Synthesis and Intramolecular Cyclization of Diethylphosphono-Substituted Allenic Glycols

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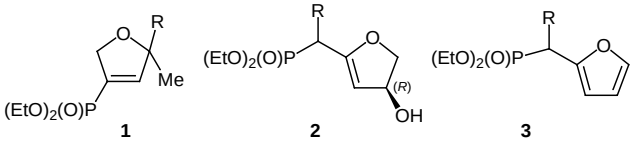
Abstract: This paper describes a convenient and efficient synthesis of new (2*R*)-5-substituted-5-(diethylphosphono)-penta-3,4-dien-1,2-diols. Phosphorylated allenic glycols are stable enough compounds, but under basic conditions they cyclized to (3*R*)-5-(3-hydroxy-2,3-dihydrofuryl)(diethylphosphono)alkanes through intramolecular nucleophilic addition of the terminal alkoxide to the central carbon atom of the allene system. Treatment of (3*R*)-5-(3-hydroxy-2,3-dihydrofuryl)(diethylphosphono)alkanes with a catalytic amount of *p*-toluenesulfonic acid in chloroform at 40–45 °C for 0.5 hours afforded diethylphosphono(2-furyl)alkanes.

Key words: cyclization, furans, 2,3-dihydrofurans, phosphaallenes, phosphorus heterocycles

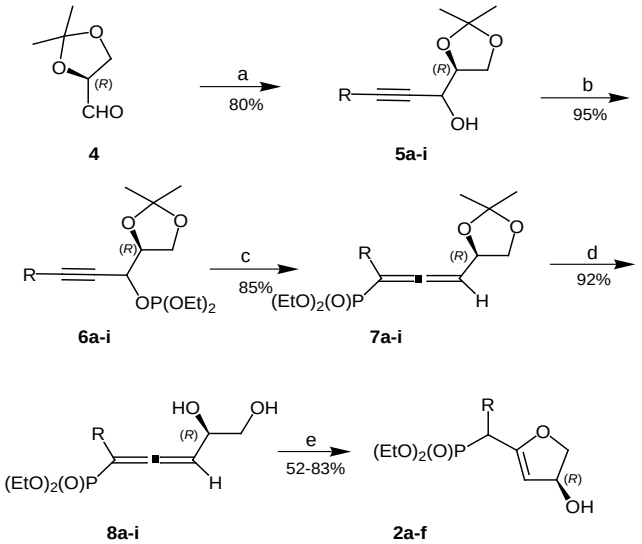
Allenes and their derivatives have received considerable attention as useful building blocks and intermediates in organic synthesis.[1,2] The introduction of different functional groups makes it possible to expand the range of possible synthetic reactions of allenes. Synthesis of allenic alcohols can be of interest with this in view. In the literature, several examples of cyclizations of allenic alcohols to 2,5-dihydrofurans[3] or furans[4] have been described. Application of this approach to phosphorus-containing allenes can open the way to phosphorylated furans and dihydrofurans. However, relatively little work has been performed on the synthesis and study of intramolecular cyclization of phosphorylated allenic carbinols.[5,6] Recently, we have described an easy synthesis of 4-(diethylphosphono)-2,5-dihydrofurans **1** from of diethylphosphono-substituted α-allenic carbilnols (Scheme 1).[6]



Scheme 1

In continuation of our earlier work on the synthesis of 1,2- and 1,3-alkadienes,[7] and in connection with our interest in developing new synthetic strategies for the construction of phosphonic heterocycles,[6,8] we herein present the synthesis of (3*R*)-5-(3-hydroxy-2,3-dihydrofuryl)(diethylphosphono)alkanes **2** from (2*R*)-*5*-substituted-5-(diethylphosphono)penta-3,4-dien-1,2-diols **8** and diethylphosphono(2-furyl)alkanes **3** using phosphorus containing allenes **8** as intermediates.

The diethylphosphono-2,3-dihydrofurans **2** were synthesized by a simple and efficient three-step procedure via propargylic alcohols **5a**–**i** and phosphorylated diols **8a**–**i** (Scheme 2). The starting material, 2,3-*O*-isopropylidene-D-glyceraldehyde **4**, was prepared from D-mannitol. D-mannitol has been ketalized using a variety of methods[9] to provide 1,2:5,6-diisopropylidene-D-mannitol. We selected the procedure reported by Chittenden,[10] which uses catalytic stannous chloride ($SnCl_2$) and 2,2-dimethoxypropane and obtained the ketal in ~60% yield. The 1,2:5,6-diisopropylidene-D-mannitol was converted to D-glyceraldehyde **4** with a silica gel-supported sodium metaperiodate reagent in powder form.[11] The propargyl alcohols were prepared in ~80% yield by a standard procedure, starting from acetylenes and D-glyceraldehyde **4**.[12]



(a) CR≡CMgBr; (b) $ClP(OEt)_2$, Et_3N, Et_2O, -40 °C; (c) r.t., 24 h; (d) MeOH, H^+, 50 °C, 1h; (e) Et_3N, 45 °C, 48 h.

R = H (**a**); C_6H_5 (**b**); p-$CH_3C_6H_4$ (**c**); $HOCH_2$ (**d**); CH_3OCH_2 (**e**); $CH(OH)CH_3$ (**f**); n-C_4H_9 (**g**); n-C_5H_{11} (**h**); n-C_6H_{13} (**i**).

Scheme 2

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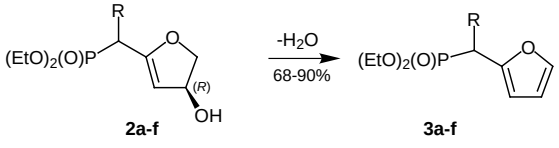
Phosphorylated allenes **8** were synthesized directly from propargylic alcohols **5a**–**i** in ~70% yield by Horner–Mark [2,3]-sigmatropic rearrangement[13] of the unstable phosphites **6** generated in situ by reaction with diethyl chlorophosphite in the presence of triethylamine in diethyl ether. ^{31}P NMR spectroscopy was used to monitor the reaction. The deprotection of the isopropylidene group proceeded in high yield upon treating phosponates **7** with 1 M HCl in methanol at 50–60 °C. Compounds **8a**–**i** were stable enough to be handled at ambient temperature. Analytically pure allenes **8a**–**i** were isolated as colorless or pale yellow oils by column chromatography on silica gel.

The glycols **8a**–**i** were obtained as mixtures of two diastereomers (^{31}P NMR spectral data, in 1:1–1.4 ratio) resulting from chirality of the allenic group. The chemical shift of phosphorus is characteristic for compounds with a 4-coordinate phosphorus atom linked with an *sp*^{2}-hybridized carbon atom. The extremely low-field position of the allenic central carbon atom resonance (near 210 ppm relative to tetramethylsilane) allows for the immediate identification of the allenic moiety by ^{13}C NMR spectroscopy.[14] The chemical shift for signals of the allenic central carbon atom of phosphorylated allene **8** is δ = 211–212 ppm.

The phosphorylated allenic glycols are stable compounds, but under basic conditions they cyclize to 2,3-dihydrofurans by nucleophilic addition of the terminal alkoxide to the central carbon atom of the allene system. Reactions were performed in the presence of triethylamine in anhydrous chloroform at 45–50 °C for 48 hours. Cyclizations of **8a**–**f** were monitored by TLC and ^{1}H NMR spectral data. Inspection of the ^{1}H NMR spectrum of the crude material showed a high conversion of **8a**–**f** to dihydrofurans **2a**–**f**. When the substituents R were sterically bulky (R = *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_6H_{13}), attempts to cyclize glycols **8g**–**i** with triethylamine were unsuccessful, affording only trace amounts of 2,3-dihydrofurans (^{1}H NMR analysis). All of the 2,3-dihydrofurans were isolated as colorless oils by column chromatography on alumina.

The 2,3-dihydrofurans **2a**–**f** can lead to α-substituted furans, a system that occurs in a number of natural products.[4b] Reaction of **2a**–**f** with a catalytic amount of *p*-toluenesulfonic acid at 40–45 °C for 2 hours led to diethylphosphonofurans **3a**–**f** (monitored by TLC on silica gel), which were isolated as stable colorless oils by column chromatography on silica gel (Scheme 3).



2a-f **3a-f**

R = H (**a**); C_6H_5 (**b**); p-$CH_3C_6H_4$ (**c**); $HOCH_2$ (**d**); CH_3OCH_2 (**e**); $CH(OH)CH_3$ (**f**).

Scheme 3

Compounds **2a**–**f** and **3a**–**f** were identified by IR, ^{1}H, ^{13}C and ^{31}P NMR spectral data. For example, the IR spectra of compounds **3a**–**f** displayed absorption bands of the phosphoryl group at 1249–1259 cm^{-1}, double bonds at ~1570, 1600 cm^{-1}, and hydroxyl group at 3350–3660 cm^{-1} (for **3d**, **3f**). The ^{1}H NMR spectrum of the 2,3-dihydrofurans **2a**–**f** showed signals of the protons for ethoxy groups, and the signals at 4.9 and 5.3 ppm related to the protons at C-3 and C-4, respectively. The chemical shifts of the corresponding tertiary and quaternary ethylenic carbon, respectively at 101–102 and 154–157 ppm, confirms the presence of the enol ether[15] in **2a**–**f**. The chemical shift δ_P = 23–25 ppm for **2a**–**f** and **3a**–**f** is characteristic for compounds with a 4-coordinate phosphorus atom linked with an *sp*^{3}-hybridized carbon atom.

In summary, we have described an easy and convenient method for the preparation of synthetically valuable (3*R*)-5-(3-hydroxy-2,3-dihydrofuryl)(diethylphosphono)alkanes from (2*R*)-5-substituted-5-(diethylphosphono)-penta-3,4-dien-1,2-diols as starting materials. Treatment of (3*R*)-5-(3-hydroxy-2,3-dihydrofuryl)(diethylphosphono)alkanes with a catalytic amount of *p*-toluenesulfonic acid in chloroform afforded diethylphosphono(2-furyl)alkanes. Future studies on this potentially important synthetic methodology are currently in progress. Applications of phosphorylated allenes to the synthesis of interesting phosphonic heterocycles will be reported in due course.

NMR spectra were recorded on a Bruker CXP-200 spectrometer at 200 MHz (^{1}H), 81.01 MHz (^{31}P) and 50.3 MHz (^{13}C). Chemical shifts for ^{1}H and ^{13}C NMR are reported in ppm relative to TMS as internal standard. ^{31}P downfield shifts (δ) are expressed with a positive sign, relative to external 85% H_3PO_4 in H_2O. IR spectra (films) were recorded on a Bruker IFS-113 spectrometer. Column chromatography was performed with Fluka Silica gel 60 (0.035–0.070 mm). Preparative TLC was performed on Fluka Silica gel/TLC-cards (20 × 20 × 0.2 cm). All reagents were of commercial quality or were purified before use. Organic solvents were purified and dried by standard procedures.[16] Propargyl alcohol was protected by reaction with ethyl vinyl ether to afford the ether in nearly quantitative yield by standard procedures.[12] The details of the preparation of O-protected propargyl alcohol have been described earlier.[7a]

(2*R*)-5-(Diethylphosphono)penta-3,4-dien-1,2-diol (8a)

Purified anhyd THF (100 mL) was placed in a 50-mL flask, acetylene was introduced through a gas-inlet tube at the rate of 2–3 L/h, and the stirrer was started. After 30 min, ethynylmagnesium bromide [prepared from magnesium turnings (0.48 g, 0.02 g-atom), and ethyl bromide (2.4 g, 0.022 mol) in THF (25 mL)] was added over 2 h; the temperature of the reaction increased 5–10 °C, and the mixture was stirred at 30–35 °C for 1 h. The mixture was cooled in an ice bath and 2,3-*O*-isopropylidene-D-glyceraldehyde, (3.12 g, 0.024 mol) in THF (15 mL) was added over 15 min. The mixture was then stirred and heated to 40–45 °C for a further 2 h. The mixture was cooled and sat. NH_4Cl was added carefully to dissolve the solid components. The two layers were separated and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic fractions were dried (K_2CO_3) and the solvent was evaporated in vacuo. To a solution of crude acetylenic alcohol **5a** (2.3 g, 0.0148 mol) in Et_2O (50 mL) under N_2 was added Et_3N (1.62 g, 0.016 mol) and the mixture was cooled to –50 °C. A solution of diethyl chlorophosphite

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(2.18 g, 0.014 mol) in Et_2O (10 mL) was added dropwise and the mixture was then stirred at –50 °C over 1 h, and at r.t. for 24 h. The solid was removed by filtration and the solvent was evaporated in vacuo. The crude phosphorylated allene **7a** was dissolved in MeOH (20 mL) and 35% HCl (1–2 drops) was added. The solution was stirred at 50–60 °C for 2 h and the solvent was evaporated in vacuo. The crude product was isolated by column chromatography on silica gel ($CHCl_3$–MeOH, 10:1.2) to yield **8a** (2.4 g, 52%) as an oil. TLC (diastereomeric mixture): R_f = 0.53, 0.56 ($CHCl_3$–MeOH, 10:1.3).

IR (film): ν = 1230, 1959, 3360, 3667 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.32 (dt, 6 H, J_{H-H} = 7.2 Hz, J_{H-P} = 1.6 Hz, 2 CH_3), 3.67 (m, 2 H, C*H*$_2$OH), 3.80 (br s, 2 H, 2 OH), 4.08 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.40 (br s, 1 H, C*H*OH), 5.44 (m, 1 H, HC=), 5.62 (ddd, 1 H, J_{H-H} = 6.5 Hz, J_{H-H} = 6.6 Hz, J_{H-P} = 13.1 Hz, HC=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.20 (d, J_{C-P} = 6.5 Hz, 2 CH_3), 62.68 (d, J_{C-P} = 6.8 Hz, 2 CH_2OP), 62.68 (d, J_{C-P} = 6.9 Hz, 2 CH_2OP), 65.79 (d, J_{C-P} = 4.0 Hz, CH_2OH), 69.95 (d, J_{C-P} = 4.1 Hz, CH_2OH), 69.14 (d, J_{C-P} = 6.3 Hz, CH_2OH), 69.22 (d, J_{C-P} = 6.4 Hz, CH_2OH), 81.57 (d, J_{C-P} = 193.7 Hz, =CH-P), 81.62 (d, J_{C-P} = 193.6 Hz, =CH-P), 94.07 (d, J_{C-P} = 16.0 Hz, =CH), 94.42 (d, J_{C-P} = 15.8 Hz, =CH), 211.13 (s, =C=), 211.94 (s, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 14.08, 14.12.

Anal. Calcd for $C_9H_{17}PO_5$ (236.23): C, 45.76; H, 7.20; P, 13.14. Found: C, 45.71; H, 7.19; P, 13.09.

(2*R*)-5-Phenyl-5-(diethylphosphono)penta-3,4-dien-1,2-diol (8b); Typical Procedure

A solution of ethylmagnesium bromide [prepared from magnesium turnings (0.48 g, 0.02 g-atom), and ethyl bromide (2.4 g, 0.022 mol) in anhyd Et_2O (100 mL)] was cooled to 0 °C, and ethynylbenzene (2.14 g, 0.021 mol) was added dropwise. The solution was stirred for 15 min at 0 °C, warmed to 34–35 °C, stirred for 2 h, and then cooled to 0 °C. A solution of 2,3-*O*-isopropylidene-D-glyceraldehyde (2.73 g, 0.021 mol) in Et_2O (15 mL) was added dropwise. After stirring for 2 h at 34–35 °C, the reaction was cooled to 0 °C, and quenched with sat. NH_4Cl. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried (K_2CO_3), filtered, and concentrated in vacuo to afford crude propargyl alcohol **5b**. To a solution of crude alcohol **5b** (3.25 g, 0.014 mol) in Et_2O (50 mL) under N_2 was added Et_3N (1.62 g, 0.016 mol) and the mixture was cooled to –50 °C. A solution of diethyl chlorophosphite (2.18 g, 0.014 mol) in Et_2O (10 mL) was added dropwise and the mixture was then stirred at –50 °C over 1 h, and at r.t. for 5 h. The solid was removed by filtration and the solvent was evaporated in vacuo. The crude phosphorylated allene **7b** was dissolved in CH_3OH (20 mL) and 35% HCl (1–2 drops) was added. The solution was stirred at 50–60 °C for 2 h and the solvent was evaporated in vacuo. The crude product was isolated by column chromatography on silica gel ($CHCl_3$–MeOH, 10:1.2) to yield **8b** (3.4 g, 54%) as an oil. TLC (diastereomeric mixture): R_f = 0.45, 0.43 ($CHCl_3$–MeOH, 10:1).

IR (film): ν = 1248, 1584, 1600, 1950, 3365, 3689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.32 (dt, 6 H, J_{H-H} = 7.3 Hz, J_{H-P} = 1.7 Hz, 2 CH_3), 3.74 (m, 2 H, C*H*$_2$OH), 4.20 (dq, 4 H, J_{H-H} = 7.3 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.42 (br s, 2 H, 2 OH), 5.31 (br s, 1 H, C*H*OH), 5.88 (dd, 1 H, J_{H-H} = 5.6 Hz, J_{H-P} = 11.9 Hz, HC=), 7.32 (m, 3 H, Ph), 7.54 (m, 2 H, Ph).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.15 (d, J_{C-P} = 6.5 Hz, 2 CH_3), 62.77 (d, J_{C-P} = 5.4 Hz, 2 CH_2OP), 62.84 (d, J_{C-P} = 5.9 Hz, 2 CH_2OP), 65.90 (d, J_{C-P} = 3.7 Hz, CH_2O), 65.95 (d, J_{C-P} = 4.0 Hz, CH_2O), 69.54 (d, J_{C-P} = 5.8 Hz, CHOH), 69.59 (d, J_{C-P} = 6.0 Hz, CHOH), 96.04 (d, J_{C-P} = 15.1 Hz, =CH), 96.41 (d, J_{C-P} = 15.2 Hz, =CH), 98.63 (d, J_{C-P} = 186.3 Hz, =CH-P), 98.63 (d, J_{C-P} = 187.1 Hz, =CH-P), 127.30 (d, J_{C-P} = 6.0 Hz, Ph), 127.35 (d, J_{C-P} = 6.0 Hz, Ph), 127.68 (s, Ph), 128.14 (s, Ph), 128.44 (s, Ph), 209.89 (d, J_{C-P} = 4.4 Hz, =C=), 210.63 (d, J_{C-P} = 5.0 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.87, 16.56.

Anal. Calcd for $C_{15}H_{21}PO_5$ (312.30): C, 57.69; H, 6.77; P, 9.92. Found: C, 57.56; H, 6.70; P, 9.82.

(2*R*)-5-Tolyl-5-(diethylphosphono)penta-3,4-dien-1,2-diol (8c)

Prepared from propargylic alcohol **5c** (3.69 g, 0.015 mol), anhyd Et_2O (75 mL), Et_3N (1.717 g, 0.017 mol), and diethyl chlorophosphite (2.34 g, 0.015 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:1.2) afforded 3.6 g (74%) of **8c**. TLC (diastereomeric mixture): R_f = 0.46, 0.45 ($CHCl_3$–MeOH, 10:1.0).

IR (film): ν = 1246, 1593, 1615, 1953, 3369, 3683 cm^{-1}.

^1H NMR ($CHCl_3$): δ = 1.31 (dt, 6 H, J_{H-H} = 7.2 Hz, J_{H-P} = 1.8 Hz, 2 CH_3), 2.39 (s, 3 H, CH_3), 3.62 (m, 2 H, CH_2OH), 4.18 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.22 (br s, 2 H, 2 OH), 5.27 (br s, 1 H, C*H*OH), 5.86 (dd, 1 H, J_{H-H} = 5.6 Hz, J_{H-P} = 11.9 Hz, HC=), 7.28 (d, 2 H, Tol), 7.41 (d, 2 H, Tol).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.13 (d, J_{C-P} = 6.6 Hz, 2 CH_3), 21.24 (s, CH_3), 62.53 (d, J_{C-P} = 5.7 Hz, 2 CH_2OP), 62.32 (d, J_{C-P} = 6.1 Hz, 2 CH_2OP), 65.55 (d, J_{C-P} = 3.4 Hz, CH_2OH), 66.05 (d, J_{C-P} = 4.2 Hz, CH_2OH), 69.49 (d, J_{C-P} = 6.0 Hz, CHOH), 69.85 (d, J_{C-P} = 6.0 Hz, CHOH), 98.17 (d, J_{C-P} = 15.3 Hz, =CH), 98.85 (d, J_{C-P} = 15.2 Hz, =CH), 99.87 (d, J_{C-P} = 187.4 Hz, =CH-P), 99.94 (d, J_{C-P} = 188.4 Hz, =CH-P), 127.21 (s, Tol), 127.44 (d, J_{C-P} = 6.0 Hz, Tol), 127.53 (d, J_{C-P} = 6.0 Hz, Tol), 128.17 (s, Tol), 128.52 (s, Tol), 210.52 (d, J_{C-P} = 4.8 Hz, =C=), 210.72 (d, J_{C-P} = 5.1 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.42, 16.73.

Anal. Calcd for $C_{16}H_{23}PO_5$ (326.33): C, 58.89; H, 7.10; P, 9.45. Found: C, 59.03; H, 7.10; P, 9.53.

(2*R*)-5-(Diethylphosphono)hexa-3,4-dien-1,2,6-triol (8d)

Prepared from propargylic alcohol **5d** (2.84 g, 0.011 mol), anhyd Et_2O (50 mL), Et_3N (1.212 g, 0.012 mol), and diethyl chlorophosphite (1.716 g, 0.011 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:1.2) afforded 1.76 g (60%) of **8d**. TLC (diastereomeric mixture): R_f = 0.35, 0.34 ($CHCl_3$–MeOH, 10:1.2).

IR (film): ν = 1228, 1956, 3343, 3678 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.32 (dt, 6 H, J_{H-H} = 7.1 Hz, J_{H-P} = 1.6 Hz, 2 CH_3), 3.65 (m, 2 H, C*H*$_2$OH), 4.10 (dq, 4 H, J_{H-H} = 7.1 Hz, J_{H-P} = 6.6 Hz, 2 CH_2OP), 4.25 (m, 2 H, C*H*$_2$OH), 4.37 (m, 1 H, J_{H-P} = 10.6 Hz, C*H*OH), 4.6 (br s, 2 H, 2 OH), 5.70 (dm, 1 H, J_{H-P} = 12.6 Hz, HC=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.11 (d, J_{C-P} = 6.5 Hz, 2 CH_3), 59.16 (d, J_{C-P} = 10.8 Hz, CH_2OH), 62.76 (d, J_{C-P} = 7.4 Hz, 2 CH_2OP), 62.90 (d, J_{C-P} = 7.6 Hz, 2 CH_2OP), 65.45 (d, J_{C-P} = 4.4 Hz, CH_2OH), 65.69 (d, J_{C-P} = 4.0 Hz, CH_2OH), 69.20 (d, J_{C-P} = 6.0 Hz, CHOH), 69.28 (d, J_{C-P} = 6.0 Hz, CHOH), 96.81 (d, J_{C-P} = 15.5 Hz, =CH), 96.89 (d, J_{C-P} = 15.5 Hz, =CH), 97.74 (d, J_{C-P} = 186.0 Hz, =CH-P), 97.76 (d, J_{C-P} = 186.1 Hz, =CH-P), 207.16 (d, J_{C-P} = 4.9 Hz, =C=), 207.21 (d, J_{C-P} = 5.4 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 17.56, 17.59.

Anal. Calcd for $C_{10}H_{19}PO_6$ (266.23): C, 45.12; H, 7.12; P, 11.63. Found: C, 45.09; H, 7.19; P, 11.63.

(2*R*)-5-(Diethylphosphono)-6-methoxyhexa-3,4-dien-1,2-diol (8e)

Prepared from propargylic alcohol **5e** (3.4 g, 0.017 mol), anhyd Et_2O (75 mL), Et_3N (1.82 g, 0.018 mol), and diethyl chlorophosphite (2.65 g, 0.017 mol). Workup and chromatography ($CHCl_3$–

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MeOH, 10:1.2) afforded 2.95 g (62%) of **8e**. TLC (diastereomeric mixture): R_f = 0.39, 038 ($CHCl_3$–MeOH, 10:1.0).

IR (film): ν = 1227, 1959, 3388, 3668 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.31 (dt, 6 H, J_{H-H} = 7.2 Hz, J_{H-P} = 1.7 Hz, 2 CH_3), 3.35 (s, 3 H, OCH_3), 3.65 (m, 2 H, C*H*$_2$OH), 4.02 (m, 2 H, C*H*$_2$$OCH_3$), 4.12 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.20 (br s, 2 H, 2 OH), 4.37 (br s, 1 H, C*H*OH), 5.58 (dm, 1 H, J_{H-P} = 12.51 Hz, HC=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.20 (d, J_{C-P} = 6.5 Hz, 2 CH_3), 58.10 (s, OCH_3), 62.76 (d, J_{C-P} = 6.0 Hz, 2 CH_2OP), 65.57 (d, J_{C-P} = 4.0 Hz, CH_2O), 65.76 (d, J_{C-P} = 4.0 Hz, CH_2O), 69.22 (d, J_{C-P} = 6.1 Hz, CH-OH), 69.31 (d, J_{C-P} = 6.0 Hz, CH_2O), 93.95 (d, J_{C-P} = 188.0 Hz, =CH-P), 93.96 (d, J_{C-P} = 188.0 Hz, =CH-P), 95.59 (d, J_{C-P} = 15.9 Hz, =CH), 96.80 (d, J_{C-P} = 15.9, =CH), 208.72 (d, J_{C-P} = 5.1 Hz, =C=), 209.21 (d, J_{C-P} = 5.6 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 17.44, 16.46.

Anal. Calcd for $C_{11}H_{21}PO_6$ (280.25): C, 47.14; H, 7.55; P, 11.05. Found: C, 47.12; H, 7.43; P, 11.16.

(2*R*)-5-(Diethylphosphono)hepta-3,4-dien-1,2,6-triol (8f)

Prepared from propargylic alcohol **5f** (2.00 g, 0.01 mol), anhyd Et_2O (75 mL), Et_3N (1.21 g, 0.012 mol), and diethyl chlorophosphite (1.56 g, 0.01 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:1.2) afforded 1.82 g (65%) of **8f**. TLC (diastereomeric mixture): R_f = 0.45, 0.51 ($CHCl_3$–MeOH, 10:1.5).

IR (film): ν = 1231, 1954, 3386, 3680 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.30 (dt, 6 H, J_{H-H} = 7.2 Hz, J_{H-P} = 1.9 Hz, 2 CH_3), 1.33 (d, 3 H, J_{H-P} = 7.8 Hz, CH_3), 3.68 (m, 2 H, CH_2OH), 4.15 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.35 (br m, 1 H, C*H*(OH)CH_3, 4.44 (m, 1 H, C*H*OH), 4.81 (br s, 2 H, 2 OH), 5.68 (dm, 1 H, J_{H-P} = 12.4 Hz, HC=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.11 (d, J_{C-P} = 6.5 Hz, 2 CH_3), 16.13 (d, J_{C-P} = 6.4 Hz, 2 CH_3), 22.71 (d, J_{C-P} = 4.2 Hz, CH_3), 22.79 (d, J_{C-P} = 4.4 Hz, CH_3), 22.84 (d, J_{C-P} = 4.0 Hz, CH_3), 22.88 (d, J_{C-P} = 4.2 Hz, CH_3), 62.85 (d, J_{C-P} = 6.0 Hz, 2 CH_2OP), 62.88 (d, J_{C-P} = 5.9 Hz, 2 CH_2OP), 62.95 (d, J_{C-P} = 6.1 Hz, 2 CH_2OP), 63.03 (d, J_{C-P} = 6.0 Hz, 2 CH_2OP), 64.68 (s, CH), 64.77 (s, CH), 64.89 (s, CH), 65.00 (s, CH), 65.61 (d, J_{C-P} = 6.3 Hz, CH), 65.68 (d, J_{C-P} = 6.0 Hz, CH), 65.85 (d, J_{C-P} = 6.1 Hz, CH), 65.91 (d, J_{C-P} = 6.2 Hz, CH), 69.32 (d, J_{C-P} = 6.2 Hz, CH_2OH), 69.44 (d, J_{C-P} = 6.0 Hz, CH_2OH), 69.49 (d, J_{C-P} = 6.1 Hz, CH_2OH), 69.54 (d, J_{C-P} = 6.0 Hz, CH_2OH), 96.81 (d, J_{C-P} = 15.0 Hz, =CH), 96.88 (d, J_{C-P} = 15.0 Hz, =CH), 97.56 (d, J_{C-P} = 15.5. Hz, =CH), 97.75 (d, J_{C-P} = 15.4 Hz, =CH), 101.62 (d, J_{C-P} = 184.2 Hz, =CHP), 101.67 (d, J_{C-P} = 184.5 Hz, =CHP), 102.53 (d, J_{C-P} = 185.5 Hz, =CHP), 102.67 (d, J_{C-P} = 185.3 Hz, =CHP), 206.53 (d, J_{C-P} = 5.2 Hz, =C=), 206.61 (d, J_{C-P} = 5.5 Hz, =C=), 206.75 (d, J_{C-P} = 5.2 Hz, =C=), 206.81 (d, J_{C-P} = 5.2 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 17.83, 17.98, 18.02, 18.07.

Anal. Calcd for $C_{11}H_{21}PO_6$ (280.25): C, 47.14; H, 7.55; P, 11.05. Found: C, 47.20; H, 7.57; P, 10.96.

(2*R*)-5-(Diethylphosphono)nona-3,4-dien-1,2-diol (8g)

Prepared from propargylic alcohol **5g** (3.71 g, 0.0175 mol), anhyd Et_2O (75 mL), Et_3N (1.92 g, 0.019 mol), and diethyl chlorophosphite (2.73 g, 0.0175 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:1.2) afforded 3.73 g (73%) of **8g**. TLC (diastereomeric mixture): R_f = 0.36, 0.38 ($CHCl_3$–MeOH, 10:1.0).

IR (film): ν = 1225, 1955, 3380, 367 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.91 (t, 3 H, J_{H-H} = 7.9 Hz), 1.35 (m, 8 H, CH_2 + 2 CH_3), 1.48 (m, 2 H, CH_2), 2.12 (ddt, 2 H, J_{H-H} = 3.2 Hz, J_{H-P} = 10.76 Hz, J_{H-H} = 8.45 Hz, CH_2), 3.61 (m, 2 H, C*H*$_2$OH), 3.90 (br s, 2 H, 2 OH), 4.08 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.32 (br m, 1 H, C*H*(OH), 5.52 (ddm, 1 H, J_{H-H} = 3.11, J_{H-P} = 13.2 Hz, J_{H-H} = 5.30 Hz, HC=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 13.74 (s, CH_3), 16.22 (d, J_{C-P} = 6.4 Hz, 2 CH_3), 22.07 (s, CH_2), 27.56 (d, J_{C-P} = 5.3 Hz, CH_2), 30.05 (d, J_{C-P} = 6.5 Hz, CH_2), 62.47 (d, J_{C-P} = 6.0 Hz, 2 CH_2OP), 65.69 (d, J_{C-P} = 3.9 Hz, CH_2OH), 66.04 (d, J_{C-P} = 4.7 Hz, CH_2OH), 69.36 (d, J_{C-P} = 6.3 Hz, CHOH), 69.51 (d, J_{C-P} = 6.5 Hz, CHOH), 95.26 (d, J_{C-P} = 16.2 Hz, =CH), 95.72 (d, J_{C-P} = 16.4 Hz, =CH), 96.15 (d, J_{C-P} = 184.2 Hz, =CH-P), 96.38 (d, J_{C-P} = 185.0 Hz, =CH-P), 207.55 (d, J_{C-P} = 6.1 Hz, =C=), 208.67 (d, J_{C-P} = 6.8 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 19.72, 19.77.

Anal. Calcd for $C_{13}H_{25}PO_5$ (292.31): C, 53.42; H, 8.62; P, 10.60. Found: C, 53.43; H, 8.56; P, 10.65.

(2*R*)-5-(Diethylphosphono)deca-3,4-dien-1,2-diol (8h)

Prepared from propargylic alcohol **5h** (4.07 g, 0.018 mol), anhyd Et_2O (75 mL), Et_3N (1.97 g, 0.0195 mol), and diethyl chlorophosphite (2.80 g, 0.018 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:1.2) afforded 4.13 g (75%) of **8h**. TLC (diastereomeric mixture): R_f = 0.40, 042 ($CHCl_3$–MeOH, 10:1.0).

IR (film): ν = 1228, 1948, 3388, 3668 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.89 (t, 3 H, J_{H-H} = 7.7 Hz, CH_3), 1.30 (m 10 H, 2 CH_2 + 2 CH_3), 1.47 (m, 2 H, CH_2), 2.11 (ddt, 2 H, J_{H-H} = 3.12 Hz, J_{H-P} = 10.83 Hz, J_{H-H} = 8.00 Hz, CH_2), 3.61 (m, 2 H, C*H*$_2$OH), 3.94 (br s, 2 H, 2 OH), 4.08 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.32 (br m, 1 H, J_{H-H} = 5.3 Hz, J_{H-P} = 11.72 Hz, C*H*(OH), 5.53 (ddm, 1 H, J_{H-H} = 3.12, J_{H-P} = 13.18 Hz, J_{H-H} = 5.30 Hz, HC=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 14.01 (s, CH_3), 16.29 (d, J_{C-P} = 6.5 Hz, 2 CH_3), 22.36 (s, CH_2), 27.68 (d, J_{C-P} = 6.6 Hz, CH_2), 27.70 (d, J_{C-P} = 6.5 Hz, CH_2), 27.88 (d, J_{C-P} = 5.2 Hz, CH_2), 27.92 (d, J_{C-P} = 5.3 Hz, CH_2), 31.20 (s, CH_2), 31.23 (s, CH_2), 62.52 (d, J_{C-P} = 6.0 Hz, CH_2O), 65.78 (d, J_{C-P} = 4.0 Hz, CH_2O), 66.13 (d, J_{C-P} = 4.4 Hz, CH_2O), 69.48 (d, J_{C-P} = 6.3 Hz, CHOH), 69.57 (d, J_{C-P} = 6.4 Hz, CHOH), 95.29 (d, J_{C-P} = 16.4 Hz, =CH), 95.76 (d, J_{C-P} = 16.4 Hz, =CH), 96.27 (d, J_{C-P} = 184.2 Hz, =CH-P), 96.46 (d, J_{C-P} = 184.6 Hz, =CH-P), 207.60 (d, J_{C-P} = 5.9 Hz, =C=0), 208.67 (d, J_{C-P} = 6.8 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 20.45, 20.49.

Anal. Calcd for $C_{14}H_{27}PO_5$ (306.33): C, 54.89; H, 8.88; P, 10.11. Found: C, 54.78; H, 8.99; P, 9.97.

(2*R*)-5-(Diethylphosphono)undeca-3,4-dien-1,2-diol (8i)

Prepared from propargylic alcohol **5i** (3.84 g, 0.016 mol), anhyd Et_2O (75 mL), Et_3N (1.77 g, 0.0175 mol), and diethyl chlorophosphite (2.50 g, 0.016 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:1.2) afforded 3.58 g (70%) of **8i**. TLC (diastereomeric mixture): R_f = 0.46, 0.47 ($CHCl_3$–MeOH, 10:1).

IR (film): ν = 1226, 1951, 3348, 3688 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.91 (t, 3 H, J_{H-H} = 7.8 Hz, CH_3), 1.31 (m 12 H, 3 CH_2 + 2 CH_3), 1.50 (m, 2 H, CH_2), 2.13 (ddt, 2 H, J_{H-H} = 3.11 Hz, J_{H-P} = 11.00 Hz, J_{H-H} = 8.15 Hz, CH_2), 3.67 (m, 2 H, C*H*$_2$OH), 4.08 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.2 (br s, 2 H, 2 OH), 4.36 (br m, 1 H, J_{H-H} = 4.8 Hz, J_{H-P} = 11.70 Hz, C*H*(OH), 5.53 (ddm, 1 H, J_{H-H} = 3.12 Hz, J_{H-P} = 13.20 Hz, J_{H-H} = 4.80 Hz, HC=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 13.88 (s, CH_3), 15.88 (d, J_{C-P} = 6.9 Hz, CH_3), 16.11 (d, J_{C-P} = 6.5 Hz, CH_3), 22.34 (s), 22.42 (s), 27.78 (d, J_{C-P} = 5.7 Hz, CH_2), 27.86 (d, J_{C-P} = 6.5 Hz, CH_2), 28.57 (s, CH_2), 31.36 (s, CH_2), 62.35 (d, J_{C-P} = 6.0 Hz, 2 CH_2OP), 65.73 (d, J_{C-P} = 4.0 Hz, CH_2OH), 66.05 (d, J_{C-P} = 4.6 Hz, CH_2OH), 69.38 (d, J_{C-P} = 6.5 Hz, CHOH), 69.53 (d, J_{C-P} = 6.5 Hz,

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CHOH), 95.02 (d, J_{C-P} = 16.3 Hz, =CH), 95.52 (d, J_{C-P} = 16.4 Hz, =CH), 95.95 (d, J_{C-P} = 184.6 Hz, =CH-P), 96.11 (d, J_{C-P} = 185.0 Hz, =CH-P), 208.42 (d, J_{C-P} = 6.8 Hz, =C=), 207.50 (d, J_{C-P} = 6.1 Hz, =C=).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 20.32, 20.46.

Anal. Calcd for $C_{15}H_{29}PO_5$ (320.36): C, 56.24; H, 9.12; P, 9.67. Found: C, 56.17; H, 8.99; P, 9.53.

(3*R*)-5-(3-Hydroxy-2,3-dihydrofuryl)(diethylphosphono)-methane (2a); Typical Procedure

To a solution of **8a** (2.36 g, 0.01 mol) and anhyd $CHCl_3$ (10 mL) was added Et_3N (0.1 g, 0.001 mol). After stirring for 48 h at 45–50 °C, the reaction mixture was concentrated. Chromatography on silica gel ($CHCl_3$–MeOH, 10:0.4) yielded **2a** (1.96 g, 83%) as an oil.

$[\alpha]_{546}$ +79.5 (*c* 1.1, CH_2Cl_2); R_f = 0.37 ($CHCl_3$–MeOH, 10:0.4).

IR (film): ν = 1247, 1678, 3385 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.31 (dt, 6 H, J_{H-H} = 7.2 Hz, J_{H-P} = 1.9 Hz, 2 CH_3), 2.78 (d, 2 H, J_{H-P} = 20.0 Hz, CH_2-P), 3.60 (br d, 1 H, J_{H-H} = 7.6 Hz, OH), 4.11 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.27 (m, 2 H, CH_2), 4.90 (br m, 1 H, C*H*OH), 5.13 (m, 1 H, HC=).

^{13}C NMR ($CDCl_3$): δ = 16.17 (d, J_{C-P} = 6.2 Hz, 2 CH_3), 26.56 (d, J_{C-P} = 140.8 Hz, CH_2-P), 62.20 (d, J_{C-P} = 6.3 Hz, 2 CH_2OP), 62.32 (d, J_{C-P} = 6.1 Hz, 2 CH_2OP), 73.60 (d, J_{C-P} = 1.7 Hz, CHOH), 78.41 (s, CH_2), 102.26 (d, J_{C-P} = 9.4 Hz, =CH), 153.49 (d, J_{C-P} = 9.5 Hz, =C-O).

^{31}P NMR ($CDCl_3$): δ = 25.12.

Anal. Calcd for $C_9H_{17}PO_5$ (236.20): C, 45.76; H, 7.25; P, 13.11. Found: C, 45.66; H, 7.00; P, 13.02.

(3*R*)-5-(3-Hydroxy-2,3-dihydrofuryl)(diethylphosphono)-(phenyl)methane (2b)

Prepared from allene **8b** (3.12 g, 0.01 mol), anhyd $CHCl_3$ (15 mL), and Et_3N (0.1 g, 0.001 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.5) afforded 2.25 g (72%) of **2b**.

R_f = 0.48 ($CHCl_3$–MeOH, 10:0.5).

IR (film): ν = 1254, 1587, 1604, 1671, 3374 cm^{-1}.

^{1}H NMR ($CDCl_3$) (diastereomeric mixture): δ = 1.10 (dt, 3 H, J_{H-H} = 7.2 Hz, J_{H-P} = 1.9 Hz, CH_3), 1.31 (m, 3 H, CH_3), 3.02 (br s, 1 H, J_{H-H} = 7.5 Hz, OH), 3.09 (br s, 1 H, J_{H-H} = 8.1 Hz, OH), 3.73 (m, 1 H, CH-Ph), 3.97 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 7.0 Hz, 2 CH_2OP), 4.10 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 4.29 (m, 2 H, CH_2), 4.97 (br m, 1 H, C*H*OH), 5.35 (m, 1 H, CH=), 7.31 (m, 3 H, Ph), 7.48 (m, 2 H, Ph).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.15 (d, J_{C-P} = 6.0 Hz, 2 CH_3), 16.19 (d, J_{C-P} = 6.0 Hz, CH_3), 16.35 (d, J_{C-P} = 6.0 Hz, 2 CH_3), 16.39 (d, J_{C-P} = 6.0 Hz, CH_3), 45.45 (d, J_{C-P} = 138.2 Hz, CH-P), 45.47 (d, J_{C-P} = 139.4 Hz, CH-P), 62.3 (d, J_{C-P} = 7.9 Hz, CH_2OP), 62.78 (d, J_{C-P} = 7.1 Hz, CH_2OP), 63.09 (d, J_{C-P} = 7.9 Hz, CH_2OP), 63.18 (d, J_{C-P} = 7.1 Hz, CH_2OP), 73.81 (s, HCOH), 78.53 (d, J_{C-P} = 2.5 Hz, CH_2), 102.75 (d, J_{C-P} = 6.9 Hz, CH=), 102.81 (d, J_{C-P} = 6.2 Hz, CH=), 127.66 (d, J_{C-P} = 2.7 Hz, Ph), 127.71 (d, J_{C-P} = 2.6 Hz, Ph), 128.53 (d, J_{C-P} = 2.3 Hz, Ph), 129.4 (d, J_{C-P} = 3.5 Hz, Ph), 129.53 (d, J_{C-P} = 3.7 Hz, Ph), 133.39 (d, J_{C-P} = 7.2 Hz, Ph), 133.53 (d, J_{C-P} = 7.4 Hz, Ph), 157.84 (d, J_{C-P} = 8.4 Hz, =C-O), 157.92 (d, J_{C-P} = 7.1 Hz, =C-O).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 23.34, 23.53.

Anal. Calcd for $C_{15}H_{21}PO_5$ (312.30): C, 57.69; H, 6.77; P, 9.92. Found: C, 57.51; H, 6.70; P, 9.82.

(3*R*)-5-(3-Hydroxy-2,3-dihydrofuryl)diethylphosphonotolyl-methane (2c)

Prepared from allene **8c** (3.26 g, 0.01 mol), anhyd $CHCl_3$ (15 mL), and Et_3N (0.1 g, 0.001mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.5) afforded 2.25 g (69%) of **2c**.

R_f = 0.5 ($CHCl_3$–MeOH, 10:0.5).

IR (film): ν = 1249, 1589, 1614, 1672, 3377 cm^{-1}.

^{1}H NMR ($CDCl_3$) (diastereomeric mixture): δ = 1.22 (dt, 3 H, J_{H-H} = 7.3 Hz, J_{H-P} = 1.1 Hz, CH_3), 1.31 (m, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 3.12 (br s, 1 H, J_{H-H} = 7.6 Hz, OH), 3.19 (br s, 1 H, J_{H-H} = 8.0 Hz, OH), 3.79 (m, 1 H, C*H*-Ph), 3.93 (dq, 4 H, J_{H-H} = 7.3 Hz, J_{H-P} = 6.9 Hz, 2 CH_2OP), 4.13 (dq, 4 H, J_{H-H} = 7.3 Hz, J_{H-P} = 6.9 Hz, 2 CH_2OP), 4.24 (m, 2 H, CH_2), 4.92 (br m, 1 H, C*H*OH), 5.31 (m, 1 H, CH=), 7.33 (m, 3 H, Ar-H), 7.48 (m, 2 H, Ar-H).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.17 (d, J_{C-P} = 6.0 Hz, CH_3), 16.20 (d, J_{C-P} = 6.0 Hz, CH_3), 16.24 (d, J_{C-P} = 6.0 Hz, CH_3), 16.38 (d, J_{C-P} = 6.0 Hz, CH_3), 21.31 (s, CH_3), 45.32 (d, J_{C-P} = 138.9 Hz, CH-P), 45.47 (d, J_{C-P} = 139.2 Hz, CH-P), 62.27 (d, J_{C-P} = 7.8 Hz, CH_2OP), 62.75 (d, J_{C-P} = 7.4 Hz, CH_2OP), 63.05 (d, J_{C-P} = 7.6 Hz, CH_2OP), 63.15 (d, J_{C-P} = 7.3 Hz, CH_2OP), 73.78 (s, HC-OH), 78.56 (d, J_{C-P} = 2.6 Hz, CH_2), 102.54 (d, J_{C-P} = 6.9 Hz, CH=), 102.84 (d, J_{C-P} = 6.4 Hz, CH=), 127.83 (d, J_{C-P} = 2.6 Hz, Tol), 127.94 (d, J_{C-P} = 2.8 Hz, Tol), 128.54 (d, J_{C-P} = 2.3 Hz, Tol), 130.1 (d, J_{C-P} = 3.6 Hz, Tol), 130.10 (d, J_{C-P} = 3.6 Hz, Tol), 134.19 (d, J_{C-P} = 7.1 Hz, Tol), 134.81 (d, J_{C-P} = 7.3 Hz, Ph), 157.84 (d, J_{C-P} = 8.4 Hz, =C-O), 157.92 (d, J_{C-P} = 7.1 Hz, =C-O).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 23.38, 23.61.

Anal. Calcd for $C_{16}H_{23}PO_5$ (326.33): C, 58.89; H, 7.10; P, 9.49. Found: C, 59.03; H, 7.10; P, 9.53.

(3*R*)-2-[5-(3-Hydroxy-2,3-dihydrofuryl)]-2-(diethylphosphono)ethane-1-ol (2d)

Prepared from allene **8d** (2.66 g, 0.01 mol), anhyd $CHCl_3$ (10 mL), and Et_3N (0.1 g, 0.001 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.5) afforded 1.6 g (60%) of **2d**.

TLC (diastereomeric mixture): R_f = 0.32, 039 ($CHCl_3$–MeOH, 10:0.9).

IR (film): ν = 1249, 1681, 3380, 3650 cm^{-1}.

^{1}H NMR (CD_3OD) (diastereomeric mixture): δ = 1.32 (dt, 6 H, J_{H-H} = 7.2 Hz, J_{H-P} = 1.8 Hz, 2 CH_3), 3.12 (dt, 1 H, J_{H-H} = 6.9 Hz, J_{H-P} = 22.0 Hz, C*H*-P), 3.64 (br s, 2 H, 2OH), 3.98 (m, 2 H, C*H*$_2$OH), 4.12 (dq, 4 H, J_{H-H} = 7.2 Hz, J_{H-P} = 6.6 Hz, 2 CH_2OP), 4.31 (m, 2 H, CH_2), 4.91 (br m, 1 H, C*H*OH), 5.24 (dd, 1 H, J_{H-H} = 2.6 Hz, J_{H-P} = 4.2 Hz, CH=).

^{13}C NMR (CD_3OD) (diastereomeric mixture): δ = 14.65 (d, J_{C-P} = 5.7 Hz, CH_3), 14.77 (d, J_{C-P} = 5.9 Hz, CH_3), 41.29 (d, J_{C-P} = 135.5 Hz, CH-P), 41.45 (d, J_{C-P} = 135.9 Hz, HC-P), 58.00 (s, CH_2OH), 58.63 (s, CH_2OH), 62.10 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.16 (d, J_{C-P} = 7.0 Hz, CH_2OP), 62.23 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.30 (d, J_{C-P} = 6.9 Hz, CH_2OP), 72.52 (d, J_{C-P} = 1.9 Hz, HC-OH), 77.26 (s, -CH_2-), 78.39 (s, -CH_2-), 101.57 (d, J_{C-P} = 9.3 Hz, CH=), 102.42 (d, J_{C-P} = 9.0 Hz, CH=), 154.37 (d, J_{C-P} = 8.4 Hz, =C-O), 155.34 (d, J_{C-P} = 9.5 Hz, =C-O).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 25.35, 25.32.

Anal. Calcd for $C_{10}H_{19}PO_6$ (266.23): C, 45.12; H, 7.19; P, 11.63. Found: C, 45.08; H, 7.12; P, 11.52.

(3*R*)-2-[5-(3-Hydroxy-2,3-dihydrofuryl)-2-(diethylphosphono)-1-methoxyethane (2e)

Prepared from allene **8e** (2.8 g, 0.01 mol), anhyd $CHCl_3$ (15 mL), and Et_3N (0.1 g, 0.001 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.5) afforded 1.45 g (52%) of **2e**.

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R_f = 0.36 ($CHCl_3$–MeOH, 10:0.5).

IR (film): ν = 1246, 1672, 3381, 3652 cm^{-1}.

^1H NMR ($CDCl_3$) (diastereomeric mixture): δ = 1.31 (dt, 6 H, J_{H-H} = 7.1 Hz, J_{H-P} = 1.2 Hz, 2 CH_3), 3.10 (dt, 1 H, J_{H-H} = 7.0 Hz, J_{C-P} = 21.5 Hz, CH-P), 3.37 (s, 3 H, OCH_3), 3.79 (m, 2 H, C*H*$_2$OH), 3.83 (br s, 1 H, J_{H-H} = 7.8 Hz, OH), 4.10 (dq, 4 H, J_{H-H} = 7.1 Hz, J_{H-P} = 6.7 Hz, 2 CH_2OP), 4.20 (m, 2 H, -CH_2-), 4.93 (br m, 1 H, C*H*OH), 5.20 (dd, 1 H, J_{H-H} = 2.6 Hz, J_{H-P} = 4.2 Hz, CH=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.02 (d, J_{C-P} = 5.9 Hz, 2 CH_3), 16.17 (d, J_{C-P} = 5.9 Hz, 2 CH_3), 42.03 (d, J_{C-P} = 136.4 Hz, HC-P), 42.27 (d, J_{C-P} = 136.6 Hz, HC-P), 58.07 (s, OCH_3), 59.72 (s, *C*H$_2$OCH$_3$), 59.85 (s, *C*H$_2$OCH$_3$), 62.12 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.17 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.21 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.24 (d, J_{C-P} = 6.9 Hz, CH_2OP), 72.41 (d, J_{C-P} = 2.0 Hz, HC-OH), 72.41 (d, J_{C-P} = 2.0 Hz, HCOH), 77.31 (s, -CH_2-), 78.45 (s, -CH_2-), 101.31 (d, J_{C-P} = 9.2 Hz, CH=), 102.53 (d, J_{C-P} = 9.3 Hz, CH=), 154.13 (d, J_{C-P} = 8.5 Hz, =C-O), 155.30 (d, J_{C-P} = 9.4 Hz, =C-O).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 25.61, 25.67.

Anal. Calcd for $C_{11}H_{21}PO_6$ (280.25): C, 47.14; H, 7.55; P, 11.05. Found: C, 47.19; H, 7.50; P, 11.20.

(3*R*)-1-[5-(3-hydroxy-2,3-dihydrofuryl)-1-(diethylphosphono)-propane-2-ol (2f)

Prepared from allene **8f** (2.8 g, 0.01 mol), anhyd $CHCl_3$ (12 mL), and Et_3N (0.1 g, 0.001 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:1.0) afforded 1.54 g (55%) of **2f**.

TLC (diastereomeric mixture): R_f = 0.40, 0.42 ($CHCl_3$–MeOH, 10:1).

IR (film): ν = 1245, 1678, 3358, 3662 cm^{-1}.

^1H NMR ($CDCl_3$) (diastereomeric mixture): δ = 1.31 (m, 9 H, 3CH_3), 2.80, 2.92 (dd, 1 H, J_{H-H} = 6.0, 6.6 Hz, J_{C-P} = 22.0 Hz, CH-P), 4.10 (m, 6 H, 2 CH_2OP + 2 OH), 4.25 (m, 2 H, -CH_2-), 4.56 (br m, 1 H, CH_3-C*H*OH), 4.87 (br m, 1 H, C*H*OH), 5.15, 5.25 (dd, 1 H, J_{H-H} = 2.7 Hz, J_{H-P} = 3.6 Hz, CH=).

^{13}C NMR ($CDCl_3$) (diastereomeric mixture): δ = 16.14 (d, J_{C-P} = 6.2 Hz, CH_3), 16.20 (d, J_{C-P} = 6.0 Hz, CH_3), 21.06 (d, J_{C-P} = 10.0 Hz, CH_3), 21.15 (d, J_{C-P} = 9.9 Hz, CH_3), 21.43 (d, J_{C-P} = 8.0 Hz, CH_3), 46.26 (d, J_{C-P} = 136.16 Hz, HC-P), 46.47 (d, J_{C-P} = 136.16 Hz, HC-P), 46.65 (d, J_{C-P} = 136.16 Hz, HC-P), 62.17 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.40 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.83 (d, J_{C-P} = 6.8 Hz, CH_2OP), 62.87 (d, J_{C-P} = 6.7 Hz, CH_2OP), 65.93 (d, J_{C-P} = 3.0 Hz, HCOH), 65.86 (d, J_{C-P} = 3.0 Hz, HCOH), 66.05 (d, J_{C-P} = 2.9 Hz, HCOH), 73.17 (d, J_{C-P} = 1.8 Hz, HCOH), 73.20 (d, J_{C-P} = 1.8 Hz, HCOH), 73.37 (d, J_{C-P} = 1.8 Hz, HCOH), 78.07 (s, -CH_2-), 78.16 (s, -CH_2-), 78.23 (s, -CH_2-), 103.16 (d, J_{C-P} =8.2 Hz, CH=), 103.46 (d, J_{C-P} = 9.5 Hz, CH=), 104.07 (d, J_{C-P} = 8.6 Hz, CH=), 154.94 (d, J_{C-P} = 7.6 Hz, =C-O), 155.41 (d, J_{C-P} = 8.1 Hz, =C-O), 155.67 (d, J_{C-P} = 8.1 Hz, =C-O).

^{31}P NMR ($CDCl_3$) (diastereomeric mixture): δ = 25.65, 25.89, 25.22, 26.35.

Anal. Calcd for $C_{11}H_{21}PO_6$ (280.25): C, 47.14; H, 7.55; P, 11.05. Found: C, 47.19; H, 7.50; P, 11.20.

Diethylphosphono(2-furyl)methane (3a); Typical Procedure

To a solution of **2a** (0.24 g, 0.001 mol) in $CHCl_3$ (10 mL) was added *p*-toluenesulfonic acid (86 mg, 0.0005 mol). After stirring for 0.5 h at 40–45 °C, the reaction mixture was concentrated in vacuo. Chromatography on silica gel ($CHCl_3$–MeOH, 10:0.4) yield **3a** (0.2 g, 90%) as an oil.

R_f = 0.72 ($CHCl_3$–MeOH, 10:0.4).

IR (film): ν = 1260, 158, 1490 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.30 (dt, 6 H, J_{H-H} = 7.1 Hz, J_{H-P} = 1.9 Hz, 2 CH_3), 3.23 (d, 2 H, J_{H-P} = 20.0 Hz, CH_2), 4.08 (dq, 4 H, J_{H-H} = 7.1 Hz, J_{H-P} = 6.8 Hz, 2 CH_2OP), 6.25 (m, 1 H, =CH), 6.32 (m, 1 H, =CH), 7.32 (m, 1 H, =CH-O).

^{13}C NMR ($CDCl_3$): δ = 16.22 (d, J_{C-P} = 6.0 Hz, 2 CH_3), 26.54 (d, J_{C-P} = 143.6 Hz, CH_2-P), 62.18 (d, J_{C-P} = 6.6 Hz, 2 CH_2OP), 108.08 (d, J_{C-P} = 7.5 Hz, =CH), 110.66 (d, J_{C-P} = 3.1 Hz, =CH), 141.79 (d, J_{C-P} = 3.3 Hz, =CH-O), 145.50 (d, J_{C-P} = 9.6 Hz, =C).

^{31}P NMR ($CDCl_3$): δ = 24.45.

Anal. Calcd for $C_9H_{15}PO_4$ (218.20): C, 49.54; H, 6.93; P, 14.20. Found: C, 49.46; H, 6.80; P, 14.09.

Diethylphosphono(2-furyl)phenylmethane (3b)

Prepared from a solution of dihydrofuran **2b** (0.31 g, 0.001 mol) in $CHCl_3$ (10 mL), and *p*-toluenesulfonic acid (86 mg, 0.0005 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.3) afforded 0.26 g (89%) of **3b**.

R_f = 0.79 ($CHCl_3$–MeOH, 10:0.5).

IR (film): ν = 1255, 1575, 1564, 1602 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.11 (dt, 3 H, J_{H-H} = 7.3 Hz, J_{H-P} = 1.2 Hz, CH_3), 1.21 (dt, 3 H, J_{H-H} = 7.1 Hz, J_{H-P} = 1.2 Hz, CH_3), 4.00 (m, 4 H, 2 CH_2OP), 4.55 (d, 2 H, J_{H-P} = 25.3 Hz, CH-P), 6.34 (m, 1 H, =CH), 6.51 (m, 1 H, =CH), 7.32 (m, 5 H, Ar), 7.48 (m, 1 H, =CH-O).

^{13}C NMR ($CDCl_3$): δ = 16.21 (d, J_{C-P} = 5.8 Hz, CH_3), 16.32 (d, J_{C-P} = 5.8 Hz, CH_3), 45.28 (d, J_{C-P} = 140.1 Hz, CH-P), 62.89 (d, J_{C-P} = 7.0 Hz, CH_2OP), 62.96 (d, J_{C-P} = 7.0 Hz, CH_2OP), 108.72 (d, J_{C-P} = 5.1 Hz, =CH), 110.63 (d, J_{C-P} = 2.1 Hz, =CH), 127.48 (d, J_{C-P} = 2.8 Hz, Ph), 128.53 (d, J_{C-P} = 2.3 Hz, Ph), 129.38 (d, J_{C-P} = 6.3 Hz, Ph), 134.41 (d, J_{C-P} = 6.4 Hz, Ph), 142.79 (d, J_{C-P} = 2.2 Hz, =CH-O), 149.73 (d, J_{C-P} = 2.8 Hz, =C).

^{31}P NMR ($CDCl_3$): δ = 23.68.

Anal. Calcd for $C_{15}H_{19}PO_4$ (294.29): C, 61.22; H, 6.51; P, 10.53. Found: C, 61.18; H, 6.45; P, 10.46.

Diethylphosphono(2-furyl)tolylmethane (3c)

Prepared from a solution of dihydrofuran **2c** (0.33 g, 0.001 mol) in $CHCl_3$ (10 mL), and *p*-toluenesulfonic acid (86 mg, 0.0005 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.3) afforded 0.27 g (88%) of **3c**.

R_f = 0.80 ($CHCl_3$–MeOH, 10:0.5).

IR (film): ν = 1255, 1575, 1564, 1598, 1602 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.11 (dt, 3 H, J_{H-H} = 7.3 Hz, J_{H-P} = 1.2 Hz, CH_3), 1.21 (dt, 3 H, J_{H-H} = 7.1 Hz, J_{H-P} = 1.2 Hz, CH_3), 2.38 (s, 3 H, CH_3), 4.0 (m, 4 H, 2 CH_2OP), 4.55 (d, 2 H, J_{H-P} = 25.3 Hz, CH-P), 6.34 (m, 1 H, =CH), 6.51 (m, 1 H, =CH, Tol), 7.32 (m, 5 H, Tol), 7.48 (m, 1 H, =CH-O).

^{13}C NMR ($CDCl_3$): δ = 16.30 (d, J_{C-P} = 5.9 Hz, 2 CH_3), 16.32 (d, J_{C-P} = 5.8 Hz, CH_3), 21.25 (s, CH_3), 46.03 (d, J_{C-P} = 139.3 Hz, CH-P), 62.63 (d, J_{C-P} = 7.0 Hz, CH_2OP), 62.86 (d, J_{C-P} = 7.0 Hz, CH_2OP), 108.34 (d, J_{C-P} = 5.3 Hz, =CH), 109.38 (d, J_{C-P} = 2.1 Hz, =CH), 127.48 (d, J_{C-P} = 2.8 Hz, Tol), 128.53 (d, J_{C-P} = 2.3 Hz, Tol), 129.38 (d, J_{C-P} = 6.3 Hz, Tol), 134.41 (d, J_{C-P} = 6.4 Hz, Tol), 142.79 (d, J_{C-P} = 2.2 Hz, =CH-O), 149.73 (d, J_{C-P} = 2.8 Hz, =C).

^{31}P NMR ($CDCl_3$): δ = 23.72.

Anal. Calcd for $C_{16}H_{21}PO_4$ (308.31): C, 62.33; H, 6.87; P, 10.05. Found: C, 62.39; H, 6.84 ; P, 10.17.

2-(Diethylphosphono)-2-(2-furyl)ethane-1-ol (3d)

Prepared from a solution of dihydrofuran **2d** (0.27 g, 0.001 mol) in $CHCl_3$ (10 mL), and *p*-toluenesulfonic acid (86 mg, 0.0005 mol).

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Workup and chromatography ($CHCl_3$–MeOH, 10:0.5) afforded 0.22 g (88%) of **3d**.

R_f = 0.66 ($CHCl_3$–MeOH, 10:0.9).

IR (film): ν = 1258, 1583, 1599, 3372 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.23 (dt, 3 H, J_{H-H} = 7.1 Hz, J_{H-P} = 1.6 Hz, CH_3), 1.31 (dt, 3 H, J_{H-H} = 7.0 Hz, J_{H-P} = 1.4 Hz, CH_3), 3.45 (br s, 1 H, OH), 3.53 (dt, 1 H, J_{H-P} = 22.4 Hz, CH-P), 3.95 (m, 2 H, CH_2), 4.08 (dq, 4 H, J_{H-H} = 7.1 Hz, J_{H-P} = 6.6 Hz, 2 CH_2OP), 6.35 (m, 2 H, 2 =CH), 7.39 (m, 1 H, =CH-O).

^{13}C NMR ($CDCl_3$): δ = 16.08 (d, J_{C-P} = 5.9 Hz, CH_3), 16.12 (d, J_{C-P} = 5.9 Hz, CH_3), 41.24 (d, J_{C-P} = 138.5 Hz, CH-P), 60.57 (d, J_{C-P} = 1.6 Hz, $HOCH_2$), 62.21 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.67 (d, J_{C-P} = 6.9 Hz, CH_2OP), 108.26 (d, J_{C-P} = 6.9 Hz, =CH), 110.54 (d, J_{C-P} = 2.9 Hz, =CH), 141.85 (d, J_{C-P} = 3.1 Hz, =CH-O), 147.85 (d, J_{C-P} = 7.9 Hz, C=).

^{31}P NMR ($CDCl_3$): δ = 25.2.

Anal. Calcd for $C_{10}H_{17}PO_5$ (248.21): C, 48.39; H, 6.90; P, 12.48. Found: C, 48.35; H, 6.84; P, 12.42.

2-(Diethylphosphono)-2-(2-furyl)-1-methoxyethane (3e)
Prepared from a solution of dihydrofuran **2e** (0.28 g, 0.001 mol) in $CHCl_3$ (10 mL), and *p*-toluenesulfonic acid (86 mg, 0.0005 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.5) afforded 0.17 g (65%) of **3e**.

R_f = 0.43 ($CHCl_3$–MeOH, 10:0.5).

IR (film): ν = 1255, 1580, 1602 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.20 (dt, 3 H, J_{H-H} = 7.0 Hz, J_{H-P} = 1.8 Hz, CH_3), 1.31 (dt, 3 H, J_{H-H} = 7.0 Hz, J_{H-P} = 1.8 Hz, CH_3), 3.29 (s, 3 H, CH_3), 3.42 (dt, 1 H, J_{H-P} = 22.0 Hz, CH-P), 3.98 (m, 2 H, CH_2), 4.11 (dq, 4 H, J_{H-H} = 7.0 Hz, J_{H-P} = 6.7 Hz, 2 CH_2OP), 6.29 (m, H, =CH), 6.47 (m, H, =CH), 7.34 (m, 1 H, O-HC=).

^{13}C NMR ($CDCl_3$): δ = 16.05 (d, J_{C-P} = 6.0 Hz, CH_3), 16.11 (d, J_{C-P} = 6.0 Hz, CH_3), 42.71 (d, J_{C-P} = 136.3 Hz, CH-P), 57.42 (s, OCH_3), 59.12 (d, J_{C-P} = 2.1 Hz, CH_2OCH_3), 62.68 (d, J_{C-P} = 7.0 Hz, CH_2OP), 62.81 (d, J_{C-P} = 6.9 Hz, CH_2OP), 109.03 (d, J_{C-P} = 6.9 Hz, =CH), 110.26 (d, J_{C-P} = 3.0 Hz, =CH), 142.75 (d, J_{C-P} = 3.0 Hz, =CH-O), 148.94 (d, J_{C-P} = 8.0 Hz, =C).

^{31}P NMR ($CDCl_3$): δ = 25.8.

Anal. Calcd for $C_{11}H_{19}PO_5$ (262.24): C, 50.38; H, 7.30; P, 11.81. Found: C, 50.27; H, 7.18; P, 11.72.

1-(Diethylphosphono)-1-(2-furyl)propane-2-ol (3f)
Prepared from a solution of dihydrofuran **2f** (0.28 g, 0.001 mol) in $CHCl_3$ (10 mL), and *p*-toluenesulfonic acid (86 mg, 0.0005 mol). Workup and chromatography ($CHCl_3$–MeOH, 10:0.8) afforded 1.6 g (60%) of **3f**.

TLC (diastereomeric mixture): R_f = 0.63, 0.67 ($CHCl_3$–MeOH, 10:0.8).

IR (film): ν = 1250, 1585, 1600 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.15 (m, 3 H, J_{H-H} = 1.6, 0.6 Hz, J_{H-P} = 1.8, 6.3, 6.7 Hz, CH_3), 1.31 (m, 6 H, J_{H-H} = 7.1 Hz, J_{H-P} = 1.0 Hz, 2 CH_3), 2.93 (dd, 1 H, J_{H-H} = 0.52 Hz, J_{H-p} = 15.3 Hz, CH-P), 3.26 (dd, J_{H-H} = 8.9 Hz, J_{H-P} = 20.8 Hz, CH-P), 3.32 (dd, J_{H-H} = 2.7 Hz, J_{H-P} = 24.1 Hz, CH-P), 3.65 (br s, 1 H, OH), 3.80 (m, 1 H, CH-OH), 4.11 (m, 4 H, $2CH_2OP$), 4.40 (m, 1 H, CHOH), 6.27, 6.49 (m, 1 H, =CH), 6.35, 6.40 (m, 1 H, =CH), 7.38, 7.40 (m, 1 H, O-HC=).

^{13}C NMR ($CDCl_3$): δ = 16.15 (d, J_{C-P} = 5.9 Hz, CH_3), 16.21 (d, J_{C-P} = 5.9 Hz, CH_3), 16.26 (d, J_{C-P} = 6.0 Hz, CH_3), 20.83 (d, J_{C-P} = 13.5 Hz, CH_3), 21.52 (d, J_{C-P} = 13.1 Hz, CH_3), 44.87 (d, J_{C-P} = 139.8 Hz, CH-P), 46.59 (d, J_{C-P} = 137.5 Hz, CH-P), 62.05 (d, J_{C-P} = 7.2 Hz, CH_2OP), 62.43 (d, J_{C-P} = 6.9 Hz, CH_2OP), 62.98 (d, J_{C-P} = 7.0 Hz, CH_2OP), 63.29 (d, J_{C-P} = 7.0 Hz, CH_2OP), 65.68 (d, J_{C-P} = 3.5 Hz, CHOH), 66.91 (d, J_{C-P} = 2.8 Hz, CHOH), 108.64 (d, J_{C-P} = 6.7 Hz, =CH), 109.85 (d, J_{C-P} = 6.3 Hz, =CH), 110.60 (d, J_{C-P} = 2.8 Hz, =CH), 110.76 (d, J_{C-P} = 2.7 Hz, =CH), 141.89 (d, J_{C-P} = 3.0 Hz, =CH-O), 142.03 (d, J_{C-P} = 3.0 Hz, =CH-O), 146.49 (d, J_{C-P} = 4.4 Hz, =C), 148.00 (d, J_{C-P} = 8.58 Hz, =CH-).

^{31}P NMR ($CDCl_3$): δ = 25.09.

Anal. Calcd for $C_{11}H_{19}PO_5$ (262.24): C, 50.38; H, 7.30; P, 11.81. Found: C, 50.47; H, 7.35; P, 11.80.

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