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Carbon−Carbon Bond Formation of Alkenylphosphonates by Aldehyde Insertion into Zirconacycle Phosphonates

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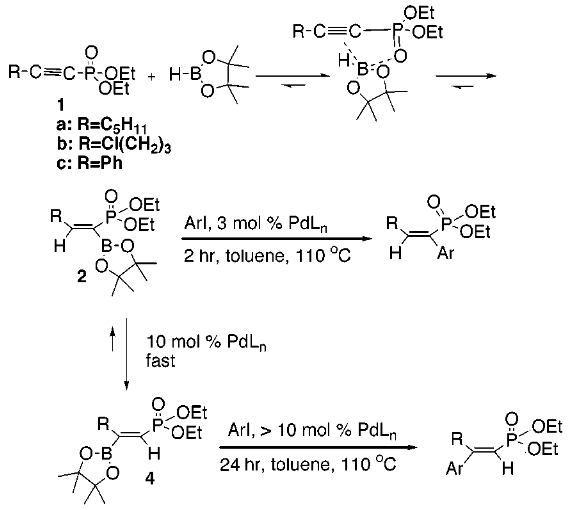
Ethyl 1-butynylphosphonate reacts with $Cp_2ZrCl_2/2n$-BuLi to give a three-membered zirconacycle that readily inserts aldehydes. Hydrolysis of the intermediate five-membered zirconacycles leads to two products, **4** and **5**. In the major product, **5**, the aldehyde inserts into C2 of the zirconacycle, while in the minor product, **4**, the aldehyde inserts into C1. Products **5** are obtained in 38−75% isolated yields. Products **4** are obtained in approximately 1−12%. Essentially, only compounds **5** are produced with *ortho*-substituted aldehydes. The regio- and stereochemistry of **4** and **5** were determined by $^3J_{PH}$, $^2J_{PC2}$, and $^3J_{PC3}$ coupling constants.

Vinylphosphonates are an important group of compounds that have found use in organic transformations.[1] The double bond in vinylphosphonates can be converted to aziridines,[2] epoxidized,[3] and C-glycosylated.[4] It reacts with organocuprate reagents that can be further transformed.[5] Vinylphosphonates are also useful reagents for the synthesis of biologically active compounds or as investigative reagents.[6] The synthesis of vinylphosphonates is varied. However, the synthesis of vinylphosphonates by addition of organometallic reagents to 1-alkynylphosphonates though attractive has not received much attention and includes *syn*-addition of organocuprates,[7] reaction of α-stannylated phosphonates with aldehydes to give *E*/*Z* mixtures of 1,2-disubstituted vinylphosphonates,[8] *anti* hydrotelluration,[9] Heck reactions using aryldiazonium salts,[10] α-lithiation of *β*-oxy or *β*-thio vinylphosphontes,[11] NaH-catalyzed olefination of benzenesulfinylmethylphosphonates,[12] and addition of sodium organyl chalcogenolates.[13] We have recently started to investigate the addition of organometallic reagents to 1-alkynylphosphonates. One such reaction is hydroboration. For instance, we have discovered that the hydroboration of 1-alkynylphosphonates with pinacolborane can be controlled to place boron on either C1 or C2 of the triple bond by proper use of base, catalyst, and reaction time.[14] In conjunction with Suzuki coupling, we developed a highly stereospecific synthesis of vinylphosphonates (Scheme 1).

Scheme 1



Zirconacycles are very useful intermediates in organic transformations.[15] Another very useful reaction of triple

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[1] For a recent review, see: (a) Minam I, T.; Motoyoshiya, J. *Synthesis* **1992,** 333. Afarinkia, K.; Binch, H. M.; Modi, C. *Tetrahedron Lett.* **1998**, *39*, 7419.

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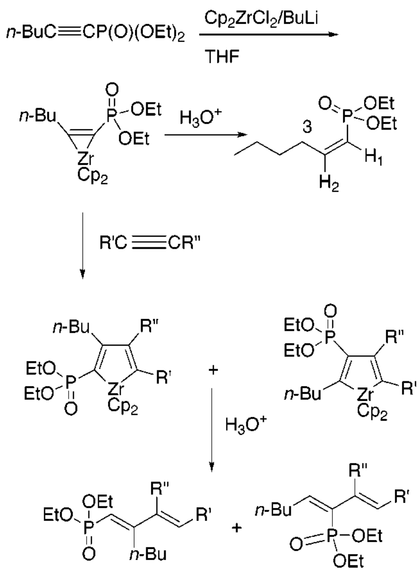
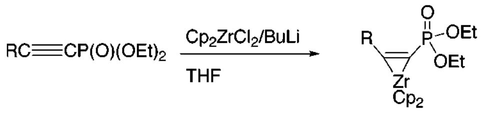
10.1021/jo010424r CCC: $20.00

Scheme 2



bonds that we have begun to explore is zirconacycle formation of 1-alkynylphosphonates[16] (eq 1).[17]


(1)

Thus, hydrolysis of the zirconacycles provided *cis*-vinylphosphonates, and subsequent insertion reactions of the three-membered zirconacycles with different alkynes provided access to 1,3-butadienylphosphonates (Scheme 2).[18]

As a continuation of the study of metalation reactions of 1-alkynylphosphonates, we now report our results on the insertion of aldehydes into three-membered zirconacycles generated from 1-alkynylphosphonates to give the equivalent of Baylis−Hillman[19] type carbon−carbon bond formation of alkenylphosphonates. Compounds such as **4** are readily converted to allenes by treatment with base under Horner−Wadsworth−Emmons conditions.[20]

When zirconacycles **1**, prepared by reaction of diethylhexynylphosphonate and 2*n*-BuLi/Cp_2ZrCl_2, is treated with an aldehydes and the reaction hydrolyzed, two products are obtained, **4** and **5** (Scheme 3). The reaction was followed by ^{31}P NMR of products **4** and **5** which absorbed in the 18−19.5 ppm range. The starting alkynylphosphonates absorb around −5 ppm. The reaction was accompanied by various amounts of *cis*-diethyl-1-hexenylphosphonate which absorbed at 17.7 ppm. The major product, **5** (Table 2), occurs by insertion of the aldehydes into C2 of the zirconacycle, apparently due to steric factors. Evidence for this are the very low yields of **4** obtained with *o*-anisaldehyde (Table 1, entry h) and 2,4-dichlorobenzaldehyde (Table 1, entry (i). In each case less than 1% of compound **4** was detected by ^{31}P of the crude reaction mixture and was not isolated. The reaction proceeds for both aromatic and aliphatic aldehydes (Table 1, entry g). Products **4** and **5** were readily purified by silica gel chromatography.

Scheme 3

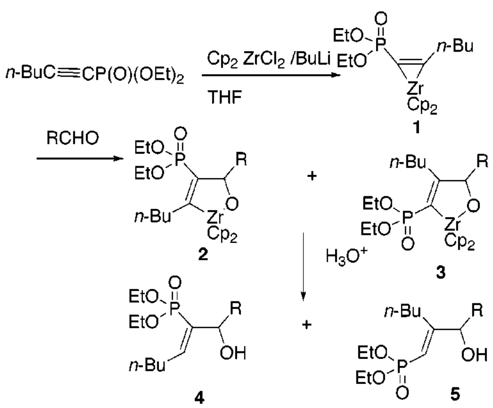
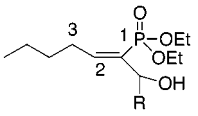


Table 1. Selected NMR Data and Yields of 4



entry	R	equiv of ald.	convn[a] (%)	isol. yield (%)	$^3J_{PH}$ (Hz)	$^2J_{PC2}$ (Hz)	$^3J_{PC3}$ (Hz)
a	phenyl	1.2	98	10	47	9.7	6.8
b	PhCH=CH	1.2	98	11	47	7.8	6.6
c	1,4-benzodioxane	1.2	95	9	48	9.4	6.8
d	*p*-F-C_6H_4	2	75	11	47	9.2	6.7
e	1-naphthyl	2	65	12	47	9.4	6.6
f	*p*-MeO-C_6H_4	2	65	7	47	9.4	6.6
g	C_6H_{13}	2	95	8	48	9.4	6.8
h	*o*-MeO-C_6H_4	2	96	<1	*b*	*b*	*b*
i	2,4-dichloro-C_6H_3	2	70	<1	*b*	*b*	*b*

[a] The total conversion was determined by ^{31}P NMR of the crude reaction mixture. [b] Not isolated.

The stereochemistry of the two isomers was determined by NMR analysis of the coupling constants. In compounds **4**, the doublet of triplets in the double bond region (6.1−6.4 ppm) indicates that the aldehyde coupling was on C1. The large $^3J_{PH}$ coupling constants (47−48 Hz) of **4**, and the relatively small $^3J_{PC3}$ coupling constants (6.6−6.8 Hz) indicate that the H2 is in the *trans* position to phosphorus and C3 is in the *cis* position, consistent with the *Z* configuration assigned to **4**.

Compound 5. The doublet in the region (~6 ppm) corresponds to the hydrogen on the C_1 (H_1) which indicates that the aldehyde coupling was on C_2. Also the relatively large $^3J_{PC3'}$ coupling constants of the alcoholic carbon C3′ (21−22 Hz) and the relatively small $^3J_{PC3}$ coupling constant of C3 (6.6−6.8 Hz) indicate that the *E* isomer was obtained as shown in Table 2. The ^{31}P NMR chemical shifts of compound **4** are (0.5−0.8 ppm) lower than the chemical shifts of compound **5**.

In the zirconation step we used a 10% excess of Cp_2ZrCl_2 to ensure that all alkylnylphosphonate was converted. In the case of benzaldehyde, cinnimaldehyde, and 1,4-benzodioxane-6-carboxyaldehyde, a 20% excess of aldehyde was introduced while with the other aldehydes 2 equiv was used since 1 equiv did not give high yields.

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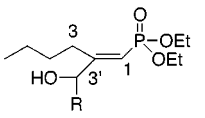
Table 2. Selected NMR Data of 5



entry	R	equiv of ald.	convn^a (%)	isol. yield (%)	$^{3}J_{PH}$ (Hz)	$^{2}J_{PC2}$ (Hz)
a	phenyl	1.2	98	75	6.8	21.2
b	PhCH═CH	1.2	98	76	6.8	21.4
c	1,4-benzodioxane	1.2	95	71	6.8	21.5
d	*p*-F-C_6H_4	2	75	48	6.6	21.6
e	1-naphthyl	2	65	38	6.8	21.2
f	*p*-MeO-C_6H_4	2	65	38	6.8	21.1
g	C_6H_{13}	2	95	70	7.1	21.4
h	*o*-MeO-C_6H_4	2	96	72	6.9	21.7
i	2,4-dichloro-C_6H_3	2	70	47	6.7	22.1

[a] The total conversion was determined by ^{31}P NMR of the crude reaction mixture.

In conclusion, we have developed a novel, stereoselective method of synthesizing vinylphosphonates by aldehyde insertion into three-membered zirconacycles. Compounds **5** originate from insertion into C2 of the zirconacycles and place the new C−C bond *trans* to the phosphonate group. Compounds **4** insert into C1 and place the new C−C bond on the same carbon as the phosphonate group. *ortho*-Substituted benzaldehydes give only **5**.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere vacuum line, and glovebox techniques were used. Solvents were purified by distillation from appropriate drying agents a under nitrogen atmosphere. Starting materials were purchased from commercial suppliers and used without further purification. ^{1}H (300 MHz) and ^{13}C NMR spectra were recorded in $CDCl_3$. ESMS analysis was performed on a LCMS.

General Procedure. A total of 1.25 mL of 1.6 M *n*-BuLi (2 mmol) was added dropwise to 0.292 g (1 mmol) of zirconocene dichloride dissolved in 5 mL of dry THF at −78 °C, and the mixture was stirred for 3 h. Then 0.2 g (0.9 mmol) of 1-hexynylphosphonate was added and the mixture was warmed gradually to room temperature and stirred overnight. Then 1.2 mmol of freshly distilled benzaldehyde was added (solid aldehydes were recrystallized and dried before use), and the mixture was stirred for an additional 24 h. The reaction mixture was worked up with dilute HCl, and the product was extracted with ether. Two isomers were obtained. The first isomer (compound **4**) showed that the aldehyde coupled to the 1-alkynylphosphonate on C_1 position to phosphorus, while the second isomer (compound **5**) showed that the aldehyde coupled at C_2 to phosphorus. These two isomers were separated on a silica gel column (75% petroleum ether (PE):25% ethyl acetate).

4a: $R_f = 0.35$ (75% PE:25% ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (t, 3H), 1.25 (t, 3H), 1.20−1.50 (overlap, 4H), 2.55 (m, 2H), 4.10 (dq, 4H), 4.51 (d, 1H, $^{3}J_{HH} = 8.1$ Hz), 5.31 (dd, 1H, $^{3}J_{PH} = 11.7$ Hz, $^{3}J_{HH} = 7.2$ Hz), 6.21−6.36 (dt, 1H, $^{3}J_{PH} = 47.1$ Hz), 7.11−7.45 (m, 5H); ^{31}P NMR (300 MHz, $CDCl_3$) δ 18.8 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0 ($^{2}J_{PC} = 9.7$ Hz), 131.1−133.3 ($^{1}J_{PC} = 169$ Hz), 128.3, 127.4, 126.6, 76.4 ($^{2}J_{PC} = 12.3$ Hz), 61.7 ($^{2}J_{PC} = 5.1$ Hz), 31.1, 30.1 ($^{3}J_{PC} = 6.8$ Hz), 22., 16.5 ($^{3}J_{PC} = 6.5$ Hz), 14.1; ESMS (MH$^+$, *m*/*z* 326). Anal. Calcd for $C_{17}H_{27}O_4P$: C, 62.56; H, 8.34; P, 9.49. Found: C, 62.43; H, 8.42; P, 9.37.

5a: $R_f = 0.31$ (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H), 1.25 (t, 3H), 1.20−1.50 (overlap, 4H), 1.90 (m, 1H), 2.62 (m, 1H), 3.41 (broad s), 4.01 (dq, 4H), 5.14 (broad s, 1H), 6.02 (d, 1H, $^{2}J_{PH} = 18.8$ Hz), 7.22−7.35 (m, 5H); ^{31}P NMR ($CDCl_3$) δ 19.5 (s); ^{13}C NMR ($CDCl_3$) δ 167.0 ($^{2}J_{PC} = 8.0$ Hz), 128.8, 128.4, 127.5, 108.8−111.3 ($^{1}J_{PC} = 190.1$), 76.1 ($^{3}J_{PC} = 21.2$ Hz), 61.1 ($^{2}J_{PC} = 5.4$ Hz), 31.6, 31.0 ($^{3}J_{PC} = 6.8$ Hz), 22.5, 16.6 ($^{3}J_{PC} = 6.3$ Hz), 14.0; ESMS (MH$^+$, *m*/*z*, 326). Anal. Calcd for $C_{17}H_{27}O_4P$: C, 62.56; H, 8.34; P, 9.49. Found: C, 62.38; H, 8.47; P, 9.36.

4b: $R_f = 0.36$ (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H), 1.27 (t, 3H), 1.20−1.50 (overlap, 4H), 2.21 (m, 2H), 4.05 (dq, 4H), 4.83 (dd, 1H, $^{3}J_{HH} = 5.4$ Hz, $^{3}J_{PH} = 20.0$ Hz), 6.27−6.43 (dt, 1H, $^{3}J_{PH} = 47$ Hz), 6.27−6.63 (overlap, 3H), 7.13−7.45 (m, 5H); ^{31}P NMR ($CDCl_3$) δ 19.0 (s); ^{13}C NMR ($CDCl_3$) δ 149.3 ($^{2}J_{PC} = 9.7$ Hz), 129.0−131.1 ($^{1}J_{PC} = 169.0$ Hz), 131.0, 129.0, 128.7, 127.5, 126.7, 76.4 ($^{2}J_{PC} = 12.6$ Hz), 61.7 ($^{2}J_{PC} = 5.1$ Hz), 30.1 ($^{3}J_{PC} = 6.8$ Hz), 22.6, 16.5 ($^{3}J_{PC} = 6.5$ Hz), 14.1; ESMS (MH$^+$, *m*/*z*, 353). Anal. Calcd for $C_{19}H_{29}O_4P$: C, 64.75; H, 8.29; P, 9.79. Found: C, 64.61; H, 8.44; P, 9.63.

5b: $R_f = 0.32$ (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H), 1.27 (t, 3H), 1.20−1.50 (overlap, 4H), 2.20 (m, 1H), 2.69 (m, 1H), 4.00 (dq, 4H), 4.24 (broad s, 1H), 4.72 (d, 1H), 5.87 (d, 1H, $^{2}J_{PH} = 15.9$ Hz), 6.05 (dd, 2H, $^{3}J_{HH} = 7.5$ Hz), 6.60 (d, 1H, $^{3}J_{HH} = 15.9$ Hz), 7.20−7.35 (m, 5H); ^{31}P NMR ($CDCl_3$) δ 19.5 (s); ^{13}C NMR ($CDCl_3$) δ 167.0 ($^{2}J_{PC} = 8.0$ Hz). 136.6, 133.4, 129.9, 128.8, 128.1, 126.8, 108.9−111.4 ($^{1}J_{PC} = 190$ Hz), 76.1 ($^{3}J_{PC} = 21.4$ Hz), 61.1 ($^{3}J_{PC} = 5.4$ Hz), 31.1 ($^{3}J_{PC} = 6.8$ Hz), 31.0, 23.0, 16.5 ($^{3}J_{PC} = 6.3$ Hz), 14.1; ESMS (MH$^+$, *m*/*z*, 353). Anal. Calcd for $C_{19}H_{29}O_4P$: C, 64.75; H, 8.29; P, 8.79. Found: C, 64.66; H, 8.40; P, 8.66.

4c: $R_f = 0.35$ (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (t, 3H), 1.20−1.50 (overlap, 4H), 2.35 (m, 2H), 4.11 (s, 4H), 4.20 (dq, 4H), 5.05 (s, 1H), 5.20 (d, 1H, $^{3}J_{PH} = 11.7$ Hz), 6.17−6.33 (dt, 1H, $^{3}J_{PH} = 48.0$ Hz), 6.70−6.90 (m, 3H); ^{31}P NMR ($CDCl_3$) δ 18.8 (s); ^{13}C NMR ($CDCl_3$) δ 149.5 ($^{2}J_{PC} = 9.4$ Hz), 131.0−133.2 ($^{1}J_{PC} = 170.0$ Hz), 143.4, 119.7, 117.6, 117.1, 116.5, 115.7, 76.4 ($^{2}J_{PC} = 13.2$ Hz), 64.5, 61.7 ($^{2}J_{PC} = 5.1$), 31.1, 30.1 ($^{3}J_{PC} = 6.8$ Hz), 22.6, 16.5 ($^{3}J_{PC} = 6.5$ Hz), 14.1; ESMS (MH$^+$, *m*/*z*, 385). Anal. Calcd for $C_{19}H_{29}O_6P$: C, 59.36; H, 7.60; P, 8.06. Found: C, 59.13; H, 7.77; P, 7.91.

5c: $R_f = 0.29$ (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.78 (t, 3H), 1.23 (t, 3H), 1.20−1.50 (overlap, 4H), 1.83 (m, 1H), 2.60 (m, 1H), 3.73 (broad s, 1H), 3.98 (dq, 4H), 4.15 (s, 4H), 4.98 (broad s, 1H), 6.00 (d, 1H, $^{2}J_{PH} = 18.0$ Hz), 6.72 (m, 3H); ^{31}P NMR($CDCl_3$) δ 19.5 (s); ^{13}C NMR ($CDCl_3$) δ 167.3 ($^{2}J_{PC} = 8.0$ Hz), 143.0, 134.0, 120.6, 117.4, 116.5, 108.3−111.0 ($^{1}J_{PC} = 190.0$ Hz), 76.1 ($^{3}J_{PC} = 21.5$ Hz), 64.1, 61.1 ($^{3}J_{PC} = 5.4$ Hz), 31.6, 31.1 ($^{3}J_{PC} = 6.8$ Hz), 23.1, 16.5 ($^{3}J_{PC} = 6.3$ Hz), 14.1; ESMS (MH$^+$, *m*/*z*, 385). Anal. Calcd for $C_{19}H_{29}O_6P$: C, 59.36; H, 7.60; P, 8.06. Found: C, 59.15; H, 7.70; P, 7.99.

4d: $R_f = 0.34$ (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H). 1.25 (t, 3H), 1.20−1.50 (overlap, 4H), 2.37 (m, 2H), 4.05 (dq, 4H), 5.30 (d, 1H, $^{3}J_{PH} = 19.5$ Hz), 6.20−6.39 (dt, 1H, $^{3}J_{PH} = 47.0$ Hz), 6.97−7.40 (m, 4H); ^{31}P NMR ($CDCl_3$) δ 18.5 (s); ^{13}C NMR ($CDCl_3$) δ 149.0 ($^{2}J_{PC} = 9.2$ Hz), 131.1−133.2 ($^{1}J_{PC} = 169.0$ Hz), 128.3, 128.2, 115.3, 115.0, 76.4 ($^{2}J_{PC} = 15.0$ Hz), 61.7 ($^{2}J_{PC} = 5.1$ Hz), 31.1, 30.1 ($^{3}J_{PC} = 6.8$ Hz), 22.6, 16.4 ($^{3}J_{PC} = 6.5$ Hz), 14.1; ESMS (MH$^+$, *m*/*z*, 344). Anal. Calcd for $C_{17}H_{26}FO_4P$: C, 59.29; H, 7.61; F, 5.52; P, 8.99. Found: C, 59.11; H, 7.77; F, 5.44; P, 8.78.

5d: $R_f = 0.27$ (70% PE:30% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3H), 1.25 (t, 3H), 1.20−1.50 (overlap, 4H), 1.89 (m, 1H), 2.61 (m, 1H), 4.00 (dq, 4H), 5.15 (broad s, 1H), 6.00 (d, 1H, $^{2}J_{PH} = 18.3$ Hz), 7.00−7.20 (m, 4H); ^{31}P NMR ($CDCl_3$) δ 19.0 (s); ^{13}C NMR ($CDCl_3$) δ 166.7 ($^{2}J_{PC} = 8.3$ Hz), 129.3, 129.2, 115.9, 115.7, 109.1−111.6 ($^{1}J_{PC} = 191.0$ Hz), 76.1 ($^{3}J_{PC} = 21.6$ Hz), 61.1 ($^{3}J_{PC} = 5.4$ Hz), 31.6, 31.1 ($^{3}J_{PC} = 6.6$ Hz), 23.1, 16.6 ($^{3}J_{PC} = 6.3$ Hz), 14.1; ESMS (MH$^+$, *m*/*z*, 344). Anal. Calcd for $C_{17}H_{26}FO_4P$: C, 59.29; H, 7.61; F, 5.52; P, 8.99. Found: C, 59.19; H, 7.74; F, 5.44; P, 8.82.

4e: $R_f = 0.38$ (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H), 1.31 (t, 3H), 1.21−1.75 (overlap, 4 H), 2.41 (m, 2H), 4.10 (dq, 4H), 4.55 (d, 1H, $^{3}J_{HH} = 8.1$ Hz), 5.55 (dd, 1H, $^{3}J_{PH} = 11.7$ Hz, $^{3}J_{HH} = 7.2$ Hz), 6.24−6.90 (dt, 1H, $^{3}J_{PH} = 46.5$ Hz), 7.10−8.00 (m, 7H); ^{31}P NMR ($CDCl_3$) δ 18.0 (s); ^{13}C NMR ($CDCl_3$) δ 150.1 ($^{2}J_{PC} = 9.4$ Hz), 140.1, 133.0, 128.0−124.2, 76.4 ($^2J_{PC}$ = 12.3 Hz), 61.7 ($^2J_{PC}$ = 5.1 Hz), 31.1, 30.1 ($^3J_{PC}$ = 6.8 Hz), 22.6, 16.4 ($^3J_{PC}$ = 6.5 Hz), 14.1; ESMS (MH^+, *m/z*, 377). Anal. Calcd for $C_{21}H_{29}O_4P$: C, 67.00; H, 7.76; P, 8.23. Found: C, 66.71; H, 7.88; P, 8.11.

5e: R_f = 0.31 (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H), 1.25 (t, 3H), 1.21−1.85 (overlap, 4H), 1.98 (m, 1H), 2.69 (m, 1H), 4.10 (dq, 4H), 5.35 (broad s, 1H), 6.13 (d, 1H, $^2J_{PH}$ = 18.0 Hz), 7.23−7.83 (m, 7H); ^{31}P NMR ($CDCl_3$) δ 19.2 (s); ^{13}C NMR ($CDCl_3$) δ 166.4 ($^2J_{PC}$ = 7.8 Hz), 138.5, 133.4, 128.9, 128.2, 128.0, 126.5, 124.7, 109.4−111.9 ($^1J_{PC}$ = 190.0 Hz), 76.1 ($^3J_{PC}$ = 21.2 Hz), 61.1 ($^3J_{PC}$ = 5.4 Hz), 31.6, 31.1 ($^3J_{PC}$ = 6.8 Hz), 23.2, 16.6 ($^3J_{PC}$ = 6.3 Hz), 14.1; ESMS (MH^+, *m/z*, 377). Anal. Calcd for $C_{21}H_{29}O_4P$: C, 67.00; H, 7.76; P, 8.23. Found: C, 66.82; H, 7.69; P, 8.19.

4f: R_f = 0.34 (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3H), 1.28 (t, 3H), 1.20−1.50 (overlap, 4H), 2.39 (m, 2H), 3.80 (s, 1H), 4.12 (dq, 4H), 5.33 (d, 1H, $^3J_{PH}$ = 19.5 Hz), 6.23−6.40 (dt, 1H, $^3J_{PH}$ = 46.8 Hz), 6.90−7.45 (m, 4H); ^{31}P NMR ($CDCl_3$) δ 18.9 (s); ^{13}C NMR ($CDCl_3$) δ 149.0 ($^2J_{PC}$ = 9.4 Hz), 132.0−134.2 ($^1J_{PC}$ = 169.0 Hz), 133.0, 131.0, 127.0, 113.0, 76.4 ($^2J_{PC}$ = 12.5 Hz), 62.1, 61.7 ($^2J_{PC}$ = 5.1 Hz), 31.1, 30.1 ($^3J_{PC}$ = 6.8 Hz), 22.6, 16.4 ($^3J_{PC}$ = 6.5 Hz), 14.1; ESMS (MH^+, *m/z*, 357). Anal. Calcd for $C_{18}H_{29}O_5P$: C, 60.66; H, 8.20; P, 8.69. Found: C, 60.73; H, 8.03; P, 8.50.

5f: R_f = 0.25 (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H), 1.29 (q, 3H), 1.20−1.51 (overlap, 4H), 1.88 (m, 1H), 2.62 (m, 1H), 3.78 (s, 3H), 4.05 (dq, 4H), 5.13 (broad s, 1H), 6.10 (d, 1H, $^2J_{PH}$ = 18.3 Hz), 6.83−7.26 (m, 4H); ^{31}P NMR ($CDCl_3$) δ 19.4 (s); ^{13}C NMR ($CDCl_3$) δ 167.1 ($^2J_{PC}$ = 7.2 Hz), 133.4, 129,0, 116,3, 114.2, 108.6−111.1 ($^1J_{PC}$ = 191.0 Hz), 76.1 ($^3J_{PC}$ = 21.1 Hz), 61.1 ($^3J_{PC}$ = 5.4 Hz), 55.5, 31.6, 31.1 ($^3J_{PC}$ = 6.6 Hz), 23.0, 16.6 ($^3J_{PC}$ = 6.3 Hz), 14.1; ESMS (MH^+, *m/z*, 357). Anal. Calcd for $C_{18}H_{29}O_5P$: C, 60.66; H, 8.20; P, 8.69. Found: C, 60.70; H, 8.12; P, 8.63.

4g: R_f = 0.46 (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.83 (2t, 6H), 1.30 (2t, 6H), 1.20−1.51 (overlap, 4H), 1.61 (m, 2H), 2.33 (m, 2H), 3.63 (broad s, 1H), 4.10 (dq, 4H), 6.23 (dt, 1H, $^2J_{PH}$ = 17.9 Hz); ^{31}P NMR ($CDCl_3$) δ 17.9 (s); ^{13}C NMR ($CDCl_3$) δ 148.3 ($^2J_{PC}$ = 9.4 Hz), 130.2−133.1 ($^1J_{PC}$ = 166.0 Hz), 74.1 ($^3J_{PC}$ = 12.4 Hz), 61.1 ($^3J_{PC}$ = 5.4 Hz), 36.1, 31.9, 31.1 ($^3J_{PC}$ = 5.6 Hz), 29.3, 25.5, 23.1, 22.8, 16.5 ($^3J_{PC}$ = 6.6 Hz), 14.1; ESMS (MH^+, *m/z*, 341). Anal. Calcd for $C_{17}H_{35}O_4P$: C, 61.08; H, 10.48; P, 9.26. Found: C, 60.88; H, 10.37; P, 9.08.

5g: R_f = 0.38 (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.85 (2t, 6H), 1.28 (2t, 6H), 1.20−1.50 (overlap, 4H), 2.13 (m, 1H), 2.63 (m, 1H), 3.30 (broad s, 1H), 3.95 (dq, 4H), 4.11 (d, 1H), 5.75 (d, 1H, $^2J_{PH}$ = 18.6 Hz); ^{31}P NMR ($CDCl_3$) δ 18.6 (s); ^{13}C NMR ($CDCl_3$) δ 169.5 ($^2J_{PC}$ = 8.0 Hz), 108.3−111.8 ($^1J_{PC}$ = 191 Hz), 74.1 ($^3J_{PC}$ = 21.4 Hz), 61.4 ($^3J_{PC}$ = 5.4 Hz), 36.0, 31.9, 31.3 ($^3J_{PC}$ = 5.6 Hz), 29.3, 25.5, 23.3, 22.8, 16.5 ($^3J_{PC}$ = 6.6 Hz), 14.1; ESMS (MH^+, *m/z*, 341). Anal. Calcd for $C_{17}H_{35}O_4P$: C, 61.08; H, 10.48; P, 9.26. Found: C, 60.92; H, 10.44; P, 9.15.

5h: R_f = 0.33 (75% PE:25% ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 0.81 (t, 3H), 1.22 (q, 3H), 1.20−1.50 (overlap, 4H), 1.95 (m, 1H), 2.65 (m, 1H), 3.51 (s, 1H), 3.70 (s, 3H), 3.95 (dq, 4H), 5.50 (broad s, 1H), 5.90 (d, ^{1}H, $^2J_{PH}$ = 18.6 Hz), 6.80−7.26 (m, 4H); ^{31}P NMR($CDCl_3$) δ 19.6 (s); ^{13}C NMR ($CDCl_3$) δ 167.5 ($^2J_{PC}$ = 8.3 Hz), 157.0, 129.0, 128.1, 121.1, 110.5, 108−111 ($^1J_{PC}$ = 190.0 Hz), 71.1 ($^3J_{PC}$ = 21.7 Hz), 61.1 ($^3J_{PC}$ = 5.4 Hz), 55.1, 31.6, 31.1 ($^3J_{PC}$ = 6.9 Hz), 23.1, 16.6 ($^3J_{PC}$ = 6.3 Hz), 14.1; ESMS (MH^+, *m/z*, 357). Anal. Calcd for $C_{18}H_{29}O_5P$: C, 60.66; H, 8.20; P, 8.69. Found: C, 60.79; H, 8.33; P, 8.78.

5i: R_f = 0.46 (75% PE:25% ethyl acetate): ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3H) 1.23 (q, 3H), 1.20−1.50 (overlap, 4H), 1.95 (m, 1H), 2.60 (m, 1H), 4.00 (dq, 4H), 5.60 (broad s, 1H), 5.95 (d, 1H, $^2J_{PH}$ = 17.7 Hz), 7.20−7.40 (m, 4H); ^{31}P NMR ($CDCl_3$) δ 18.7 (s); ^{13}C NMR ($CDCl_3$) δ 166.0 ($^2J_{PC}$ = 8.4 Hz), 137.7, 135.0, 134.2, 129.9, 129.4, 127.8, 110.2−112.8 ($^1J_{PC}$ = 190.0 Hz), 71.1 ($^3J_{PC}$ = 21.1 Hz), 61.1 ($^3J_{P\ C}$ = 5.4 Hz), 31.6, 31.1 ($^3J_{PC}$ = 6.7 Hz), 23.2, 16.6 ($^3J_{PC}$ = 6.3 Hz), 14.1; ESMS (MH^+, *m/z* 396, 397, 398, 399). Anal. Calcd for $C_{17}H_{25}Cl_2O_4P$: C, 51.67; H, 6.37; Cl, 17.49; P, 7.84. Found: C, 51,55; H, 6.19; Cl, 18.15; P, 7.66.

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