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Synthesis and selective carbocupration reaction of fluorine-containing enynic esters, enynylphosphine oxides, and enynylphosphates

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ABSTRACT

Some new fluorine-containing enynic esters, enynylphosphine oxides, and enynylphosphates were synthesized stereoselectively in good yields by the dehydrohalogenation reaction of fluoroalkylated 3-iodoacrylates, 2-iodovinylphosphonates, and 2-iodovinylphosphine oxides under basic conditions. These fluorine-containing enynic compounds could undergo carbocupration reaction with organocopper reagents and the vinylcopper intermediates formed in situ could further react with some electrophiles such as allyl bromide, phenylselenyl bromide, and iodine to give the corresponding polysubstituted fluorine-containing dienoic esters, phosphates, and phosphine oxides with high regio- and stereoselectivity.

1. Introduction

Recently, fluorine-containing compounds have drawn increasing interest owing to their unique physical and biological properties. Accordingly, considerable efforts have been devoted to the development of methodologies for the efficient and selective synthesis of fluorinated compounds.[1] Among a great diversity of fluorine-containing molecules, fluorine-containing enynes are well-known as a kind of important synthetic intermediates for the synthesis of fluorinated analogues of some biologically active molecules.[2] Therefore, significant efforts have been made toward the synthesis of fluorine-containing enynes.[3] However, to the best of our knowledge, fluorine-containing enynic esters, enynylphosphine oxides, and enynylphosphates **2** (Fig. 1, R^1=COOEt, $P(O)(OEt)_2$ or $P(O)Ph_2$) have remained unexploited. Recently, we reported the regio- and stereoselective addition of perfluoroalkyl iodides to allenes conjugated with carbon–oxygen or phosphorus–oxygen double bonds, which afforded a series of fluoroalkylated 3-iodoacrylates, 2-iodovinylphosphonates, and 2-iodovinylphosphine oxides **1**.[4] Further studies showed that these fluoroalkylated vinyl iodides could be easily transformed to the corresponding enynes **2** stereoselectively by treating with Et_3N or DBU. In this paper we report the synthesis of some fluorine-containing enynes **2** and their carbocupration reaction[5] with organocopper reagents.

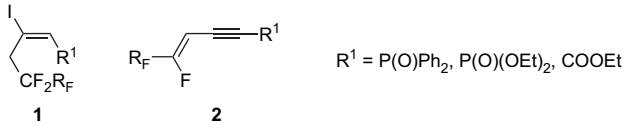

Figure 1.

2. Results and discussion

At room temperature, fluoroalkylated 2-iodovinylphosphine oxides (**1a**–**1c**) and 2-iodovinylphosphonates (**1d**–**1f**) reacted readily with triethylamine in THF. In this reaction, the elimination of both hydrogen iodide and hydrogen fluoride occurred in one step, giving the corresponding enynylphosphine oxides (**2a**–**2c**) and enynylphosphates (**2d**–**2f**), respectively. After purification, a careful analysis of the spectroscopic data of the product revealed that only isomers in *Z*-configuration were formed. The ^1H NMR spectra showed a big coupling constant (J=27–30 Hz) between the vinylic proton and fluorine, which was in agreement with the reported results.[2a,6] When 3-iodoacrylate **1g** was allowed to react with triethylamine under similar conditions, the dehydrohalogenation reaction did not occur. Raising the reaction temperature to reflux afforded a complex mixture. Fortunately, the desired product **2g** was obtained in good yield from the reaction of **1g** and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at −78 °C in Et_2O. The structure of **2a**–**g** was further proved by X-ray crystallography of **2c** (Fig. 2).[7] The results are summarized in Table 1.

The carbocupration reaction of alkynes is an effective method for the synthesis of polysubstituted olefins.[5] With these fluorine-

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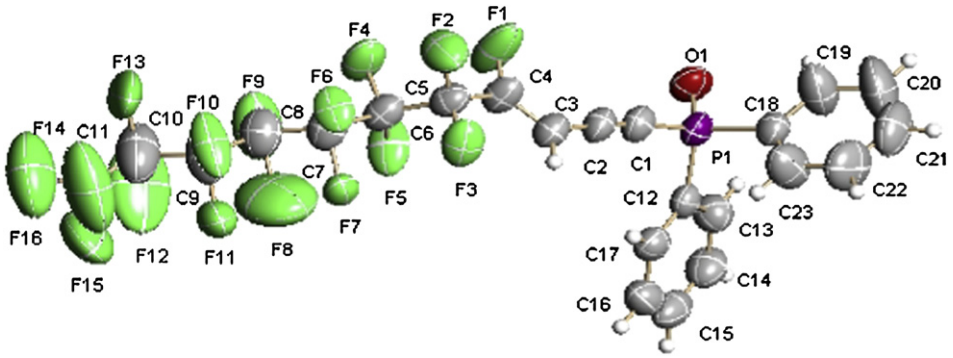
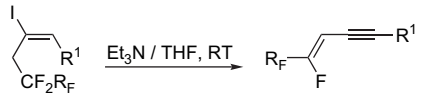


Figure 2. Crystal structure of **2c**.

Table 1
Synthesis of fluorine-containing enynic esters, enynylphosphine oxides, and enynylphosphates



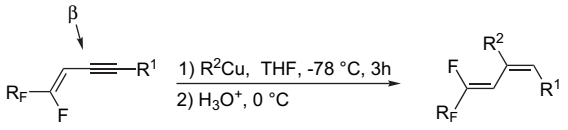
1 **2**

Entry	**1**	R^1	R_F	Product	Isolated yield (%)
1	**1a**	$P(O)Ph_2$	$ClCF_2$	**2a**	86
2	**1b**	$P(O)Ph_2$	C_3F_7	**2b**	78
3	**1c**	$P(O)Ph_2$	C_7F_{15}	**2c**	86
4	**1d**	$P(O)(OEt)_2$	$ClCF_2$	**2d**	91
5	**1e**	$P(O)(OEt)_2$	C_3F_7	**2e**	78
6	**1f**	$P(O)(OEt)_2$	C_7F_{15}	**2f**	89
7	**1g**	COOEt	C_3F_7	**2g**	90[a]

[a] DBU was employed instead of Et_3N at −78 °C in Et_2O.

containing enynes **2** in hand, we next investigated their carbocupration reaction with some organocopper reagents. Using THF as solvent, **2** reacted readily with organocopper reagents prepared from CuCl and lithium reagent or Grignard reagent at −78 °C. After quenching with saturated ammonium chloride solution, the corresponding diene products **3** were obtained in moderate to good yields. The results are summarized in Table 2. Again the reaction showed high regio- and stereoselectivity. In all cases, the addition reaction took place at the β-position of enynes **2** in a cis-addition

Table 2
The carbocupration reaction of **2** with organocopper reagents



2 **3**

Entry	R^1	R_F	R^{2a}	Product	Isolated yield (%)
1	$P(O)Ph_2$	$ClCF_2$	Et	**3a**	87
2	$P(O)Ph_2$	$ClCF_2$	*n*-Bu	**3b**	78
3	$P(O)Ph_2$	$ClCF_2$	*n*-$C_{12}H_{25}$	**3c**	67
4	$P(O)Ph_2$	$ClCF_2$	4-ClC_6H_4	**3d**	76
5	$P(O)Ph_2$	$ClCF_2$	4-$MeOC_6H_4$	**3e**	72
6	$P(O)Ph_2$	$ClCF_2$	1-Naphthyl	**3f**	87
7	$P(O)(OEt)_2$	$ClCF_2$	Et	**3g**	72
8	$P(O)(OEt)_2$	C_3F_7	*n*-Bu[b]	**3h**	93
9	$P(O)(OEt)_2$	C_7F_{15}	*n*-C_8H_{17}	**3i**	80
10	$P(O)(OEt)_2$	C_7F_{15}	1-Naphthyl	**3j**	85
11	COOEt	C_3F_7	*n*-Bu[b]	**3k**	78

[a] Copper reagents were prepared from Grignard reagent and CuCl, unless otherwise noted.
[b] Copper reagents were prepared from *n*-BuLi and CuCl.

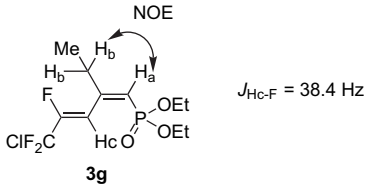


Figure 3.

manner exclusively, and only one isomer was formed. The stereoselectivity of the reaction was consistent with previous studies.[5] The regioselectivity can be rationalized in terms of the stabilization effect of ester group, phosphine oxide group, or phosphate group on the carbanion intermediate formed during the reaction.

The structure of **3** was determined by their NMR spectra and the NOESY experiment of compound **3g** (Fig. 3). The big coupling constant of the vinylic proton H_c and fluorine indicates a trans configuration. The NOESY experiment of compound **3g** showed that there was a strong correlation between the vinylic proton H_a and proton H_b in ethyl group, revealing that H_a and the ethyl group are in the cis configuration. Additionally, no NOE is observed between the vinylic proton H_c and H_b, indicating that **3g** is in the *s-trans* conformation.

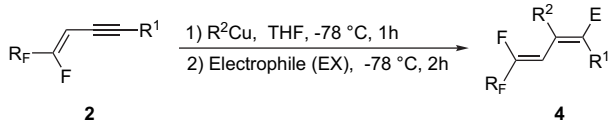
According to the literature[5] and above experimental results, vinylcopper species were involved in the reaction and they were very likely to react with other electrophiles added to the reaction mixture to give olefin derivatives. Following previous experiments, we examined the feasibility of the reaction of vinylcopper intermediates formed in situ with some electrophiles. As expected, when electrophiles such as allyl bromide, phenylselenyl bromide, and iodine were added to the above reaction system, the corresponding coupling products **4a–h** were obtained in satisfactory yields. The results are summarized in Table 3.

The structure of **4** was also determined by their NMR spectra and the NOESY experiment of **4a**. As shown in Figure 4, the NOE between H_d in the allyl group and H_e in the ethyl group was observed, while no NOE was found between the vinylic proton H_f and H_e in the ethyl group.

3. Conclusion

In summary, we have developed a convenient method for the stereoselective synthesis of fluorine-containing enynic esters, enynylphosphine oxides, and enynylphosphates from fluoroalkylated 3-iodoacrylates, 2-iodovinylphosphine oxides, and 2-iodovinylphosphonates under mild conditions. The carbocupration reaction of these fluoroalkylated enynes with copper reagents derived from organolithium or Grignard reagents gave the corresponding polysubstituted fluorine-containing dienoic esters,

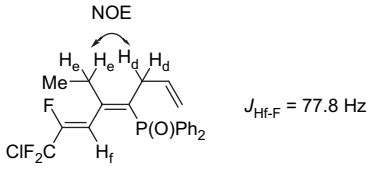
Table 3
The reaction of **2** with organocopper reagents and electrophiles



2 **4**

Entry	R^1	R_F	R^2[a]	Electrophile (EX)	Product	Isolated yield (%)
1	$P(O)Ph_2$	$ClCF_2$	Et[b]		**4a**	77
2	$P(O)Ph_2$	$ClCF_2$	Et[b]	I_2	**4b**	75
3	$P(O)Ph_2$	C_7F_{15}	*n*-Bu	I_2	**4c**	75
4	$P(O)(OEt)_2$	C_3F_7	*n*-Bu		**4d**	89
5	$P(O)(OEt)_2$	C_3F_7	*n*-Bu	I_2	**4e**	82
6	$P(O)(OEt)_2$	C_3F_7	*n*-Bu	PhSeCl	**4f**	85
7	$P(O)(OEt)_2$	C_7F_{15}	*n*-Bu		**4g**	78
8	COOEt	C_3F_7	*n*-Bu	I_2	**4h**	75

[a] Copper reagents were prepared from *n*-BuLi and CuCl, unless otherwise noted.
[b] Copper reagents were prepared from Grignard reagent and CuCl.



4a

Figure 4.

phosphates, and phosphine oxides with high regio- and stereoselectivity.

4. Experimental

4.1. General experimental procedure

Melting points were measured with a Temp-Melt apparatus and uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AM-300 instruments with TMS as the internal standard. ^{19}F NMR and ^{31}P NMR spectra were recorded on the same spectrometer using $CFCl_3$ and 85% H_3PO_4 as external standards, respectively. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra and high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 and a Finnigan MAT-8430 spectrometer, respectively. Elemental analyses were performed by this institute. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium before use. Starting materials **1** were prepared in our laboratory by previous reported procedures.[4] All other chemicals were commercially available and were used as received.

4.2. Typical procedure for the synthesis of 2

To a THF solution (10 mL) of fluoroalkylated 2-iodovinylphosphonate or 2-iodovinylphosphine oxide **1** (1 mmol) was added the THF solution (2 mL) of Et_3N (3 mmol) at room temperature. The mixture was stirred at room temperature for a few hours (monitored by TLC). After the reaction, the mixture was poured into H_2O (20 mL) and extracted with Et_2O (3×20 mL). The combined organic layer was washed with saturated NaCl solution (20 mL), dried over Na_2SO_4, and evaporated in vacuo. The crude product was subjected to column chromatography using petroleum ether/ethyl acetate as eluent to give **2**.

*4.2.1. (Z)-5-Chloro-4,5,5-trifluoropent-3-en-1-ynyl-(diphenyl)phosphine oxide (**2a**)*

White solid, mp: 52–53 °C; IR (KBr): 3060, 2990, 2920, 2188, 2162, 1674, 1591, 1485, 1440, 1350, 1255, 1211, 1157, 1123, 981 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.79–7.52 (4H, m), 7.51–7.38 (6H, m), 5.79 (1H, dd, J_1=27.6 Hz, J_2=3.3 Hz); ^{19}F NMR ($CDCl_3$): δ −61.15 (2F, d, J=15.2 Hz), −106.70 (1F, m); ^{31}P NMR ($CDCl_3$): δ 9.14; MS (EI) *m*/*z* (%): 355 (6.00), 261 (16.12), 230 (69.60), 195 (100.00). Anal. Calcd for $C_{17}H_{11}ClF_3OP$: C, 57.57; H, 3.13; Cl, 10.00. Found: C, 57.18; H, 3.27; Cl, 10.26.

*4.2.2. (Z)-4,5,5,6,6,7,7,7-Octafluorohept-3-en-1-ynyl-(diphenyl)phosphine oxide (**2b**)*

Yellow oil; IR (neat): 3060, 2982, 2927, 2198, 1673, 1591, 1485, 1440, 1367, 1211, 1123, 1061, 1034, 999 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.88–7.81 (4H, m), 7.62–7.48 (6H, m), 5.94 (1H, dd, J_1=29.6 Hz, J_2=2.7 Hz); ^{19}F NMR ($CDCl_3$): δ −80.34 (3F, m), −106.14 (1F, m), −119.02 (2F, m), −126.67 (2F, m); ^{31}P NMR ($CDCl_3$): δ 9.64; MS (ESI) *m*/*z* (%): 439. Anal. Calcd for $C_{19}H_{11}F_8OP$: C, 52.07; H, 2.53. Found: C, 52.15; H, 2.68.

*4.2.3. (Z)-4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Hexadecafluoroundec-3-en-1-ynyl(diphenyl)phosphine oxide (**2c**)*

White solid, mp: 67–68 °C; IR (KBr): 3062, 2100, 1684, 1592, 1485, 1440, 1374, 1253, 1205, 1147, 1122, 1070, 989 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.88–7.81 (4H, m), 7.62–7.48 (6H, m), 5.95 (1H, dd, J_1=27.9 Hz, J_2=2.4 Hz); ^{19}F NMR ($CDCl_3$): δ −80.75 (3F, m), −106.11 (1F, m), −118.23 (2F, m), −121.95 (4F, m), −122.47 (4F, m), −126.11 (2F, m); ^{31}P NMR ($CDCl_3$): δ 9.22; MS (ESI) *m*/*z* (%): 639. Anal. Calcd for $C_{23}H_{11}F_{16}OP$: C, 43.28; H, 1.74. Found: C, 43.13; H, 2.00.

*4.2.4. (Z)-Diethyl 4,5,5,5-tetrafluoropent-3-en-1-ynylphosphonate (**2d**)*

Colorless oil; IR (neat): 3051, 2991, 2913, 2197, 1674, 1480, 1446, 1395, 1351, 1269, 1159, 1027, 982 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.77 (1H, dd, J_1=27.9 Hz, J_2=3.9 Hz), 4.27–4.15 (4H, m), 1.42–1.36 (6H, m); ^{19}F NMR ($CDCl_3$): δ −61.27 (2F, d, J=15.2 Hz), −106.99 (1F, m); ^{31}P NMR ($CDCl_3$): δ −8.46; MS (ESI) *m*/*z* (%): 291. Anal. Calcd for $C_9H_{11}ClF_3O_3P$: C, 37.20; H, 3.82. Found: C, 37.07; H, 3.96.

*4.2.5. (Z)-Diethyl 4,5,5,6,6,7,7,7-octafluorohept-3-en-1-ynylphosphonate (**2e**)*

Yellow oil. IR (neat): 3056, 2991, 2914, 2201, 1675, 1481, 1447, 1396, 1369, 1267, 1234, 1126, 1030, 981 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.92 (1H, dd, J_1=28.2 Hz, J_2=3.9 Hz), 4.28–4.14 (4H, m), 1.43–1.35 (6H, m); ^{19}F NMR ($CDCl_3$): δ −81.01 (3F, m), −107.22 (1F, m), −119.64 (2F, m), −127.29 (2F, m); ^{13}C NMR ($CDCl_3$): δ 156.41 (dt, J_1=276.8 Hz, J_2=33.8 Hz), 95.18, 89.81 (dd, J_1=288.4 Hz, J_2=6.9 Hz), 85.70 (d, J=52.1 Hz), 63.56, 15.69; ^{31}P NMR ($CDCl_3$): δ −7.98; MS (ESI) *m*/*z* (%): 375; HRMS calcd for $C_{11}H_{12}F_8O_3P$ (M+H): 375.0391; found: 375.0398.

*4.2.6. (Z)-Diethyl 4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-hexadecafluoroundec-3-en-1-ynylphosphonate (**2f**)*

Yellow oil; IR (neat): 3059, 2991, 2913, 2188, 1673, 1481, 1447, 1395, 1356, 1250, 1210, 1149, 1028, 985 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.86 (1H, dd, J_1=28.2 Hz, J_2=3.9 Hz), 4.22 (4H, q, J=7.5 Hz), 1.40 (6H, t, J=7.5 Hz); ^{19}F NMR ($CDCl_3$): δ −80.77 (3F, m), −106.38 (1F, m), −118.31 (2F, m), −121.83 (4F, m), −122.58 (4F, m), −126.16 (2F, m); ^{13}C NMR ($CDCl_3$): δ 156.89 (dt, J_1=251.8 Hz, J_2=28.1 Hz), 95.22, 90.06 (dd, J_1=222.3 Hz, J_2=2.3 Hz), 85.87 (d, J=38.7 Hz), 63.77, 15.94; ^{31}P NMR ($CDCl_3$): δ −7.62; MS (ESI) *m*/*z* (%): 575; HRMS calcd for $C_{15}H_{12}F_{16}O_3P$ (M+H): 575.0263; found: 575.0281.

4.3. Synthesis of (*Z*)-ethyl 5,6,6,7,7,8,8,8-octafluorooct-4-en-2-ynoate (2g)

To an etheral solution (20 mL) of (*E*)-ethyl 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooct-2-enoate **1g** (1 mmol) was added the etheral solution (2 mL) of DBU (2 mmol) at −78 °C. After stirring at the

same temperature for 1 h, the reaction mixture was poured into the cold NH_4Cl solution (20 mL) and the resulted mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with saturated NaCl solution (20 mL), dried over Na_2SO_4, and evaporated in vacuo. The crude product was subjected to column chromatography using petroleum ether/ethyl acetate (20:1) as eluent to give **2g**.

*4.3.1. (Z)-Ethyl 5,6,6,7,7,8,8,8-octafluorooct-4-en-2-ynoate (**2g**)*

Yellow oil; IR (neat): 3095, 2991, 2233, 1724, 1370, 1237, 1127, 1072 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.78 (1H, d, J=28.5 Hz), 4.22 (2H, q, J=7.2 Hz), 1.27 (3H, t, J=7.2 Hz); ^{19}F NMR ($CDCl_3$): δ −80.86 (3F, t, J=9.3 Hz), −107.15 (1F, m), −119.52 (2F, m), −127.22 (2F, m); ^{13}C NMR ($CDCl_3$): δ 156.13 (dt, J_1=282.7 Hz, J_2=28.1 Hz), 152.60, 95.11, 90.08 (d, J=6.8 Hz), 73.11, 62.64, 13.83; MS (EI) m/z (%): 265 (100.00), 238 (28.77), 219 (13.43), 119 (49.45); HRMS calcd for C_8HF_8O (M−EtO): 264.9900; found: 264.9900.

4.4. Typical procedure for the reaction of 2 with organocopper reagents derived from Grignard reagents

Under nitrogen atmosphere, CuCl (2 mmol) was added to the solution of ethylmagnesium bromide in THF (10 mL) prepared from magnesium turning (2 mmol) and ethyl bromide (2 mmol) at −40 °C. After stirring for 30 min at that temperature, the reaction mixture was cooled to −78 °C and the solution of **2** (0.5 mmol) in THF (2 mL) was added. After stirring for 3 h at −78 °C, the mixture was allowed to warm to −10 °C and quenched with saturated NH_4Cl solution. The resulted mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with saturated NaCl solution (20 mL), dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give **3**.

*4.4.1. (1Z,3Z)-5-Chloro-2-ethyl-4,5,5-trifluoropenta-1,3-dienyl(diphenyl)phosphine oxide (**3a**)*

Yellow oil; IR (neat): 3062, 2977, 2940, 2881, 1749, 1681, 1583, 1485, 1465, 1438, 1365, 1266, 1195, 1147, 1050, 990 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.74–7.67 (4H, m), 7.58–7.44 (7H, m), 6.15 (1H, d, J=22.2 Hz), 2.61 (2H, q, J=7.2 Hz), 1.16 (3H, t, J=7.2 Hz); ^{19}F NMR ($CDCl_3$): δ −59.27 (2F, d, J=15.8 Hz), −119.76 (1F, m); ^{31}P NMR ($CDCl_3$): δ 21.91; MS (ESI) m/z (%): 385. Anal. Calcd for $C_{19}H_{17}ClF_3OP$: C, 59.31; H, 4.45. Found: C, 59.38; H, 4.53.

*4.4.2. (Z)-2-((Z)-3-Chloro-2,3,3-trifluoroprop-1-enyl)hex-1-enyl(diphenyl)phosphine oxide (**3b**)*

White solid, mp: 87–88 °C; IR (KBr): 3059, 2962, 2933, 1677, 1583, 1487, 1459, 1437, 1373, 1265, 1185, 1146, 1120, 1052, 957 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.73–7.66 (4H, m), 7.55–7.44 (7H, m), 6.13 (1H, d, J=22.5 Hz), 2.56 (2H, t, J=7.2 Hz), 1.51–1.49 (2H, m), 1.41–1.36 (2H, m), 0.92 (3H, t, J=6.9 Hz); ^{19}F NMR ($CDCl_3$): δ −59.25 (2F, d, J=17.2 Hz), −119.72 (1F, m); ^{31}P NMR ($CDCl_3$): δ 21.69; MS (ESI) m/z (%): 413. Anal. Calcd for $C_{21}H_{21}ClF_3OP$: C, 61.10; H, 5.13. Found: C, 61.06; H, 5.12.

*4.4.3. (Z)-2-((Z)-3-Chloro-2,3,3-trifluoroprop-1-enyl)tetradec-1-enyl(diphenyl)phosphine oxide (**3c**)*

White solid, mp: 58–59 °C; IR (KBr): 3057, 2997, 2932, 2854, 1680, 1589, 1469, 1438, 1377, 1344, 1265, 1175, 1138, 1118, 1060, 962 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.73–7.66 (4H, m), 7.56–7.44 (7H, m), 6.12 (1H, d, J=22.5 Hz), 2.55 (2H, t, J=6.9 Hz), 1.52–1.49 (20H, m), 0.88 (3H, t, J=6.9 Hz); ^{19}F NMR ($CDCl_3$): δ −59.24 (2F, d, J=16.4 Hz), −119.71 (1F, m); ^{31}P NMR ($CDCl_3$): δ 21.77; MS (ESI) m/z (%): 525. Anal. Calcd for $C_{29}H_{37}ClF_3OP$: C, 66.34; H, 7.10. Found: C, 66.56; H, 6.80.

*4.4.4. (1E,3Z)-5-Chloro-2-(4-chlorophenyl)-4,5,5-trifluoropenta-1,3-dienyl(diphenyl)phosphine oxide (**3d**)*

White solid, mp: 144–145 °C; IR (KBr): 3059, 2991, 1683, 1592, 1557, 1490, 1438, 1401, 1361, 1264, 1232, 1183, 1142, 1096, 1033, 1014, 945 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.78–7.72 (4H, m), 7.59–7.49 (7H, m), 7.35–7.26 (4H, m), 6.45 (1H, d, J=20.7 Hz); ^{19}F NMR ($CDCl_3$): δ −59.84 (2F, d, J=17.4 Hz), −113.12 (1F, m); ^{31}P NMR ($CDCl_3$): δ 21.31; MS (ESI) m/z (%): 467. Anal. Calcd for $C_{23}H_{16}Cl_2F_3OP$: C, 59.12; H, 3.45. Found: C, 59.13; H, 3.67.

*4.4.5. (1E,3Z)-5-Chloro-4,5,5-trifluoro-2-(4-methoxyphenyl)penta-1,3-dienyl(diphenyl)phosphine oxide (**3e**)*

White solid, mp: 120–121 °C; IR (KBr): 3056, 2986, 2841, 1684, 1606, 1559, 1513, 1437, 1361, 1294, 1253, 1179, 1142, 1039, 940 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.80–7.73 (4H, m), 7.54–7.42 (6H, m), 7.35–7.31 (3H, m), 6.90 (2H, d, J=8.4 Hz), 6.45 (1H, d, J=20.3 Hz), 3.83 (3H, s); ^{19}F NMR ($CDCl_3$): δ −59.73 (2F, d, J=14.1 Hz), −114.22 (1F, m); ^{31}P NMR ($CDCl_3$): δ 21.35; MS (ESI) m/z (%): 463. Anal. Calcd for $C_{24}H_{19}ClF_3O_2P$: C, 62.28; H, 4.14. Found: C, 62.05; H, 4.39.

*4.4.6. (1E,3Z)-5-Chloro-4,5,5-trifluoro-2-(naphthalen-1-yl)penta-1,3-dienyl(diphenyl)phosphine oxide (**3f**)*

White solid, mp: 124–125 °C; IR (KBr): 3061, 2986, 1671, 1570, 1508, 1437, 1359, 1259, 1188, 1146, 1122, 1067, 1048, 993 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.15 (1H, d, J=33.0 Hz), 7.89–7.75 (7H, m), 7.56–7.35 (10H, m), 6.44 (1H, d, J=23.7 Hz); ^{19}F NMR ($CDCl_3$): δ −59.75 (2F, d, J=16.1 Hz), −115.56 (1F, m); ^{31}P NMR ($CDCl_3$): δ 21.48; MS (ESI) m/z (%): 483. Anal. Calcd for $C_{27}H_{19}ClF_3OP$: C, 67.16; H, 3.97. Found: C, 67.20; H, 3.93.

*4.4.7. Diethyl (1Z,3Z)-5-chloro-2-ethyl-4,5,5-trifluoropenta-1,3-dienylphosphonate (**3g**)*

Colorless oil; IR (neat): 3078, 2983, 2942, 1750, 1683, 1591, 1460, 1393, 1369, 1245, 1150, 1052, 965 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.27 (1H, d, J=38.4 Hz), 5.67 (1H, d, J=14.1 Hz), 4.09 (4H, q, J=7.5 Hz), 2.54 (2H, q, J=7.5 Hz), 1.33 (6H, t, J=7.5 Hz), 1.14 (3H, t, J=7.5 Hz); ^{19}F NMR ($CDCl_3$): δ −59.45 (2F, d, J=15.8 Hz), −119.68 (1F, m); ^{13}C NMR ($CDCl_3$): δ 153.42, 149.20 (dt, J_1=203.5 Hz, J_2=23.3 Hz), 119.37 (dd, J_1=151.9 Hz, J_2=3.1 Hz), 106.17, 61.85, 30.41, 16.29, 12.52; ^{31}P NMR ($CDCl_3$): δ 18.09; MS (ESI) m/z (%): 321; HRMS calcd for $C_{11}H_{18}ClO_3F_3OP$ (M+H): 321.0628; found: 321.0643.

*4.4.8. Diethyl (1Z,3Z)-4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-hexadecafluoro-2-octylundeca-1,3-dienylphosphonate (**3i**)*

Colorless oil; IR (neat): 3078, 2933, 2860, 1683, 1590, 1490, 1368, 1320, 1242, 1151, 1105, 1028, 966 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.31 (1H, dd, J_1=39.3 Hz, J_2=1.2 Hz), 5.69 (1H, d, J=14.4 Hz), 4.09 (4H, q, J=6.9 Hz), 2.49 (2H, t, J=7.8 Hz), 1.50–1.43 (2H, m), 1.35–1.27 (16H, m), 0.88 (3H, t, J=7.2 Hz); ^{19}F NMR ($CDCl_3$): δ −80.80 (3F, t, J=10.2 Hz), −117.15 (2F, m), −119.48 (1F, m), −121.93 (4F, m), −122.75 (4F, m), −126.15 (2F, m); ^{13}C NMR ($CDCl_3$): δ 151.94, 146.3 (dt, J_1=205.3 Hz, J_2=22.5 Hz), 120.79 (dd, J_1=137.7 Hz, J_2=2.7 Hz), 110.90, 61.88, 37.78, 31.78, 29.24, 29.11, 28.28, 22.61, 16.25, 16.18, 14.00; ^{31}P NMR ($CDCl_3$): δ 17.58; MS (ESI) m/z (%): 689; HRMS calcd for $C_{23}H_{30}F_{16}O_3P$ (M+H): 689.1672; found: 689.1650.

*4.4.9. Diethyl (1E,3Z)-4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-hexadecafluoro-2-(naphthalen-1-yl)undeca-1,3-dienylphosphonate (**3j**)*

Yellow oil; IR (neat): 3050, 2988, 1918, 1716, 1509, 1364, 1244, 1220, 1151, 1105, 1052, 1024, 970 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.88–7.86 (2H, m), 7.74–7.34 (2H, m), 7.52–7.43 (3H, m), 7.35–7.31 (1H, m), 5.96 (1H, d, J=17.7 Hz), 4.22 (4H, q, J=6.3 Hz), 1.38 (6H, t, J=6.3 Hz); ^{19}F NMR ($CDCl_3$): δ −80.76 (3F, t, J=10.2 Hz), −115.11 (1F, m), −117.49 (2F, m), −121.93 (4F, m), −122.73 (4F, m), −126.12 (2F, m); ^{13}C NMR ($CDCl_3$): δ 149.03, 147.4 (dt, J_1=207.3 Hz, J_2=24.0 Hz),

138.22, 138.00, 133.37, 130.38, 129.11, 128.52, 126.59, 125.41 (dd, J_1=124.4 Hz, J_2=3.5 Hz), 126.24, 125.18, 124.48, 111.47, 62.28, 16.38; ^{31}P NMR ($CDCl_3$): δ 16.26; MS (ESI) *m*/*z* (%): 703; HRMS calcd for $C_{25}H_{20}F_{16}O_3P$ (M+H): 703.0889; found: 703.0868.

4.5. Typical procedure for the reaction of 2 with organocopper reagents derived from *n*-BuLi

To a solution of CuCl (0.32 mmol) in THF (5 mL) was added 0.2 mL (0.32 mmol) of *n*-BuLi (1.6 M hexane solution) at −78 °C under an atmosphere of nitrogen. The mixture was stirred for 30 min and **2** (0.24 mmol) was added. After stirring at −78 °C for 3 h, the reaction mixture was allowed to warm to −10 °C and quenched with saturated NH_4Cl solution (10 mL), extracted with Et_2O (3×20 mL). The combined organic layer was washed with saturated NaCl solution (20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give **3**.

*4.5.1. Diethyl (1Z,3Z)-2-butyl-4,5,5,6,6,7,7,7-octafluorohepta-1,3-dienylphosphonate (**3h**)*

Yellow oil; IR (neat): 3065, 2938, 2878, 1683, 1590, 1373, 1350, 1235, 1188, 1122, 1054, 1029, 962 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.33 (1H, dd, J_1=39.0 Hz, J_2=1.8 Hz), 5.70 (1H, d, J=14.4 Hz), 4.14–4.04 (4H, m), 2.51 (2H, t, J=8.1 Hz), 1.50–1.40 (4H, m), 1.35 (6H, t, J=7.2 Hz), 0.93 (3H, t, J=7.2 Hz); ^{19}F NMR ($CDCl_3$): δ −80.95 (3F, t, J=9.3 Hz), −118.37 (2F, m), −119.97 (1F, m), −127.31 (2F, m); ^{13}C NMR ($CDCl_3$): δ 151.85, 146.41 (dt, J_1=275.4 Hz, J_2=27.7 Hz), 120.74 (dd, J_1=182.6 Hz, J_2=4.1 Hz), 110.65, 61.80, 37.41, 30.35, 22.15, 16.13, 13.57; ^{31}P NMR ($CDCl_3$): δ 15.20; MS (EI) *m*/*z* (%): 390 (81.69), 375 (6.19), 43 (100.00); HRMS calcd for $C_{15}H_{21}F_8O_3P$: 432.1101; found: 432.1107.

*4.5.2. (2Z,4Z)-Ethyl 3-butyl-5,6,6,7,7,8,8,8-octafluoroocta-2,4-dienoate (**3k**)*

Yellow oil; IR (neat): 3094, 2966, 2939, 2879, 1717, 1683, 1614, 1469, 1383, 1355, 1235, 1157, 1122, 1037, 963 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.54 (1H, d, J=39.9 Hz), 5.86 (1H, s), 4.19 (2H, q, J=7.2 Hz), 2.47 (2H, t, J=7.8 Hz), 1.50–1.32 (4H, m), 1.30 (3H, t, J=7.2 Hz), 0.93 (3H, t, J=7.2 Hz); ^{19}F NMR ($CDCl_3$): δ −81.44 (3F, t, J=10.8 Hz), −118.81 (2F, m), −119.87 (1F, m), −127.79 (2F, m); ^{13}C NMR ($CDCl_3$): δ 165.40, 148.31, 122.34, 110.05, 60.45, 36.22, 30.58, 22.65, 14.10, 13.72; MS (EI) *m*/*z* (%): 368 (4.48), 339 (8.04), 326 (94.86), 171 (100.00); HRMS calcd for $C_{14}H_{16}F_8O_2$: 368.1023; found: 368.1022.

4.6. Typical procedure for the reaction of 2 with organocopper reagents derived from Grignard reagents and electrophiles

Under nitrogen atmosphere, CuCl (2 mmol) was added to the solution of ethylmagnesium bromide in THF (10 mL) prepared from magnesium turning (2 mmol) and ethyl bromide (2 mmol) at −40 °C. After stirring for 30 min at that temperature, the reaction mixture was cooled to −78 °C and a solution of **2** (0.5 mmol) in THF (2 mL) was added. The resulted mixture was stirred at −78 °C for 1 h, then allyl bromide or iodine (2 mmol) was added slowly to the mixture. After stirring for 2 h, the mixture was allowed to warm to room temperature and quenched with saturated NH_4Cl solution (20 mL). The resulted mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with saturated NaCl solution (20 mL) (in the case of iodine, the solution of $Na_2S_2O_3$ was added until the color disappeared), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give **4**.

*4.6.1. (4Z,6Z)-8-Chloro-5-ethyl-7,8,8-trifluoroocta-1,4,6-trien-4-yl(diphenyl)phosphine oxide (**4a**)*

White solid, mp: 87–88 °C; IR (KBr): 3078, 2977, 2941, 1680, 1636, 1574, 1483, 1470, 1434, 1358, 1314, 1269, 1176, 1140, 1116, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.69–7.64 (4H, m), 7.52–7.44 (6H, m), 7.34 (1H, d, J=77.8 Hz), 5.44–5.34 (1H, m), 4.89 (1H, d, J=10.2 Hz), 4.78 (1H, d, J=17.1 Hz), 2.99 (2H, dd, J_1=16.8 Hz, J_2=5.7 Hz), 2.57 (2H, q, J=7.4 Hz), 1.11 (3H, t, J=7.4 Hz); ^{19}F NMR ($CDCl_3$) δ −59.19 (2F, d, J=15.2 Hz), −122.15 (1F, m); ^{13}C NMR ($CDCl_3$): δ 150.18, 147.11 (dt, J_1=201.9 Hz, J_2=24.1 Hz), 132.73 (d, J=118.0 Hz), 131.87, 131.84, 131.74, 128.51, 128.39, 116.79, 108.07, 34.47, 25.88, 12.90; ^{31}P NMR ($CDCl_3$): δ 31.47; MS (ESI) *m*/*z* (%): 425. Anal. Calcd for $C_{22}H_{21}ClF_3OP$: C, 62.20; H, 4.98. Found: C, 62.02; H, 4.93.

*4.6.2. (1E,3Z)-5-Chloro-2-ethyl-4,5,5-trifluoro-1-iodopenta-1,3-dienyl(diphenyl)phosphine oxide (**4b**)*

Colorless oil; IR (neat): 3062, 2983, 2938, 1725, 1672, 1592, 1485, 1439, 1265, 1176, 1130, 1061 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82–7.65 (5H, m), 7.57–7.45 (6H, m), 2.82 (2H, q, J=7.8 Hz), 1.12 (3H, t, J=7.8 Hz); ^{19}F NMR ($CDCl_3$): δ −59.25 (2F, m), −119.26 (1F, m); ^{13}C NMR ($CDCl_3$): δ 156.94, 146.81 (dt, J_1=203.85 Hz, J_2=23.2 Hz), 132.40, 132.30, 131.47 (d, J=82.5 Hz), 128.48, 128.35, 106.40, 37.64, 11.63; ^{31}P NMR ($CDCl_3$): δ 32.42; MS (ESI) *m*/*z* (%): 511; HRMS calcd for $C_{19}H_{17}ClF_3IOP$ (M+H): 510.9697; found: 510.9715.

4.7. Typical procedure for the reaction of 2 with organocopper reagents derived from *n*-BuLi and electrophiles

To a solution of CuCl (0.32 mmol) in THF (5 mL) was added 0.2 mL (0.32 mmol) of *n*-BuLi (1.6 M hexane solution) at −78 °C under an atmosphere of nitrogen. After stirring for 30 min, **2** (0.27 mmol) was added. The mixture was stirred at −78 °C for 1 h. Then allyl bromide, phenylselenyl bromide or iodine (1 mmol) was added dropwise or in portion. After stirring for 2 h, the mixture was allowed to warm to room temperature and quenched with saturated NH_4Cl solution (10 mL). The resulted mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with saturated NaCl solution (20 mL) (in the case of iodine, the solution of $Na_2S_2O_3$ was added until the color disappeared), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give **4**.

*4.7.1. (1E,3Z)-2-Butyl-4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-hexadecafluoro-1-iodoundeca-1,3-dienyl(diphenyl)phosphine oxide (**4c**)*

White solid, mp: 75–76 °C; IR (KBr): 3066, 2971, 2939, 1666, 1519, 1439, 1371, 1206, 1151, 1118, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.81–7.67 (5H, m), 7.59–7.42 (6H, m), 2.83 (2H, t, J=7.2 Hz), 1.52–1.41 (4H, m), 0.95 (3H, t, J=7.2 Hz); ^{19}F NMR ($CDCl_3$): δ −80.86 (3F, t, J=8.7 Hz), −117.25 (2F, m), −119.42 (1F, m), −121.99 (4F, m), −122.76 (4F, m), −126.18 (2F, m); ^{31}P NMR ($CDCl_3$): δ 31.98; MS (ESI) *m*/*z* (%): 823. Anal. Calcd for $C_{27}H_{20}F_{16}OP$: C, 39.44; H, 2.45. Found: C, 39.73; H, 2.40.

*4.7.2. Diethyl (4Z,6Z)-5-butyl-7,8,8,9,9,10,10,10-octafluorodeca-1,4,6-trien-4-ylphosphonate (**4d**)*

Yellow oil; IR (neat): 3083, 2984, 2936, 2877, 1679, 1639, 1575, 1447, 1393, 1349, 1233, 1188, 1158, 1121, 1027, 954 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 (1H, dd, J_1=39.3 Hz, J_2=2.1 Hz), 5.86–5.77 (1H, m), 5.13–5.07 (2H, m), 4.14–3.99 (4H, m), 3.18 (2H, dd, J_1=17.4 Hz, J_2=5.7 Hz), 2.49 (2H, t, J=7.8 Hz), 1.38–1.33 (4H, m), 1.30 (6H, t, J=7.2 Hz), 0.92 (3H, t, J=6.9 Hz); ^{19}F NMR ($CDCl_3$): δ −81.01 (3F, m), −118.17 (2F, m), −123.44 (1F, m), −127.36 (2F, m); ^{13}C NMR ($CDCl_3$): δ 147.12, 144.24 (dt, J_1=204.1 Hz, J_2=22.3 Hz), 134.56, 130.74 (d, J=132.4 Hz), 116.24, 113.09, 61.94, 34.09, 31.80, 30.60, 22.83, 16.15,

13.69; ^{31}P NMR ($CDCl_3$): δ 18.46; MS (ESI) m/z (%): 473; HRMS calcd for $C_{18}H_{26}F_8O_3P$ (M+H): 473.1486; found: 473.1484.

*4.7.3. Diethyl (1E,3Z)-2-butyl-4,5,5,6,6,7,7,7-octafluoro-1-iodohepta-1,3-dienylphosphonate (**4e**)*

Yellow oil; IR (neat): 3080, 2966, 2936, 2877, 1676, 1532, 1469, 1393, 1365, 1233, 1160, 1122, 1025, 961 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47 (1H, dd, J_1=37.5 Hz, J_2=2.4 Hz), 4.20–4.05 (4H, m), 2.79 (2H, t, J=7.5 Hz), 1.49–1.43 (4H, m), 1.36 (6H, t, J=7.2 Hz), 0.96 (3H, t, J=6.9 Hz); ^{19}F NMR ($CDCl_3$): δ −80.84 (3F, t, J=9.9 Hz), −118.31 (2F, m), −119.91 (1F, m), −127.19 (2F, m); ^{13}C NMR ($CDCl_3$): δ 154.57, 144.09 (dt, J_1=275.2 Hz, J_2=26.6 Hz), 110.60, 97.57 (d, J=186.2 Hz), 63.15, 42.80, 29.32, 22.53, 15.99, 13.69; ^{31}P NMR ($CDCl_3$): δ 9.28; MS (ESI) m/z (%): 559; HRMS calcd for $C_{15}H_{21}F_8IO_3P$ (M+H): 559.0140; found: 559.0130.

*4.7.4. Diethyl (1E,3Z)-2-butyl-4,5,5,6,6,7,7,7-octafluoro-1-(phenylselanyl)hepta-1,3-dienylphosphonate (**4f**)*

Yellow oil; IR (neat): 3075, 2964, 2935, 2876, 1674, 1579, 1531, 1478, 1440, 1364, 1233, 1188, 1159, 1122, 1052, 1024, 963 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.44 (1H, dd, J_1=38.1 Hz, J_2=2.1 Hz), 7.36–7.33 (2H, m), 7.18–7.15 (3H, m), 3.99–3.79 (4H, m), 2.83 (2H, t, J=7.2 Hz), 1.25–1.19 (4H, m), 1.11 (6H, t, J=6.9 Hz), 0.78 (3H, t, J=6.9 Hz); ^{19}F NMR ($CDCl_3$): δ −80.86 (3F, t, J=9.6 Hz), −118.18 (2F, m), −120.03 (1F, m), −127.13 (2F, m); ^{13}C NMR ($CDCl_3$): δ 156.40, 144.84 (dt, J_1=267.2 Hz, J_2=27.2 Hz), 131.83, 131.1, 129.95 (d, J=104.0 Hz), 129.18, 127.08, 112.53, 62.64, 37.53, 30.80, 22.64, 16.10, 13.58; ^{31}P NMR ($CDCl_3$): δ 13.47; MS (ESI) m/z (%): 588; HRMS calcd for $C_{21}H_{25}F_8O_3PSe$ (M+Na): 611.0471; found: 611.0467.

*4.7.5. Diethyl (4Z,6Z)-5-butyl-7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-hexadecafluorotetradeca-1,4,6-trien-4-ylphosphonate (**4g**)*

Yellow oil; IR (neat): 3080, 2962, 2930, 2871, 1700, 1678, 1629, 1464, 1362, 1245, 1211, 1151, 994 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.43 (1H, dd, J_1=41.1 Hz, J_2=2.4 Hz), 5.86–5.73 (1H, m), 5.14–5.07 (2H, m), 4.14–3.99 (4H, m), 3.18 (2H, dd, J_1=17.7 Hz, J_2=5.7 Hz), 2.48 (2H, t, J=9.3 Hz), 1.43–1.35 (4H, m), 1.31 (6H, t, J=6.9 Hz), 0.92 (3H, t, J=7.5 Hz); ^{19}F NMR ($CDCl_3$) δ −80.91 (3F, t, J=10.7 Hz), 117.00 (2F, m), −121.99 (4F, m), −123.03 (4F, m), −123.16 (1F, m), −126.23 (2F, m); ^{13}C NMR ($CDCl_3$) δ 147.14, 144.42 (dt, J_1=202.4 Hz, J_2=24.1 Hz), 134.60, 130.86 (d, J=129.6 Hz), 116.20, 113.19, 61.87, 34.11, 31.78, 30.62, 22.82, 16.12, 13.63; ^{31}P NMR ($CDCl_3$) δ 18.39; MS (ESI) m/z (%): 673; HRMS calcd for $C_{22}H_{26}F_{16}IO_3P$ (M+H): 673.1359; found: 673.1368.

*4.7.6. (2E,4Z)-Ethyl 3-butyl-5,6,6,7,7,8,8,8-octafluoro-2-iodoocta-2,4-dienoate (**4h**)*

Yellow oil; IR (neat): 3090, 2966, 2938, 2879, 1727, 1468, 1350, 1233, 1123, 1031, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.56 (1H, d, J=35.7 Hz), 4.26 (2H, q, J=7.2 Hz), 2.64 (2H, t, J=7.8 Hz), 1.42–1.35 (4H, m), 1.30 (3H, t, J=6.9 Hz), 0.93 (3H, t, J=7.2 Hz); ^{19}F NMR ($CDCl_3$): δ −81.23 (3F, m); −118.99 (2F, m), −121.77 (1F, m), −127.76 (2F, m); ^{13}C NMR ($CDCl_3$): δ 164.91, 145.48, 144.37 (dt, J_1=194.3 Hz, J_2=20.6 Hz), 110.13, 96.27, 62.72, 40.55, 29.31, 22.50, 14.07, 13.67; MS (EI) m/z (%): 494 (12.22), 449 (11.36), 424 (49.68), 297 (100.00); HRMS calcd for $C_{14}H_{15}F_8IO_2$: 493.9989; found: 493.9995.

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References and notes

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7. The crystal structure of **2c** has been deposited as supplementary publication No. CCDC-691263 at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.