Convenient and Efficient Access to Fluoroalkylated Vinylphosphonates via Highly Regio- and Stereoselective Hydrometalation or Carbometalation Reactions of Fluorine-Containing Alkynylphosphonates

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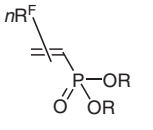
Abstract: The hydrostannation, carbocupration, and carbozincation reactions of fluorinated alkynylphosphonates were investigated. The hydrostannation reaction proceeded smoothly without an additive (e.g., BEt_3/O_2, AIBN) to give the corresponding vinylstannanes in a highly regio- and stereoselective manner. Various cuprates, prepared from organolithium, Grignard, and organozinc reagents, could participate nicely in the carbocupration reactions, the corresponding adducts were obtained in good to high yields. Dialkylzinc reagents reacted smoothly with the alkynylphosphonates even in the absence of copper salt to afford the corresponding adducts in good yields.

Key words: fluoroalkenes, alkynylphosphonates, hydrostannation, carbocupration, carbozincation, regioselective, stereoselective

Vinylphosphonates are recognized as extremely valuable compounds because of their widespread applications.[1] They are employed as synthetic intermediates in the preparation of biologically and pharmacologically active molecules,[2] as well as in other organic transformations,[3] and they are utilized in polymers,[4] agricultural chemicals,[5] or flame retardants.[6]

Fluorine-containing materials are also very important molecules and have attracted great interest in recent years in the medicinal, pharmaceutical, and agricultural fields, among others, owing to the enhanced biological or physiological activity exerted by fluorine(s).[7] Consequently, it is not surprising that much effort has recently been devoted towards the development of new methodologies for the synthesis of fluorinated vinylphosphonates **1** (Figure 1).[8]

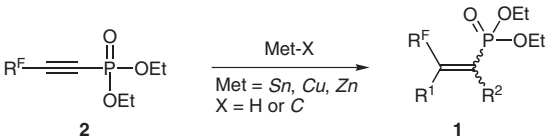
However, to the best of our knowledge, methods for the stereoselective preparation of such molecules are still quite limited. We now report in detail a new synthetic method for the preparation of fluoroalkylated vinylphosphonates **1** via highly regio- and stereoselective hydrometalation and carbometalation reactions of fluorine-containing alkynylphosphonates **2** (Scheme 1).



1

R^F = F, CF_3, CHF_2, etc.

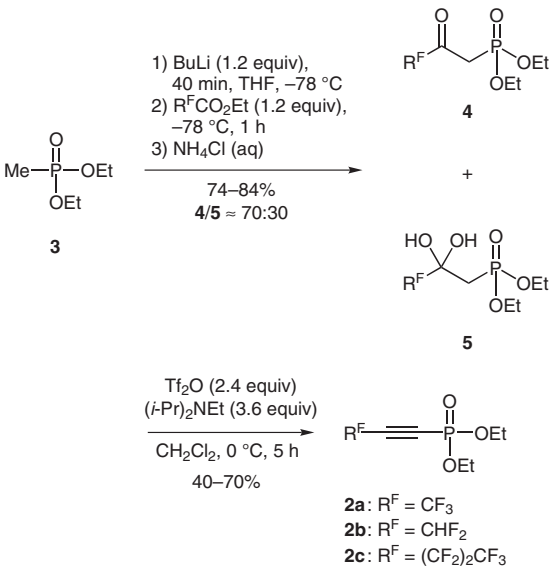
Figure 1



2 **1**

R^F = CHF_2, CF_3, $H(CF_2)_3$

Scheme 1 Intended research program



3 **4** **5**

2a: $R^F = CF_3$
2b: $R^F = CHF_2$
2c: $R^F = (CF_2)_2CF_3$

Scheme 2 Preparation of fluorinated alkynylphosphonates **2a–c**

The starting phosphonates **2** were prepared with slight modifications of the reported procedure (Scheme 2).[9] Thus, treatment of diethyl methylphosphonate (**3**) with butyllithium (1.2 equiv) at –78 °C for 40 minutes followed by addition of ethyl perfluoroalkanoate (1.2 equiv) gave the mixture of β-ketophosphonate **4** and its hydrate **5** in 74–84% yield in a ratio of ca. 70:30. This mixture was subjected to trifluoromethansulfonic anhydride (2.4 equiv) and *N*,*N*-diisopropylethylamine (3.6 equiv) in dichloromethane at 0 °C for five hours, the desired fluorinated alkynylphosphonates **2a–c** were obtained in 40–70% yield.

Initial studies with the thus-obtained alkynylphosphonates **2** focused on the hydrostannation reaction (Table 1).

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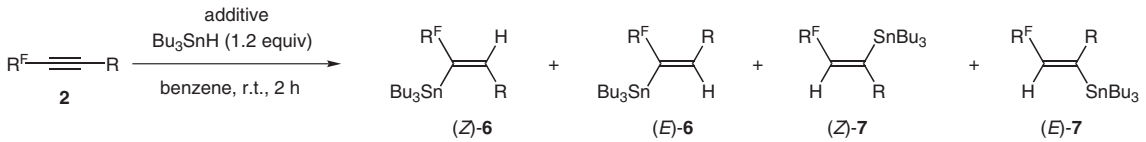
Table 1 Hydrostannation Reaction of Fluorine-Containing Alkynylphosphonates



Entry	R^F	R	Additive	Yield[a] (%) of **6** + **7**	Ratio[a]	
					6/7	*Z*/*E*
1[b]	CF_3	4-ClC_6H_4	Et_3B	99 (95)[10]	100:0	**6a**: 100:0
2[b]	CF_3	4-$MeOC_6H_4$	Et_3B	99 (90)[10]	100:0	**6b**: 98:2
3[b]	CF_3	4-ClC_6H_4	–	3[10]	100:0	**6a**: 100:0
4[b]	CF_3	4-$EtO_2CC_6H_4$	–	65[10]	35:65	**6c**: 0:100, **7c**: 0:100
5[b]	CF_3	4-$O_2NC_6H_4$	–	65[10]	21:79	**6d**: 0:100, **7d**: 0:100
6	CF_3	$P(O)(OEt)_2$	–	99 (91)	0:100	**7e**: 100:0
7	CHF_2	$P(O)(OEt)_2$	–	72 (69)	0:100	**7f**: 100:0
8	$(CF_2)_2CF_3$	$P(O)(OEt)_2$	–	66 (50)	0:100	**7g**: 100:0

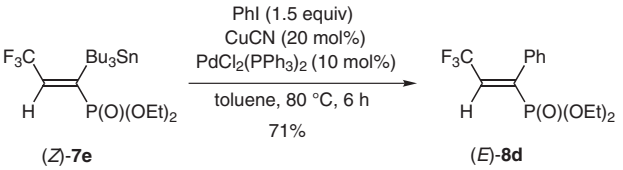
[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[b] Performed in toluene at 0 °C for 4 h.

We have already reported the hydrostannation reaction of fluoroalkylated alkynes containing various aromatic substituents.[10] Thus, as shown in Table 1, entries 1–3, the alkynes bearing halogen or an electron-donating group on the benzene ring underwent hydrostannation only in the presence of a catalytic amount of triethylborane, giving the corresponding vinylstannanes (*Z*)-**6a–c** in a highly regio- and stereoselective manner. On the other hand, the reaction of the alkynes bearing an electron-withdrawing group on the benzene ring took place smoothly even in the absence of triethylborane to give a mixture of (*E*)-**6** and (*E*)-**7** isomers in a ratio of ca. 30:70 (Table 1, entries 4 and 5).

Very surprisingly, treatment of diethyl 3,3,3-trifluoroprop-1-ynylphosphonate (**2a**) with tributylstannane without any additive in benzene at room temperature for two hours gave the corresponding *Z*-adduct (*Z*)-**7e**, exclusively (Table 1, entry 6). As shown in entries 7 and 8, changing the fluoroalkyl group from trifluoromethyl to difluoromethyl, or heptafluoropropyl did not influence the reaction, (*Z*)-**7f** and (*Z*)-**7g** were obtained with excellent regio- and stereoselectivity.

The obtained vinylstannane (*Z*)-**7e** was subjected to the Stille coupling reaction (Scheme 3).[11] Thus, treatment of (*Z*)-**7e** with iodobenzene (1.5 equiv) in the presence of copper(I) cyanide (20 mol%) and dichlorobis(triphenylphosphine)palladium(II) (10 mol%) in toluene at 80 °C for six hours gave the corresponding coupling product (*E*)-**8d** in 71% yield.

We next examined the carbocupration reaction using various carbon nucleophiles, such as organolithium, Grignard, and organozinc reagents,[12] as summarized in Table 2.

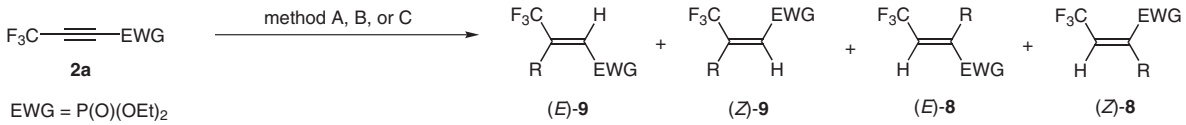


Scheme 3 Stille coupling of a fluorine-containing vinylstannane with iodobenzene

The reaction of **2a** with butyllithium in the absence of copper salts was investigated (Table 2, entry 1). Thus, treatment of **2a** with butyllithium (2.4 equiv) in tetrahydrofuran at –60 °C for two hours afforded a complex mixture; none of the desired product was detected. On the other hand, the addition of an equimolar amount of copper(I) cyanide had a significant influence on the reaction. Thus, the desired alkenylphosphonate (*Z*)-**9a** was obtained exclusively (Table 2, entry 2); no other regio- and stereoisomers were observed. Similarly, various organolithium reagents were investigated. Methyllithium and *sec*-butyllithium were found to be good reagents for this carbocupration reaction, affording the corresponding adducts in high yields with high regio- and stereoselectivity (Table 2, entries 3 and 4). The use of phenyllithium caused a slight decrease of the chemical yield, while the regio- and stereoselectivity still remained excellent (Table 2, entry 5).

We also studied the reaction using various Grignard reagents as shown in Table 2, entries 6–15. The employment of butylmagnesium bromide without a copper salt resulted in complete consumption of the starting alkyne but with the formation of a very low yield of the adduct, though (*E*)-**9a** was obtained exclusively. As shown in entries 7–10, alkyl Grignard reagents (e.g., BuMgBr,

Table 2 Carbocupration or Carbozincation Reaction of Trifluoromethylated Acetylenic Phosphonates



Entry	Organometallic reagent (R-Met)	Method[a]	Product **9**, **8**	Yield[b] (%) of **9** + **8**	Isomer ratio[b]	
					9/8	*E*/*Z*
1	BuLi	A[c]	**a**	0	100:0	**9a**: 0:100
2	BuLi	A	**a**	99 (75)	100:0	**9a**: 0:100
3	MeLi	A	**b**	86 (79)	100:0	**9b**: 0:100
4	*s*-BuLi	A	**c**	72 (64)	100:0	**9c**: 0:100
5	PhLi	A	**d**	54 (44)	100:0	**9d**: 0:100
6	BuMgBr	B[c]	**a**	13	100:0	**9a**: 100:0
7	BuMgBr	B	**a**	99 (91)	100:0	**9a**: 5:95
8	MeMgBr	B	**b**	73 (69)	100:0	**9b**: 0:100
9	CyMgBr	B	**e**	61 (53)	100:0	**9e**: 1:99
10	*s*-BuMgBr	B	**c**	70 (51)	100:0	**9c**: 2:98
11	PhMgBr	B	**d**	81 (61)	100:0	**9d**: 13:87
12	4-$F_3CC_6H_4MgBr$	B	**f**	86 (69)	100:0	**9f**: 21:79
13	4-$MeOC_6H_4MgBr$	B	**g**	79 (78)	100:0	**9g**: 9:91
14	3-$MeOC_6H_4MgBr$	B	**h**	93 (82)	100:0	**9h**: 10:90
15	2-$MeOC_6H_4MgBr$	B	**i**	62 (53)	100:0	**9i**: 19:81
16	Et_2Zn	A[c]	**j**	20[d]	100:0	**9j**: 64:36
17	Et_2Zn	A	**j**	79 (61)	62:38	**9j**: 0:100 **8j**: 0:100
18	Me_2Zn	A	**b**	73 (62)	100:0	**9b**: 0:100
19	*i*-Pr_2Zn	A	**k**	84 (69)	85:15	**9k**: 0:100 **8k**: 0:100
20	Ph_2Zn	A	**d**	75 (67)	100:0	**9d**: 0:100
21	Et_2Zn	C	**j**	77 (71)	100:0	**9j**: 62:38
22	Me_2Zn	C	**b**	13[e]	100:0	**9b**: 0:100
23[f]	Me_2Zn	C	**b**	7[g]	100:0	**9b**: 0:100
24	*i*-Pr_2Zn	C	**k**	22[h]	100:0	**9k**: 0:100
25[f]	*i*-Pr_2Zn	C	**k**	87 (45)	100:0	**9k**: 6:94
26	Ph_2Zn	C	**d**	68 (39)	100:0	**9d**: 40:60

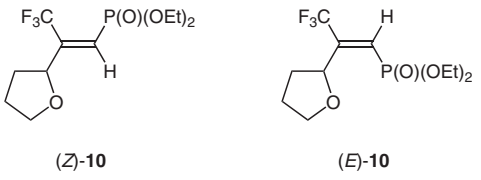
[a] Method A: 1. RLi or R_2Zn, CuCN, THF, –60 °C, 2 h, 2. aq NH_3–MeOH; Method B: 1. RMgBr, CuCN, THF, –60 °C, 2 h, 2. aq NH_3–MeOH; Method C: R_2Zn, THF, –40 °C, 14 h, 2. aq NH_4Cl.
[b] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[c] In the absence of CuCN.
[d] The starting alkyne was recovered in 44% yield.
[e] The product (*Z*)-**10** was obtained in 37% yield.
[f] Hexane was used as solvent instead of THF.
[g] The starting material was recovered in only 24% yield.
[h] The product (*E*)-**10** was obtained in 34% yield.

MeMgBr, CyMgBr, and *s*-BuMgBr) gave the corresponding trisubstituted adducts (*Z*)-**9** in a highly regio- and stereoselective manner in good to high yields. However, switching the Grignard reagents from alkyl to aryl Grignard reagents, such as phenyl-, 4-(trifluoromethyl)phenyl-, 4-, 3-, and 2-methoxyphenylmagnesium bromide, caused a slight decrease of the stereoselectivity (ratio for **9** *E*/*Z* 20:80–10:90) (Table 2, entries 11–15). Additionally, we examined the reaction with commercially available organozinc reagents as described in Table 2, entries 16–20. Even in the absence of copper(I) cyanide, diethylzinc could react with **2a** to give the corresponding adducts, (*E*)-**9j** and (*Z*)-**9j** in 20% yield, together with 44% of the recovered alkyne (Table 2, entry 16).[13] The addition of copper(I) cyanide brought about a significant improvement of the chemical yields. As shown in entries 17 and 19, diethylzinc or diisopropylzinc could participate nicely in the carbocupration reaction, (*Z*)-**9j**,**k** and (*Z*)-**8j**,**k** were obtained in good to high yields as an isomeric mixture.

Very interestingly, dimethylzinc and diphenylzinc were found to be good reagents, the adducts (*Z*)-**9b**,**d** were afforded in a highly regio- and stereoselective manner (Table 2, entries 18 and 20); no other regio- and stereoisomers were detected.

Finally, we attempted the carbozincation reaction because diethylzinc reacted with **2a** even in the absence of a copper salt to give the carbometalated adduct together with the recovery of a large amount of the starting material (Table 2, entry 16). After several attempts, we found that **2a** reacted smoothly with 2.4 equivalents of diethylzinc in tetrahydrofuran at –40 °C for 14 hours to give the corresponding adduct **9j** in 77% yield as a stereoisomeric mixture (Table 2, entry 21). However, dimethylzinc and diisopropylzinc were observed to be less reactive, the desired products were obtained in poor yields (Table 2, entries 22 and 24). After careful examination, it was found that the low yields resulted from the formation of (*Z*)-**10** or (*E*)-**10** in the reaction in 37% or 34% yield, respectively, with dimethylzinc or diisopropylzinc (Figure 2). As the tetrahydro-2-furyl moiety in these byproducts may come from the solvent, we performed the reaction of **2a** with dimethyl- or diisopropylzinc in hexane, instead of tetrahydrofuran. As a result, the reaction with diisopropylzinc took place smoothly, the desired adduct (*Z*)-**9k** was afforded preferentially in high yield (Table 2, entry 25), while dimethylzinc did not give a satisfactory result (Table 2, entry 23). It is noteworthy that the use of diphenylzinc caused a significant decrease of the stereoselectivity, (*E*)-**9d** and (*Z*)-**9d** were obtained in a stereorandom manner in a good yield (Table 2, entry 26).

The structures of new compounds (*E*)-**8d**, (*E*)-**9a–k**, (*Z*)-**10**, and (*E*)-**10** were confirmed by ^{19}F and ^{13}C NMR spectroscopy (Table 3).[14] Thus, the doublet (^3J = 7.5 Hz) in ^{19}F NMR was assigned to the CF_3CH= group, while the singlets in ^{19}F NMR are characteristic for CF_3CR= (R ≠ H). In the ^{13}C NMR analysis, the small $^3J_{C1\text{-}P}$ (~10 Hz) or the large $^3J_{C2\text{-}P}$ coupling constants (15–32 Hz) are consistent



(*Z*)-**10** (*E*)-**10**

37% [$R_2Zn = Me_2Zn$] 34% [$R_2Zn = (i\text{-}Pr)_2Zn$]

Figure 2 Byproduct in the case of the carbozincation with dimethylzinc or diisopropylzinc

with the *Z* or *E* configuration of R^1 or R^2 with respect to phosphorus, respectively.

The vinylstannanes (*Z*)-**7e–g** were determined as the *Z*-isomer based on the stereochemistry of (*Z*)-**8d** as well as the chemical shifts of ^{19}F NMR spectra.

In summary, we have investigated the hydrostannation, carbocupration, and carbozincation reactions of fluorinated alkynylphosphonates in detail. The hydrostannation took place smoothly even in the absence of triethylborane, giving the corresponding *Z*-adducts exclusively in good to high yields. The reaction with various copper reagents derived from organolithium, Grignard, and organozinc reagents, also proceeded smoothly to give the corresponding *Z*-adducts in a highly regio- and stereoselective manner. Additionally, organozinc reagents, which are well known to be much less reactive, than organolithium and Grignard reagents, reacted smoothly with fluorinated alkynylphosphonates even in the absence of a copper salt at –40 °C, the corresponding adducts were obtained in good to high yields.

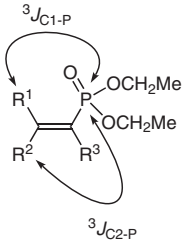
IR spectra were taken on a JASCO FT/IR-4100 type A spectrophotometer; film on a NaCl plate. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-500 NMR spectrometer and a JEOL JNM-AL 400 NMR spectrometer in $CDCl_3$ soln with TMS as internal reference. A JEOL JNM-EX90A (84.21 MHz) FT-NMR spectrometer and a JEOL JNM-AL 400 NMR spectrometer were used for determining the yield of the products with C_6F_6. ^{19}F NMR (376.05 MHz) spectra was measured with a JEOL JNM-AL 400 NMR spectrometer in $CDCl_3$ soln with $CFCl_3$ as internal standard. ^{31}P NMR (161.70 MHz) spectra was measured with a JEOL JNM-AL 400 NMR spectrometer in $CDCl_3$ soln with Ph_3P as external standard. ^{13}C and ^{31}P NMR spectra were proton decoupled. HRMS were taken on a Hitachi M-80B mass spectrometer by EI, CI, and FAB methods.

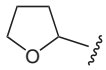
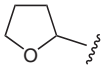
All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. TLC was performed on aluminum sheets coated with Merck silica gel 60 F_{254} plates, and column chromatography was carried out using Wacogel C-200 as adsorbent.

Diethyl (*Z*)-3,3,3-Trifluoro-1-(tributylstannyl)prop-1-enylphosphonate [(*Z*)-7e]; Typical Procedure for Hydrostannation

To a soln of diethyl 3,3,3-trifluoroprop-1-ynylphosphonate (**2a**, 60 mg, 0.25 mmol) in benzene (3 mL) was added Bu_3SnH (87 mg, 0.3 mmol) at r.t. and the soln was stirred at r.t. for 2 h. The mixture was quenched with aq NH_4Cl and it was then extracted with EtOAc (3 ×). The combined organic layers were dried (anhyd Na_2SO_4) and concentrated in vacuo. The residue was chromatographed (silica gel, hexane–EtOAc, 3:1) to afford (*Z*)-**7e** (0.119 g, 91%).

Table 3 Determination of the Stereochemistry with the C–P Coupling Constants



Compound	R^1	R^2	R^3	$^3J_{C1-P}$ (Hz)	$^3J_{C2-P}$ (Hz)	Multiplicity[a]
(*E*)-**8d**	H	CF_3	Ph	–	31.4	d[b]
(*Z*)-**8j**	CF_3	H	Et	9.6	–	d[b]
(*Z*)-**9a**	CF_3	Bu	H	9.0	16.8	s
(*Z*)-**9b**	CF_3	Me	H	8.3	19.0	s
(*Z*)-**9c**	CF_3	*s*-Bu	H	9.7	15.5	s
(*Z*)-**9d**	CF_3	Ph	H	8.3	18.4	s
(*Z*)-**9e**	CF_3	Cy	H	9.8	15.5	d[c]
(*E*)-**9j**	Et	CF_3	H	5.8	32.2	s
(*Z*)-**9j**	CF_3	Et	H	9.6	17.3	s
(*Z*)-**10**	CF_3		H	9.1	15.0	s
(*E*)-**10**		CF_3	H	6.6	30.6	s

[a] In ^{19}F NMR.
[b] $^3J_{F-H}$ coupling = 7.5 Hz.
[c] A long-range coupling, $^4J_{F-P}$ = 4.9 Hz.

IR (neat): 2958, 2924, 2873, 2856, 1465, 1392, 1378, 1319, 1278, 1246, 1146, 1026, 962, 911, 877, 841, 794, 748, 671 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 9 H), 1.11–1.13 (m, 6 H), 1.31–1.34 (m, 12 H), 1.48 (m, 6 H), 4.01–4.13 (m, 4 H), 7.23 (qd, *J* = 7.5, 34.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.78, 13.42, 16.16, 26.96, 28.52, 61.81 (d, *J* = 5.6 Hz), 122.25 (dq, *J* = 37.6, 268.4 Hz), 141.48 (q, *J* = 34.7 Hz), 147.10 (qd, *J* = 5.5, 124.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.69 (d, *J* = 7.5 Hz, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.01 (s, 1 P).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{39}F_3O_3PSn$: 521.1454; found: 521.1426.

Diethyl (*Z*)-3,3-Difluoro-1-(tributylstannyl)prop-1-enylphosphonate [(*Z*)-7f]

IR (neat): 2958, 2959, 2872, 2855, 1704, 1464, 1363, 1244, 1131, 1081, 1030, 962, 882, 795, 740 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 9 H), 1.06–1.10 (m, 6 H), 1.27–1.34 (m, 12 H), 1.44–1.50 (m, 6 H), 4.03–4.07 (m, 4 H), 6.04 (ddt, *J* = 2.2, 5.5, 55.5 Hz, 1 H), 7.21 (dtd, *J* = 5.5, 8.8, 33.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.86, 13.53, 16.32 (d, *J* = 6.4 Hz), 27.10, 28.65, 61.76 (d, *J* = 6.1 Hz), 113.86 (dt, *J* = 41.4, 237.7 Hz), 144.12 (td, *J* = 10.9, 128.0 Hz), 147.65 (t, *J* = 25.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –112.26 (dd, *J* = 7.1, 56.0 Hz, 2 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.30–22.40 (m, 1 P).

HRMS (FAB): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{39}F_2NaO_3PSn$: 527.1527; found: 527.1539.

Diethyl (*Z*)-3,3,4,4,5,5,5-Heptafluoro-1-(tributylstannyl)pent-1-enylphosphonate [(*Z*)-7g]

IR (neat): 2959, 2925, 2873, 1604, 1456, 1353, 1231, 1178, 1118, 1052, 964, 907, 786 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.4 Hz, 9 H), 1.08–1.11 (m, 6 H), 1.25–1.35 (m, 13 H), 1.44–1.50 (m, 5 H), 4.04–4.13 (m, 4 H), 7.27 (td, *J* = 13.8, 34.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.17, 13.54, 16.30 (d, *J* = 6.4 Hz), 27.13, 28.64, 62.04 (d, *J* = 5.9 Hz), 108.46–119.14 (m, 2 C), 139.34 (t, *J* = 21.9 Hz), 150.07 (td, *J* = 6.8, 121.5 Hz), 151.56.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –127.44 (s, 2 F), –112.69 (s, 2 F), –80.78 (t, *J* = 9.8 Hz, 3 F), 151.56.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.79 (t, *J* = 4.4 Hz, 1 P).

HRMS (FAB): *m*/*z* $[M - H]^+$ calcd for $C_{21}H_{38}F_7O_3PSn$: 621.1390; found: 621.1422.

Diethyl (*E*)-3,3,3-Trifluoro-1-phenylprop-1-en-1-ylphosphonate [(*E*)-8d]; Typical Procedure for the Stille Coupling Reaction

To soln of $PdCl_2(PPh_3)_2$ (18 mg, 0.025 mmol, 10 mol%) in toluene (3 mL) was added (*Z*)-**7e** (0.130 g, 0.25 mmol), CuCN (45 mg, 0.050 mmol, 20 mol%), and PhI (0.042 mL, 0.375 mmol) and the mixture was heated to 80 °C and stirred at this temperature for 6 h. The mixture was quenched with aq NH_4Cl and then it was extracted with Et_2O (3 ×). The combined organic layers were dried (anhyd Na_2SO_4) and concentrated in vacuo. The residue was chromatographed (silica gel, hexane–EtOAc, 1: 1) to afford (*E*)-**8d** (54 mg, 71%).

IR (neat): 2985, 1738, 1648, 1494, 1445, 1393, 1356, 1281, 1254, 1193, 1140, 1052, 1024, 976, 771 (m), 728, 699, 594 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.1 Hz, 6 H), 4.09–4.13 (m, 4 H), 6.75 (dq, *J* = 7.7, 24.0 Hz, 1 H), 7.24–7.26 (m, 2 H), 7.36–7.39 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.19 (d, *J* = 6.6 Hz), 63.17 (d, *J* = 5.8 Hz), 121.62 (dq, *J* = 31.4, 273.6 Hz), 128.11 (q, *J* = 1.7 Hz), 128.71 (d, *J* = 2.5 Hz), 130.23 (dq, *J* = 11.5, 33.9 Hz), 130.74 (d, *J* = 11.6 Hz), 132.15 (d, *J* = 5.8 Hz), 143.40 (qd, *J* = 7.5, 127.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –58.62 (d, *J* = 7.5 Hz, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.88–12.11 (m, 1 P).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{17}F_3O_3P$: 309.0868; found: 309.0875.

Diethyl (*Z*)-2-(Trifluoromethyl)hex-1-enylphosphonate [(*Z*)-9a]; Typical Procedure, Method A, for Carbocupration Using Various Organolithium or Organozinc Reagents

To a soln of CuCN (53 mg, 0.6 mmol) in THF (1 mL) was added 1.6 M BuLi in hexane (0.38 mL, 0.6 mmol) at –60 °C and the soln was stirred for 10 min. To this soln was added dropwise **2a** (58 mg, 0.25 mmol) in THF (1 mL). The mixture was stirred at –60 °C for 2 h and then quenched with aq NH_3–MeOH (1:5, 6 mL) and extracted with Et_2O (3 ×). The combined organic layers were dried (anhyd Na_2SO_4) and concentrated in vacuo. The residue was chromatographed (silica gel, hexane–EtOAc, 1:1) to afford (*Z*)-**9a** (54 mg, 75%).

Diethyl (*Z*)-3,3,3-Trifluoro-2-phenylprop-1-enylphosphonate [(*Z*)-9d]; Typical Procedure, Method B, for Carbocupration Using Various Grignard Reagents

To a soln of CuCN (53 mg, 0.6 mmol) in THF (1 mL) was added a THF soln of PhMgBr (0.6 mmol, prepared readily from Mg and PhBr) at –60 °C and the whole was stirred for 10 min, then allowed to warm to –20 °C. After stirring the mixture for 30 min, it was again cooled to –60 °C, and to this soln was added dropwise **2a** (58 mg, 0.25 mmol) in THF (1 mL). The mixture was stirred at –60 °C for 2 h, and was then quenched with aq NH_3–MeOH (1:5, 6 mL). The soln was extracted with Et_2O (3 ×). The combined organic layers were dried (anhyd Na_2SO_4) and concentrated in vacuo. The residue was chromatographed (silica gel, hexane–EtOAc, 1:1) to afford (*Z*)-**9d** (47 mg, 61%).

Diethyl (*Z*)-2-(Trifluoromethyl)but-1-enylphosphonate [(*Z*)-9j]; Typical Procedure, Method C, for Carbozincation

To a soln of **2a** (58 mg, 0.25 mmol) in THF (1 mL) added 1.0 M Et_2Zn in hexane (0.6 mL) at –40 °C. The mixture was stirred at –40 °C for 14 h, and then quenched with aq NH_4Cl. The soln was extracted with EtOAc (3 ×). The combined organic layers were dried (anhyd Na_2SO_4) and concentrated in vacuo. The residue was chromatographed (silica gel, hexane–EtOAc, 1:1) to afford (*Z*)-**9j** (46 mg, 71%).

Diethyl (*Z*)-2-(Trifluoromethyl)hex-1-enylphosphonate [(*Z*)-9a]

IR (neat): 2962, 2933, 2874, 1729, 1649, 1456, 1378, 1259, 1227, 1175, 1133, 1054, 1028, 967, 794 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.4 Hz, 3 H), 1.33 (t, *J* = 7.1 Hz, 6 H), 1.36 (q, *J* = 7.4 Hz, 2 H), 1.46–1.51 (m, 2 H), 2.31 (t, *J* = 7.4 Hz, 2 H), 4.12 (dq, *J* = 7.1, 7.1 Hz, 4 H), 5.94 (d, *J* = 9.4 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.72, 16.20 (d, *J* = 5.7 Hz), 22.02, 29.32, 33.07 (qd, *J* = 1.6, 16.5 Hz), 62.28 (d, *J* = 5.8 Hz), 122.14 (dq, *J* = 9.0, 276.1 Hz), 122.62 (qd, *J* = 3.3, 189.4 Hz), 148.03 (d, *J* = 31.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.95 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.34–10.51 (m, 1 P).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{21}F_3O_3P$: 289.1181; found: 289.1183.

Diethyl (*Z*)-3,3,3-Trifluoro-2-methylprop-1-enylphosphonate [(*Z*)-9b]

IR (neat): 2986, 2934, 2910, 1648, 1480, 1448, 1371, 1258, 1180, 1103, 1029, 968, 845, 795, 762, 609, 569 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.0 Hz, 6 H), 2.05 (m, 3 H), 4.12 (dq, *J* = 7.0, 7.0 Hz, 4 H), 5.98 (qd, *J* = 1.2, 9.7 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.22 (d, *J* = 6.6 Hz), 20.43 (qd, *J* = 2.5, 19.0 Hz), 62.3 (d, *J* = 5.7 Hz), 121.89 (dq, *J* = 8.3, 274.5 Hz), 123.73 (dq, *J* = 3.3, 189.3 Hz), 143.7 (q, *J* = 33.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –65.58–65.57 (m, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.58–9.69 (m, 1 P).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_8H_{15}F_3O_3P$: 247.0712; found: 247.0701.

Diethyl (*Z*)-3-Methyl-2-(trifluoromethyl)pent-1-enylphosphonate [(*Z*)-9c]

IR (neat): 2964, 2910, 1638, 1456, 1389, 1332, 1261, 1221, 1026, 865, 797, 432 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.4 Hz, 3 H), 1.13 (d, *J* = 6.8 Hz, 3 H), 1.33 (t, *J* = 7.1 Hz, 6 H), 1.39–1.46 (m, 1 H), 1.54–1.62 (m, 1 H), 2.46 (dq, *J* = 2.3, 6.8 Hz, 1 H), 4.12 (dq, *J* = 7.1, 7.1 Hz, 4 H), 5.93 (d, *J* = 9.3 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.42, 16.23 (d, *J* = 6.5 Hz), 19.94, 28.86, 37.76 (d, *J* = 15.5 Hz), 62.24–62.32 (m), 121.61 (qd, *J* = 6.9, 190.5 Hz), 122.45 (dq, *J* = 9.7, 276.8 Hz), 153.0 (q, *J* = 30.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.74 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.3–11.5 (m, 1 P).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{21}F_3O_3P$: 289.1181; found: 289.1175.

Diethyl (*Z*)-3,3,3-Trifluoro-2-phenylprop-1-enylphosphonate [(*Z*)-9d]

IR (neat): 2985, 1621, 1496, 1362, 1261, 1195, 1177, 1135, 1052, 1026, 972, 831, 795, 763, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.37 (t, *J* = 7.1 Hz, 6 H), 4.20 (dq, *J* = 7.1, 7.1 Hz, 4 H), 6.27 (d, *J* = 8.9 Hz, 1 H), 7.40–7.44 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.28 (d, *J* = 6.5 Hz), 62.50 (d, *J* = 6.1 Hz), 121.83 (dq, *J* = 8.3, 276.7 Hz), 126.46 (qd, *J* = 2.9, 188.0 Hz), 127.56, 128.63, 129.86, 134.86 (d, *J* = 18.4 Hz), 146.57 (d, *J* = 32.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –60.36 (s, *J* = 2.0 Hz, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.69–9.72 (m, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{17}F_3O_3P$: 309.0868; found: 309.0880.

Diethyl (*E*)-3,3,3-Trifluoro-2-phenylprop-1-enylphosphonate [(*E*)-9d]

IR (neat): 2985, 2933, 1735, 1496, 1478, 1445, 1369, 1259, 1180, 1134, 1099, 1026, 976, 795, 772, 751, 702, 673, 606 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.1 Hz, 6 H), 3.71–3.94 (m, 4 H), 6.52–6.55 (m, 1 H), 7.42 (br s, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.06 (d, *J* = 6.6 Hz), 62.18 (d, *J* = 6.2 Hz), 122.12 (dq, *J* = 30.0, 275.8 Hz), 123.36 (qd, *J* = 4.6, 191.6 Hz), 128.14, 129.13 (d, *J* = 1.3 Hz), 129.65, 131.27 (d, *J* = 7.0 Hz), 146.26 (q, *J* = 31.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –68.20 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.29–11.46 (m, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{17}F_3O_3P$: 309.0868; found: 309.0864.

Diethyl (*Z*)-2-Cyclohexyl-3,3,3-trifluoroprop-1-enylphosphonate [(*Z*)-9e]

IR (neat): 2932, 2857, 1641, 1451, 1391, 1348, 1313, 1256, 1167, 1131, 1026, 965, 845, 796 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13–1.25 (m, 2 H), 1.33 (t, *J* = 7.0 Hz, 8 H), 1.67–1.74 (m, 2 H), 1.81–1.88 (m, 4 H), 2.30 (t, *J* = 11.4 Hz, 1 H), 4.12 (dq, *J* = 7.4, 7.4 Hz, 4 H), 5.93 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.18 (d, *J* = 6.5 Hz), 25.62, 26.23, 32.56, 40.67 (qd, *J* = 1.1, 15.5 Hz), 62.2 (d, *J* = 6.1 Hz), 121.23 (qd, *J* = 3.4, 190.4 Hz), 122.43 (dq, *J* = 9.8, 276.9 Hz), 153.02 (q, *J* = 29.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.39 (d, *J* = 4.9 Hz, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.63 (q, *J* = 3.1 Hz, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{23}F_3O_3P$: 315.1338; found: 315.1308.

Diethyl (*Z*)-3,3,3-Trifluoro-2-[4-(trifluoromethyl)phenyl]prop-1-enylphosphonate [(*Z*)-9f]

IR (neat): 2987, 1620, 1362, 1328, 1261, 1178, 1132, 1069, 1053, 1022, 973, 847, 827, 672, 615, 465 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (t, *J* = 7.2 Hz, 6 H), 4.17–4.25 (m, 4 H), 6.31 (d, *J* = 8.4 Hz, 1 H), 7.5–7.7 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.23 (d, *J* = 5.7 Hz), 62.75 (d, *J* = 6.6 Hz), 121.51 (dq, *J* = 8.2, 276.1 Hz), 123.60 (q, *J* = 271.9 Hz), 125.65 (q, *J* = 4.1 Hz), 128.08, 128.55 (qd, *J* = 2.4, 187.6 Hz), 131.83 (q, *J* = 33.0 Hz), 138.30 (qd, *J* = 1.6, 19.0 Hz), 145.06 (dq, *J* = 1.7, 33.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –60.42 (s, 3 F), –63.47 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.83 (q, *J* = 2.1 Hz, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{16}F_6O_3P$: 377.0742; found: 377.0755.

Diethyl (*Z*)-3,3,3-Trifluoro-2-(4-methoxyphenyl)prop-1-enylphosphonate [(*Z*)-9g]

IR (neat): 2985, 2938, 2909, 2843, 1606, 1514, 1464, 1444, 1361, 1177, 1134, 1027, 970, 828, 790, 737, 588, 492 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.2 Hz, 6 H), 3.81 (s, 3 H), 4.17 (dq, *J* = 7.2, 7.2 Hz, 4 H), 6.20 (d, *J* = 8.8 Hz, 1 H), 6.88–6.93 (m, 2 H), 7.34–7.36 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.22 (d, *J* = 6.6 Hz), 55.21, 62.42 (d, *J* = 23.2 Hz), 114.01, 121.93 (dq, *J* = 8.2, 276.1 Hz), 124.37 (qd, *J* = 2.5, 189.3 Hz), 126.87, 127.06, 129.02, 130.60, 146.01 (dq, *J* = 1.7, 33.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –60.31 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.08–10.38 (m, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}F_3O_4P$: 339.0974; found: 339.0963.

Diethyl (*Z*)-3,3,3-Trifluoro-2-(3-methoxyphenyl)prop-1-enylphosphonate [(*Z*)-9h]

IR (neat): 2985, 1600, 1578, 1489, 1434, 1360, 1290, 1135, 1059, 1025, 977, 852, 793, 704, 474 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (t, *J* = 6.8 Hz, 6 H), 3.82 (s, 3 H), 4.20 (dq, *J* = 6.8, 6.8 Hz, 4 H), 6.27 (d, *J* = 8.8 Hz, 1 H), 6.92–6.99 (m, 3 H), 7.29–7.31 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.18 (d, *J* = 5.8 Hz), 55.26, 62.51 (d, *J* = 6.5 Hz), 113.26, 115.27, 119.83, 121.25, 121.71 (dq, *J* = 8.3, 276.1 Hz), 126.48 (qd, *J* = 3.3, 187.6 Hz), 129.66, 136.02 (dd, *J* = 1.7, 20.0 Hz), 146.33 (dq, *J* = 1.6, 33.0 Hz), 159.48.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –60.43 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.62 (q, *J* = 2.9 Hz, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}F_3O_4P$: 339.0974; found: 339.0963.

Diethyl (*Z*)-3,3,3-Trifluoro-2-(2-methoxyphenyl)prop-1-enylphosphonate [(*Z*)-9i]

IR (neat): 2985, 2842, 1631, 1600, 1582, 1492, 1464, 1438, 1353, 1260, 1173, 1024, 970, 784, 756, 606 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (t, *J* = 7.2 Hz, 6 H), 3.81 (s, 3 H), 4.15–4.22 (m, 4 H), 6.17 (d, *J* = 10.4 Hz, 1 H), 6.90–6.97 (m, 2 H), 7.15–7.18 (m, 1 H), 7.34–7.39 m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.21 (d, *J* = 6.6 Hz), 55.56, 62.45 (d, *J* = 6.6 Hz), 110.99, 120.48, 121.39 (dq, *J* = 8.3, 276.1 Hz), 124.80 (qd, *J* = 1.7, 18.2 Hz), 127.73 (qd, *J* = 3.3, 183.4 Hz), 129.99, 131.00, 145.20 (dq, *J* = 1.7, 34.7 Hz), 156.90.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –60.95 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.23–9.27 (m, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}F_3O_4P$: 339.0974; found: 339.0973.

Diethyl (*Z*)-2-(Trifluoromethyl)but-1-enylphosphonate [(*Z*)-9j]

IR (neat): 2984, 2942, 1446, 1391, 1373, 1326, 1259, 1224, 1178, 1134, 1027, 970, 856, 795 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 7.3 Hz, 3 H), 1.33 (t, *J* = 7.1 Hz, 6 H), 2.35–2.39 (m, 2 H), 4.13 (dq, *J* = 7.1, 7.1 Hz, 4 H), 5.93 (d, *J* = 9.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.15, 16.19 (d, *J* = 6.5 Hz), 26.09 (qd, *J* = 1.7, 17.3 Hz), 62.25 (d, *J* = 6.1 Hz), 121.68 (qd, *J* = 3.4, 190.4 Hz), 122.17 (dq, *J* = 9.6, 276.7 Hz), 149.18 (q, *J* = 31.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –64.29 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.71 (q, *J* = 2.9 Hz, 1 P).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_9H_{17}F_3O_3P$: 261.0868; found: 261.0859.

Diethyl (*E*)-2-(Trifluoromethyl)but-1-enylphosphonate [(*E*)-9j]

IR (neat): 2985, 2945, 1650, 1446, 1393, 1351, 1322, 1250, 1181, 1132, 1025, 970, 859, 797 (s), 762 (m), 642 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16–1.20 (m, 3 H), 1.34 (t, *J* = 7.6 Hz, 6 H), 2.68 (dq, *J* = 2.4, 7.2 Hz, 2 H), 4.12 (m, 4 H), 6.13 (dd, *J* = 1.6, 12.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.50 (d, *J* = 2.4 Hz), 16.27, 21.6 (d, *J* = 5.8 Hz), 62.16 (d, *J* = 5.7 Hz), 119.92 (qd, *J* = 5.8, 189.4 Hz), 123.02 (dq, *J* = 32.2, 276.1 Hz), 150.81 (dq, *J* = 9.9, 28.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –69.04 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.80 (q, *J* = 1.5 Hz, 1 P).

HRMS (FAB): *m/z* [M + H]$^+$ calcd for $C_9H_{17}F_3O_3P$: 261.0868; found: 261.0876.

Diethyl (*Z*)-1-Ethyl-3,3,3-trifluoroprop-1-enylphosphonate [(*Z*)-8j]

IR (neat) 2983, 2938, 1648, 1446, 1393, 1368, 1283, 1240, 1138, 1104, 1023, 968, 795, 760, 677 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (t, *J* = 7.3 Hz, 3 H), 1.34 (t, *J* = 7.1 Hz, 6 H), 2.43–2.47 (m, 2 H), 4.11–4.20 (m, 4 H), 6.1 (dq, *J* = 8.84, 43.62 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.82 (d, *J* = 5.4 Hz), 16.18 (d, *J* = 6.4 Hz), 28.90 (d, *J* = 8.7 Hz), 62.49 (d, *J* = 6.3 Hz), 121.41 (dq, *J* = 9.6, 271.4 Hz), 128.17 (dq, *J* = 5.7, 37.2 Hz), 145.07 (dq, *J* = 5.0, 170.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –58. 01 (d, *J* = 7.5 Hz, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.34–11.53 (m, 1 P).

HRMS (FAB): *m/z* [M + H]$^+$ calcd for $C_9H_{17}F_3O_3P$: 261.0868; found: 261.0874.

Diethyl (*Z*)-2-(Trifluoromethyl)-3-methylbut-1-enylphosphonate [(*Z*)-9k]

IR (neat): 2980, 2939, 1638, 1469, 1391, 1327, 1258, 1223, 1189, 1167, 1135, 1100, 1028, 966, 839, 795, 483 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, *J* = 6.8 Hz, 6 H), 1.32 (t, *J* = 7.1 Hz, 6 H), 2.69 (dq, *J* = 6.8, 6.8 Hz, 1 H), 4.11 (dq, *J* = 7.1, 7.1 Hz, 4 H), 5.95 (d, *J* = 6.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.19 (d, *J* = 6.5 Hz), 21.85, 30.91 (d, *J* = 15.8 Hz), 62.25 (d, *J* = 6.2 Hz), 120.85 (qd, *J* = 3.4, 190.5 Hz), 122.46 (dq, *J* = 9.9, 277.3 Hz), 153.86 (q, *J* = 29.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.11 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.41–11.45 (m, 1 P).

HRMS (FAB): *m/z* [M + H]$^+$ calcd for $C_{10}H_{19}F_3O_3P$: 275.1025; found: 275.1030.

Diethyl (*Z*)-3,3,3-Trifluoro-2-(tetrahydrofuran-2-yl)prop-1-enylphosphonate [(*Z*)-10]

IR (neat): 2986, 2910, 1649, 1444, 1391, 1333, 1259, 1208, 1168, 1139, 1053, 1025, 969, 795 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (dt, *J* = 1.2, 7.2 Hz, 6 H), 1.75–1.80 (m, 1 H), 1.91–1.97 (m, 2 H), 2.27–2.32 (m, 1 H), 3.88 (dt, *J* = 6.8, 8.0 Hz, 1 H), 3.97 (td, *J* = 7.2, 7.6 Hz, 1 H), 4.10–4.17 (m, 4 H), 4.59 (t, *J* = 7.2 Hz, 1 H), 6.41 (dd, *J* = 1.6, 10.4 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.19 (dd, *J* = 3.3, 6.5 Hz), 25.58, 31.95 (d, *J* = 1.7 Hz), 62.30 (dd, *J* = 6.1, 9.0 Hz), 68.75, 76.29 (qd, *J* = 3.3, 15.0 Hz), 120.60 (qd, *J* = 3.3, 189.4 Hz), 121.71 (dq, *J* = 9.1, 276.1 Hz), 148.31 (q, *J* = 31.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –61.49 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.07 (q, *J* = 2.9 Hz, 1 P).

HRMS (FAB): *m/z* [M + H]$^+$ calcd for $C_{12}H_{19}F_3O_4P$: 303.0974; found: 303.0979.

Diethyl (*E*)-3,3,3-Trifluoro-2-(tetrahydrofuran-2-yl)prop-1-enylphosphonate [(*E*)-10]

IR (neat): 2985, 2887, 1638, 1446, 1393, 1370, 1252, 1165, 1051, 1025, 970, 858, 838, 794, 746, 482 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.2 Hz, 6 H), 1.88–2.05 (m, 3 H), 2.30–2.36 (m, 1 H), 3.85 (td, *J* = 4.8, 8.0 Hz, 1 H), 4.01 (dt, *J* = 7.2, 7.2 Hz, 1 H), 4.07–4.16 (m, 4 H), 5.23 (dt, *J* = 0.8, 7.2 Hz, 1 H), 6.22 (td, *J* = 1.2, 10.4 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.25 (dd, *J* = 4.1, 6.6 Hz), 26.20, 32.38, 62.27 (dd, *J* = 5.7, 14.9 Hz), 69.18, 75.38 (d, *J* = 6.6 Hz), 121.54 (qd, *J* = 5.4, 189.3 Hz), 122.26 (dq, *J* = 30.6, 276.9 Hz), 149.44 (dq, *J* = 9.9, 27.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –64.77 (s, 3 F).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.67 (q, *J* = 1.5 Hz, 1 P).

HRMS (FAB): *m/z* [M + H]$^+$ calcd for $C_{11}H_{19}F_3O_4P$: 303.0974; found: 303.0961.

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