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Stereoselective Synthesis of Perfluoroalkylated (*E*, *E*)-Dienes from Perfluoroalkylated Alkynes. The Synthesis of Fluorinated Analogs of Lepidoptera Pheromones

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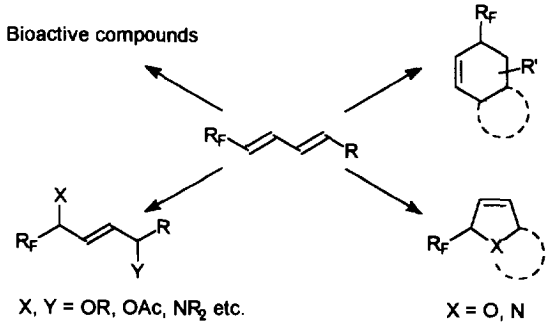
Abstract: $Pd(dba)_2$ -HOAc catalyzed the isomerization of 1-perfluoroalkyl-1-alkynes to give 1-perfluoroalkyl-(1E, 3E)-dienes in good yield and stereoselectivity; the fluorinated analogs of Lepidoptera species sex pheromone attractants were synthesized applying this method.

INTRODUCTION

Conjugated dienes are important synthetic intermediates widely used in the construction of cyclic and multifunctionalized systems.[1] Accordingly, fluorine-containing 1, 3-dienes, such as 1-perfluoroalkyl-1, 3-dienes, not only may serve as biologically active compounds,[2a] but also are valuable building blocks for the synthesis of selectively fluorinated compounds [2b] (**Scheme 1**). For example, Diels-Alder reaction leads to



Scheme 1

carbocyclic compounds while metal catalyzed oxidation may give heterocyclic or polyfunctionalized structures with perfluoroalkyl substitution. However, the methods for preparing perfluoroalkylated 1, 3-dienes are up to now limited and suffer from lack of generality. Only perfluoroalkylated dienes with another electron-withdrawing group or with specific substitution pattern could be obtained.[3,4] Concerning the potential changes in the metabolism, lipid solubility and volatibility of biologically active molecules through introduction of

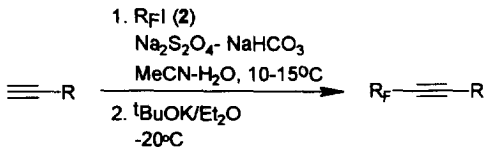
fluorine atoms,[5] we are interested in the influence of fluorine atoms upon some bioactive dienic natural products. Herein, we report a convenient method to prepare 1-perfluoroalkyl-(1*E*, 3*E*)-dienes and the synthesis of fluorinated analogs of the sex pherc mone attractants of Lepidoptera species.

In the continuing study of the reactivity of electron-deficient alkynes, we have developed the transition metal-catalyzed alkyne-diene isomerization.[6] Recently, we[7] and Trost's group[8] independently published the results on phosphine-catalyzed isomerization of electron-deficient acetylenic compounds to *E*, *E*-dienes. Considering the electron-withdrawing perfluoroalkyl group, a perfluoroalkyl-substituted alkyne is also an eletron-deficient alkyne, so we set out to explore the possibility of synthesizing perfluoroalkylated 1, 3-dienes by isomerization of perfluoroalkylated alkynes.

RESULTS AND DISCUSSION

1-Perfluoroalkyl-1-alkynes **3** are prepared easily from terminal alkynes by perfluoroalkyl iodide addition[9] and subsequent HI elimination[10] (**Table 1**). Unfortunately, our first trials on the isomerization of **3** using phosphine as the catalyst all failed. Thus, no reaction occurred when **3** was heated with triphenylphosphine in aromatic solvent, while more reactive tributylphosphine induced defluorination[11] of the starting material and resulted in unidentifiable tarry substances.

Table 1 Preparation of Perfluoroalkylated Alkynes 3.



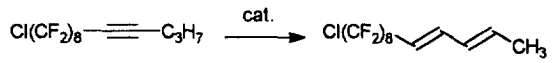
1 3

3	R_F	R	Yield (%)
3a	$Cl(CF_2)_2$	n-C_6H_{13}	47
3b	$Cl(CF_2)_2$	n-C_8H_{17}	74
3c	$Cl(CF_2)_2$	$(CH_2)_9OH$	82
3d	$Cl(CF_2)_4$	n-C_3H_7	52
3e	$Cl(CF_2)_4$	n-C_5H_{11}	73
3f	$Cl(CF_2)_4$	$(CH_2)_6OH$	76
3g	$Cl(CF_2)_8$	n-C_3H_7	78

We then turned to investigate the reaction under transition metal-catalyzed conditions. In our previous work on transition metal-catalyzed isomerization of acetylenic compounds, two mechanisms were postulated: 1. through repeated metal hydride addition-elimination (using M-H complexes or zero valent palladium as the

catalyst precursor). 2. through metal assisted phosphine catalysis(using high valent metal-phosphine complexes). Thus two types of catalytic systems were studied on substrate **3g** and the results are listed in **Table 2**. As shown in the table, while $Pd(dba)_2$-PPh_3 and $PdCl_2(PPh_3)_2$ can not effect the isomerization, both $Pd(dba)_2$-HOAc-PPh_3 and $Pd(OAc)_2$-PPh_3 systems gave reasonable yields of diene product **4g**. It occurred to us that the real catalyst is a Pd-H species generated from zero valent Pd and an active hydrogen source,[12] although it is still unclear what is the H-source in the case of $Pd(OAc)_2$-PPh_3 catalytic system (entry 5, **Table 2**). The difference between $Pd(OAc)_2$ and $PdCl_2$ may be rationalized by the fact that $Pd(OAc)_2$ is easily reduced by Ph_3P to Pd(0)[13] which in turn transforms to Pd-H species. This is supported by the formation of metallic

Table 2. Isomerization reaction of 3g using different catalytic systems.[a]



entry	catalyst (mol%)	type[b]	additive (mol%)	T(°C)	time (h)	product (%)[c]
1	$Pd(dba)_2$(10) Ph_3P(40)	A	none	110	24	No reaction
2	$Pd(dba)_2$(5) Ph_3P(20)	A	HOAc (20)	80	48	Partial conversion[d]
3	$Pd(dba)_2$(5) Ph_3P(20)	A	HOAc (20)	110	12	**4g**(82)
4	$PdCl_2(PPh_3)_2$(5) PPh_3(10)	B	none	110	48	No reaction
5	$Pd(OAc)_2$(5) Ph_3P(20)	B	none	110	10	**4g**(63)[e]

[a] Reaction conditions: A mixture of **3g**(0.5mmol), catalyst and additive in $PhCH_3$ (2mL) was stirred at specified temperature under Ar. The reaction was monitored by TLC and ^{19}F NMR.

[b] A: Pd(0) catalyst; B: Pd(II) catalyst.

[c] Isolated yield by column chromatography.

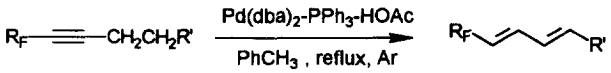
[d] The yield was not determined.

[e] Pd metal precipitated out during the reaction.

palladium during the reaction. An analoguous reduction of $PdCl_2$, on the other hand, is much difficult, so $PdCl_2(PPh_3)_2$ failed to catalyze the isomerization. The ineffectiveness of $PdCl_2$-PPh_3 system also suggested that Pd(II) assisted nucleophilic catalysis of phosphine does not work here.

Using $Pd(dba)_2$-HOAc catalytic system in $PhCH_3$ solvent, other substrates also isomerized smoothly to give perfluoroalkylated dienes in moderate to good yields. High *E*, *E*-stereoselectivity was obtained for all the isomerization products (**Table 3**).

Table 3. $Pd(dba)_2$-PPh_3-HOAc Catalyzed Isomerization of 1-Perfluoroalkyl-1-Alkynes 3.



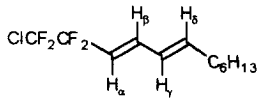
3 **4**

entry	substrate			product	Yield
	number	R_F	R'		(%)[a]
1	**3b**	$Cl(CF_2)_2$	n-C_6H_{13}	**4b**	80
2[b]	**3c**	$Cl(CF_2)_2$	$(CH_2)_7OH$	**4c'**	88
3	**3e**	$Cl(CF_2)_4$	n-C_3H_7	**4e**	75
4	**3f'**	$Cl(CF_2)_4$	$(CH_2)_4OAc$	**4f'**	75
5[b]	**3f**	$Cl(CF_2)_4$	$(CH_2)_4OH$	**4f'**	76
6	**3g**	$Cl(CF_2)_8$	CH_3	**4g**	82
7[b]	**9**	CF_3	$(CH_2)_7OH$	**5a**	85
8[b]	**10**	CF_3CF_2	$(CH_2)_8OH$	**6a**	86

[a] Isolated yield by column chromatography.

[b] 1eq of Ac_2O was added besides $Pd(dba)_2$, PPh_3 and HOAc. The corresponding acetylated product was obtained.

The double bond configuration of the diene products was established based on the H-H coupling constants in ^1H NMR spectra.[6] Four vinylic protons were well resolved in 300 MHz ^1H NMR using C_6D_6 as the solvent. The coupling constant between H_γ and H_δ, 15.0Hz and the large J value for H_β (15.4Hz) indicated two trans double bonds (**Figure 1**). The *E*, *E*-configuration was also supported by the 990cm^{-1} absorption peak in infrared spectra.[14]

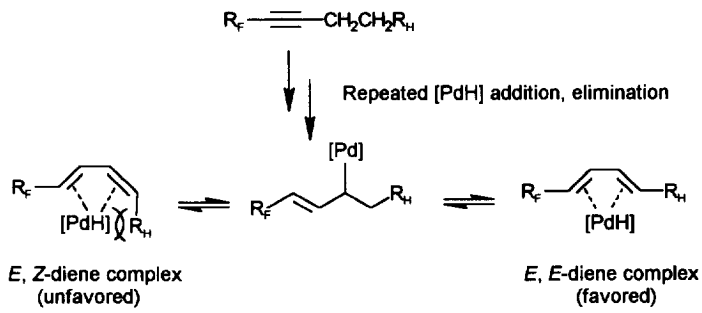


4b

H_α	7.20-7.00	m
H_β	6.60	ddt(J=15.4, 10.4, 2.1Hz)
H_γ	5.68	dd(J=15.0, 10.4 Hz)
H_δ	5.42	dt(J=15.0, 6.7Hz)

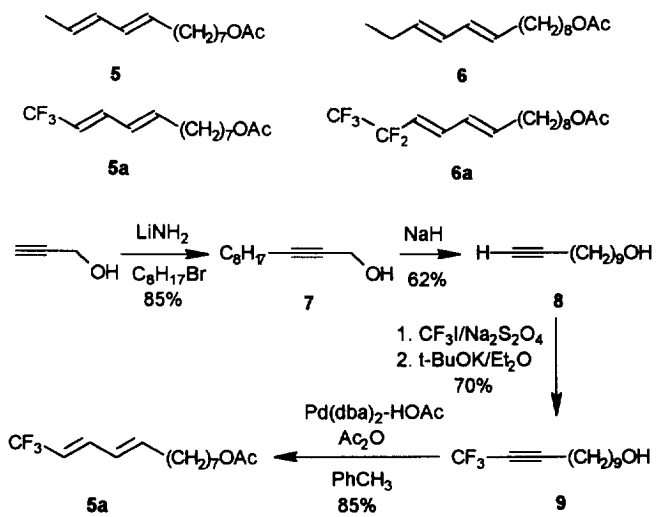
Figure 1

The high *E*, *E*-stereoselectivity might be account for by the relative thermodynamic stability between different diene isomers and the template effect of palladium, especially the latter [6]. As shown in **Scheme 2**, the equilibriums favoring *E*, *E*-diene complex may result in the highly selective formation of *E*, *E*-dienes.



Scheme 2

A number of natural products have conjugated *E*, *E*-diene or polyene moiety.[15] For example, **5** and **6** are the sex pheromone attractants of Lepidoptera species[16] (**Scheme 3**). They were used to attract and capture male moths of *M. latiferranus*, a serious pest of filbernuts in some parts of America. In order to study the influence of fluorine atoms upon the biological properties of these molecules and to illustrate the utility of our isomerization method, we synthesized their partially fluorinated analogs **5a** and **6a** according to the route shown in **Scheme 3**. Trifluoromethyl alkynol **9** was prepared by a CF_3I addition-HI elimination sequence from 10-undecyn-1-ol **8**. **9** was then isomerized and acetylated in one step to **5a**, giving an overall yield of 31% starting from propargyl alcohol. **6a** was similarly prepared, in an overall yield of 41%.



Scheme 3

As described above, we have developed a new route to prepare perfluoroalkylated (1*E*, 3*E*)-dienes from readily available materials and successfully used this method to synthesize fluorinated insect pheromones. The generality and high stereoselectivity of this method are noteworthy. The reaction also reveals some insight of

the isomerization mechanism of a different type of alkynes. Further applications of this novel synthesis, especially the elaboration of the perfluoroalkylated 1, 3-dienes to carbocyclic or heterocyclic compounds, are now under investigation.

EXPERIMENTAL SECTION

General Methods. Melting points are uncorrected. IR spectra were run on a Shimadzu IR440 instrument. ^{1}H NMR were recorded with TMS as internal standard on a Varian EM390 or an Bruker XL300 spectrometer. ^{19}F NMR spectra were recorded on an Varian EM356 spectrometer using $CFCl_3$ as external standard. MS data (EI) were obtained on a Finnigan 4201 spectrometer and HRMS data were obtained on an Finnigan MAT 8430 spectrometer. The analytical samples were purified by bulb-to-bulb distillation after column chromatography.

General Procedure for Preparation of 1-Perfluoroalkyl-1-alkynes 3. To a stirred solution of perfluoroalkyl iodide **2** (10mmol) and 1-alkyne **1** (10mmol) in a mixed solvent of MeCN (15mL) and water (10mL), was added $NaHCO_3$ (1.00g, 12mmol) and $Na_2S_2O_4$ (2.08g, 12mmol). Stirring was continued at 10-15°C for 30min. The resulting mixture was diluted with water (20mL) and extracted with ethyl ether (30mL × 3). The combined organic layer was washed with brine (20mL × 2), dried ($MgSO_4$) and concentrated under reduced pressure to give the crude adduct. The adduct diluted in anhydrous ether (20mL) was added to a stirred suspension of ^{t}BuOK (25mmol) in anhydrous ether (10mL) at -20°C. The mixture was stirred at -20°C for 1h and 0°C for another 2h. 3N HCl (10mL) was then added and the organic layer was separated, dried over anhydrous $MgSO_4$. After the solvent was removed by distillation, low boiling product was purified by fractional distillation and high boiling product by column chromatography on silica gel.

Preparation of **9** and **10** was similar to the general procedure except that the gaseous CF_3I and C_2F_5I was bubbled into the mixture of $NaHCO_3$, $Na_2S_2O_4$, MeCN and water.

1-Chloro-1, 1, 2, 2-tetrafluoro-3-decyne (3a) bp 174-176°C. ^{1}H NMR(90MHz/CCl_4): 2.30(t, J=5.0Hz, 2H), 1.95-1.00(m, 8H), 0.85(t, J=6.0Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -71.0(m, 2F), -96.0(m, 2F) ppm; IR: 2950, 2850, 2250, 1470, 980 cm^{-1}; MS m/z: 247[M^+(^{37}Cl)+1](1.6), 245[M^+(^{35}Cl)+1](4.0), 232(6.8), 148(13.3), 129(14.1), 69(53.3), 55(81.6), 43(100); Anal. Calcd. for $C_{10}H_{13}ClF_4$: C, 49.09; H, 5.36. Found: C, 48.91; H, 4.97.

1-Chloro-1, 1, 2, 2-tetrafluoro-3-dodecyne (3b) bp 210-212°C. ^{1}H NMR(90MHz/CCl_4): 2.23(t, J=5.2Hz, 2H), 1.8-1.0(m, 12H), 0.80(t, J=6.0Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -70.7(m, 2F), -96.1(m, 2F) ppm; IR: 2930, 2870, 2260, 1280, 915 cm^{-1}; MS m/z: 274[M^+(^{37}Cl)](0.3), 272[M^+(^{35}Cl)](1.0), 253(4.6), 215(54.7), 97(25.9), 55(100), 43(74.9); Anal. Calcd. for: $C_{12}H_{17}ClF_4$, 82.85; H, 6.28. Found: C, 52.66; H, 6.50.

13-Chloro-12, 12, 13, 13-tetrafluorotridec-10-yn-1-ol (3c) bp 145-148°C/10mmHg. ^{1}H NMR(90MHz/CCl_4): 3.52(t, J=5.4Hz, 2H), 2.50-2.17(m, 2H), 1.80-1.10(m, 15H) ppm; ^{19}F NMR(56MHz/CCl_4): -70.6(m, 2F), -96.2(m, 2F) ppm; IR: 3300, 2920, 2850, 2230, 1480, 1240, 1100, 840, 780 cm^{-1}; MS m/z: 304[M$^+$(^{37}Cl)](3.7), 302[M$^+$(^{35}Cl)](11.6), 285(5.0), 243(30.7), 229(51.6), 215(40.7), 95(39.5), 81(45.1), 69(79.0), 55(100), 43(34.8); HRMS Calcd. for $C_{13}H_{19}ClF_4O$: 302.1060; Found: 302.1014.

1-Chloro-1, 1, 2, 2, 3, 3, 4, 4-octafluoro-5-nonyne (3d) bp 155-157°C. ^{1}H NMR(90MHz/CCl_4): 2.15(t, J=6.0Hz, 2H), 1.80-1.25(m, 2H), 0.85(t, J=7.0Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -68.4(m, 2F), -97.0(m, 2F), -119.7(m, 2F), -122.2(m, 2F) ppm; IR: 2950, 2850, 2250, 1470, 1380, 1160, 850 cm^{-1} ; MS m/z: 305[M$^+$(^{37}Cl)+1](5.0), 303[M$^+$(^{35}Cl)+1](5.4), 281(2.6), 257(1.7), 157(10.6), 107(21.4), 61(36.4), 55(9.6), 43(100); Anal. Calcd. for $C_9H_7ClF_8$: C, 35.72; H, 2.33. Found: C, 35.80; H, 2.38.

1-Chloro-1, 1, 2, 2, 3, 3, 4, 4-octafluoro-5-undecyne (3e) bp 190-192°C; ^{1}H NMR(90MHz/CCl_4): 2.25(t, J=5.5Hz, 2H), 1.80-1.10(m, 6H), 0.80(t, J=6.0Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -67.8(m, 2F), -95.6(m, 2F), -119.0(m, 2F), -121.4(m, 2F) ppm; IR: 2950, 2930, 2850, 2250, 1470, 1190, 700 cm^{-1}; MS m/z: 332[M$^+$(^{37}Cl)](3.2), 331[M$^+$(^{35}Cl)+1](10), 286(17.4), 268(15.8), 181(13.2), 149(17.6), 71(35.0), 57(36.6), 43(100); Anal. Calcd. for $C_{11}H_{11}ClF_8$: C, 39.96; H, 3.35. Found: C, 40.06; H, 3.20.

12-Chloro-9, 9, 10, 10, 11, 11, 12, 12-octafluorododec-7-yn-1-ol (3f) bp 88-90°C/8mmHg. ^{1}H NMR(90MHz/CCl_4): 3.60(t, J=6.0Hz, 2H), 2.25(t, J=6.4Hz, 2H), 2.60(br, 1H), 1.80-1.10(m, 8H) ppm; ^{19}F NMR(56MHz/CCl_4): -67.8(m, 2F), -95.6(m, 2F), -119.0(m, 2F), -121.4(m, 2F) ppm; IR: 3350, 2950, 2870, 2250, 1190, 1135, 750 cm^{-1}; MS m/z: 362[M$^+$(^{37}Cl)](0.5), 360[M$^+$(^{35}Cl)](1.0), 346(2.7), 344(6.8), 301(18.9), 281(20.1), 85(10.5), 69(16.7), 61(29.6), 55(100); Anal. Calcd. for $C_{12}H_{13}ClF_8O$: C, 39.96, H, 3.63. Found: C, 39.57; H, 3.38.

1-Chloro-1, 1, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8-hexadecafluoro-9-tridecyne (3g) bp 75-76°C/10mmHg. ^{1}H NMR(90MHz/CCl_4): 2.10(t, J=6.0Hz, 2H), 1.90-1.20(m, 2H), 0.82(t, J=7.0Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -69.4(m, 2F), -97.8(m, 2F), -119.0~ -125.4(m, 12F) ppm; IR: 2930, 2250, 1470, 1190, 980, 700 cm^{-1}; MS m/z: 485[M$^+$(^{37}Cl)-F](0.5), 483[M$^+$(^{35}Cl)-F](1.8), 457(1.9), 291(6.1), 157(47.1), 117(100), 97(26.2), 69(23.2), 42(18.5). Anal. Calcd. for $C_{13}H_7ClF_{16}$: C, 31.06; H, 1.40. Found: C, 30.72; H, 1.16.

12, 12, 12-Trifluorododec-10-yn-1-ol (9) bp 132-134°C/10mmHg. ^{1}H NMR(90MHz/CCl_4): 3.44(t, J=6.0Hz, 2H), 2.96(brs, 1H), 2.46-1.96(m, 2H), 1.80-1.10(m, 14H) ppm; ^{19}F NMR(56MHz/CCl_4): -48.8(s, 3F) ppm; IR: 3350, 2950, 2850, 2250, 1460, 1280, 1130, 785 cm^{-1}; MS m/z: 236(M$^+$)(2.1), 219(2.2), 177(16.4), 175(13.2), 163(27.2), 149(31.9), 69(66.4), 55(100), 43(40.1). HRMS: Calcd. for $C_{12}H_{17}F_3$: 218.1282; Found: 218.1258.

13, 13, 14, 14, 14-Pentafluorotetradec-11-yn-1-ol (10) bp 78-80°C/1mmHg. ^{1}H NMR(90MHz/CCl_4): 3.53(t, J=5.5Hz, 2H), 2.60-2.15(2H), 1.90-1.10(m, 17H) ppm; ^{19}F NMR(56MHz/CCl_4): -85.1(m, 3F),

-100.2(m, 2F) ppm; IR: 3350, 2950, 2870, 2250, 1465, 1370, 1220, 1120, 1080 cm^{-1} ; MS m/z: 300(M^+)(1.5), 282(4.5), 263(11.7), 213(30.1), 133(52.8), 55(100), 43(46.2); HRMS Calcd. for $C_{14}H_{19}F_5$: 282.1407; Found: C, 282.1399.

12-Acetoxy-1-Chloro-1, 1, 2, 2, 3, 3, 4, 4-octafluoro-5-dodecyne (3f') was prepared by acetylation of **3f**. bp 85-87°C/ 10mmHg. ^1H NMR(90MHz/CCl_4): 4.05(t, J=5.5Hz, 2H), 2.42(t, J=6.0Hz, 2H), 1.98(s, 3H), 1.80-1.10(m, 8H) ppm; ^{19}F NMR(56MHz/CCl_4): -67.8(m, 2F), -95.6(m, 2F), -119.0(m, 2F), -121.4(m, 2F) ppm; IR: 2950, 2870, 2250, 1740, 1465, 1370, 1220, 1120, 780 cm^{-1}; MS m/z: 405[$M^+(^{37}Cl)$+1](0.7), 403[$M^+(^{35}Cl)$+1](1.7), 383(3.2), 343(18.3), 323(18.3), 85(9.2), 69(16.6), 61(29.6), 43(100); Anal. Calcd. for $C_{14}H_{15}ClF_8O_2$: C, 41.75; H, 3.75. Found: C, 41.52; H, 3.70.

Typical Procedure for the Isomerization of 1-Perfluoroalkyl-1-alkyne. A solution of **3b** (1.0mmol), $Pd(dba)_2$ (0.10mmol), PPh_3 (0.20mmol), HOAc (1.0mmol) in 2mL $PhCH_3$ was degassed and protected under argon. The mixture was then stirred at 110°C and monitored by ^{19}F NMR. The reaction was completed in 24h. The solvent was evacuated and flash chromatography on silica gel (eluent: petroleum ether) gave **4b**.

1-Chloro-1, 1, 2, 2-tetrafluorododeca-3*E*, 5*E*-diene (4b) bp 70-72°C/4mmHg. ^1H NMR(300MHz/C_6D_6): 7.20-7.00(m, 1H), 6.60(ddt, J=15.4, 10.4, 2.1Hz,1H), 5.68(dd, J=15.0, 10.4Hz, 1H), 5.42(dt, J=15.0, 6.7Hz, 1H), 2.20(t, J=6.5Hz, 2H), 1.60-1.20(m, 8H), 0.85(t, J=6.4Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -71.0(m, 2F), -107.3(m, 2F) ppm; IR: 2950, 2850, 1660, 1360, 1200, 990, 750 cm^{-1}; MS m/z: 272[$M^+(^{37}Cl)$-2](0.6), 270[$M^+(^{35}Cl)$-2](6.8), 239(10.8), 200(5.8), 167(9.3), 149(100), 105(36.3), 69(53.1), 57(62.1), 43(51.3); Anal. Calcd. for $C_{12}H_{17}ClF_4$: C, 52.85; H, 6.28; H, 52.90; H, 6.20.

13-Acetoxy-1-chloro-1, 1, 2, 2-tetrafluorotrideca-3*E*, 5*E*-diene (4c') bp 150-152°C/15mmHg. ^1H NMR(300MHz/$CDCl_3$): 7.20-7.05(m, 1H), 6.75(ddt, J=15.4, 9.8, 2.0Hz, 1H), 6.08(dd, J=15.0, 9.8Hz, 1H), 5.62(dt, J=15.0, 6.5Hz, 1H), 4.05(t, J=6.8Hz, 2H), 2.25-2.05(m, 2H), 2.05(s, 3H), 1.70-1.50(m, 2H), 1.50-1.20(m, 8H) ppm; ^{19}F NMR(56MHz/CCl_4): -71.0(m, 2F), -96.2(m, 2F) ppm; IR: 2920, 2850, 1740, 1660, 1365, 1150, 1090, 990, 780 cm^{-1}; MS m/z: 346[$M^+(^{37}Cl)$](1.8), 344[$M^+(^{35}Cl)$](4.8), 308(23.9), 295(6.9), 282(22.6), 143(27.2), 129(44.6), 93(63.8), 55(41.7), 43(100); Anal. Calcd. for $C_{15}H_{21}ClF_4O_2$: C, 52.26; H, 6.14. Found: C, 52.52; H, 6.17.

1-Chloro-1, 1, 2, 2, 3, 3, 4, 4-octafluoroundeca-5*E*, 7*E*-diene (4e) bp 48-50°C/10mmHg. ^1H NMR(300MHz/$CDCl_3$): 7.20-7.00(m, 1H), 6.70(ddt, J=15.4, 10.6, 2.0Hz, 1H), 6.04(dd, J=15.0, 10.6Hz, 1H), 5.62(dt, J=15.0, 6.5Hz, 1H), 2.20(q, J=6.5Hz, 2H), 1.60-1.20(m, 2H), 0.85(t, J=6.7Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -67.2(m, 2F), -110.5(m ,2F), -119.5(m, 2F), -122.0(m, 2F) ppm; IR: 2950, 2850, 1660, 1240, 1200, 990, 830 cm^{-1} ; MS m/z: 334[$M^+(^{37}Cl)$+2](1.0), 332[$M^+(^{35}Cl)$+2](3.2), 286(18.5), 268(11.2), 149(19.7), 71(35.0), 57(56.1), 43(100); Anal. Calcd. for $C_{11}H_{11}ClF_8$: C, 39.96; H, 3.35. Found: C, 39.56; H, 3.51.

12-Acetoxy-1-Chloro-1, 1, 2, 2, 3, 3, 4, 4-octafluorododeca-5*E*, 7*E*-diene (4f') bp 136-138°C/15mmHg. ^{1}H NMR(300MHz/C_6D_6): 7.20-7.00(m, 1H), 6.61(ddt, J=15.4, 10.6, 2.1Hz, 1H), 5.64(dd, J=15.0, 10.6Hz, 1H), 5.42(dt, J=15.0, 7.0Hz, 1H), 3.92(t, J=6.5Hz, 2H), 1.75(s, 3H), 1.80-1.60(m, 2H), 1.40-0.95(m, 4H) ppm; ^{19}F NMR(56MHz/CCl_4): -67.2(m, 2F), -110.5(m, 2F), -119.2(m, 2F), -122.0(m, 2F) ppm; IR: 2920, 2850, 1740, 1660, 1360, 1240, 1200, 990, 750 cm^{-1}; MS m/z: 404[M^+(^{37}Cl)](0.5), 402[M^+(^{35}Cl)](1.0), 366(3.3), 236(16.3), 205(9.2), 177(9.2), 131(70.8), 91(40.0), 55(13.3), 43(100); Anal. Calcd. for $C_{14}H_{15}ClF_8O_2$: C, 41.75; H, 3.75. Found: C, 41.45; H, 3.72.

1-Chloro-1, 1, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8-hexadecafluoroundeca-9*E*, 11*E*-diene (4g) bp 75-77°C/10mmHg. ^{1}H NMR(300MHz/C_6D_6): 7.30-7.00(m, 1H), 6.60(ddt, J=15.5, 10.5, 2.0Hz, 1H), 5.96(dd, J=16.0, 10.5Hz, 1H), 5.42(dq, J=16.0, 6.6Hz, 1H), 1.45(d, J=6.6Hz, 3H) ppm; ^{19}F NMR(56MHz/CCl_4): -68.4(m, 2F), -111.5(m, 2F), -120.9(m, 2F), -121.5~ -123.0(m, 8F), -123.8(m, 2F) ppm; IR: 3010, 2920, 1660, 1360, 1240, 990, 700 cm^{-1}; MS m/z: 485[M^+(^{37}Cl)-F](0.5), 483[M^+(^{35}Cl)-F](1.6), 291(15.9), 242(15.3), 157(100), 117(92.6), 97(26.4), 69(27.2), 42(18.5); Anal. Calcd. for $C_{13}H_7ClF_{16}$: C, 31.06; H, 1.40; Found: C, 31.30; H, 1.11.

12-Acetoxy-1, 1, 1-trifluorododeca-2*E*, 4*E*-diene (5a) oil. ^{1}H NMR(300MHz/$CDCl_3$): 7.20-7.00(m, 1H), 6.70(ddq, J=15.5, 9.6, 2.0Hz, 1H), 6.00(dd, J=15.5, 9.6Hz, 1H), 5.58(dt, J=15.5, 6.5Hz, 1H), 4.05(t, J=6.7Hz, 2H), 2.15(q, J=6.5Hz, 2H), 2.06(s, 3H), 1.70-1.55(m, 2H), 1.50-1.20(m, 8H) ppm; ^{19}F NMR(56MHz/CCl_4): -62.6(m, 3F) ppm; IR: 2920, 2820, 1740, 1660, 1240, 1110, 990 cm^{-1}; MS m/z: 279(M^++1)(0.4), 258(48.5), 219(22.2), 148(48.4), 116(43.4), 79(82.0), 67(40.8), 43(100); HRMS: Calcd. for $C_{14}H_{21}F_2O_2$: 258.1431; Found: 258.1476.

14-Acetoxy-1, 1, 1, 2, 2-pentafluorotetradeca-3*E*, 5*E*-diene (6a) oil. ^{1}H NMR(300MHz/$CDCl_3$): 7.20-7.05(m, 1H), 6.75(ddt, J=15.4, 9.8, 2.0Hz, 1H), 6.08(dd, J=15.0, 9.8Hz, 1H), 5.62(dt, J=15.0, 6.5Hz, 1H), 4.05(t, J=6.8Hz, 2H), 2.25-2.05(m, 2H), 2.05(s, 3H), 1.70-1.50(m, 2H), 1.50-1.20(m, 10H) ppm; ^{19}F NMR(56MHz/CCl_4): -69.3(m, 3F), -108.5(m, 2F) ppm; IR: 2920, 2850, 1740, 1660, 1150, 1090, 990, 780 cm^{-1} ; MS m/z: 342(M^+)(5.0), 306(25.0), 293(7.1), 280(21.5), 141(29.1), 127(44.6), 91(64.5), 57(42.1), 43(100). Anal. Calcd. for $C_{16}H_{23}F_5O_2$: C, 56.13; H, 6.77. Found: C, 55.97; H, 6.88.

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