Carbocupration of Diethyl 1-Alkynyl Phosphonates: Stereo- and Regioselective Synthesis of 1,2,2-Trisubstituted Vinyl Phosphonates

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Introduction

The synthesis of stereoselectively substituted alkenes is one of the interesting topics in organic synthesis. The chemistry of organocopper(I) reagents has especially received a great deal of attention regarding cis-conjugate addition reactions with acetylenic compounds.[1] In the case of addition to functionalized acetylenes, α,*β*-acetylenic esters undergo a facile conjugate addition reaction with lithium diorganocuprates,[2] with cis addition taking place exclusively. 1-Alkynyl sulfoxides and sulfones also undergo cis-conjugate addition.[3] In contrast, the reactions of organocopper(I) reagents with a number of 1-alkynyl phosphorus compounds have been observed in a few cases.[4] At the time this work was initiated, no addition of organocopper(I) reagents to 1-alkynyl phosphonates had been reported.

Vinyl phosphonates are interesting compounds owing to their synthetic utility[5] and biological activity.[6] For the preparation of the vinyl phosphonates, many reports are found in the literature.[5,7] In contrast, for the synthetic methods of 2,2-dialkyl vinylic phosphonates, a few methods are known. One of these methods is the copper-catalyzed Arbuzov reaction,[8] having some limitations with the preparation of starting compounds. Recently, we have reported a new synthetic route for the stereodefined vinylic phosphonates via *t*-BuOK-induced cleavage of dihydrofuran derivatives.[9] However, synthetic methods for stereocontrolled 1,2,2-trisubstituted vinylic phosphonates appear to have never been reported.

Herein, we report a synthetic route (Scheme 1), results (Table 1) for the preparation of vinylic phosphonates by the additions of organocopper(I) reagents to 1-alkynyl phosphonates (**1**).[10] By subsequent capture of the inter-

Table 1. Preparation of Diethyl 2,2-Disubstituted Vinyl Phosphonates by the Reaction of 1-Alkynylphosphonates with Copper(I) Reagents (electrophile = H^+)

R	Copper(I) reagents/ time(h)/ Temp	Product	yield(%)[a]	$3^s/3^a$ [a b]
H	$Et_2CuMgBr$/ 1/ rt	Et_2O_3P, H, H, Et **a**	85	only 3^s
n-Bu	$Me_2CuMgBr$/ 1.5/ rt	Et_2O_3P, *n*-Bu, H, Me **b**	85	only 3^s
n-Bu	$Et_2CuMgBr$/ 1/ rt	Et_2O_3P, *n*-Bu, H, Et **c**	92	only 3^s
n-Bu	*n*-Bu_2CuLi_2I/ 1/ rt	Et_2O_3P, *n*-Bu, H, *n*-Bu **d**	93	–
n-Bu	Ph_2CuLi_2I/ 1/ rt	Et_2O_3P, *n*-Bu, H, Ph **e**	95	only 3^s
n-Hex	$Me_2CuMgBr$/ 2/ rt	Et_2O_3P, *n*-Hex, H, Me **f**	92	only 3^s
CH_2OBn	$Me_2CuMgBr$/ 1/ rt	Et_2O_3P, CH_2OBn, H, Me **g**	90	only 3^s
Ph	*n*-Bu_2CuLi_2I/ 0.2/ -10 °C[c]	Et_2O_3P, Ph, H, *n*-Bu **h**	94	only 3^s
t-Bu	$Me_2CuMgBr$ or Me_2CuLi_2I/ 0.5/ reflux[d]	Et_2O_3P, Me, H, *t*-Bu **i**	96	only 3^a
t-Bu	$Et_2CuMgBr$/ 6/ rt	Et_2O_3P, Et, H, *t*-Bu **j**	94	only 3^a
t-Bu	*n*-Bu_2CuLi_2I/ 2/ rt	Et_2O_3P, *n*-Bu, H, *t*-Bu **k**	97	only 3^a

[a] Isolated yields. [b] Other isomers were not detected in the GC and NMR studies. [c] Another isomer (**e**) was detected as the major product ($3^s/3^a = 0.67$) at room temperature (1 h). [d] No reaction at room temperature.

Scheme 1

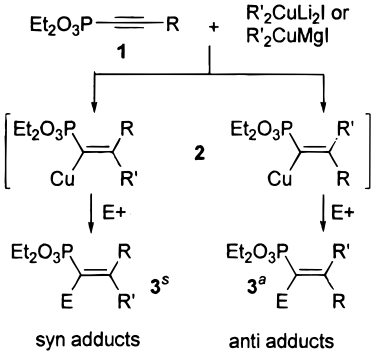

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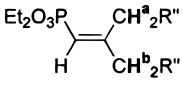
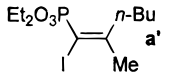
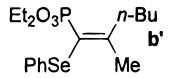
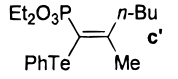
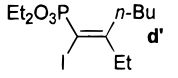
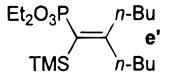
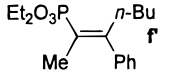
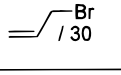
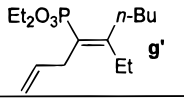
Table 2. NMR Data Due to the Allylic Methyl for Vinylic Phosphonates (in $CDCl_3$, ppm(δ) Downfield range from tetramethylsilane and ^{31}P coupling constants (J) range)



	H^a	H^b
ppm(δ) range	2.30~2.50	1.80~2.10
J range(Hz)	1.90~2.40	< 0.78

R" were hydrogen or alkyl groups. When R" was alkoxy group, δ was shifted more downfield(4.45) but *J* was similar value

Table 3. Preparation of Diethyl 1,2,2-Trisubstituted Vinyl Phosphonates by the Reaction of 1-Hexynylphosphonates with Copper(I) Reagents and Several Electrophiles

Copper(I) reagents	Electrophile/ time(min) at rt	Product[a]	yield(%)[b]
$Me_2CuMgBr$	I_2/ 10	 **a'**	97
$Me_2CuMgBr$	PhSeBr / 20	 **b'**	40[c]
$Me_2CuMgBr$	PhTeI / 20	 **c'**	80
$Et_2CuMgBr$	I_2/ 10	 **d'**	98
n-Bu_2CuLi_2I	TMSCl / 30	 **e'**	82
Ph_2CuLi_2I	MeI/ 60	 **f'**	85
$Et_2CuMgBr$	 / 30	 **g'**	88

[a] Stereoselectivity was retained from vinylic copper intermediates (Table 1). [b] Isolated yields. [c] 1-Brominated vinylic phosphonate was obtained in a considerable amount as a side product.

mediate 1-phosphonyl-2,2-dialkyl vinylcopper compounds (**2**) with several electrophiles, we obtained the 1,2,2-trisubstituted vinylic phosphonates (**3**) having high regio- and stereoselectivity in reasonably good yields (Table 3).

Results and Discussion

Preliminary experiments involved the treatment of diethyl 1-alkynyl phosphonates with copper(I) reagents (1.5 equiv), followed by a protolysis with saturated ammonium chloride solution (E = H). As indicated in the Table 1, the reaction proceeds well for copper(I) reagents derived from copper iodide. In all cases attack of the alkyl copper(I) reagents on diethyl 1-alkynyl phosphonates occurred at the 2-position exclusively without side reactions. The regioselectivity can be rationalized in terms of a carbanion stabilization by the phosphonyl group.

In all reactions involving the possible formation of geometrical isomers, the NMR spectra of the crude vinylic phosphonates showed the stereospecific formation of essentially only *one* isomer.

It was found that the 1-alkynyl phosphonates undergo a smooth, stereospecific cis-addition of copper(I) reagents when R = H, *n*-Bu, *n*-Hex, CH_2OBn, Ph, but not *t*-Bu. When R = Ph, the product was only one isomer at −10 °C, but a mixture (e, h) with the anti adduct as the major product at room temperature. When R was *t*-Bu, we obtained the anti-addition products exclusively to our surprise. In case of R = *t*-Bu, R′ = Et, the reaction time was very long. When the reaction time was 1 h, the quenched mixture includes the starting compound and only the anti-product (j).

The structures of the 2,2-dialkyl vinylic phosphonates were characterized by one- or two-dimensional NOE techniques and HRMS. On the basis of these defined structures, the ^1H NMR absorption due to the allylic methyl protons in the 2,2-dialkyl vinyl phosphonates showed the lowest downfield peaks and larger phosphorus coupling constants when they were cis rather than trans to the phosphonate group (Table 2).

The poor reactivity of Me_2CuLi_2I and $Me_2CuMgBr$ toward alkylacetylenes is well-known,[11] and so their lower reactivity toward 1-alkynyl phosphonates required longer times and higher reaction temperatures. Addition took place even with a terminal acetylenic phosphonate with no observable abstraction of the acetylenic proton with the organocopper reagent ($Et_2CuMgBr$). R'_2CuLi_2I or $R'_2CuMgBr$ showed similar reactivity in the conversion of 1-alkynyl phosphonates into vinyl phosphonates.

The α-phosphonyl vinylcopper(I) species (**2**) as 1-metallic vinyl phosphonates are very important intermediates because they react with a variety of eletrophiles to give the vinyl phosphonate derivatives. These intermediates react with several electrophiles having transmetalation properties (I, Te, Se),[12] and the α-phosphonyl vinylcopper-(I) species (**2**) are fairly stable. Vinylcopper(I) species usually dimerize rapidly above −10 °C,[11] but solutions of our adducts can be stirred at refluxing (THF) temperature during several minutes without detectable dimerization. Because of the pronounced thermal stability of the intermediary adducts, the presence of stabilizing agents such as trimethyl phosphite prior to the addition of the electrophile is not required.

The α-functionalization of vinyl phosphonates was performed by adding several electrophiles to the α-phosphonyl vinylcopper(I) intermediates at −78 °C followed by warming to rt. After workup, the vinyl phosphonates were obtained as indicated in Table 3. 1-Iodovinylphosphonates were obtained by treating the intermediary adducts with iodine. When phenyltelluryl iodide, phenylselenyl bromide, or trimethylsilyl chloride was added, vinylic phosphonates substituted with an electron-withdrawing group were formed, bearing a PhTe,[13] PhSe,[14] or Me_3Si[15] group in the α-position. In case of PhSeBr, the 1-bromo-substituted vinylic phosphonate was obtained in a considerable amount as a side product.

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Allylation and methylation were carried out with allyl bromide and methyl iodide, respectively. However, in case of the attempted acylation of α-phosphonyl vinylcopper-(I) intermediates with acetyl chloride and benzoyl chloride, complications occurred because of the isomerization of unstable vinylic phosphonates containing a strong electron-withdrawing α-acyl group and 2,2-dialkyl groups. Therefore, we could not prepare the corresponding α-acyl vinylic phosphonates successfully.

In conclusion, the reaction of organocopper(I) reagents with 1-alkynylphosphonates affords a rapid entry into a variety of vinylic phosphonates with high regio- and stereoselectivity and with high yields in a one-pot process. 1-Alkynyl phosphonates (**1**) are easily converted into 1-phosphonyl-2,2-dialkyl vinylcopper(I) intermediates (**2**) by treatment with organocopper(I) reagents. The adducts (**2**) react with a variety of electrophiles to give the vinyl phosphonate derivatives (**3**) RR′C=C(E)PO_3Et_2 (E = H, I, Me, allyl, SePh, TePh, $SiMe_3$). The stereochemistry of the carbocupration of 1-alkynyl phosphonates with organocopper(I) reagents are observed as only syn-addition (R = H, *n*-Bu, *n*-Hex, CH_2OBn, Ph) and unexpected anti-addition in the case of R = *t*-Bu.

Experimental Section

General. All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. THF was distilled from Na/benzophenone ketyl. ^{1}H-, ^{13}C-, and NOE-NMR spectra were recorded at 300 MHz in $CDCl_3$, using TMS or residual $CHCl_3$ as internal references.

Synthesis of Diethyl 2,2-Dialkyl Vinylic Phosphonates (a−k). General Procedure. Diethyl 1-alkynylphosphonates (**1**)[10] (1 mmol) in THF (3 mL) were added to the organocopper(I) reagents[1] (1.5 equiv) at −78 °C. The reaction mixtures were allowed to warm at −10 °C, room temperature, or refluxing (THF) temperature during several hours (Table 1), followed by protolysis with saturated aqueous NH_4Cl, and the products (colorless oil) were isolated by extraction with diethyl ether, drying ($MgSO_4$), concentration, and silica gel chromatography (EtOAc:hexane = 1:1), respectively.

(*E*)-1-(Diethyl phosphonato)-1-propene (a): ^{1}H NMR δ 6.67−6.84 (m, 1H), 5.49−5.63 (m, 1H), 3.93−4.04 (m, 4H), 2.11−2.20 (m, 2H), 1.22−1.30 (m, 6H), 0.95−1.03 (m, 3H); ^{13}C NMR δ 154.936 (d, *J* = 4.5), 115.61(d, *J* = 187.35), 61.413 (d, *J* = 5.55), 26.93 (d, *J* = 22.2), 16.22 (d, *J* = 6.30), 11.71.

(*Z*)-1-(Diethyl phosphonato)-2-methyl-1-hexene (b): ^{1}H NMR δ 5.29 (d, 1H, *J* = 18.88), 3.93−4.03 (m, 4H), 2.40−2.43 (m, 2H), 1.63 (s, 3H), 1.30−1.40 (m, 4H), 1.21−1.28 (m, 6H), 0.85 (t, 3H, *J* = 7.31); ^{13}C NMR δ 163.63 (d, *J* = 7.43), 122.12 (d, *J* = 188.175), 61.00 (d, *J* = 5.55), 34.72 (d, *J* = 6.68), 30.25 (d, *J* = 1.8), 25.44 (d, *J* = 24.6), 22.62, 16.24 (d, *J* = 6.6), 13.82; HRMS exact mass calcd for $C_{11}H_{23}O_3P$ (M^+): 234.1384, found: 234.1392.

(*Z*)-1-(Diethyl phosphonato)-2-ethyl-1-hexene (c): ^{1}H NMR δ 5.18 (d, 1H, *J* = 18.28), 3.85−3.95 (m, 4H), 2.33−2.38 (m, 2H), 2.04 (q, 2H, *J* = 7.37), 1.22−1.30 (m, 4H), 1.14−1.22 (m, 6H), 0.90 (t, 3H, *J* = 6.78), 0.76 (t, 3H, *J* = 7.08); ^{13}C NMR δ 163.56 (d, *J* = 6.90), 109.62 (d, *J* = 189.075), 60.78 (d, *J* = 5.55), 33.46 (d, *J* = 7.05), 30.64 (d, *J* = 7.05), 30.48 (d, *J* = 2.55), 22.60, 16.06 (d, *J* = 6.45), 13.62, 11.63; HRMS exact mass calcd for $C_{12}H_{25}O_3P$ (M^+): 248.1541, found: 248.1550.

1-(Diethyl phosphonato)-2-(*n*-butyl)-1-hexene (d): ^{1}H NMR δ 5.18 (d, 1H, *J* = 18.64), 3.85−3.94 (m, 4H), 2.31−2.37 (m, 2H), 2.00 (t, 2H, *J* = 7.08), 1.20−1.32 (m, 8H), 1.13−1.18 (m, 6H), 0.73−0.78 (m, 6H); ^{13}C NMR δ 167.29 (d, *J* = 6.75), 110.65 (d, *J* = 188.25), 60.75 (d, *J* = 5.55), 37.59 (d, *J* = 22.28), 33.24 (d, *J* = 7.05), 30.46 (d, *J* = 1.88), 29.44, 22.59, 22.05, 16.05 (d, *J* = 6.45), 13.81, 11.56; HRMS Exact mass calcd for $C_{14}H_{29}O_3P$ (M+): 276.1854, found: 276.1877.

(*E*)-1-(Diethyl phosphonato)-2-phenyl-1-hexene (e): ^{1}H NMR δ 7.22−7.31 (m, 5H), 5.65 (d, 1H, *J* = 17.15), 3.97−4.10 (m, 4H), 2.85−2.95 (m, 2H), 1.20−1.28 (m, 10H), 0.75−0.80 (m, 3H); ^{13}C NMR δ 163.52 (d, *J* = 8.63), 140.90 (d, *J* = 23.63), 128.59, 128.22, 126.17, 113.58 (d, *J* = 188.625), 61.11 (d, *J* = 5.70), 32.13 (d, *J* = 6.50), 30.69 (d, *J* = 3.53), 22.42, 16.13 (d, *J* = 2.48), 13.60.

(*Z*)-1-(Diethyl phosphonato)-2-methyl-1-octene (f): ^{1}H NMR δ 5.17 (dd, 1H, *J* = 19.06, 1.10), 3.61−3.91 (m, 4H), 2.29−2.35 (m, 2H), 1.71 (s, 3H), 1.20−1.40 (m, 2H), 0.95−1.20 (m, 12H), 0.69 (t, 3H, *J* = 6.46); ^{13}C NMR δ 163.22 (d, *J* = 7.58), 111.95 (d, *J* = 188.33), 60.64 (d, *J* = 4.05), 34.67 (d, *J* = 6.6), 31.32, 28.92, 27.64 (d, *J* = 1.88), 25.14 (d, *J* = 24.6), 22.17, 15.96 (d, *J* = 6.53), 13.63.

(*Z*)-1-(Diethyl phosphonato)-2-methyl-1-propenyl benzyl ether (g): ^{1}H NMR δ 7.24−7.32 (m, 5H), 5.51 (d, 1H, *J* = 23.20), 4.46 (s, 2H), 4.45 (d, 2H, *J* = 2.41), 3.96−4.06 (m, 4H), 1.98d, 3H, *J* = 0.74), 1.25−1.29 (m, 6H); ^{13}C NMR δ 158.29 (d, *J* = 21.53), 137.69, 128.10, 127.46, 127.37, 114.47 (d, *J* = 186.08), 72.43, 69.82 (d, *J* = 7.05), 61.30 (d, *J* = 5.55), 23.17 (d, *J* = 22.8), 16.30 (d, *J* = 6.6).

(*Z*)-1-(Diethyl phosphonato)-2-phenyl-1-hexene (h): ^{1}H NMR δ 7.24−7.33 (m, 5H), 5.68 (d, 1H, *J* = 17.7), 3.69−3.86 (m, 4H), 2.46 (t, 2H, *J* = 6.59), 1.20−1.45 (m, 4H), 1.04−1.08 (m, 6H), 0.61−0.66 (m, 3H); ^{13}C NMR δ 163.31 (d, *J* = 3.75), 139.67 (d, *J* = 23.63), 127.78, 127.59, 127.33 (d, *J* = 1.73), 113.77 (d, *J* = 188.83), 61.09 (d, *J* = 6.08), 41.11 (d, *J* = 20.85), 29.51, 22.08, 16.02 (d, *J* = 8.25), 13.75.

(*E*)-1-(Diethyl phosphonato)-2-(*tert*-butyl)-1-propene (i): ^{1}H NMR δ 5.37 (dd, 1H, *J* = 17.70, 0.71), 3.92−4.00 (m, 4H), 2.00 (dd, 3H, *J* = 3.00, 0.67), 1.17−1.25 (m, 6H), 1.01 (s, 9H); ^{13}C NMR δ 170.23 (d, *J* = 4.88), 109.01 (d, *J* = 187.50), 60.99 (d, *J* = 5.63), 38.25 (d, *J* = 20.03), 24.48, 16.36 (d, *J* = 8.03), 16.20 (d, *J* = 6.3).

(*E*)-1-(Diethyl phosphonato)-2-(*tert*-butyl)-1-butene (j): ^{1}H NMR δ 5.36 (d, 1H, *J* = 16.22), 3.93−4.01 (m, 4H), 2.48 (qd, 2H, *J* = 7.47, 1.96), 1.20−1.27 (m, 6H), 1.09 (t, 3H, *J* = 7.44), 1.05 (s, 9H); ^{13}C NMR δ 176.17 (d, *J* = 5.85), 108.76 (d, *J* = 187.65), 61.00 (d, *J* = 5.78), 38.87 (d, *J* = 20.55), 29.06, 23.47 (d, *J* = 7.58), 16.24 (d, *J* = 8.03) 15.73 (d, *J* = 2.7).

(*E*)-1-(Diethyl phosphonato)-2-(*tert*-butyl)-1-hexene (k): ^{1}H NMR δ 5.27 (d, 1H, *J* = 16.03), 3.83−3.93 (m, 4H), 2.29−2.35 (m, 2H), 1.30−1.41 (m, 2H), 1.18−1.27 (m, 2H), 1.10−1.17 (m, 6H), 0.94 (s, 9H), 0.75 (t, 3H, *J* = 7.25); ^{13}C NMR δ 174.67 (d, *J* = 5.85), 108.71 (d, *J* = 188.18), 60.74 (d, *J* = 5.78), 38.61 (d, *J* = 20.63), 33.31 (d, *J* = 2.40), 30.47 (d, *J* = 7.35), 28.92, 23.27, 16.06 (d, *J* = 6.38), 13.51.

Synthesis of Diethyl 1,2,2-Trisubstituted Vinylphosphonates (a′−g′). General Procedure. Diethyl 1-hexynylphosphonates (1 mmol) in THF (3 mL) were added to the organocopper(I) reagents (1.5 equiv) at −78 °C, and the reaction mixtures were allowed to warm at room temperature for several hours (Table 1). The reaction mixtures were then cooled to −78 °C and several electrophiles (in the cases of **a′**, **d′**, iodine (2 mmol, 0.508 g, in THF (6 mL)); in the case of **b′**, phenyl selenyl bromide (2 mmol, 0.470 g, in THF (4 mL)); in the case of **c′**, phenyltelluryl iodide (2 mmol) (prepared by reaction of diphenyl ditelluride (1.0 mmol, 0.410 g) with iodine (1.0 mmol, 0.254 g) in THF (5 mL) for 1 h at rt); in the case of **e′**, trimethylsilyl chloride (2 mmol, 0.220 g, in THF (3 mL)); in the case of **f′**, methyl iodide (2 mmol, 0.13 mL, neat); in the case of **g′**, allyl bromide (2 mmol, 0.242 g in THF (3 mL))) were added dropwise. The reaction mixtures were allowed to warm to rt and were stirred for several minutes (Table 2) before quenching with saturated NH_4Cl (aq), and the products (colorless oil) were isolated by extraction with diethyl ether, drying ($MgSO_4$), evaporation, and silica gel chromatography (in the cases of **a′**, **b′**, **c′**, **d′**, EtOAc:hexane = 1: 4; in the cases of **e′**, **f′**, **g′**, EtOAc:hexane = 1:1), respectively.

(*E*)-1-(Diethyl phosphonato)-1-iodo-2-methyl-1-hexene (a′): ^{1}H NMR δ 3.95−4.02 (m, 4H), 2.74 (td, 2H, *J* = 7.33, 1.83), 2.04 (t, 3H, *J* = 1.67), 1.30−1.40 (m, 4H), 1.21−1.28 (m, 6H), 0.80 (t, 3H, *J* = 7.22); ^{13}C NMR δ 166.23 (d, *J* = 13.8), 85.17 (d, *J* = 194.1), 62.18 (d, *J* = 5.40), 38.63 (d, *J* = 4.65), 32.80 (d, *J* = 16.13), 30.71 (d, *J* = 1.65), 22.38, 16.01 (d, *J* = 6.75), 13.69; HRMS exact mass calcd for $C_{11}H_{22}IO_3P$ (M^+): 360.0351, found: 360.0339.

(*E*)-1-(Diethyl phosphonato)-1-phenylselenyl-2-methyl-1-hexene (b′): ^{1}H NMR δ 7.11−7.31 (m, 5H), 3.92−4.06 (m, 4H), 2.82 (td, 2H, *J* = 7.50, 1.83), 2.12 (d, 3H, *J* = 2.14), 1.45−1.51 (m, 2H), 1.33−1.40 (m, 2H), 1.15−1.20 (m, 6H), 0.90 (t, 3H, *J* = 7.22); ^{13}C NMR δ 170.76 (d, *J* = 16.5), 132.62, 129.37, 128.92,

125.95, 113.60 (d, J = 191.93), 62.07 (d, J = 6.00), 37.52 (d, J = 5.78), 31.16 (d, J = 1.65), 26.31 (d, J = 16.43), 22.78, 16.14 (d, J = 6.75), 13.86; HRMS exact mass calcd for $C_{17}H_{27}O_3PSe$ (M^+): 390.0863, found: 390.0820.

(*E*)-1-(Diethyl phosphonato)-1-phenyltelluryl-2-methyl-1-hexene (c′): ^{1}H NMR δ 7.55−7.58 (m, 2H), 7.14−7.17 (m, 3H), 3.98−4.07 (m, 4H), 2.85 (td, 2H, J = 7.44, 1.90), 2.15 (d, 3H, J = 1.79), 1.40−1.44 (m, 2H), 1.29−1.36 (m, 2H), 1.21−1.26 (m, 6H), 0.88 (t, 3H, J = 7.26); ^{13}C NMR δ 171.82 (d, J = 11.1), 136.00, 129.22, 127.18, 116.61, 103.09 (d, J = 176.63), 62.06 (d, J = 5.93), 37.56 (d, J = 7.28), 32.13 (d, J = 19.58), 31.37 (d, J = 1.58), 22.77, 16.27 (d, J = 6.6), 13.88; HRMS exact mass calcd for $C_{17}H_{27}O_3PTe$ (M^+): 440.0760, found: 440.0705.

(*E*)-1-(Diethyl phosphonato)-1-iodo-2-ethyl-1-hexene (d′): ^{1}H NMR δ 3.89−4.00 (m, 4H), 2.68 (td, 2H, J = 7.34, 1.75), 2.34 (q, 2H, J = 7.51), 1.23−1.35 (m, 4H), 1.18−1.20 (m, 6H), 0.92 (t, 3H, J = 7.49), 0.77 (t, 3H, J = 7.18); ^{13}C NMR δ 170.67 (d, J = 12.53), 84.22 (d, J = 192.98), 62.09 (d, J = 5.33), 37.95 (d, J = 15.68), 33.95 (d, J = 4.65), 31.14 (d, J = 1.73), 22.51, 15.92 (d, J = 6.53), 13.57, 11.22 (d, J = 2.33); HRMS exact mass calcd for $C_{12}H_{24}IO_3P$ (M^+): 374.0508, found: 374.0524.

1-(Diethyl phosphonato)-1-trimethylsilyl-2-(*n*-butyl)-1-hexene (e′): ^{1}H NMR δ 3.89−3.96 (m, 4H), 2.63−2.65 (m, 2H), 2.22 (t, 2H, J = 6.92), 1.25−1.40 (m, 8H), 1.20−1.24 (m, 6H), 0.82−0.88 (m, 6H), 0.16 (t, 9H, J = 0.83); ^{13}C NMR δ 177.75, 122.85 (d, J = 147.38), 60.38 (d, J = 5.7), 38.63 (d, J = 28.05), 36.06 (d, J = 10.95), 32.22 (d, J = 2.10), 31.53 (d, J = 1.65), 23.03, 22.96, 16.24 (d, J = 6.68), 13.91, 13.90, 2.31 (d, J = 2.18); HRMS exact mass calcd for $C_{17}H_{37}O_3PSi$ (M^+): 348.2250, found: 348.2217.

(*E*)-1-(Diethyl phosphonato)-1-methyl-2-(phenyl)-1-hexene (f′): ^{1}H NMR δ 7.23−7.33 (m, 3H), 7.01−7.043 (m, 2H), 4.05−4.12 (m, 4H), 2.79−2.83 (m, 2H), 2.62 (d, 3H, J = 13.71), 1.29−1.32 (m, 6H), 1.20−1.26 (m, 4H), 0.78 (t, 3H, J = 6.67); ^{13}C NMR δ 168.58 (d, J = 12.45), 142.03 (d, J = 22.43), 128.12, 127.32 (d, J = 0.98), 126.93, 120.37 (d, J = 175.13), 61.20 (d, J = 5.70), 36.46 (d, J = 6.75), 30.34 (d, J = 1.95), 22.66, 18.20 (d, J = 11.40), 16.31 (d, J = 6.30), 13.83.

(*Z*)-1-(Diethyl phosphonato)-1-allyl-2-(ethyl)-1-hexene (g′): ^{1}H NMR δ 5.65−5.80 (m, 1H), 4.91−5.01 (m, 1H), 3.90−4.00 (m, 4H), 2.95 (dd, 2H, J = 17.52 J = 5.80), 2.45−2.50 (m, 2H), 2.11 (qd, 2H, J = 7.46, 0.77), 1.28−1.40 (m, 4H), 1.21−1.26 (m, 6H), 0.96 (t, 3H, J = 7.35), 0.86 (t, 3H, J = 7.07); ^{13}C NMR δ 162.56 (d, J = 11.18), 136.23 (d, J = 1.65), 120.08 (d, J = 177.00), 114.81, 61.00 (d, J = 5.555), 33.78, 33.65 (d, J = 3.53), 31.24 (d, J = 2.25), 25.87 (d, J = 19.13), 23.04, 16.22 (d, J = 6.53), 13.89, 12.61 (d, J = 2.55); HRMS exact mass calcd for $C_{15}H_{29}O_3P$ (M^+): 288.1854, found: 288.1831.

Supporting Information Available: ^{1}H NMR, ^{13}C NMR, HRMS, NOE spectra of compounds **a**−**k**, **a′**−**g′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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