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A study of the 1,2-addition of group IV metallacycles derived from 1-alkynylphosphonates to conjugated enones

Ofir Baum, Abed Al Aziz Quntar, Valery M. Dembitsky and Morris Srebnik*

Department of Medicinal Chemistry and Natural Products†*, School of Pharmacy, Hebrew University Jerusalem, POB 12065, Jerusalem 91120, Israel*

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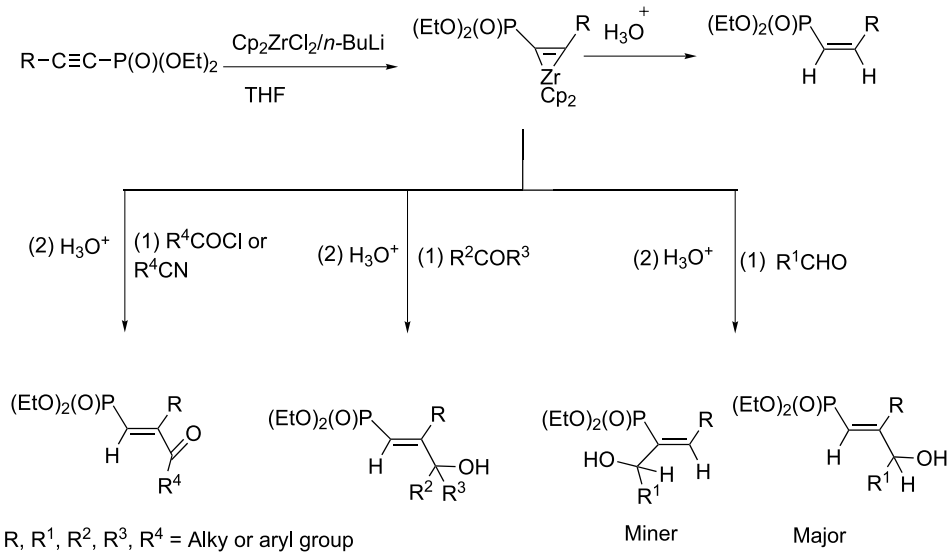
Abstract—Addition of group IV cyclopropenemetallocycles to conjugated enones indicates that the reaction course is mostly dependent on the metallocyle and the enone moiety. The zirconacycle affords the unrearranged products **3**. On the other hand, some rearranged products, 1,3-butadienylphosphonates, are obtained when titanacycles are used.

1. Introduction

Stereodefined vinylphosphonates are an important class of compounds that have interesting biological activity,[1] and are useful intermediates in further organic transformations.[2] Recently, we have prepared various types of stereodefined vinylphosphonates including *cis*-vinylphosphonates, 1,3-butadienylphosphonates,[3] 1-(hydroxymethyl)vinylphosphonates, 2-(hydroxymethyl)vinylphosphonates,[4] 3-oxo-vinylphosphonates,[5] 3-aminovinylphosphonates,[6] and various other di- and tri-substituted vinylphosphonates, (Scheme 1).[7]

As part of our ongoing program to synthesize stereodefined vinylphosphonates from group IV metals, we were interested in studying the addition of metallocyclopropenes to structurally diverse enones. The 1,2-addition has not been reported and could provide several interesting types of stereo defined vinylphosphonates. In this paper we report our initial results.



Scheme 1.

Keywords: Metallocycle; Zirconacycle; Titanacycle; 1,3-Butadienylphosphonates; Enones; Allylic rearrangement.
* Corresponding author. Tel.: +972-2-675-7301; fax: +972-2-675-8201; e-mail address: msrebni@md2.huji.ac.il
† Affiliated with the David R. Bloom Center for Pharmaceutics at the Hebrew University in Jerusalem.

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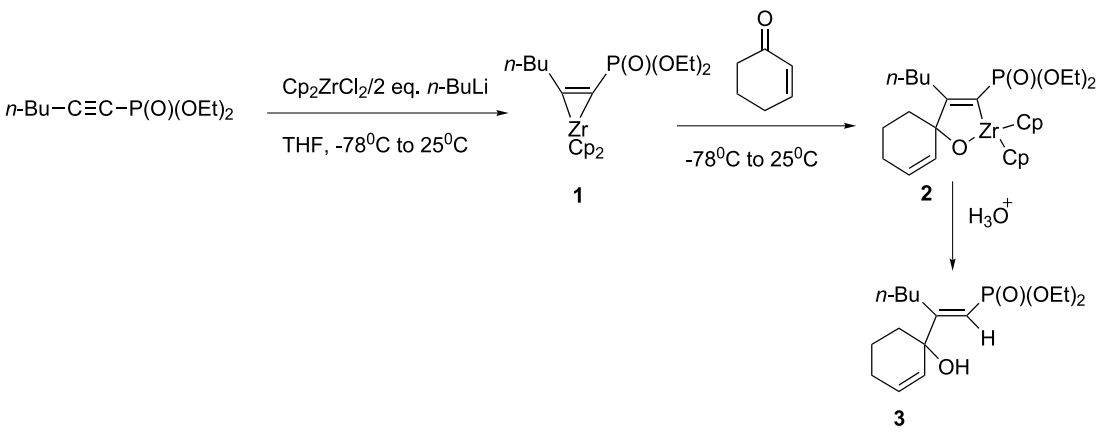


Scheme 2.

Table 1. Preparation and selectivity of **3** and **4**

Entry	Enone	Reactions with Ti		Reactions with Zr	
		Rearranged **4** (%)	Un-rearranged **3** (%)	Rearranged **4** (%)	Un-rearranged **3** (%)
a	Cyclohexenone	100	0	0	100
b	Cycloheptenone	100	0	0	100
c	4,4-Dimethylcyclohexenone	0	100	0	100
d	Methyl vinyl ketone	0	100	0	100

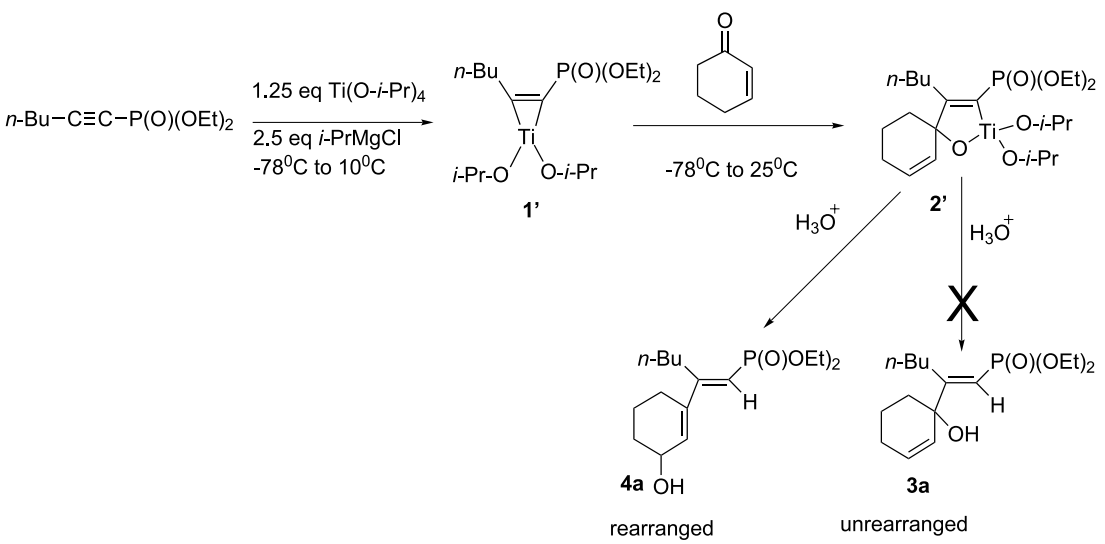
2. Results and discussion

When diethyl 1-hexynylphosphonate was treated with Cp_2ZrCl_2/2 *n*-BuLi, zirconacyclopropene **1** were produced.[8] When **1** was treated with 2-cyclohexen-1-one, the five membered ring zirconacylces **2**, were obtained, which upon workup, compounds **3a** was afforded, (Scheme 2).

The structure of **3** was determined by NMR, LCMS, and UV spectroscopy. These diallylic alcohols are new types of vinylphosphonates which have not been reported before. The results are listed in Table 1.

The regio- and stereochemistry of compounds **3** were determined by NMR analysis and phosphorous carbon coupling constants. The presence of doublet in the ^{1}H NMR, due to the phosphorous splitting of the vinylic hydrogen in the region (4.9–5.8 ppm) in ^{1}H NMR is indicative that the enone coupling was on C2 to phosphorous. In addition, the large $^3J_{PC}$ of the alcoholic carbon (22.0–22.7 Hz) of the inserted enone moiety, compared to the small $^3J_{PC}$ of the allylic carbon of *n*-Bu (~7 Hz) is consistent with *cis* configuration of *n*-Bu group with respect to phosphorous, whereas the inserted enone moieties are in *trans* position to phosphorous (Table 3).

Diallylic alcohol compounds are of increasing interests. Besides possessing significant biological activity,[9] they are



Scheme 3.

Table 2. UV data of selected **3** and **4**

Compound	λ_{max} (nm)	ε	Conc. (M) in methanol
3c	252 (sh)	869	6.9×10^{-4}
3d	250	1469	1.4×10^{-4}
4a	251	8614	7.1×10^{-4}
4b	251	8642	1.8×10^{-4}

important intermediates in organic transformation. They are transformed to epoxy alcohols,[10] to bicyclic allylic alcohols and ethers.[11] Moreover, they are interesting intermediates in the asymmetric synthesis of polyhydroxylated celastracease sesquiterpene core.[10]

In contrast to the results obtained with the zirconacyclopropenes, reaction of diethyl 1-hexynylphosphonate with Ti(O-*i*Pr)$_4$/2 *i*PrMgCl, followed by cyclohexenone gave after workup the rearranged products,[12] butadienylphosphonate **4**, which was isolated as the sole product (Scheme 3).

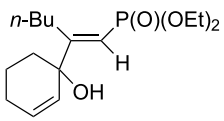
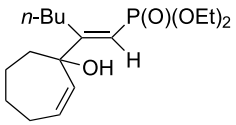
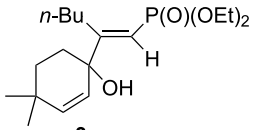
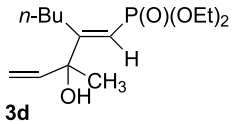
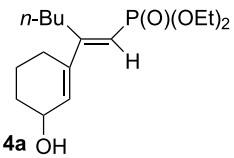
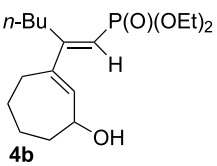
Initially, compounds **3**, were expected to be obtained after the acidic workup, but the allylic rearranged products **4** were obtained in two examples (Table 1). However, under the same acidic workup, 4,4-dimethylcyclohexenone and methyl vinyl ketone gave unrearranged products **3**. The results are listed in Table 1, and selected UV data are listed in Table 2.

The regio- and the stereochemistry of compounds **4** were determined from the NMR data and the coupling constants. The small $^3J_{PC}$ values of *n*-Bu (~7 Hz) compared to the larger $^3J_{PC}$ values of the vinylic carbon ~20 Hz is indicative *cis* position of *n*-Bu to the phosphorous and *trans* position of the enone moiety (Table 3).

The UV data (Table 2) are consistent with the NMR analysis. The diallylic alcohols **3c** and **3d** have relatively a small ε, while ε of the rearranged compounds **4a** and **4b** are >8000.

No rearranged products **4** were detected in the zirconacycle reactions, whereas rearrangement occurred on two occasions with the titanacycles. Since all reactions were

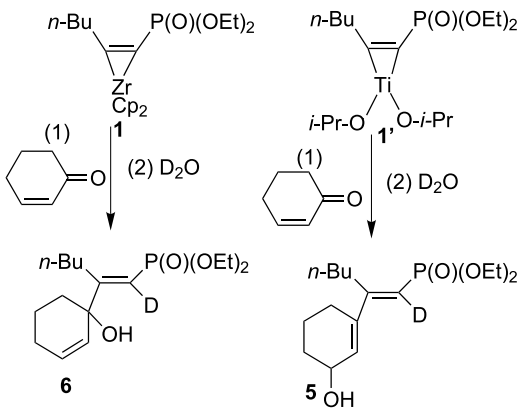
Table 3. Structure and selected NMR data for **3** and **4**

Entry	Structure of **3** and **4**	$^2J_{PH}$ (Hz)	$^3J_{PC}$ (Hz) of enone moiety	$^3J_{PC}$ (Hz) of (*n*-Bu)	δ ^{31}P NMR
3a	 **3a**	17.1	22.7	7.1	19.31
3b	 **3b**	17.4	22.6	7.0	20.48
3c	 **3c**	17.4	22.6	6.9	20.17
3d	 **3d**	16.8	22.0	6.9	20.32
4a	 **4a**	17.1	23.8	7.0	20.31
4b	 **4b**	15.5	23.8	6.9	20.08

purified on silica gel chromatography, silica gel is ruled out as cause of the rearrangement.[10]

To get insight into the rearrangement and the mechanism, the reaction mixture with the Ti reagent was also worked up under neutral and basic conditions. Rearrangement product **4a** was obtained in all cases. In addition, when **3a** was subjected to Lewis acid catalysis, complex reaction mixtures were obtained with no detection of product **4a**.

All this seems to indicate that rearrangement takes place on the titanacycle, possibly by ring expansion of the titanacycle. At any rate, the C–Ti bond is intact prior to work up as indicated by deuterium labeling (attempts to monitor the reaction by NMR were unsuccessful). When the reaction mixture was quenched with D_2O and D_2SO_4, GCMS analysis of the deuterium quenched rearranged and un-rearranged products **5**, **6** indicated only one stable atom of deuterium is incorporated on C1 to the phosphorous (Scheme 4).



Scheme 4.

Dienylphosphonates are of considerable synthetic interest. They undergo a variety of reactions including 1,3-dipolar additions,[13] cycloaddition with CH_2N_2,[14] and [2+2] cycloadditions.[15] In addition, these compounds possess biological activities by themselves.[16] Synthesis of these compounds are few in number. In the literature there is no general method for their preparation. They have been prepared by isomerization of 1-alkynylphosphonates in the presence of palladium salts,[17] by Knoevenagel reaction,[15] by reaction of unsaturated cyanophosphonates with *N*-tosylsulfonylimines.[18]

3. Conclusions

In this study, various stereodefined vinylphosphonates were prepared by addition of group IV metallacycles to enones. When the enones were added to the zirconacyclopropenes, the unrearranged products, 3-hydroxy allylic vinylphosphonates, **3** were obtained. On the other hand, the reaction course of the enones with the titanacyclopropenes was dependent on the enone moiety, in which, in certain cases, the rearranged 1,3-butadienylphosphonates products **4** were obtained. The use of different workup media, i.e., acidic, neutral, and basic, has no influence on the rearrangement.

4. Experimental

4.1. General comments

All reactions were carried out under dry nitrogen atmosphere using pre heated dry glassware. All the solvents that were used were dried and distilled from sodium–benzophenone mixture prior to use. Starting materials were used as purchased from commercial suppliers without further purification. ^1H (300 MHz), ^{13}C (75.4 MHz) and ^{31}P (121 MHz) NMR spectra were recorded in $CDCl_3$. ESMS analysis was performed on a LCMS. UV was used to determine the maximum absorbance.

General procedure for **4** (*reactions of enones with titanacycles*). To a 50 ml round bottom flask containing a solution of 0.355 g of $Ti(O\text{-}iPr)_4$ (1.25 mmol) dissolved in 10 ml of dry diethyl ether, 1.25 ml of iPrMgCl 2 M in ether (2.5 mmol) were introduced at −78 °C followed by the addition of 0.218 g of diethyl-1-hexynylphosphonate (1 mmol). The reaction mixture was allowed to warm gradually, over a period of 4 h to 5 °C. Then the reaction was cooled again to −78 °C and 1.1 mmol of the enone was added. The reaction was allowed to warm gradually to 25 °C overnight. After acidic workup the product was extracted by dietyl ether (2×20), dried over magnesium sulphate, and was purified on silica gel, using petroleum ether–ethyl acetate.

General procedure for **3** (*reactions of enones with zirconacycles*). To a 50 ml round bottom flask charged with 0.292 g of Cp_2ZrCl_2 (1.25 mmol) dissolved in 6 ml of dry THF, 1 ml of 2 M solution of *n*-BuLi was introduced at −78 °C. After 4 h of stirring in the range −50 to −30 °C, 0.26 g (0.9 mmol) of 1-hexynylphosphonate was added, the reaction mixture was allowed to warm gradually to 25 °C and left stirring over night. Then the reaction was cooled again to −78 °C and 1.1 mmol of the enone was added. The reaction was allowed to warm gradually to 25 °C over night followed by acidic work-up with diluted hydrochloric acid (1 M). The product was extracted in diethyl ether, and dried over magnesium sulphate, and was isolated on silica gel column chromatography, using petroleum ether–ethyl acetate.

General procedure for **5** *and* **6**. The same procedure for **3** and **4** except the D_2O workup instead of H_3O^+.

4.2. Spectroscopic data

4.2.1. Compound 3a. 50% isolated yield; (30% petroleum ether: 70% ethyl acetate); R_f=0.42; ^1H NMR (300 MHz: δ 0.84 (t, 3H, J_{HH}=7.5 Hz), 1.27 (t, 6H, J_{HH}=6.6 Hz), 1.29–1.99 (overlap, 10H), 2.42 (m, 2H), 2.50 (broad s, 1H), 3.90–4.01 (m, 4H), 5.47–5.51 (d, 1H, J_{HH}=9.9 Hz), 5.69–5.74 (d, 1H, $^2J_{PH}$=17.1 Hz), 5.88 (m, 1H); ^{31}P NMR (121 MHz): δ 19.31; ^{13}C NMR (75.4 MHz): δ 13.7, 16.2 (d, $^3J_{PC}$=6.5 Hz), 18.5, 23.4, 24.7, 30.1 (d, $^3J_{PC}$=7.1 Hz, *cis*), 33.2, 35.5, 61.1 (d, $^2J_{PC}$=5.7 Hz), 74.3 (d, $^3J_{PC}$=22.7 Hz, trans), 111.0 (d, $^1J_{PC}$=189.4 Hz), 130.5, 131.3, 170.96 (d, $^2J_{PC}$=6.6 Hz); ESMS (MH^+, *m/z*, 317.4). Anal. calcd for $C_{16}H_{29}O_4P$: C, 60.74; H, 9.24; P, 9.79. Found: C, 60.64; H, 9.36; P, 9.70%.

4.2.2. Compound 3b. 54% isolated yield; (30% petroleum ether: 70% ethyl acetate); R_f=0.44; ^{1}H NMR (300 MHz): δ 0.91 (t, 3H, J_{HH}=7.5 Hz), 1.23–1.51 (m, 8H), 1.51–2.01 (m, 6H), 2.15–2.21 (m, 2H), 2.36–2.46 (m, 2H), 2.54–2.63 (m, 2H), 3.37 (s, broad, 1H), 4.00–4.12 (m, 4H), 5.50 (d, 1H, J_{HH}=11.8 Hz) 5.78 (d, 1H, $^2J_{PH}$=17.4 Hz), 5.80–5.89 (m, 1H); ^{31}P NMR (121 MHz): δ 20.48; ^{13}C NMR (75.4 Hz): δ 13.9, 16.39 (d, $^3J_{PC}$=6.6 Hz), 22.9, 23.7, 26.7, 27.1, 30.1 (d, $^3J_{PC}$=7.0 Hz, *cis*), 33.5, 37.6, 61.3 (d, 2C, $^2J_{PC}$=5.8 Hz), 80.6 (d, $^3J_{PC}$=22.6 Hz), 111.2 (d, $^1J_{PC}$=188 Hz), 132.1, 136.0, 170.9 (d, $^2J_{PC}$=6.9 Hz); ESMS (MH^+, *m/z*, 331.2). Anal. calcd for $C_{17}H_{31}O_4P$: C, 61.80; H, 9.46; P, 9.37. Found: C, 61.66; H,9.40; P, 9.31%.

4.2.3. Compound 3c. 55% isolated yield; (30% petroleum ether: 70% ethyl acetate); R_f=0.53; ^{1}H NMR (300 MHz): δ 0.72–0.90 (m, 3H), 0.96 (s, 3H), 1.00 (s, 3H), 1.29 (m, 6H), 1.32–1.87 (overlap, 8H), 2.41 (m, 2H), 4.02 (m, 4H), 5.35 (d, 1H, J_{HH}=9.9 Hz), 5.61 (d, 1H, J_{HH}=10.2 Hz), 5.73 (d, 1H, $^2J_{PH}$=17.4 Hz); ^{31}P NMR (121 Hz): d 20.17; ^{13}C NMR (75.4 MHz): δ 14.0, 16.5, 16.6, 23.7, 27.7, 29.9, 30.3 (d, $^3J_{PC}$=6.9 Hz, *cis*), 31.9, 32.9, 33.3, 33.5 (d, $^3J_{PC}$=2.3 Hz), 61.4, 61.4, 74.7 (d, $^3J_{PC}$=22.6 Hz), 111.2 (d, $^1J_{PC}$= 188.9 Hz), 128.2, 141.5, 171.0 (d, $^2J_{PC}$=6.9 Hz); UV: 252 nm/869; ESMS (MH^+, *m/z*, 345.3). Anal. calcd for $C_{18}H_{33}O_4P$: C, 62.77; H, 9.66; P, 8.99. Found: C, 62.59; H,9.70; P, 8.81%.

4.2.4. Compound 3d. 50% isolated yield; (50% petroleum ether: 50% ethyl acetate); R_f=0.36; ^{1}H NMR (300 MHz): δ 0.75 (t, 3H, J_{HH}=6.9 Hz), 1.18 (t, 6H, J_{HH}=7.2 Hz), 1.29 (s, 3H), 1.22–1.39 (overlap, 4H), 2.29 (t, 2H, J_{HH}=8.4 Hz), 3.55 (s, broad, 1H), 3.90 (m, 4H), 4.96 (d, 1H, J_{HH}=10.8 Hz), 5.13 (d, 1H, $^2J_{PH}$=16.8 Hz), 5.69–5.82 (m, 2H); ^{31}P NMR (121 MHz); δ 20.32; ^{13}C NMR (75.4 MHz): δ 14.2, 16.6, 16.6, 23.2, 26.4, 30.1 (d, $^3J_{PC}$=6.9 MHz, *cis*), 32.8, 60.9 (d, $^2J_{PC}$=5.7 Hz), 76.4 (d, $^3J_{PC}$= 22.0 Hz) 109.8 (d, $^1J_{PC}$=189.8 Hz), 113.1, 142.7, 170.0 (d, $^2J_{PC}$=7.2 MHz); UV: 266 nm/2439; ESMS (MH^+, *m/z*, 291.1). Anal. calcd for $C_{14}H_{27}O_4P$: C, 57.92; H, 9.37; P, 10.67. Found: C, 57.78; H, 9.40; P, 10.52%.

4.2.5. Compound 4a. 50% isolated yield; (30% petroleum ether: 70% ethyl acetate); R_f=0.11; ^{1}H NMR (300 MHz): δ 0.75 (t, 3H, J_{HH}=6.9 Hz), 1.07–1.47 (overlap,12H), 1.66–2.03 (overlap, 5H), 2.45–2.58 (m, 2H), 3.86–3.99 (m, 4H), 4.17 (s, 1H, broad), 5.36 (d, 1H, $^2J_{PH}$=17.1 Hz), 5.96 (s, 1H); ^{31}P NMR (121 MHz) δ 20.31; ^{13}C NMR (75.4 Hz): δ 14.0, 14.2, 16.4, 16.4, 19.8, 23.1, 26.3, 31.5 (d, $^3J_{PC}$= 7.0 Hz, *cis*), 32.1, 60.5, 61.5, 66.3, 110.5 (d, $^1J_{PC}$=191.1 Hz), 131.9, 138.4 (d, $^3J_{PC}$=23.8 Hz), 163.6 (d, $^2J_{PC}$=8.3 Hz); UV: 251 nm/8614; ESMS (MH^+, *m/z*, 317.4). Anal. calcd for $C_{16}H_{29}O_4P$: C, 60.74; H, 9.24; P, 9.79. Found: C, 60.70; H, 9.33; P, 9.70%.

4.2.6. Compound 4b. 50% isolated yield; (30% petroleum ether: 70% ethyl acetate); R_f=0.11; ^{1}H NMR (300 MHz): δ 0.86 (m, 3H, J_{HH}=7.2 Hz), 1.27 (t, 6H, J_{HH}=2.1 Hz), 1.31–2.38 (overlap, 13H), 2.63 (m, 2H), 4.06 (m, 4H), 4.47 (m, 1H), 4.94 (d, 1H, $^2J_{PH}$=15.0 Hz), 5.97 (s, 1H); ^{31}P NMR (121 MHz): δ 20.08; ^{13}C NMR (75.4 Hz): δ 14.2, 16.6, 16.6 (d, $^3J_{PC}$=6.9 Hz), 19.7, 23.3, 26.4, 30.8 (d, $^3J_{PC}$=6.9 Hz, *cis*), 31.7, 32.2, 61.6 (d, $^2J_{PC}$=5.4 Hz), 66.7,111.5 (d, $^1J_{PC}$=190 Hz), 138.1, 142.4 (d, $^3J_{PC}$=23.8 Hz), 166.1 (d, $^2J_{PC}$=8.1 Hz); UV: 251 nm/8642; ESMS (MH^+, *m/z*, 331.2). Anal. calcd for $C_{17}H_{31}O_4P$: C, 61.80; H, 9.46; P, 9.37. Found: C, 61.66; H, 9.40; P, 9.23%.

4.2.7. Compound 5. 45% isolated yield; (30% petroleum ether: 70% ethyl acetate); R_f=0.10; ^{1}H NMR (300 MHz): δ 0.75 (t, 3H, J_{HH}=6.9 Hz), 1.07–1.47 (overlap,12H), 1.66–2.03 (overlap, 5H), 2.45–2.58 (m, 2H), 3.86–3.99 (m, 4H), 4.17 (s, 1H, broad), 5.96 (s, 1H); ^{31}P NMR (121 MHz) δ 20.31; ^{13}C NMR (75.4 Hz): δ 14.0, 14.2, 16.4, 16.4, 19.8, 23.1, 26.3, 31.5 (d, $^3J_{PC}$=7.0 Hz, *cis*), 32.1, 60.5, 61.5, 66.3, 110.5 (d, $^1J_{PC}$=191.1 Hz), 131.9, 138.4 (d, $^3J_{PC}$=23.8 Hz), 163.6 (d, $^2J_{PC}$=8.3 Hz); ESMS (MH^+, *m/z*, 318.4).

4.2.8. Compound 6. 48% isolated yield; (30% petroleum ether: 70% ethyl acetate); R_f=0.40; ^{1}H NMR (300 MHz: δ 0.84 (t, 3H, J_{HH}=7.5 Hz), 1.27 (t, 6H, J_{HH}=6.6 Hz), 1.29–1.99 (overlap, 10H), 2.42 (m, 2H), 2.50 (broad s, 1H), 3.90–4.01 (m, 4H), 5.47–5.51 (d, 1H, J_{HH}=9.9 Hz), 5.88 (m, 1H); ^{31}P NMR (300 MHz): δ 19.31; ^{13}C NMR (75.4 MHz): δ 13.7, 16.2 (d, $^3J_{PC}$=6.5 Hz), 18.5, 23.4, 24.7, 30.1 (d, $^3J_{PC}$=7.1 Hz, *cis*), 33.2, 35.5, 61.1 (d, $^2J_{PC}$=5.7 Hz), 74.3 (d, $^3J_{PC}$=22.7 Hz, trans), 111.0 (d, $^1J_{PC}$=189.4 Hz), 130.5, 131.3, 170.96 (d, $^2J_{PC}$=6.6 Hz); ESMS (MH^+, *m/z*, 318.4).

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