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A kinetic separation method for the stereoselective preparation of 1-fluorovinylphosphonates from *E/Z* mixtures of 1-bromo-1-fluoroolefins

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Abstract

Reaction of *E/Z* mixtures of 1-bromo-1-fluoroolefins with diethylphosphite and catalytic $Pd(PPh_3)_4$ in triethylamine at 30–40°C gave predominately the (*E*)-isomer of the 1-fluorovinylphosphonate (*E/Z* ≥ 95:5) in good yields. Pure (*E*)-1-fluorovinylphosphonate could be readily obtained by chromatographic separation of the 95:5 *E/Z* mixture. Pure (*Z*)-1-bromo-1-fluoroolefin could be recovered and phosphorylated at 70°C to give pure (*Z*)-1-fluorovinylphosphonate in 51–60% yield. Thus, *E/Z* mixtures of 1-bromo-1-fluoroolefins could be kinetically separated into pure (*E*)- and (*Z*)-1-fluorovinylphosphonates. This methodology provides an unequivocal route to the isomerically pure (*E*)- and (*Z*)-1-fluorovinylphosphonates from the readily available 1-bromo-1-fluoroolefins.

Keywords: Fluorinated phosphonates; Phosphonates; α-Fluorovinylphosphonates; Kinetic separation

1. Introduction

Naturally occurring phosphate-containing molecules play important roles in various cellular processes, including signal transduction. Therefore, nonhydrolyzable phosphate mimetics have received considerable attention, and α,α-difluorophosphonates, α-fluorophosphonates and α-fluorovinylphosphonates as phosphate isosteres have been used in an effective manner to overcome the lability of the phosphate group [1–3]. α-Fluorovinylphosphonates have also been utilized as precursors of α-fluorophosphonates, via hydrogenation reactions. This methodology was initially employed by Blackburn and Rashid for the enantiospecific synthesis of α-fluoromethylene-phosphonate analogs of 3-phospho-D-glyceric acid [4]. Similar preparations of α-fluorophosphonate analogs of phosphopeptide mimetics [5] and potential enzyme inhibitors [6] were subsequently employed by other workers. One of the main problems in the preparation of α-fluorovinylphosphonates has been the inability to prepare isomerically pure α-fluorovinylphosphonates. Although there are useful methods to obtain (*E*)-α-fluorovinylphosphonates, there is a paucity of routes for the preparation of (*Z*)-α-fluorovinylphosphonates [3]. A route to isomerically pure (*E*)- and (*Z*)-α-fluorovinylphosphonates is a challenging synthetic problem — although an important problem. Catalytic asymmetric hydrogenation could provide a useful route to optically active α-fluorophosphonates.

In this work, we address the problem of isomerically pure (*E*)- and (*Z*)-α-fluorovinylphosphonates. Subsequent work will address the catalytic asymmetric hydrogenation of these isomerically pure α-fluorovinylphosphonates.

The Wadsworth–Emmons–Horner reaction and the Peterson olefination reaction have been the primary synthetic routes for the preparation of *E/Z* mixtures of α-fluorovinylphosphonates. Blackburn and Parratt reported that treatment of $[(^{i}PrO)_2P(O)]_2CFLi$ with aldehydes and ketones produced *E/Z* mixtures of α-fluorovinylphosphonates in 56–95% yields [7,8]. Schlewer and coworkers utilized the lithium salt of diethyl-1-fluoro-1-trimethylsilylmethylphosphonate to prepare a 1/1 *E/Z* mixture of α-fluorovinylphosphonates from aromatic aldehydes [6]. O'Hagan and coworkers [9], and Savignac and coworkers [10] simultaneously reported a similar Peterson olefination route with aldehydes and ketones. Savignac and coworkers later demonstrated that treatment of $[(EtO)_2P(O)]_2CFLi$ with aromatic aldehydes and aliphatic ketones at low temperatures led mainly to the (*E*)-isomer of the α-fluorovinylphosphonates [11].

Recent work by Hammond and coworkers has illustrated an elegant preparation of 1-fluoroallenylphosphonate [12].

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Iodination of diethyl-1-fluoro-1,2-propadienephosphonate gave 91% of (*E*)-diethyl-1-fluoro-2,3-di-iodo-1-propenephosphonate, an excellent intermediate for further functional group transformations. Several α-fluorovinylphosphonates were stereospecifically prepared from the di-iodo intermediate. Hydroamination of the 1-fluoroallenylphosphonate, however, gave *E/Z* mixtures of products in some cases.

The attempted conjugate addition of organocopper reagents with 3-(diethylphosphonodifluoromethyl)but-2-enoate failed [5]. The reaction unexpectedly gave an organocopper-mediated reduction product, (*E*)-α-fluorovinylphosphonate via the reaction of $(EtO)_2P(O)Na$ with ethyl-3,3-difluoro-2-[(trimethylsilyl)methyl]propenate [13]. Xu and Zemlicka used DBN to eliminate HF from (*E*)-diethyl-4-(adenin-9-yl)-3-bromo-1,1-difluoro-2-butene-1-phosphonate to give 21% of *E/Z*-diethyl-4-(adenin-9-yl)-3-bromo-1-fluoro-1,3-butadiene-1-phosphonate [14].

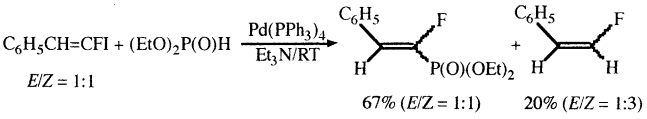
An attractive route to arylphosphonates was developed by Ohshiro and coworkers. Reaction of dialkylphosphonates with aryl bromides or iodides in the presence of triethylamine and catalytic tetrakis(triphenylphosphine)palladium gave good to excellent yields of the corresponding arylphosphonates [15]. Xu and Li extended this methodology to the preparation of vinylphosphinates from alkenyl bromides [16]. The configuration of the double bond is maintained in the vinylphosphinate. McCarthy and coworkers employed this methodology in the stereospecific formation of α-fluorovinylphosphonates from the corresponding 1-fluoro-1-iodoalkene derivative [3]. However, further application of this elegant methodology has been limited by the difficulties associated with the stereospecific preparation of isomerically pure (*E*)- and (*Z*)-1-fluoro-1-iodoolefins [17].

2. Results and discussion

The methodology developed by Ohshiro and coworkers [15], Xu and Li [16], and McCarthy and coworkers [3] suggested that the stereospecific conversion of 1-halo-1-fluoroolefins to 1-fluorovinylphosphonates via Pd(0) catalyzed phosphorylation would be the most direct, stereospecific entry to α-fluorovinylphosphonates. However, as noted by McCarthy and coworkers [3], there is no general stereospecific route to 1-halo-1-fluoroolefins. The Wadsworth–Emmons–Horner reaction, Peterson olefination, and Wittig approaches to this class of olefins generally give *E/Z* mixtures. Rolando and coworkers has developed a multi-step route to (*Z*)-1-bromo-1-fluoroolefins, but the methodology seems to be applicable only to aryl derivatives and requires several steps [18]. Consequently, we decided to investigate *E/Z* mixtures of 1-halo-1-fluoroolefins to determine if kinetic separation (on phosphorylation) could be utilized to prepare isomerically pure (*E*)- and (*Z*)-α-fluorovinylphosphonates from *E/Z* mixtures.

Our initial work investigated the phosphorylation reaction of the *E/Z* mixture of $C_6H_5CH{=}CFI$, prepared by a Wadsworth–Emmons–Horner reaction, as shown below:

$$(EtO)_2P(O)CHFI + C_6H_5CHO \xrightarrow[-78^\circ C]{LDA/THF} C_6H_6CH{=}CFI, \quad 54\%\ (E/Z = 1{:}1)$$



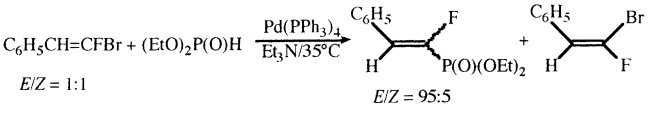
Phosphorylation of the above *E/Z* mixture with diethylphosphite using Pd(0) catalysis gave a reasonable yield of the α-fluorovinylphosphonates, but also produced a significant amount of reduction product. Reduction of organic halides with a combination of diethylphosphite/Et_3N is well established in the chemical literature [19,20]. The formation of the reduction product may account for the lower yields in some of the phosphorylation reactions reported by McCarthy and coworkers [3]. When we monitored this reaction by ^{19}F NMR, some interesting features in this reaction were observed:

1. The (*E*)-isomer of the 1-fluoro-1-iodostyrene reacted faster than the (*Z*)-isomer; formation of the (*E*)-isomer of the α-fluorovinylphosphonate was faster than its corresponding (*Z*)-isomer. For example, after 24 h at RT, an *E/Z* ratio of 3:1 $C_6H_5CH{=}CFP(O)(OEt)_2$ was observed; all the (*E*)-$C_6H_5CH{=}CFI$ had been consumed and significant amounts of (*Z*)-$C_6H_5CH{=}CFI$ remained.
2. After 7 days at RT, both *E/Z*-isomers had been consumed to give the *E/Z* ratios of products noted in the above equation. Consequently, some modest kinetic separation was observed but not sufficient enough to accomplish our goal of preparing isomerically pure (*E*)- and (*Z*)-α-fluorovinylphosphonates.

Next, we studied the corresponding 1-bromo-1-fluoroolefins, which can be readily prepared by Wittig methodology developed in our laboratory [21–23].

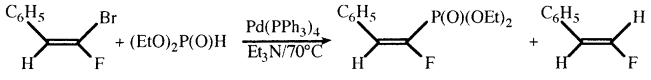
$$2Ph_3P + CFBr_3 + RCHO \xrightarrow[70^\circ C]{triglyme} E/Z\text{-}RCH{=}CFBr + Ph_3PO + Ph_3PBr_2$$

When 1-bromo-1-fluorostyrene was used as the substrate in the phosphorylation reaction, no reduction product was detected at lower temperatures (RT → 40°C).



At 35°C, the formation of the (*E*)-α-fluorovinylphosphonate was significantly more selective than the corresponding

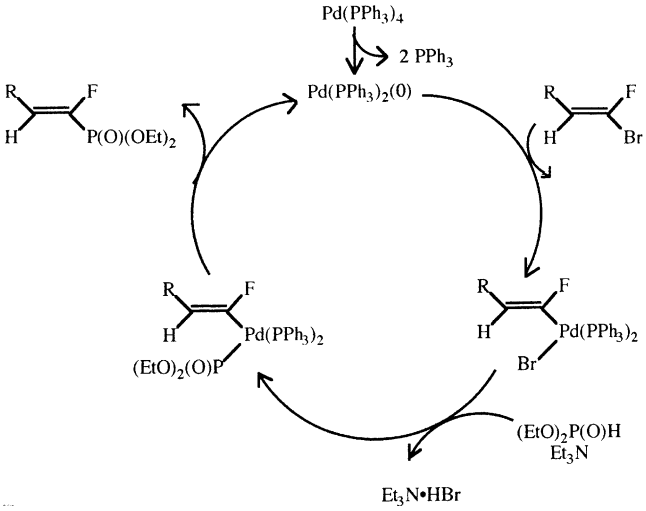
vinyliodide analog noted earlier. When all the (*E*)-C_6H_5CH=CFBr had been consumed, the *E*/*Z*-ratio of C_6H_5CH=CFP(O)$(OEt)_2$ isomers was 95:5, and large amounts of pure (*Z*)-C_6H_5CH=CFBr could be readily recovered (cf. Experimental Section). The (*Z*)-1-bromo-1-fluoroolefins could be readily converted to isomerically pure (*Z*)-C_6H_5CH=CFP(O)$(OEt)_2$ via phosphorylation at higher temperatures. At these higher temperatures, the competitive reduction:



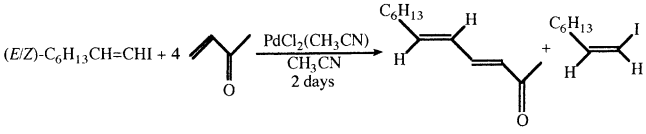
reaction became significant, but 50–60% yields of isomerically pure (*Z*)-vinylphosphonate could be isolated. The 95:5 mixture of *E*/*Z*-C_6H_5CH=CFP(O)$(OEt)_2$ could be separated by silica gel chromatography and isomerically pure (*E*)-vinylphosphonate isolated in reasonable yields. Table 1 summarizes similar results with various *E*/*Z*-mixtures of RCH=CFBr. Note that R– can be both aryl and alkyl. In Table 1, the isolated yield of pure (*E*)-vinylphosphonate is based on total olefin utilized in the reaction (not on the percentage of (*E*)-C_6H_5CH=CFBr in the original *E*/*Z* mixture). The *E*/*Z* product ratio in Table 1 represents the *E*/*Z* ratio detected in the reaction mixture; the small amounts of (*Z*)-vinylphosphonate were removed on chromatographic isolation.

The (*E*)- and (*Z*)-configuration of the α-fluorovinylphosphonates were assigned on the magnitude of the J_{H-F} coupling constants. The (*E*)-isomers exhibited J_{H-F} of ∼40 Hz and the (*Z*)-isomers exhibited J_{H-F} of ∼30 Hz, consistent with *trans* J_{H-F} > *cis* J_{H-F} in other olefinic derivatives [24].

The formation of the α-fluorovinylphosphonates can be rationalized by the normal three-step pathway for palladium catalyzed reactions, as illustrated below:



There are few reports in the literature regarding different reactivities of (*E*)- and (*Z*)-isomers in palladium catalyzed reactions. Weisenfeld and coworkers [25] reported that reaction of the *E*/*Z* mixture of 1-iodo-1-octene with four equivalents of methylvinylketone resulted in total conversion of the (*E*)-olefin to the conjugated diene; the (*Z*)-olefin was unreactive:



Reactions of 1,1-dichloroolefins with Grignard or organozinc reagents in the presence of $PdCl_2$(dppb) resulted in the formation of mono-coupled product. The chloride *trans* to

Table 1
Stereoselective preparation of 1-fluorovinylphosphonates

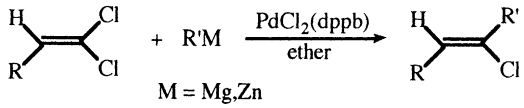
RCH=CFBr + $(EtO)_2P(O)H \xrightarrow[Et_3N/h/T°C]{Pd(PPh_3)_4}$ RCH=CFP(O)$(OEt)_2$

Compound no.	R	*E*/*Z*	Temperature (°C)/time (h)	Yield (%)[a]	*E*/*Z* Pdt. Ratio
1	$(CH_3)_2CH$	7:3	40/24	55	96:4[b]
2	C_6H_5	1:1	35/24	45	95:5[b]
3	C_7H_{15}	1:1	40/24	45	95:5[b]
4	$2,4(CH_3)_2C_6H_3$	3:2	40/24	56	94:6[b]
5	*p*-ClC_6H_4	3:2	40/24	44	96:4[b]
6	$C_6H_5(CH_3)CH$	3:2	40/24	49	92:8[b]
7	$(CH_3)_2CH$	0/100	reflux (24)	53	0/100
8	C_6H_5	0/100	70/24	51	0/100
9	C_7H_{15}	0/100	75/24	60	0/100
10	$2,4(CH_3)_2C_6H_3$	0/100	reflux (24)	52	0/100
11	*p*-ClC_6H_4	0/100	reflux (24)	55	0/100
12	$C_6H_5(CH_3)CH$	0/100	reflux (24)	56	0/100

[a] Yield of pure (*E*)- or pure (*Z*)-isomer after chromatography of the reaction mixture; yield is based on the initial amount of total olefin utilized in the reaction.

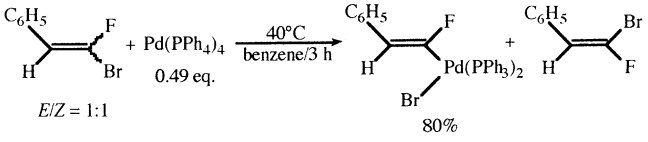
[b] *E*/*Z* product ratio in the reaction mixture before chromatography; the (*Z*)-isomer was separated by chromatography of the reaction mixture.

the R-group in the olefin was replaced by the R′-group of the Grignard reagent [26,27]. The replacement:



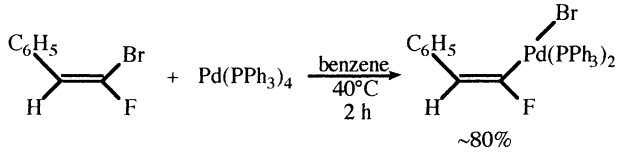
of the *cis* chloride was hampered by the steric effect of the vicinal *cis*-substituent. Similar steric effects were observed in the cross-coupling reaction of (*E*)- and (*Z*)-1-bromo-1-alkenes with alkynyl organozinc reagents by Rossi and coworkers [28–31].

In order to learn more details of the formation of the α-fluorovinylphosphonates and more importantly to understand which step in the mechanistic process (oxidative-addition, metathesis, or reductive elimination) is responsible for the kinetic separation observed, we carried out the following qualitative experiments. Thus, where a 1:1 (*E*/*Z*) mixture of $C_6H_5CH{=}CFBr$ was reacted with 0.49 equivalents of $Pd(PPh_3)_4$ at 40°C (benzene) for 3 h, the (*E*)-olefin was selectively consumed. After vacuum removal of solvent, the remaining solids were washed with ether to remove PPh_3 and unreacted olefin.

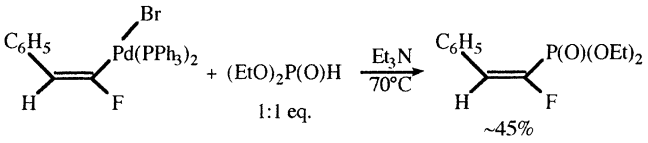


The (*E*)-palladium complex was obtained in ~80% yield. NMR data for this complex was consistent with the structure assigned in the above equation: ^{19}F NMR ($CDCl_3$): −44.9 (dt, $J = 53.5$ Hz, $J = 15.2$ Hz) ppm. ^1H NMR ($CDCl_3$): vinylhydrogen at 4.71 (d, $J = 53.7$ Hz) ppm; ^{31}P NMR ($CDCl_3$): 22.8 (d, $J = 15.3$ Hz). When this complex was treated with 1 equivalent of diethylphosphite and Et_3N at room temperature, the formation of ~80% (*E*)-$C_6H_5CH{=}CFP(O)(OEt)_2$ was complete in 8 h.

When 0.95 mmol of $Pd(PPh_3)_4$ was treated with 1.0 mmol of (*Z*)-1-bromo-1-fluorostyrene in benzene, the corresponding (*Z*)-complex was formed at 40°C in 2 h in ~80% yield. After



removal of solvent and removal of solids with ether, the (*Z*)-complex was obtained in ~80% yield. No (*Z*)-complex was formed at room temperature (18 h). NMR data was consistent with the structure assigned in the above equation. ^{19}F NMR ($CDCl_3$): −50.1 (dt, $J = 29.3$ Hz, $J = 16$ Hz) ppm; ^1H NMR ($CDCl_3$): vinylhydrogen at 5.32 (d, $J = 30.0$ Hz) ppm; ^{31}P NMR ($CDCl_3$): 22.3 (d, $J = 16.1$ Hz) ppm. When the (*Z*)-complex was treated with 1:1 equivalents of diethylphosphite and excess Et_3N at 70°C, the corresponding (*Z*)-α-fluoro-vinylphosphonate was formed in ~45% yield along with ~10% (*Z*)-$C_6H_5CH{=}CFH$. Only a trace of the vinylphosphonate was detected by ^{19}F NMR of the reaction mixture at room temperature after 48 h.



The above experiments indicate that the formation of the (*E*)-palladium complex is faster than the formation of the (*Z*)-palladium complex. Thus, the kinetic separation observed in our work is due to the faster oxidative addition of palladium to the (*E*)-1-bromo-1-fluoroolefin. The subsequent steps in the mechanism (metathesis and reductive elimination) are also faster for the (*E*)-palladium complex. Thus, when a mixture of (*E*)- and (*Z*)-palladium complexes was treated with 1:1 equivalents of diethylphosphite in Et_3N, formation of (*E*)-$C_6H_5CH{=}CFP(O)(OEt)_2$ was observed (by ^{19}F NMR) after 3 h at room temperature. No (*Z*)-$C_6H_5CH{=}CFP(O)(OEt)_2$ was detected after 3 days at room temperature. Thus, the kinetic separation of the *E*/*Z*-mixture of 1-bromo-1-fluoroolefins is dictated by the selective formation of the (*E*)-palladium complex. Moreover, the subsequent steps in the overall mechanism also appeared to be controlled by steric effects in the palladium intermediates.

3. Conclusions

The preparation of isomerically pure (*E*)-1-fluorovinylphosphomates can be accomplished via the kinetic separation of phosphorylation reactions of *E*/*Z*-mixtures of 1-bromo-1-fluoroolefins with diethylphosphite and triethylamine in the presence of $Pd(PPh_3)_4$ at RT to 40°C. The recovered (*Z*)-1-bromo-1-fluoroolefin can be similarly phosphorylated to the corresponding isomerically pure (*Z*)-1-fluorovinylphosphonate at 70–80°C. Qualitative mechanistic experiments indicate that the kinetic separation occurs in the oxidative-addition step of the reaction. Thus, the *E*/*Z*-mixtures of 1-bromo-1-fluorolefins, which are readily prepared, can be utilized to give isomerically pure both (*E*)- and (*Z*)-1-fluorovinylphosphonates.

4. Experimental

4.1. General

All reactions were monitored by ^{19}F NMR analysis of the reaction mixture on either a 90 or 300 MHz spectrometer.

The ^{1}H, ^{19}F, ^{13}C and ^{31}P NMR spectra of final products were obtained on a 300 MHz spectrometer ($CDCl_3$, $CFCl_3$ or TMS internal references). FT-IR spectra were recorded on the pure sample on NaCl plate. Low resolution mass spectral analyses were performed at 70 eV in the electron-impact mode on a single-quadrapole instrument interfaced to a gas chromatograph fitted with an OV-101 column. High resolution mass spectral analyses were performed by the University of Iowa, high resolution mass spectroscopy facility at 70 eV in the electron impact mode. GLPC analyses were performed on a 5% OV-101 column and thermal conductivity detector.

4.2. Materials

THF was distilled from sodium benzophenone ketyl at atmospheric pressure prior to use. Tetrakis(triphenylphosphine) palladium was prepared by Coluson's procedure [32]. Aldehydes were commercial samples and were distilled prior to use. The *E/Z* mixtures of 1-bromo-1-fluoroolefins were prepared from the corresponding aldehydes and [Ph_3P=CFBr] as described in the literature [23]. $(EtO)_2$-P(O)CHFI was prepared by iodination of $(EtO)_2$-P(O)CFHZnBr [33]. Et_3N was dried over NaH and distilled from NaH.

4.3. A representative procedure for the preparation of an (E)-α-fluorovinylphosphonate

4.3.1. Diethyl-(1E)-1-fluoro-3-methyl-but-1-enephosphonate, (E)-$(CH_3)_2$CHCH=CFP(O)$(OEt)_2$ (1)

A 25 ml dry flask equipped with a condenser, stir bar and a N_2 tee was charged with 0.23 g (0.199 mmol) of $Pd(PPh_3)_4$, 0.76 g (5.5 mmol) of diethylphosphite, 2.0 ml of Et_3N and 0.85 g (5 mmol) of a ^{i}PrCH=CFBr mixture (E/Z = 7:3). The reaction mixture was stirred at 40°C until no (*E*)-olefin remained by ^{19}F NMR analysis of the reaction mixture (~24 h). The reaction mixture was directly purified by silica gel chromatography (pentane 100%, then 40:60 ethylacetate:hexane); 0.21 g of pure (*Z*)-^{i}PrCH=CFBr was recovered (0.64 g, 3.8 mmol of olefins consumed), and 0.62 g (55%) of (*E*)-^{i}PrCH=CFP(O)$(OEt)_2$ was isolated. GLPC > 99% ^{1}H NMR ($CDCl_3$): 5.82 (dtm, J = 40 Hz, J = 7.7 Hz, 1H),4.08–4.22 (m, 4H), 2.84–2.96 (m, 1H), 1.36 (td, J = 7.1 Hz, J = 1.1 Hz, 6H), 1.1 (dd, J = 6.8 Hz, J = 1:1 Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −132.9 (dd, J = 102.5 Hz, J = 40 Hz) ppm. ^{13}C NMR ($CDCl_3$): 148 (dd, J = 273 Hz, J = 236 Hz), 132.8 (dd, J = 26.5 Hz, J = 5 Hz), 62.7 (d, J = 5.5 Hz), 24.3 (dd, J = 10 Hz, J = 5 Hz), 21.8, 16.0 (d, J = 6 Hz) ppm. ^{31}P NMR ($CDCl_3$): 6.1 (d, J = 103 Hz) ppm. GC–MS: 224 (M^+, 17), 209 (2), 196 (9), 168 (37), 153 (45), 138 (100), 127 (32), 111 (91), 94 (12), 82 (42). TLC: R_f = 0.35 (hexanes:ethyl acetate = 1:1). HRMS: Calcd. for $C_9H_{18}FO_3P$: 224.0977; Found: 224.0997. FT-IR (neat, NaCl plate): 2875 (m), 1664 (s), 1446 (s), 1166 (w), 840 (s).

4.3.2. Diethyl-(1E)-1-fluoro-2-phenylethenephosphonate; (E)-C_6H_5CH=CFP(O)$(OEt)_2$ (2)

Similarly, the reaction of 1.0 g (5 mmol) (freshly prepared) C_6H_5CH=CFBr (E/Z = 1:1) with 0.76 g (5.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.23 g, 0.199 mmol) and 2.0 ml of Et_3N at 35°C (24 h) gave 0.48 g of pure (*Z*)-C_6H_5CH=CFBr (0.52 g, 2.5 mmol of olefins consumed) and 0.58 g (45%) of pure (*E*)-C_6H_5CH=CFP(O)$(OEt)_2$. GLPC > 99%. ^{1}H NMR ($CDCl_3$): 7.4–7.6 (m, 5H), 6.7 (dd, J = 42, J = 8.6 Hz, 1H), 4.22 (m 4H), 1.39 (t, J = 7.1 Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −127 (dd, J = 98 Hz, J = 43 Hz) ppm. ^{13}C NMR ($CDCl_3$): 149 (dd, J = 286 Hz, J = 236 Hz), 130 (dd, J = 14 Hz, J = 2 Hz), 129 (d, J = 8 Hz), 128.5 (d, J = 2 Hz), 128, 122 (d, J = 30 Hz), 62 (d, J = 6 Hz), 15 (d, J = 6 Hz) ppm. ^{31}P NMR ($CDCl_3$): 6.3 (d, J = 98 Hz) ppm. GC–MS: 258 (M^+, 72), 230 (5), 185 (61), 167 (27), 149 (77), 129 (70), 102 (100), 65 (88). TLC: R_f = 0.34 (hexane:ethyl acetate = 1:1). HRMS: Calcd. for $C_{12}H_{16}FO_3P$: 258.0821; Found: 258.0819. FT-IR (neat, NaCl plate): 2985 (m), 1213 (m), 1162 (s), 798 (s).

4.3.3. Diethyl-1(E)-1-fluoronon-1-enephosphonate; (E)-C_7H_{15}CH=CFP(O)$(OEt)_2$ (3)

Similarly, the reaction of 1.12 g (5 mmol) of C_7H_{15}CH=CFBr (*E/Z*: 1:1) with 0.76 g (5.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.23 g, 0.199 mmol) and 3.0 ml of Et_3N at 40°C (24 h) gave 0.5 g pure (*Z*)-C_7H_{15}CH=CFBr (0.62 g, 2.78 mmol of olefins consumed) and 0.63 g (45%) of (*E*)-C_7H_{15}CH=CFP(O)$(OEt)_2$ (E/Z = 95 : 5). ^{1}H NMR ($CDCl_3$): 6.0 (dq, J = 40 Hz, J = 8 Hz, 1H), 4.2 (m, 4H), 2.4 (qt, J = 7 Hz, J = 2 Hz, 2H), 1.3–1.5 (m, 16H), 0.9 (t, J = 3.5 Hz, 3H) ppm. ^{19}F NMR ($CDCl_3$): −132.4 (dd, J = 103 Hz, J = 40 Hz) ppm. ^{13}C NMR ($CDCl_3$): 150 (dd, J = 273 Hz, J = 236 Hz), 127 (dd, J = 28 Hz, J = 16 Hz), 63 (d = 6 Hz), 31.6, 28.9, 28.8, 28.2 (m), 24 (dd, J = 10 Hz, J = 5 Hz) 22.4, 16 (d, J = 7 Hz), 13.9 ppm. ^{31}P NMR ($CDCl_3$): 6.2 (d, J = 103 Hz) ppm. GC–MS: 280 (M^+, 5), 251 (7), 183 (63), 170 (28), 155 (49), 138 (100), 127 (91), 111 (58). TLC: R_f = 0.30 (hexane:ethyl acetate = 1:1). HRMS: Calcd. for $C_{13}H_{26}FO_3P$: 280.1603; Found: 280.1622. FT-IR (neat, NaCl plate); 2983 (s), 2929 (vs), 1666 (vs), 1141 (vs).

4.3.4. Diethyl-(1E)-1-fluoro-2(2′,4′-dimethyl)phenylethenephosphonate, (E)-2,4$(CH_3)_2$–C_6H_3CH=CFP(O)$(OEt)_2$ (4)

Similarly, the reaction of 1.15 g (5 mmol) of 2,4-$(CH_3)_2C_6H_3$CH=CFBr (E/Z = 3:2) with 0.76 g (5.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.23 g, 0.199 mmol) and 3.0 ml of Et_3N at 40°C (24 h) gave 0.40 g pure (*Z*)-2,4-dimethyl[C_6H_3CH=CFBr] (0.75 g, 3.27 mmol of olefins consumed) and 0.80 g (56%) of (*E*)-2,4-dimethyl[C_6H_3CH=CFP(O)$(OEt)_2$] (E/Z = 94:6). ^{1}H NMR ($CDCl_3$): 7.7 (d, J = 4 Hz, 1H), 7.0 (s, 3H), 6.9

(dd, $J = 42$ Hz, $J = 9$ Hz, 1H), 4.2–4.3 (m, 4H), 2.3 (s, 3H), 2.4 (s, 3H), 1.4 (t, $J = 7$ Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −129.2 (dd, $J = 100$ Hz, $J = 42$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 149 (dd, $J = 285$ Hz, $J = 237$ Hz), 139.4 (d, $J = 1.4$ Hz), 137 (d, $J = 1$ Hz), 131.1, 129.8 (dd, $J = 12$ Hz, $J = 1.4$ Hz), 126.8, 126.7 (dd, $J = 13$ Hz, $J = 1.5$ Hz), 120.2 (d, $J = 30$ Hz), 63.0 (d, $J = 5.5$ Hz), 21.2, 19.9, 16.2 (d, $J = 6$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 6.8 (d, $J = 100$ Hz) ppm. GC–MS: 286 (M^+, 57), 266 (20), 238 (13), 210 (60), 157 (36), 146 (54), 129 (100), 115 (51). TLC: $R_f = 0.40$ (hexanes:ethyl acetate = 1:1). HRMS: Calcd. for $C_{14}H_{20}FO_3P$: 286.1134; Found: 286.1113. FT-IR (neat, NaCl plate): 2985 (m), 2912 (s), 1444 (s), 1164 (m), 836 (vs).

*4.3.5. Diethyl-(1E)-1-fluoro-2-(4′-chlorophenyl)ethenephosphonate, (E)-p-ClC_6H_4CH=CFP(O)$(OEt)_2$ (**5**)*

Similarly, the reaction of 1.18 g (5 mmol) of *p*-ClC_6H_4CH=CFBr ($E/Z = 3{:}2$) with 0.76 g (5.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.23 g, 0.199 mmol) and 3.0 ml of Et_3N at 40°C (24 h) gave 0.45 g pure (*Z*)-*p*-ClC_6H_4CH=CFBr (0.73 g, 3.10 mmol of olefins consumed) and 0.65 g (45%) of (E)-*p*-ClC_6H_4CH=CFP(O)$(OEt)_2$ ($E/Z = 96{:}4$). ^{1}H NMR ($CDCl_3$): 7.4–7.6 (m, 4H), 6.7 (dd, $J = 42$ Hz, $J = 9$ Hz, 1H), 4.1–4.3 (m, 4H), 1.4 (td, $J = 7$ Hz, $J = 0.6$ Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −126 (dd, $J = 97$ Hz, $J = 42$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 150 (dd, $J = 287$ Hz, $J = 236$ Hz), 135 (d, $J = 3.6$ Hz), 131 (d, $J = 8$ Hz), 129.5 (dd, $J = 14.5$ Hz, $J = 1.4$ Hz), 128.9, 121.7 (d, $J = 30$ Hz), 63.2 (d, $J = 5.4$ Hz), 16.1 (d, $J = 6.2$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 5.7 (d, $J = 97$ Hz) ppm. GC–MS: 292 (M^+, 62), 294 (26), 264 (6), 244 (16), 218 (55), 201 (14), 183 (72), 136 (100), 119 (50), 101 (21), 93 (40). TLC: $R_f = 0.30$ (hexanes:ethyl acetate = 1:1). HRMS: Calcd. for $C_{12}H_{15}{}^{35}ClFO_3P$: 292.0431; Found: 292.0436. FT-IR: (neat, NaCl plate): 2985 (m), 2935 (s), 1592 (s), 1164 (m), 796 (s).

*4.3.6. Diethyl-(1E)-1-fluoro-3-phenylbut-1-enephosphonate, (E)-$C_6H_5(CH_3)$CHCH=CFP(O)$(OEt)_2$ (**6**)*

Similarly, the reaction of 1.15 g (5 mmol) of C_6H_5-(CH_3)CHCH=CFBr ($E/Z = 3{:}2$) with 0.76 g (5.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.23 g, 0.199 mmol) and 2.0 ml of Et_3N at 40°C (48 h) gave 0.40 g of pure (*Z*)-$C_6H_5(CH_3)$CHCH=CFBr (0.75 g, 3.30 mmol of olefins consumed) and 0.70 g (49%) of (*E*)-C_6H_5-(CH_3)CHCH=CFP(O)$(OEt)_2$ (100% (*E*)). GLPC > 99%. ^{1}H NMR ($CDCl_3$): 7.2–7.4 (m, 5H), 6.1 (ddd, $J = 39$ Hz, $J = 10$ Hz, $J = 8$ Hz, 1H), 4.0–4.3 (m, 5H), 1.4 (d, $J = 7$ Hz, 3H), 1.3 (dt, $J = 21$ Hz, $J = 7$ Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −132 (dd, $J = 102$ Hz, $J = 39$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 149 (dd, $J = 275$ Hz, $J = 235$ Hz), 143.5, 131 (dd, $J = 28$ Hz, $J = 6$ Hz), 128.6, 126.7, 126.6, 62.9 (dd, $J = 5$ Hz, $J = 2.5$ Hz), 34.8 (dd, $J = 10$ Hz, $J = 4$ Hz), 21.1, 16.1 (t, $J = 6$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 5.8 (d, $J = 102$ Hz) ppm. GC–MS: 286 (M^+, 6), 266 (15), 238 (11), 210 (33), 148 (21), 128 (100), 115 (13), 105 (5), 77 (9). TLC: $R_f = 0.35$ (hexane-s:ethyl acetate = 1:1). HRMS: Calcd. for $C_{14}H_{20}FO_3P$: 286.1134; Found: 286.1157. FT-IR (neat, NaCl plate): 2981 (s), 2933 (vs), 1592 (vs), 1454 (vs), 1164 (s), 975 (m), 796 (s).

*4.3.7. A representative procedure for the preparation of (Z)-α-fluorovinylphosphonate; diethyl-(1Z)-1-fluoro-3-methylbut-1-enephosphonate; (Z)-$(CH_3)_2$CHCH=CFP(O)$(OEt)_2$ (**7**)*

A 25 ml flask equipped with a condenser, a stir bar, and a N_2 tee was charged with 0.42 g (2.5 mmol) of (*Z*)-$(CH_3)_2$CHCH=CFBr, 0.11 g (0.1 mmol) of $Pd(PPh_3)_4$, 0.41 g (3 mmol) of diethylphosphite and 2.0 ml of Et_3N. The reaction mixture was stirred at reflux for 24 h. The reaction mixture was directly purified by silica gel chromatography (hexanes 100%, then 40:60 ethyl acetate:hexanes); 0.30 g (53%) OF (*Z*)-$(CH_3)_2$CHCH=CFP(O)$(OEt)_2$ (100% *Z*) was isolated. GLPC > 99%. ^{1}H NMR ($CDCl_3$): 5.9 (ddd, $J = 32$ Hz, $J = 29$ Hz, $J = 11$ Hz, 1H), 4.16–4.22 (m, 4H), 3.21–3.38 (m, 1H), 1.4 (td, $J = 7$ Hz, $J = 0.5$ Hz, 6H), 1.1 (dd, $J = 7$ Hz, $J = 1$ Hz, 6H) ppm. ^{19}F NMR (CDCl): −125 (dd, $J = 106$ Hz, $J = 29$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 147.9 (dd, $J = 264$ Hz, $J = 229$ Hz), 134 (dd, $J = 31$ Hz, $J = 10$ Hz), 62.8 (d, $J = 5$ Hz), 24.7 (d, $J = 7$ Hz), 23.1 (t, $J = 2$ Hz), 16.1 (d, $J = 6$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 4.5 (d, $J = 106$ Hz) ppm. GC–MS: 224 (M^+, 32), 196 (26), 168 (100), 153 (31), 147 (17), 138 (12), 111 (19), 101 (12), 87 (16), 83 (36). TLC: $R_f = 035$ (hexane:ethyl acetate = 1:1).

*4.3.8. Diethyl-(1Z)-1-fluoro-2-phenylethenephosphonate, (Z)-C_6H_5CH=CFP(O)$(OEt)_2$ (**8**)*

Similarly, the reaction of 1.01 g (5 mmol) of (*Z*)-C_6H_5CH=CFBr with 0.76 g (5.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.23 g, 0.199 mmol) and 3.0 ml of Et_3N at 70°C (24 h) gave 0.65 g (51%) of (*Z*)-C_6H_5CH=CFP(O)$(OEt)_2$ (100% (*Z*). GLPC > 99%, ^{1}H NMR ($CDCl_3$): 7.34–7.49 (m, 5H), 7.1 (t, $J = 29$ Hz), 1H), 4.1 (m, 4H), 1.2 (t, $J = 7$ Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −116.5 (dd, $J = 110$ Hz, $J = 29$ Hz), ppm. ^{13}C NMR ($CDCl_3$): 151 (dd, $J = 267$ Hz, $J = 230$ Hz), 130 (dd, $J = 11$ Hz, $J = 2$ Hz), 129.4 (m), 128.6, 128.1, 125.5 (dd, $J = 28$ Hz, $J = 20$ Hz), 63 (d, $J = 6$ Hz), 16 (d, $J = 7$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 4.3 (d, $J = 110$ Hz) ppm. GC–MS: 258 (M^+, 72), 185 (61), 149 (77), 129 (61), 118 (79), 102 (100), 93 (48), 65 (88). TLC: $R_f = 0.40$ (hexanes:ethyl acetate = 1:1). HRMS: Calcd. for $C_{12}H_{16}FO_3P$: 258.0821; Found: 258.0845. FT-IR (neat, NaCl plane): 3056 (s), 2935 (s), 1162 (s), 98 (s).

*4.3.9. Diethyl-(1Z)-1-fluoronon-1-enephosphonate, (Z)-$C_7H_{15}CH$=CFP(O)$(OEt)_2$ (**9**)*

Similarly, the reaction of 0.67 g (3.0 mmol) (*Z*)-$C_7H_{15}CH$=CFBr with 0.50 g. (3.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol)

and 3.0 ml of Et_3N at 75°C (24 h) gave 0.5 g (60%) of (*Z*)-$C_7H_{15}CH{=}CFP(O)(OEt)_2$ (100% *Z*). GLPC > 99%. ^1H NMR ($CDCl_3$): 6.0 (ddt, $J = 32$ Hz, $J = 29$ Hz, $J = 9$ Hz), 3.99–4.18 (m, 4H), 2.35–2.44 (m. 2H), 1.19–1.37 (m, 16H), 0.81 (t, $J = 7$ Hz) ppm. ^{19}F NMR ($CDCl_3$): −122.9 (dd, $J = 106$ Hz, $J = 29$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 149 (dd, $J = 263$ Hz, $J = 229$ Hz), 128 (m), 63 (d, $J = 6$ Hz), 31.7, 29.5, 29, 28.9, 24.7 (d, $J = 6$ Hz), 22.6, 16.2 (d, $J = 6$ Hz), 14.0, ppm. ^{31}P NMR ($CDCl_3$): 5.3 (d, $J = 107$ Hz) ppm. GC–MS: 280 (M^+, 14), 223 (6), 209 (65), 181 (40), 153 (100), 138 (30), 111 (17). HRMS: Calcd. for $C_{13}H_{26}FO_3P$: 280.1603; Found: 280.1607. FT-IR (neat, NaCl plate): 2858 (s), 1444 (vs), 1186 (vs), 1164(s), 1141 (vs).

*4.3.10. Diethyl-(1Z)-1-fluoro-2-(2′,4′-dimethyl)phenylethenephosphonate, (Z)-2,4-$(CH_3)_2$-[$C_6H_3CH{=}CFP(O)(OEt)_2$] (**10**)*

Similarly, the reaction of 0.69 g (3 mmol) of (*Z*)-2,4-$(CH_3)_2C_6H_3CH{=}CFBr$ with 0.50 g (3.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol) and 2.0 ml of Et_3N at reflux (24 h) gave 0.45 g (52%) of (*Z*)-2,4$(CH_3)_2C_6H_3CH{=}CFP(O)(OEt)_2$ (100% *Z*). ^1H NMR ($CDCl_3$): 7.2 (d, $J = 8$ Hz, 1H), 7.1 (d, $J = 29$ Hz, 1H), 6.9 (m. 2H), 3.82–4.03 (m, 4H), 2.17 (s, 3H), 2.2 (s, 3H), 1.1 (t, $J = 7$ Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −117.7 (dd, $J = 112$ Hz, $J = 28$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 150.8 (dd, $J = 268$ Hz, $J = 232$ Hz), 138.7, 136.1 (dd, $J = 3$ Hz, $J = 1.2$ Hz), 130.3, 130.1, 126.7 (dd, $J = 10$ Hz, $J = 2$ Hz), 126.1, 124.1 (dd, $J = 28$ Hz, $J = 8$ Hz), 64.0 (d, $J = 6$ Hz), 21.1, 19.9, 15.9 (d, $J = 7$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 4.4 (d, $J = 111$ Hz) ppm. GC–MS: 286 (M^+, 34), 266 (15), 210 (63), 157 (30), 130 (100), 115 (55). TLC: $R_f = 0.35$ (hexanes:ethyl acetate = 1:1). HRMS: Calcd. for $C_{14}H_{20}FO_3P$: 286.1134; Found: 286.1121. FT-IR (neat, NaCl plate): 2983 (m), 2933 (s), 1454 (s), 1164 (m), 794 (m).

*4.3.11. Diethyl-(1Z)-1-fluoro-3-(4′-chlorophenylethenephosphonate, (Z)-p-$ClC_6H_4CH{=}CFP(O)(OEt)_2$) (**11**)*

Similarly, the reaction of 0.70 g (3 mmol) of (*Z*)-*p*-$ClC_6H_4CH{=}CFBr$ with 0.50 g (3.5 mmol) of diethylphosphite in the presence of $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol) and 2.0 ml of Et_3N at reflux (24 h) gave 0.49 g (55%) of (*Z*)-*p*-$ClC_6H_4CH{=}CFP(O)(OEt)_2$ (100% *Z*). GLPC > 99%. ^1H NMR ($CDCl_3$): 7.3–7.5 (m, 4H), 7.0 (dd, $J = 29$ Hz, $J = 8$ Hz, 1H), 4.0–4.2 (m, 4H), 1.3 (td, $J = 7$ Hz, $J = 0.5$ Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −115.2 (dd, $J = 108$ Hz, $J = 29$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 151.3 (dd, $J = 269$ Hz, $J = 229$ Hz), 134.7, 130.8, 128.7 (dd, $J = 12$ Hz, $J = 2$ Hz), 128.3, 124.5 (dd, $J = 28$ Hz, $J = 21$ Hz), 63.3 (d, $J = 6$ Hz), 16.0 (d, $J = 7$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 3.7 (d, $J = 108$ Hz) ppm. GC–MS: 292 (M^+, 28), 294 (11), 264 (2), 218 (33), 163 (24), 136 (100), 120 (37), 93 (50), 65 (77). TLC: $R_f = 0.35$ (hexanes:ethyl acetate = 1:1). HRMS: Calcd. for $C_{12}H_{15}{}^{35}ClFO_3P$: 292.0431; Found: 292.0440. FT-IR (neat, NaCl plate): 2985 (s), 2935 (vs), 1630 (vs), 1594 (vs), 1164 (s), 883 (s).

*4.3.12. Diethyl-(1Z)-1-fluoro-3-phenylbut-1-enephosphonate, (Z)-$C_6H_5(CH_3)CHCH{=}CFP(O)(OEt)_2$ (**12**)*

Similarly, the reaction of 0.65 g (2.5 mmol) of (*Z*)-$C_6H_5(CH_3)CHCH{=}CFBr$ with 0.50 g (3.5 mmol) of diehylphosphite in the presence of $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol) and 2.0 ml of Et_3N at reflux (24 h) gave 0.40 g (56%) of (*Z*)-$C_6H_5(CH_3)CHCH{=}CFP(O)(OEt)_2$ (100% *Z*). GLPC > 99%. ^1H NMR ($CDCl_3$): 7.28–7.34 (m, 5H), 6.20 (ddd, $J = 31$ Hz, $J = 28$ Hz, $J = 12$ Hz, 1H), 4.5–4.6 (m, 1H), 3.98–4.29 (m, 4H), 1.36–1.43 (m, 6H), 1.3 (td, $J = 7$ Hz, $J = 0.4$ Hz, 3H) ppm. ^{19}F NMR ($CDCl_3$): −123.9 (ddd, $J = 104$ Hz, $J = 28$ Hz, $J = 2.5$ Hz) ppm. ^{13}C NMR ($CDCl_3$): 148 (dd, $J = 267$ Hz, $J = 237$ Hz), 144 (t, $J = 2$ Hz), 132.4 (dd, $J = 31$ Hz, $J = 11$ Hz), 128.6, 126.8, 126.5, 62.9 (dd, $J = 6$ Hz, $J = 3$ Hz), 34.7 (dd, $J = 7$ Hz, $J = 1$ Hz), 21.9, 16.1 (dd, $J = 9$ Hz, $J = 7$ Hz) ppm. ^{31}P NMR ($CDCl_3$): 4.7 (d, $J = 105$ Hz) ppm. GC–MS: 286 (M^+, 7), 266 (31), 238 (16), 210 (38), 145 (24), 128 (100), 115 (60), 101 (13), 77 (20). TLC: $R_f = 0.35$ (hexanes:ethyl acetate = 1:1). HRMS: Calcd. for $C_{14}H_{20}FO_3P$: 286.1134; Found: 286.1125.

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