Bifunctionalized Allenes. Part XIII. A Convenient and Efficient Method for Regioselective Synthesis of Phosphorylated α-Hydroxyallenes with Protected and Unprotected Hydroxy Group

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Abstract: The paper describes a convenient and efficient method for regioselective synthesis of phosphorylated α-hydroxyallenes using an atom economical [2,3]-sigmatropic rearrangement of intermediate propargyl phosphites or phosphinites. These can be readily prepared via reaction of protected alkynols with dimethyl chlorophosphite or chlorodiphenyl phosphine respectively in the presence of a base.

Keywords: synthesis; hydroxy group protection; [2,3]-sigmatropic rearrangement; phosphorylated α-hydroxyallenes

1. Introduction

The synthesis and application of allene derivatives has had a great influence in preparative organic chemistry during the last three decades. The crucial structural characteristic of allenes is the presence of two π electron clouds separated by a single sp-hybridized carbon atom. Due to that very unique structural and electronic arrangement allenic compounds have an extraordinary reactivity profiles [1–8]. Moreover, functionalized allenes have also attracted growing attention due to their versatility as key building blocks for organic synthesis. The synthetic potential of functionalized allenes has been
thoroughly explored in recent years. The research in that area has led to the development of novel methods for the construction of a variety of functionalized heterocyclic and carbocyclic systems [9–13].

There are various methods for the construction of hydroxyallenes that include prototropic rearrangement of propargylic alcohols [14–16], metal-catalyzed nucleophilic addition of propargylic derivatives to aldehydes [17–24], Cu(I)-catalyzed reaction of propargylic chlorides with Grignard reagents [25–27], metal-catalyzed reaction of propargylic oxiranes with organometallic compounds [28–35] and ketones [36,37], reduction of alcohols, ethers, oxiranes etc. with aluminium reagents [38–40], Pd(0)-catalyzed reaction of cyclic carbonates with acetylenic compounds [41,42], SN2’ [43,44] and SN [45–47] reactions of metalled alkoxy-allenes with oxiranes and ketones [5], and other routes [48,49].

In addition there are methods [50–53] for the synthesis of phosphorus-containing allenes (phosphonates [54–59], phosphinates [60,61], and phosphine oxides [62–69]) including reactions of α-alkynols with chloride-containing derivatives of phosphorus acids followed by [2,3]-sigmatropic rearrangement. Several diethylphosphono-substituted α-allenic alcohols were prepared by Brel [70,71] directly from alcohols by Horner-Mark rearrangement of unstable propargylic phosphites.

Since the reversible interconversion of propargylic phosphites, phosphonites and phosphinites to allenyl phosphonates, phosphinates and phosphine oxides was discovered five decades ago [60,61], it has become one of the most thoroughly investigated and synthetically applied [2,3]-sigmatropic rearrangements. Numerous synthetic applications of the rearrangement have been reported, such as its use in the synthesis of allenic steroids for substrate-induced inactivation of aromatase [72], in the efficient synthesis of (2R)-2-amino-5-phosphonopentanoic acid (AP5) as a powerful and selective N-methyl-D-aspartate (NMDA) antagonist [73], in the preparation of the phosphonate analogues of phosphatidyl derivatives [74,75], and, in the synthesis of new acyclic analogues of nucleotides containing a purine or pyrimidine moiety and an allenic skeleton [76,77].

Our research program on the chemistry of the bifunctionalized allenes requires a convenient method to introduce a phosphorus-containing group such as phosphonate or phosphine oxide group as well as a hydroxyalkyl group in the first position to the allenic system of double bonds. The above-mentioned groups attract more and more researchers’ attention as useful functionalities in organic synthesis. The emphasis is particularly on the applications of these groups as temporary transformers of chemical reactivity of the allenic system in the synthesis of eventually heterocyclic compounds.

Our scientific interest on the synthesis [78] and electrophilic cyclization reactions [79] of bifunctionalized allenes reported in our previous articles let to the discovery of a convenient and efficient method for regioselective synthesis of phosphorylated α-hydroxyallenes by an atom economical [2,3]-sigmatropic rearrangement of the mediated 4-(tetrahydro-2H-pyran-2-yloxy)-propargyl phosphites or phosphinites.

2. Results and Discussion

We based our strategy for the synthesis of the phosphorylated α-hydroxyallenes on our experience in preparation of the 4-heteroatom-functionalized allencarboxylates [78] and relied on the well-precedented [2,3]-sigmatropic shift of propargylic phosphites to allene phosphonates [54–59] and propargylic phosphinites to allenyl phosphate oxides [62–69]. We were aware of the fact that a precedent exists for such an approach to the synthesis of the diethylphosphono-substituted α-allenic
alcohols [70,71], but as far as we know, a general useful method for regioselective synthesis of phosphorylated (phosphonates and phosphine oxides) α-hydroxylallenes (primary, secondary or tertiary alcohols) with protected or unprotected hygroxy group has not been reported yet.

2.1. Synthesis of Phosphorylated α-Hydroxylallenes with Protected Hydroxy Group

The main target in our research, and namely 1,1-bifunctionalized allenes, was achieved as a range of the phosphorylated α-hydroxylallenes 7, 9, 10, and 11 were prepared by applying the following four-step procedure: (i) protection of hydroxy group in the propargylic alcohols 1; (ii) subsequent reaction with Grignard reagent to give the protected alkynols 5; (iii) interaction with dimethyl chlorophosphate or chlorodiphenyl phosphine in the presence of a base; and finally (iv) [2,3]-sigmatropic rearrangement of the protected propargyl phosphites or phosphinites.

2.1.1. Synthesis of (Tetrahydro-2H-pyran-2-yloxy)-alkynols

The first step in our investigation was to examine the hydroxy group protection in the propargylic alcohols 1 with 3,4-dihydro-2H-pyran (DHP) in the presence of pyridinium p-toluenesulfonate (PPTS) [80–83] (Scheme 1 and Table 1). Thus, the formed alkynylloxy-tetrahydro-2H-pyrans 2 were isolated by distillation in essentially quantitative yields (95%–99%). Reaction of the protected propargylic compounds 2 with ethyl-magnesium bromide and subsequent dropwise addition of propargyl magnesium bromide 3 generated in situ to ketones 4 and reflux for 24 h gave the (tetrahydro-2H-pyran-2-yloxy)-alkynols 5 which were stable and were isolated by column chromatography in 53%–61% yields.

Scheme 1. Synthesis of the (tetrahydro-2H-pyran-2-yloxy)-alkynols 5.

Reagents and Conditions: (i) DHP (3,4-dihydro-2H-pyran) (1.5 eq), PPTS (0.1 eq), CH₂Cl₂, rt, 4 h, distillation; (ii) EtMgBr (1 eq), THF, reflux, 2 h; (iii) dropwise addition of 3 to R²R³C=O 4 (2 eq) (R² = Me, R³ = Et; R² = Me, R³ = Bu; R² + R³ = -(CH₂)₅-) reflux, 24 h, column chromatography.

Table 1. Synthesis of the (tetrahydro-2H-pyran-2-yloxy)-alkynols 5.

| Entry | Alcohol | R | R¹ | R² | R³ | Yield a, % |
|-------|---------|---|----|----|----|------------|
| 1     | 5a      | H | H  | Me | Et | 61         |
| 2     | 5b      | H | H  | Me | Bu | 59         |
| 3     | 5c      | H | H  | -(CH₂)₅- | 58 |
| 4     | 5d      | H | Me | Me | Et | 57         |
| 5     | 5e      | H | Me | Me | Bu | 56         |
| 6     | 5f      | H | Me | -(CH₂)₅- | 56 |
| 7     | 5g      | Me | Me | Me | Et | 54         |
| 8     | 5h      | Me | Me | Me | Bu | 53         |

a Isolated yields by chromatographic purification.
2.1.2. Synthesis of Dimethyl 1-(Tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-1,2-dieneephosphonates

Once we had the required propargyl alcohols 5 with protected hydroxyl groups, we were able to investigate the proposed reactions with the corresponding chloro-containing phosphorus reagents such as dimethyl chlorophosphite and chlorodiphenyl phosphine in the presence of a base and subsequent [2,3]-sigmatropic rearrangement of the intermediate 4-(tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-propargyl phosphites or phosphinites 6 and 8. Let us start with the dimethyl 1-(tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-1,2-dieneephosphonates 7\textit{a}–\textit{h} that can be easily prepared via an atom economical 2,3-sigmatropic rearrangement of the 4-(tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-propargyl phosphites or phosphinites 6\textit{a}–\textit{h}, intermediates formed by reaction of the (tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-alkynols 5\textit{a}–\textit{h} with dimethyl chloro-phosphate, prepared \textit{in situ} from phosphorus trichloride and 2 equiv. of methanol in the presence of triethylamine, and 2 equiv. of pyridine, according to Scheme 2 and Table 2.

\textbf{Scheme 2.} Synthesis of the dimethyl 1-(tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-1,2-dieneephosphonates 7.

\begin{center}
\begin{align*}
\text{THPO} & \quad \text{R}^1 \quad \text{R}^2 \quad \text{THPO} \\
& \quad \text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \\
\text{HO} & \quad (\text{MeO})_2\text{P} \\
\text{iv)} & \quad \text{PCl}_3 (1 \text{ eq}), \text{Et}_3\text{N} (1.1 \text{ eq}), \text{Et}_2\text{O}, -70 \degree \text{C}, 30 \text{ min stirring}, \text{pyridine} (2.2 \text{ eq}), \\
& \quad \text{MeOH} (2 \text{ eq}), \text{Et}_2\text{O}, [2,3-\sigma]-\text{rearrangement}, -70 \degree \text{C}, 1 \text{ h}, \text{rt}, 10 \text{ h}, \text{column chromatography}.
\end{align*}
\end{center}

\textbf{Table 2.} Synthesis of the dimethyl 1-(tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-1,2-dieneephosphonates 7.

\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Entry} & \textbf{Allene} & \textbf{R} & \textbf{R}^1 & \textbf{R}^2 & \textbf{R}^3 & \textbf{Yield a, \%} \\
\hline
1 & 7\textit{a} & H & H & Me & Et & 78 \\
2 & 7\textit{b} & H & H & Me & Bu & 75 \\
3 & 7\textit{c} & H & H & -(\text{CH}_2)\text{z}- & & 73 \\
4 & 7\textit{d} & H & Me & Me & Et & 74 \\
5 & 7\textit{e} & H & Me & Me & Bu & 72 \\
6 & 7\textit{f} & H & Me & -(\text{CH}_2)\text{z}- & & 75 \\
7 & 7\textit{g} & Me & Me & Me & Et & 71 \\
8 & 7\textit{h} & Me & Me & Me & Bu & 70 \\
\hline
\end{tabular}

\textit{a} Isolated yields by chromatographic purification.

2.1.3. Synthesis of 2-[2-(Diphenylphosphinoyl-2,3-dienyloxy)]-tetrahydro-2\textit{H}-pyrans

Next, the reaction of the (tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-alkynols 5\textit{a}–\textit{h} with chlorodiphenyl phosphine in the presence of triethylamine at \(-70 \degree \text{C}\) gave the expected 2-(2-diphenylphosphinoyl-2,3-dienyloxy)-tetrahydro-2\textit{H}-pyrans 9\textit{a}–\textit{h} in very good yields (Table 3) as a result of [2,3]-sigmatropic rearrangement of the 4-(tetrahydro-2\textit{H}-pyran-2-\textit{yloxy})-propargyl phosphinites 8\textit{a}–\textit{h} for 8 h at room temperature, according to the reaction sequence outlined in Scheme 3.
Table 3. Synthesis of the 2-(2-diphenylphosphinoyl-2,3-dienyloxy)-tetrahydro-2H-pyrans 9.

| Entry | Allene | R | R¹ | R² | R³ | Yield a, % |
|-------|--------|---|----|----|----|------------|
| 1     | 9a     | H | H  | Me | Et | 86         |
| 2     | 9b     | H | H  | Me | Bu | 84         |
| 3     | 9c     | H | H  | -(CH₂)₅- |    | 81         |
| 4     | 9d     | H | Me | Me | Et | 83         |
| 5     | 9e     | H | Me | Me | Bu | 82         |
| 6     | 9f     | H | Me | -(CH₂)₅- |    | 80         |
| 7     | 9g     | Me | Me | Me | Et | 80         |
| 8     | 9h     | Me | Me | Me | Bu | 78         |

a Isolated yields by chromatographic purification.

Scheme 3. Synthesis of the 2-(2-diphenylphosphinoyl-2,3-dienyloxy)-tetrahydro-2H-pyrans 9.

A new family of phosphorylated α-hydroxyallenes with protected hydroxyl group 7 and 9 were synthesized via an atom economical and regioselective [2,3]-sigmatropic rearrangement of the intermediate formed propargyl phosphites or phosphinites in the reaction of protected alkynols 5 with dimethylchloro phosphate or chlorodiphenyl phosphine in the presence of triethylamine.

2.2. Synthesis of Phosphorylated α-Hydroxyallenes with Unprotected Hydroxy Group

Compounds 7 and 9 were stable enough to be handled at ambient temperature. The hydroxy group was deprotected by stirring the ethanol solution of the protected hydroxylalkyl-allenephosphonates 7 and hydroxylalkyl-allenyl phosphine oxides 9 in the presence of 0.1 equiv. PPTS at room temperature for 6 h, according to Scheme 4 and Table 4.

Scheme 4. Synthesis of the 1-hydroxyalkyl-1,2-diene phosphonates 10, the 3-diphenylphosphinoyl-2,3-dien-1-ols 11a–c and the 3-diphenylphosphinoyl-3,4-dien-2-ols 11d–h.

Reagents and Conditions: (vii) Ph₂PCl (1 eq), Et₃N (1.1 eq), Et₂O, −70 °C; (viii) [2,3-σ]-rearrangement, −70 °C, 1 h, rt, 8 h, column chromatography.
Table 4. Synthesis of the 1-hydroxyalkyl-1,2-diene phosphonates 10, the 3-diphenylphosphinoyl-2,3-dien-2-ols 11a–c and the 3-diphenylphosphinoyl-3,4-dien-2-ols 11d–h.

| Entry | Allene | R   | R¹  | R²   | R³   | Yield a, % |
|-------|--------|-----|-----|------|------|------------|
| 1     | 10a    | H   | H   | Me   | Et   | 80         |
| 2     | 10b    | H   | H   | Me   | Bu   | 78         |
| 3     | 10c    | H   | H   | -(CH₂)₅⁻ | 77   |
| 4     | 10d    | H   | Me  | Me   | Et   | 80         |
| 5     | 10e    | H   | Me  | Me   | Bu   | 79         |
| 6     | 10f    | H   | Me  | -(CH₂)₅⁻ | 81   |
| 7     | 10g    | Me  | Me  | Me   | Et   | 79         |
| 8     | 10h    | Me  | Me  | Me   | Bu   | 78         |
| 9     | 11a    | H   | H   | Me   | Et   | 86         |
| 10    | 11b    | H   | H   | Me   | Bu   | 83         |
| 11    | 11c    | H   | H   | -(CH₂)₅⁻ | 81   |
| 12    | 11d    | H   | Me  | Me   | Et   | 87         |
| 13    | 11e    | H   | Me  | Me   | Bu   | 85         |
| 14    | 11f    | H   | Me  | -(CH₂)₅⁻ | 88   |
| 15    | 11g    | Me  | Me  | Me   | Et   | 84         |
| 16    | 11h    | Me  | Me  | Me   | Bu   | 83         |

a Isolated yields by chromatographic purification.

After a conventional work-up, all allenic products 7, 9, 10, and 11 were isolated as stable yellow or orange oils by column chromatography and identified by ¹H-, ¹³C-, and ³¹P-NMR and IR spectra as well as by elemental analysis.

3. Experimental Section

3.1. General Information

All new synthesized compounds were purified by column chromatography and characterized on the basis of NMR, IR, and microanalytical data. NMR spectra were recorded on DRX Bruker Avance-250 (¹H at 250.1 MHz, ¹³C at 62.9 MHz, ³¹P at 101.2 MHz) and Bruker Avance II + 600 (Bruker BioSpinGmbH, Karlsruhe, Germany) (¹H at 600.1 MHz, ¹³C at 150.9 MHz, ³¹P at 242.9 MHz) spectrometers for solutions in CDCl₃. All ¹H- and ¹³C-NMR experiments were measured referring to the signal of internal TMS and ³¹P-NMR experiments were measured referring to the signal of external 85% H₃PO₄. J values are given in hertz. IR spectra were recorded with an FT-IRAffinity-1 Shimadzu spectrophotometer (Shimadzu, Tokyo, Japan). Elemental analyses were carried out by the Microanalytical Service Laboratory of Faculty of Chemistry and Pharmacy, University of Sofia, Bulgaria, using Vario EL3 CHNS(O) (Elementar Analysensysteme, Hanau, Germany). Column chromatography was performed on Kieselgel F₂₅₄ 60 (70–230 mesh ASTM, 0.063–0.200 nm, Merck, Darmstadt, Germany). Et₂O and THF were distilled from Na wire/benzophenone, CH₂Cl₂ was distilled over CaH₂, other commercially available chemicals were used without additional purification unless otherwise noted. Reactions were carried out in oven dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for purity on TLC plates Kieselgel F₂₅₄ 60 (Merck).
3.2. General Procedure [80–83] for Synthesis of the Alkynyloxy-tetrahydro-2H-pyrans 2

A solution of alkynols 1 (60.0 mmol) and DHP (7.6 g, 90.0 mmol) [0.152 g/mL] in dry methylene chloride (50 mL) containing PPTS (1.5 g, 6.0 mmol) [0.03 g/mL] is stirred for 4 h at room temperature. Then the reaction was quenched with saturated NaHCO₃ and extracted with methylene chloride. The organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvent, distillation gives an essentially quantitative yield of the alkynyloxy-tetrahydro-2H-pyrans 2 (95%–99%) which are described in the literature [80–83].

3.3. General Procedure for Synthesis of (Tetrahydro-2H-pyran-2-yloxy)-alkynols 5

Ethylmagnesium bromide [prepared from magnesium (1.2 g, 50.0 mmol) [0.024 g/mL] and ethyl bromide (5.5 g, 50.0 mmol) [0.11 g/mL] in dry THF (50 mL)] is added dropwise under stirring to substituted alkynyloxy-tetrahydro-2H-pyrans 2 (50.0 mmol) and then the mixture is refluxed for 2 h. The solution of the prepared alkynyl magnesium bromides 3 is added dropwise under stirring to the ketones 4 (100.0 mmol). The mixture is refluxed for 24 h and after cooling is hydrolyzed with a saturated aqueous solution of ammonium chloride. The organic layer is separated, washed with water, and dried over anhydrous sodium sulfate. Solvent and the excess of ketone are removed by distillation. Purification of the residue is achieved by column chromatography (silica gel, Kieselgel Merck 60 F₂₅₄) with ethyl acetate-hexane (5:1). The pure products 5 had the following properties:

3-Methyl-6-(tetrahydro-2H-pyran-2-yloxy)-hex-4-yn-3-ol (5a). Colourless oil, yield: 61%. Rₓ 0.53; IR (neat, cm⁻¹): 1121 (C-O-C), 3439 (OH). ¹H-NMR (600.1 MHz): δ 1.37 (t, J = 7.2 Hz, 3H, Me-CH₂), 1.40 (s, 3H, Me-C-OH), 1.48, 1.67, 1.71, 3.59, 4.62 (overlapping multiplets, 9H, OTHP), 1.79 (m, 2H, Me-CH₂), 3.54 (s, 1H, OH), 4.29 (m, 2H, CH₂O). ¹³C-NMR (150.9 MHz) δ 9.9, 19.0, 26.1, 28.4, 30.7, 37.5, 55.0, 62.3, 66.2, 81.5, 89.4, 97.7. Anal. Calcd for C₁₂H₂₀O₃ (212.29): C 67.89, H 9.50. Found: C 67.81, H 9.44.

4-Methyl-1-(tetrahydro-2H-pyran-2-yloxy)-oct-2-yn-4-ol (5b). Colourless oil, yield: 59%. Rₓ 0.49; IR (neat, cm⁻¹): 1121 (C-O-C), 3420 (OH). ¹H-NMR (250.1 MHz): δ 0.87 (t, J = 6.5 Hz, 3H, -(CH₂)₃), 1.39 (s, 3H, Me-C-OH), 1.34–1.39, 1.48–1.80, 3.61, 4.72 (overlapping multiplets, 15H, OTHP + (CH₂)₅-Me), 2.70 (s, 1H, OH), 4.24 (m, 2H, CH₂O). ¹³C-NMR (62.9 MHz) δ = 14.7, 19.2, 23.9, 24.7, 25.6, 29.4, 30.8, 45.5, 55.3, 60.9, 64.2, 80.1, 89.0, 97.1. Anal. Calcd for C₁₄H₂₄O₃ (240.34): C 69.96, H 10.07. Found: C 70.03, H 10.12.

1-[3-(Tetrahydro-2H-pyran-2-yloxy)-prop-1-ynyl]-cyclohexanol (5c). Colourless oil, yield: 58%. Rₓ 0.48; IR (neat, cm⁻¹): 1120 (C-O-C), 3412 (OH). ¹H-NMR (250.1 MHz): δ 1.30–1.77, 1.96–2.01, 2.10–2.16, 3.54–3.72, 4.70–4.74 (overlapping multiplets, 19H, OTHP + (CH₂)₅-Me), 2.70 (s, 1H, OH), 4.27 (m, 2H, CH₂O). ¹³C-NMR (62.9 MHz) δ = 19.2, 23.2, 25.7, 26.1, 30.4, 40.0, 53.8, 62.5, 69.2, 81.0, 88.9, 96.8. Anal. Calcd for C₁₄H₂₂O₃ (238.32): C 70.56, H 10.07. Found: C 70.03, H 10.12.

3-Methyl-6-(tetrahydro-2H-pyran-2-yloxy)-hept-4-yn-3-ol (5d). Colourless oil, yield: 57%. Rₓ 0.54; IR (neat, cm⁻¹): 1122 (C-O-C), 3398 (OH). ¹H-NMR (600.1 MHz): δ 1.36 (t, J = 7.4 Hz, 3H, Me-CH₂), 1.38 (s, 3H, Me-C-OH), 1.46, 1.62, 1.71, 3.62, 4.71 (overlapping multiplets, 9H, OTHP), 1.49 (d, J = 7.0 Hz, 3H, Me-CH), 1.67 (m, 2H, Me-CH₂), 3.24 (s, 1H, OH), 4.78 (m, 1H, CH-Me). ¹³C-NMR
5-Methyl-2-((tetrahydro-2H-pyran-2-yloxy)-non-3-yn-5-ol (5e). Colourless oil, yield: 56%. Rf 0.51; IR (neat, cm$^{-1}$): 1123 (C-O-C), 3432 (OH). $^1$H-NMR (600.1 MHz): δ 0.88 (t, J = 6.3 Hz, 3H, Me-(CH$_2$)$_3$), 1.36 (s, 3H, Me-C-OH), 1.33–1.40, 1.46–1.79, 3.76, 4.78 (overlapping multiplets, 15H, OTHP + (CH$_2$)$_3$-Me), 1.52 (d, J = 6.9 Hz, 3H, Me-CH), 2.54 (s, 1H, OH), 4.66 (m, 1H, CH-Me). $^{13}$C-NMR (150.9 MHz) δ = 14.4, 20.2, 22.4, 24.2, 24.9, 26.1, 30.2, 31.0, 45.4, 62.7, 63.0, 64.4, 84.2, 88.1, 99.4. Anal. Calcd for C$_{15}$H$_{26}$O$_3$ (254.37): C 70.83, H 10.30. Found: C 70.87, H 10.23.

1-[3-(Tetrahydro-2H-pyran-2-yloxy)-but-1-ynyl]-cyclohexanol (5f). Colourless oil, yield: 56%. Rf 0.48; IR (neat, cm$^{-1}$): 1119 (C-O-C), 3429 (OH). $^1$H-NMR (250.1 MHz): δ 1.29–1.52, 1.67–1.84, 1.95–2.12, 3.50–3.87, 4.79–4.82 (overlapping multiplets, 19H, OTHP + (CH$_2$)$_5$), 1.49 (d, J = 7.0 Hz, 3H, Me-CH), 3.32 (s, 1H, OH), 4.71 (m, 1H, CH-Me). $^{13}$C-NMR (62.9 MHz) δ = 20.1, 22.5, 23.0, 24.7, 26.0, 32.4, 40.6, 61.9, 62.4, 68.9, 83.2, 90.2, 98.9. Anal. Calcd for C$_{15}$H$_{24}$O$_3$ (252.35): C 71.39, H 9.59. Found: C 71.30, H 9.66.

3,6-Dimethyl-6-((tetrahydro-2H-pyran-2-yloxy)-hept-4-yn-3-ol (5g). Colourless oil, yield: 54%. Rf 0.49; IR (neat, cm$^{-1}$): 1120 (C-O-C), 3416 (OH). $^1$H-NMR (600.1 MHz): δ 1.29–1.52, 1.67–1.84, 1.95–2.12, 3.50–3.87, 4.79–4.82 (overlapping multiplets, 15H, OTHP), 1.51 (s, 6H, 2Me), 1.68 (m, 2H, Me-CH$_2$), 3.22 (s, 1H, OH). $^{13}$C-NMR (150.9 MHz) δ = 9.3, 21.1, 25.4, 28.6, 30.0, 32.4, 35.7, 64.1, 66.3, 71.0, 82.3, 86.5, 96.4. Anal. Calcd for C$_{14}$H$_{24}$O$_3$ (240.34): C 69.96, H 10.07. Found: C 69.89, H 10.15.

2,5-Dimethyl-2-((tetrahydro-2H-pyran-2-yloxy)-non-3-yn-5-ol (5h). Colourless oil, yield: 53%. Rf 0.45; IR (neat, cm$^{-1}$): 1119 (C-O-C), 3421 (OH). $^1$H-NMR (600.1 MHz): δ 0.87 (t, J = 6.4 Hz, 3H, Me-(CH$_2$)$_3$), 1.34 (s, 3H, Me-C-OH), 1.36–1.42, 1.47–1.72, 3.59, 4.89 (overlapping multiplets, 15H, OTHP + (CH$_2$)$_3$-Me), 1.50 (s, 6H, 2Me), 2.542 (s, 1H, OH). $^{13}$C-NMR (150.9 MHz) δ = 14.7, 21.1, 24.3, 24.7, 25.7, 28.4, 30.0, 31.7, 44.2, 64.7, 64.9, 71.3, 82.4, 86.1, 96.7. Anal. Calcd for C$_{16}$H$_{28}$O$_3$ (268.39): C 71.60, H 10.52. Found: C 71.52, H 10.58.

3.4. General Procedure for Synthesis of the Dimethyl 1-((Tetrahydro-2H-pyran-2-yloxy)-1,2-dienephosphonates 7

To a solution of phosphorus trichloride (2.8 g, 20.0 mmol) [0.047 g/mL] and triethylamine (2.2 g, 22.0 mmol) [0.037 g/mL] in dry diethyl ether (60 mL) at –70 °C was added dropwise with stirring a solution of the (tetrahydro-2H-pyran-2-yloxy)-alkynols 5 (20.0 mmol) in the same solvent (20 mL). After 30 min stirring at the same temperature a solution of pyridine (3.1 g, 44.0 mmol) [0.062 g/mL] and of methanol (1.3 g, 40.0 mmol) [0.026 g/mL] in dry diethyl ether (50 mL) were added. The reaction mixture was stirred for an hour at the same temperature and for 10 h at room temperature. The mixture was then washed with water, 2 N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F$_{254}$) with a mixture of ethyl acetate and hexane (10:1) as eluent to give the pure products 7 as oils, which had the following properties:
**Dimethyl 3-methyl-1-(tetrahydro-2H-pyran-2-ylloxy)methyl-1,2-diene phosphonate (7a).** Yellow oil, yield: 78%. R$_f$ 0.58; IR (neat, cm$^{-1}$): 1119 (C=O-C), 1250 (P=O), 1958 (C=C-C). $^1$H-NMR (600.1 MHz): δ 1.07 (t, $J$ = 7.4 Hz, 3H, Me-CH$_3$), 1.53, 1.60, 1.71, 3.53, 4.32 (overlapping multiplets, 9H, OTHP), 1.80 (d, $J$ = 6.7 Hz, 3H, Me-C=), 2.07 (m, 2H, Me-CH$_2$), 3.76 (d, $J$ = 11.2 Hz, 3H, MeO), 4.14 (m, 2H, CH$_2$O). $^{13}$C-NMR (150.9 MHz) δ = 12.0 ($J$ = 7.6 Hz), 18.1 ($J$ = 6.6 Hz), 19.2, 25.5, 26.5 ($J$ = 4.2 Hz), 30.4, 52.8 ($J$ = 6.2 Hz), 61.9, 64.9 ($J$ = 10.1 Hz), 90.7 ($J$ = 191.2 Hz), 97.2, 104.6 ($J$ = 15.6 Hz), 208.6 ($J$ = 5.5 Hz). $^{31}$P-NMR (242.9 MHz): δ 20.3. Anal. Calcd for C$_{14}$H$_{25}$O$_5$P (304.32): C 55.25; H 8.28. Found: C 55.33; H 8.19.

**Dimethyl 3-methyl-1-(tetrahydro-2H-pyran-2-ylloxy)methyl-hepta-1,2-diene phosphonate (7b).** Yellow oil, yield: 75%. R$_f$ 0.59; IR (neat, cm$^{-1}$): 1121 (C=O-C), 1251 (P=O), 1956 (C=C-C). $^1$H-NMR (600.1 MHz): δ 0.90 (t, $J$ = 7.2 Hz, 3H, Me-(CH$_2$)$_3$), 1.44, 1.53, 1.60, 3.53, 4.36 (overlapping multiplets, 9H, OTHP), 1.78 (d, $J$ = 6.5 Hz, 3H, Me-C=), 1.36, 1.82, 2.05 (overlapping multiplets, 6H, Me-(CH$_2$)$_3$), 3.75 (d, $J$ = 11.2 Hz, 3H, MeO), 4.09 (m, 2H, CH$_2$O). $^{13}$C-NMR (150.9 MHz) δ = 13.9, 18.0 ($J$ = 6.7 Hz), 19.2, 22.2, 25.5, 29.4, 30.3, 32.9, 52.7 ($J$ = 6.3 Hz), 61.8, 64.9 ($J$ = 10.1 Hz), 90.3 ($J$ = 191.7 Hz), 97.3, 102.8 ($J$ = 16.2 Hz), 208.8 ($J$ = 5.4 Hz). $^{31}$P-NMR (242.9 MHz): δ 20.4. Anal. Calcd for C$_{16}$H$_{29}$O$_5$P (332.37): C 57.82, H 8.79. Found: C 57.90, H 8.72.

**Dimethyl 2-cyclohexylidene-1-(tetrahydro-2H-pyran-2-ylloxy)methyl-ethenephosphonate (7e).** Yellow oil, yield: 73%. R$_f$ 0.57; IR (neat, cm$^{-1}$): 1118 (C=O-C), 1252 (P=O), 1953 (C=C-C). $^1$H-NMR (600.1 MHz): δ 1.25–2.23, 3.55, 3.86, 4.31 (overlapping multiplets, 19H, (CH$_2$)$_5$ + OTHP), 3.74 (d, $J$ = 11.1 Hz, 3H, MeO), 4.15 (m, 2H, CH$_2$O). $^{13}$C-NMR (150.9 MHz) δ = 19.1, 25.5, 25.7, 26.5, 30.3 ($J$ = 5.9 Hz), 30.4, 52.9 ($J$ = 6.2 Hz), 62.0, 64.7 ($J$ = 10.8 Hz), 88.6 ($J$ = 190.7 Hz), 97.2, 105.1 ($J$ = 15.6 Hz), 205.6 ($J$ = 5.1 Hz). $^{31}$P-NMR (242.9 MHz): δ 21.2. Anal. Calcd for C$_{18}$H$_{30}$O$_5$P (330.36): C 58.17, H 8.24. Found: C 58.24, H 8.18.

**Dimethyl 3-methyl-1-[1-(tetrahydro-2H-pyran-2-ylloxy)-ethyl]-penta-1,2-diene phosphonate (7d).** Orange oil, yield: 74%. R$_f$ 0.44; IR (neat, cm$^{-1}$): 1122 (C=O-C), 1259 (P=O), 1951 (C=C-C). $^1$H-NMR (600.1 MHz): δ 0.95 (t, $J$ = 7.3 Hz, 3H, Me-CH$_3$), 1.41 (dd, $J$ = 6.4 Hz, $J$ = 10.2 Hz, 3H, Me-CHO), 1.51, 1.58, 1.68, 3.63, 4.38 (overlapping multiplets, 9H, OTHP), 1.74 (d, $J$ = 6.6 Hz, 3H, Me-C=), 2.04 (m, 2H, Me-CH$_2$), 3.77 (d, $J$ = 11.2 Hz, 3H, MeO), 4.67 (m, 1H, CHO). $^{13}$C-NMR (150.9 MHz) δ = 12.3 ($J$ = 7.5 Hz), 18.5 ($J$ = 6.3 Hz), 19.4, 23.4 ($J$ = 7.6 Hz), 25.5, 27.7 ($J$ = 4.6 Hz), 30.5, 52.5 ($J$ = 6.3 Hz), 62.4, 67.4 ($J$ = 10.3 Hz), 95.8, 96.4 ($J$ = 192.0 Hz), 104.4 ($J$ = 15.9 Hz), 209.2 ($J$ = 5.1 Hz). $^{31}$P-NMR (242.9 MHz): δ 20.4. Anal. Calcd for C$_{15}$H$_{25}$O$_5$P (318.35): C 56.59, H 8.55. Found: C 56.64, H 8.63.

**Dimethyl 3-methyl-1-[1-(tetrahydro-2H-pyran-2-ylloxy)-ethyl]-hepta-1,2-diene phosphonate (7e).** Orange oil, yield: 72%. R$_f$ 0.43; IR (neat, cm$^{-1}$): 1120 (C=O-C), 1254 (P=O), 1956 (C=C-C). $^1$H-NMR (600.1 MHz): δ 0.93 (t, $J$ = 7.1 Hz, 3H, Me-(CH$_2$)$_3$), 1.43 (dd, $J$ = 6.3 Hz, $J$ = 10.0 Hz, 3H, Me-CHO), 1.48, 1.55, 1.64, 3.62, 4.38 (overlapping multiplets, 9H, OTHP), 1.77 (d, $J$ = 6.6 Hz, 3H, Me-C=), 1.41, 1.74, 2.11 (overlapping multiplets, 6H, Me-(CH$_2$)$_3$), 3.76 (d, $J$ = 11.2 Hz, 3H, MeO), 4.64 (m, 1H, CHO). $^{13}$C-NMR (150.9 MHz) δ = 13.8, 18.8 ($J$ = 6.5 Hz), 19.5, 22.7, 23.5 ($J$ = 7.5 Hz), 25.7, 29.6, 30.4, 32.8, 52.3 ($J$ = 6.2 Hz), 62.3, 68.6 ($J$ = 10.2 Hz), 91.4 ($J$ = 191.7 Hz), 95.6, 103.4 ($J$ = 16.2 Hz), 209.0 ($J$ = 5.3 Hz). $^{31}$P-NMR (242.9 MHz): δ 20.5. Anal. Calcd for C$_{17}$H$_{31}$O$_5$P (346.40): C 58.94, H 9.02. Found: C 59.01, H 8.96.
Dimethyl 1-cyclohexylidenemethylene-2-(tetrahydro-2H-pyran-2-yloxy)-propanephosphonate (7f). Dark orange oil, yield: 75%. Rf 0.42; IR (neat, cm$^{-1}$): 1122 (C-O-C), 1258 (P=O), 1953 (C=C=C). $^1$H-NMR (600.1 MHz): δ 1.31–2.27, 3.57, 3.71, 4.34 (overlapping multiplets, 19H, (CH$_2$)$_5$ + OTHP), 1.42 (d, J = 6.2 Hz, 3H, Me-CHO), 3.74 (d, J = 11.1 Hz, 3H, MeO), 4.51 (m, 1H, CHO). $^{13}$C-NMR (150.9 MHz): δ 19.6, 23.5 (J = 7.6 Hz), 25.6, 24.7, 25.8, 29.4 (J = 5.7 Hz), 30.6, 52.8 (J = 6.3 Hz), 62.6, 65.8 (J = 10.6 Hz), 93.8 (J = 189.6 Hz), 94.7, 106.0 (J = 15.5 Hz), 204.3 (J = 5.0 Hz). $^{31}$P-NMR (242.9 MHz): δ 20.2. Anal. Calcd for C$_{17}$H$_{29}$O$_5$P (344.38): C 59.29, H 8.49. Found: C 59.36, H 8.43.

Dimethyl 3-methyl-1-[1-methyl-1-(tetrahydro-2H-pyran-2-yloxy)-ethyl]-penta-1,2-dienephosphonate (7g). Orange oil, yield: 71%. Rf 0.44; IR (neat, cm$^{-1}$): 1117 (C-O-C), 1252 (P=O), 1949 (C=C=C). $^1$H-NMR (600.1 MHz): δ 1.05 (t, J = 7.4 Hz, 3H, Me-CH$_2$), 1.45 (d, J = 10.3 Hz, 6H, Me$_2$CO), 1.47, 1.60, 1.64, 3.56, 4.35 (overlapping multiplets, 9H, OTHP), 1.79 (d, J = 6.6 Hz, 3H, Me-C=), 2.06 (m, 2H, Me-CH$_2$), 3.76 (d, J = 11.1 Hz, 3H, MeO). $^{13}$C-NMR (150.9 MHz) δ = 12.4, 18.4, 20.4, 25.3, 31.1 (J = 8.1 Hz), 27.7 (J = 4.8 Hz), 31.3, 51.9 (J = 6.6 Hz), 63.2, 68.4 (J = 10.0 Hz), 92.4, 99.4 (J = 194.0 Hz), 103.8 (J = 15.3 Hz), 208.5 (J = 5.0 Hz). $^{31}$P-NMR (242.9 MHz): δ 21.4. Anal. Calcd for C$_{16}$H$_{29}$O$_5$P (332.37): C 57.82, H 8.79. Found: C 57.76, H 8.87.

Dimethyl 3-methyl-1-[1-methyl-1-(tetrahydro-2H-pyran-2-yloxy)-ethyl]-hepta-1,2-dienephosphonate (7h). Orange oil, yield: 70%. Rf 0.42; IR (neat, cm$^{-1}$): 1117 (C-O-C), 1252 (P=O), 1949 (C=C=C). $^1$H-NMR (600.1 MHz): δ 0.91 (t, J = 7.2 Hz, 3H, Me-(CH$_2$)$_5$), 1.49 (d, J = 10.3 Hz, 6H, Me$_2$CO), 1.42, 1.73, 2.06 (overlapping multiplets, 6H, Me-(CH$_2$)$_3$), 1.46, 1.57, 1.62, 3.64, 4.37 (overlapping multiplets, 9H, OTHP), 1.78 (d, J = 6.6 Hz, 3H, Me-C=), 3.75 (d, J = 11.2 Hz, 3H, MeO). $^{13}$C-NMR (150.9 MHz) δ = 13.9, 19.1, 20.6, 22.5, 25.4, 30.0, 30.4 (J = 8.2 Hz), 31.4, 32.9, 53.1 (J = 6.7 Hz), 63.3, 66.4 (J = 10.3 Hz), 92.7, 98.5 (J = 190.4 Hz), 104.2 (J = 15.3 Hz), 207.4 (J = 5.1 Hz). $^{31}$P-NMR (242.9 MHz): δ 22.2. Anal. Calcd for C$_{18}$H$_{33}$O$_5$P (360.43): C 59.98, H 9.23. Found: C 60.05, H 9.29.

3.5. General Procedure for Synthesis of the 2-(2-Diphenylphosphinoyl-2,3-dienyloxy)-tetrahydro-2H-pyran 9

To a solution of the (tetrahydro-2H-pyran-2-yloxy)-alkynols 5 (20.0 mmol) and triethylamine (2.2 g, 22.0 mmol) [0.037 g/mL] in dry diethyl ether (60 mL) at −70 °C a solution of freshly distilled diphenylchlorophosphine (4.4 g, 20.0 mmol) [0.22 g/mL] in the same solvent (20 mL) was added dropwise with stirring. The reaction mixture was stirred for an hour at the same temperature and for 8 h at room temperature and then washed with water, 2 N HCl, extracted with diethyl ether, and the extract was washed with saturated NaCl, and dried over anhydrous sodium sulfate. The solvent was removed using a rotatory evaporator and the residue was purified by column chromatography on a silica gel (Kieselgel Merck 60 F$_{254}$) with ethyl acetate-hexane (10:1) to give the pure products 9 as oils, which had the following properties:

2-(2-Diphenylphosphinoyl-4-methyl-hexa-2,3-dienyloxy)-tetrahydro-2H-pyran (9a). Yellow oil, yield: 86%. Rf 0.58; IR (neat, cm$^{-1}$): 1119 (C-O-C), 1157 (P=O), 1437, 1483 (Ph), 1949 (C=C=C). $^1$H-NMR (600.1 MHz): δ 0.75 (t, J = 7.4 Hz, 3H, Me-CH$_2$), 1.27–1.82, 3.71–3.77, 4.59–4.62 (overlapping multiplets, 9H, OTHP), 1.52 (d, J = 6.2 Hz, 3H, Me-C=), 2.05 (m, 2H, Me-CH$_2$), 4.26–4.53 (m, 2H, CH$_2$O), 7.41–7.78 (m, 10H, 2Ph). $^{13}$C-NMR (150.9 MHz) δ = 11.8, 17.6 (J = 5.6 Hz), 18.9, 25.4, 26.3,
2-(2-Diphenylphosphinoyl-4-methyl-octa-2,3-dienyloxy)-tetrahydro-2H-pyran (9b). Yellow oil, yield: 84%. R<sub>f</sub> 0.57; IR (neat, cm<sup>-1</sup>): 1120 (C-O-C), 1155 (P=O), 1438, 1482 (Ph), 1954 (C=C=C). <sup>1</sup>H-NMR (600.1 MHz): δ 0.81 (t, J = 7.3 Hz, 3H, Me-CH<sub>2</sub>), 1.07–1.18, 3.41–3.45 (mm, 6H, (CH<sub>2</sub>)<sub>3</sub>-Me), 1.34–1.74, 3.71–3.77, 4.58–4.61 (overlapping multiplets, 9H, OTHP), 1.51 (d, J = 6.6 Hz, 3H, Me-C=), 4.25–4.52 (m, 2H, CH<sub>2</sub>O), 7.30–7.82 (m, 10H, 2Ph). <sup>13</sup>C-NMR (150.9 MHz) δ = 14.9, 17.7 (J = 5.6 Hz), 18.9, 22.2, 25.4, 30.1, 29.2, 32.8, 61.7, 64.3 (J = 9.6 Hz), 95.2 (J = 104.5 Hz), 97.8, 103.0 (J = 13.3 Hz), 131.5–133.4 (2Ph), 208.5 (J = 6.4 Hz). <sup>31</sup>P-NMR (242.9 MHz): δ 29.8. Anal. Calcd for C<sub>24</sub>H<sub>29</sub>O<sub>3</sub>P (396.46): C 72.63, H 7.42.

2-(3-Cyclohexylidene-2-diphenylphosphinoyl-allyloxy)-tetrahydro-2H-pyran (9c). Yellow oil, yield: 81%. R<sub>f</sub> 0.56; IR (neat, cm<sup>-1</sup>): 1123 (C-O-C), 1169 (P=O), 1436, 1490 (Ph), 1954 (C=C=C). <sup>1</sup>H-NMR (600.1 MHz): δ 0.97–1.06, 1.86–2.02, 3.40–3.44 (overlapping multiplets, 10H, (CH<sub>2</sub>)<sub>5</sub>), 1.27–1.57, 3.72–3.77, 4.58–4.60 (overlapping multiplets, 9H, OTHP), 4.29–4.51 (m, 2H, CH<sub>2</sub>O), 7.26–7.78 (m, 10H, 2Ph). <sup>13</sup>C-NMR (150.9 MHz) δ = 18.9, 21.1, 25.4, 26.3 (J = 3.8 Hz), 29.9 (J = 5.2 Hz), 30.1, 61.8, 64.1 (J = 9.6 Hz), 94.0 (J = 105.2 Hz), 97.5, 104.9 (J = 13.4 Hz), 128.1–133.0 (2Ph), 205.4 (J = 6.8 Hz). <sup>31</sup>P-NMR (242.9 MHz): δ 31.1. Anal. Calcd for C<sub>26</sub>H<sub>31</sub>O<sub>3</sub>P (422.50): C 73.91, H 7.40. Found: C 73.83, H 7.31.

2-(2-Diphenylphosphinoyl-1,4-dimethyl-hexa-2,3-dienyloxy)-tetrahydro-2H-pyran (9d). Orange oil, yield: 83%. R<sub>f</sub> 0.46; IR (neat, cm<sup>-1</sup>): 1119 (C-O-C), 1158 (P=O), 1440, 1489 (Ph), 1950 (C=C=C). <sup>1</sup>H-NMR (600.1 MHz): δ 0.84 (t, J = 7.3 Hz, 3H, Me-CH<sub>2</sub>), 1.30–1.71, 3.61–3.65, 4.56–4.59 (overlapping multiplets, 9H, OTHP), 1.43 (dd, J = 6.4 Hz, J = 9.8 Hz, 3H, Me-CHO), 1.53 (d, J = 6.4 Hz, 3H, Me-C=), 2.02 (m, 2H, Me-CH<sub>2</sub>), 4.61–4.67 (m, 1H, CHO), 7.29–7.82 (m, 10H, 2Ph). <sup>13</sup>C-NMR (150.9 MHz) δ = 12.7, 18.6 (J = 5.5 Hz), 19.5, 22.5 (J = 7.7 Hz), 22.6, 27.5 (J = 5.4 Hz), 30.6, 62.4, 64.9 (J = 9.4 Hz), 97.6 (J = 104.1 Hz), 96.7, 104.7 (J = 13.7 Hz), 129.2–134.5 (2Ph), 204.7 (J = 6.6 Hz). <sup>31</sup>P-NMR (242.9 MHz): δ 30.4. Anal. Calcd for C<sub>25</sub>H<sub>31</sub>O<sub>3</sub>P (410.49): C 73.15, H 7.61. Found: C 73.08, H 7.69.

2-(2-Diphenylphosphinoyl-1,4-dimethyl-octa-2,3-dienyloxy)-tetrahydro-2H-pyran (9e). Orange oil, yield: 82%. R<sub>f</sub> 0.45; IR (neat, cm<sup>-1</sup>): 1123 (C-O-C), 1165 (P=O), 1440, 1489 (Ph), 1949 (C=C=C). <sup>1</sup>H-NMR (600.1 MHz): δ 0.81 (t, J = 7.5 Hz, 3H, Me-CH<sub>2</sub>), 1.10–1.21, 3.50–3.55 (mm, 6H, (CH<sub>2</sub>)<sub>3</sub>-Me), 1.34–1.71, 3.62–3.67, 4.57–4.63 (overlapping multiplets, 9H, OTHP), 1.42 (dd, J = 6.4 Hz, J = 9.7 Hz, 3H, Me-CHO), 1.55 (d, J = 6.3 Hz, 3H, Me=C=), 4.52–4.57 (m, 1H, CHO), 7.29–7.82 (m, 10H, 2Ph). <sup>13</sup>C-NMR (150.9 MHz) δ = 13.8, 18.4 (J = 5.6 Hz), 19.6, 21.3, 22.2 (J = 7.5 Hz), 25.5, 30.5, 29.5, 32.9, 62.7, 65.2 (J = 9.7 Hz), 97.4, 97.9 (J = 105.0 Hz), 104.7 (J = 13.7 Hz), 129.7–134.6 (2Ph), 207.7 (J = 6.6 Hz). <sup>31</sup>P-NMR (242.9 MHz): δ 30.4. Anal. Calcd for C<sub>27</sub>H<sub>33</sub>O<sub>3</sub>P (438.54): C 73.95, H 8.04. Found: C 74.03, H 7.99.

2-(3-Cyclohexylidene-2-diphenylphosphinoyl-1-methyl-allyloxy)-tetrahydro-2H-pyran (9f). Yellow oil, yield: 80%. R<sub>f</sub> 0.45; IR (neat, cm<sup>-1</sup>): 1118 (C-O-C), 1160 (P=O), 1439, 1488 (Ph), 1949 (C=C=C). <sup>1</sup>H-NMR (600.1 MHz): δ 1.03–1.11, 1.91–1.97, 3.33–3.45 (overlapping multiplets, 10H, (CH<sub>2</sub>)<sub>5</sub>), 30.1, 61.6, 64.2 (J = 9.5 Hz), 95.9 (J = 104.4 Hz), 97.6, 104.6 (J = 13.9 Hz), 131.7–133.8 (2Ph), 208.2 (J = 6.5 Hz). <sup>31</sup>P-NMR (242.9 MHz): δ 29.5. Anal. Calcd for C<sub>24</sub>H<sub>29</sub>O<sub>3</sub>P (396.46): C 72.71, H 7.37. Found: C 72.63, H 7.42.
1.31–1.62, 3.68–3.79, 4.56–4.70 (overlapping multiplets, 9H, OTHP), 1.44 (d, J = 6.5 Hz, 3H, Me-CHO), 4.51–4.57 (m, 1H, CHO), 7.31–7.87 (m, 10H, 2Ph). 13C-NMR (150.9 MHz) δ = 20.0, 20.7, 21.7 (J = 7.4 Hz), 26.1, 26.7 (J = 3.6 Hz), 30.2, 30.4 (J = 5.3 Hz), 62.8, 67.8 (J = 9.6 Hz), 97.7, 99.8 (J = 105.0 Hz), 106.3 (J = 13.8 Hz), 127.7–134.2 (2Ph), 203.6 (J = 7.2 Hz). 31P-NMR (242.9 MHz): δ 31.2. Anal. Calcd for C27H33O3P (436.52): C 74.29, H 7.62. Found: C 74.33, H 7.69.

2-(2-Diphenylphosphinoyl-1,1,4-trimethyl-hexa-2,3-dienyloxy)-tetrahydro-2H-pyran (9g). Dark orange oil, yield: 80%. Rf 0.44; IR (neat, cm⁻¹): 1119 (C-O-C), 1154 (P=O), 1436, 1487 (Ph), 1956 (C=C=C). 1H-NMR (600.1 MHz): δ 1.03 (t, J = 7.5 Hz, 3H, Me-CH2), 1.38–1.69, 3.53–3.73, 4.61–4.77 (overlapping multiplets, 9H, OTHP), 1.47 (d, J = 10.6 Hz, 6H, Me2CO), 1.53 (d, J = 6.5 Hz, 3H, Me-C=), 2.02 (m, 2H, Me-CH2), 7.41–7.85 (m, 10H, 2Ph). 13C-NMR (150.9 MHz) δ = 12.1, 18.5 (J = 5.7 Hz), 19.4, 26.2, 28.4 (J = 5.5 Hz), 31.1, 31.2 (J = 8.0 Hz), 63.0, 68.4 (J = 9.7 Hz), 96.9, 97.8 (J = 104.7 Hz), 105.1 (J = 13.4 Hz), 127.4–133.9 (2Ph), 204.5 (J = 7.0 Hz). 31P-NMR (242.9 MHz): δ 31.7. Anal. Calcd for C26H33O3P (424.51): C 73.56, H 7.84. Found: C 73.63, H 7.92.

2-(2-Diphenylphosphinoyl-1,1,4-trimethyl-octa-2,3-dienyloxy)-tetrahydro-2H-pyran (9h). Yellow oil, yield: 78%. Rf 0.45; IR (neat, cm⁻¹): 1119 (C-O-C), 1162 (P=O), 1440, 1486 (Ph), 1953 (C=C=C). 1H-NMR (600.1 MHz): δ 1.06 (t, J = 7.6 Hz, 3H, Me-CH2), 1.09–1.22, 3.43–3.46 (mm, 6H, (CH2)3-Me), 1.29–1.64, 3.57–3.74, 4.59–4.74 (overlapping multiplets, 9H, OTHP), 1.50 (d, J = 10.5 Hz, 3H, Me2CO), 1.55 (d, J = 6.6 Hz, 3H, Me-C=), 7.37–7.84 (m, 10H, 2Ph). 13C-NMR (150.9 MHz) δ = 13.8, 18.1 (J = 5.7 Hz), 18.7, 21.7, 25.8, 30.0, 30.4, 30.7 (J = 8.2 Hz), 33.1, 62.0, 67.9 (J = 9.5 Hz), 97.3, 98.4 (J = 105.3 Hz), 104.8 (J = 13.5 Hz), 128.0–134.4 (2Ph), 205.4 (J = 7.2 Hz). 31P-NMR (242.9 MHz): δ 30.6. Anal. Calcd for C28H37O3P (452.57): C 74.31, H 8.24. Found: C 74.24, H 8.17.

3.6. General Procedure for Synthesis of the 1-Hydroxyalkyl-1,2-diene phosphonates 10, the 3-Diphenylphosphinoyl-2,3-dien-1-ols 11a–c and the 3-Diphenylphosphinoyl-3,4-dien-2-ols 11d–h

A solution of the dimethyl 1-(tetrahydro-2H-pyran-2-yloxy)-1,2-diene phosphonates 7 or the 2-(2-diphenylphosphinoyl-2,3-dienyloxy)-tetrahydro-2H-pyran 9 (5.0 mmol) and PPTS (1.13 g, 0.5 mmol) [0.113 g/mL] in ethanol (10 mL) was stirred at room temperature for 6 h. The mixture was then washed with water, extracted with methylene chloride and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F254) with a mixture of ethyl acetate and hexane (10:1) as an eluent to give the pure products 10 or 11 as oils, which had the following properties:

**Dimethyl 1-hydroxymethyl-3-methylpenta-1,2-diene phosphonate (10a).** Pale yellow oil, yield: 80%. Rf 0.45; IR (neat, cm⁻¹): 1248 (P=O), 1956 (C=C=C), 3404 (OH). 1H-NMR (250.1 MHz): δ 1.06 (t, J = 7.4 Hz, 3H, Me-CH2), 1.80 (d, J = 6.7 Hz, 3H, Me-C=), 2.04–2.12 (m, 2H, Me-CH2), 2.64 (s, 1H, OH), 3.75 (d, J = 11.8 Hz, 3H, MeO), 4.30–4.36 (m, 2H, CH2O). 13C-NMR (62.9 MHz) δ = 12.0 (J = 7.7 Hz), 18.1 (J = 6.5 Hz), 26.5 (J = 9.3 Hz), 52.8 (J = 6.3 Hz), 64.9 (J = 10.1 Hz), 90.8 (J = 191.3 Hz), 104.7 (J = 15.7 Hz), 208.7 (J = 5.6 Hz). 31P-NMR (101.2 MHz): δ 21.6. Anal. Calcd for C9H13O3P (242.20): C 49.09, H 7.78. Found: C 49.17, H 7.71.
Dimethyl 1-hydroxymethyl-3-methylhepta-1,2-diene phosphonate (10b). Pale yellow oil, yield: 78%. Rf 0.43; IR (neat, cm⁻¹): 1249 (P=O), 1958 (C=C=C), 3401 (OH). ¹H-NMR (600.1 MHz): δ 0.99 (t, J = 7.3 Hz, 3H, Me-CH₃), 1.32–1.46, 1.51–1.63, 2.03–2.09 (overlapping multiplets, 10H, Me-(CH₂)₃), 1.79 (d, J = 6.5 Hz, 3H, Me-C=), 2.64 (s, 1H, OH), 3.76 (d, J = 11.2 Hz, 3H, MeO), 4.33–4.38 (m, 2H, CH₂O). ¹³C-NMR (150.9 MHz) δ = 13.9, 18.1 (J = 6.6 Hz), 22.2, 30.3, 32.9, 52.8 (J = 6.2 Hz), 64.9 (J = 10.1 Hz), 90.4 (J = 191.5 Hz), 103.7 (J = 15.6 Hz), 208.8 (J = 5.5 Hz). ³¹P-NMR (242.9 MHz): δ 21.0. Anal. Calcd for C₁₁H₂₁O₄P (248.26): C 53.32, H 8.53. Found: C 53.30, H 8.62.

Dimethyl 2-cyclohexylidene-1-hydroxymethyl-ethenephosphonate (10c). Colourless oil, yield: 77%. Rf 0.44; IR (neat, cm⁻¹): 1259 (P=O), 1952 (C=C=C), 3412 (OH). ¹H-NMR (250.1 MHz): δ 1.22–1.37, 1.80–1.96, 3.49–3.57 (overlapping multiplets, 10H, (CH₂)₃), 2.67 (s, 1H, OH), 3.75 (d, J = 11.3 Hz, 3H, MeO), 4.23–4.29 (m, 2H, CH₂O). ¹³C-NMR (62.9 MHz): δ = 191.5, 103.7 (J = 20.8. Anal. Calcd for C₁₂H₂₃O₄P (262.28): C 54.95, H 8.78. Found: C 55.02, H 8.54.

Dimethyl 1-(1-hydroxyethyl)-3-methylhepta-1,2-diene phosphonate (10d). Yellow oil, yield: 80%. Rf 0.58; IR (neat, cm⁻¹): 1254 (P=O), 1956 (C=C=C), 3372 (OH). ¹H-NMR (600.1 MHz): δ 0.98 (t, J = 7.5 Hz, 3H, Me-CH₃), 1.42 (dd, J = 6.1 Hz, J = 10.2 Hz, 3H, Me-CHO), 1.78 (d, J = 6.6 Hz, 3H, Me-C=), 2.02–2.10 (m, 2H, Me-CH₂), 2.70 (s, 1H, OH), 3.78 (d, J = 11.6 Hz, 3H, MeO), 4.67–4.72 (m, 1H, Me-CHO). ¹³C-NMR (150.9 MHz) δ = 12.2 (J = 7.6 Hz), 18.4 (J = 6.4 Hz), 23.2 (J = 7.5 Hz), 27.4 (J = 9.2 Hz), 52.6 (J = 6.2 Hz), 66.9 (J = 192.3 Hz), 104.4 (J = 15.9 Hz), 208.9 (J = 5.4 Hz). ³¹P-NMR (242.9 MHz): δ 21.1. Anal. Calcd for C₁₁H₁₉O₄P (246.24): C 53.65, H 7.78. Found: C 53.72, H 7.73.

Dimethyl 1-(1-hydroxyethyl)-3-methylpenta-1,2-diene phosphonate (10e). Yellow oil, yield: 79%. Rf 0.57; IR (neat, cm⁻¹): 1248 (P=O), 1958 (C=C=C), 3407 (OH). ¹H-NMR (600.1 MHz): δ 1.09 (t, J = 7.4 Hz, 3H, Me-CH₂), 1.39–1.44, 1.50–1.55, 2.11–2.15 (overlapping multiplets, 10H, Me-(CH₂)₃), 1.40 (dd, J = 6.3 Hz, J = 10.3 Hz, 3H, Me-CHO), 1.77 (d, J = 6.9 Hz, 3H, Me-C=), 2.68 (s, 1H, OH), 3.77 (d, J = 11.5 Hz, 3H, MeO), 4.50–4.55 (m, 1H, Me-CHO). ¹³C-NMR (150.9 MHz) δ = 13.7, 18.7 (J = 6.4 Hz), 23.0, 23.5 (J = 7.5 Hz), 30.0, 33.0, 52.3 (J = 6.2 Hz), 68.7 (J = 10.0 Hz), 91.5 (J = 191.5 Hz), 103.2 (J = 16.1 Hz), 208.7 (J = 5.4 Hz). ³¹P-NMR (242.9 MHz): δ 21.2. Anal. Calcd for C₁₀H₁₉O₄P (234.23): C 51.28, H 8.18. Found: C 51.21, H 8.13.

Dimethyl 1-(1-hydroxyethyl)-3-methylhepta-1,2-diene phosphonate (10f). Orange oil, yield: 81%. Rf 0.59; IR (neat, cm⁻¹): 1253 (P=O), 1951 (C=C=C), 3422 (OH). ¹H-NMR (600.1 MHz): δ 1.33–1.48, 1.87–2.00, 3.12–3.20 (overlapping multiplets, 10H, (CH₂)₃), 1.38 (dd, J = 6.4 Hz, J = 9.7 Hz, 3H, Me-CHO), 2.84 (s, 1H, OH), 3.78 (d, J = 11.6 Hz, 3H, MeO), 4.64–4.69 (m, 1H, Me-CHO). ¹³C-NMR (150.9 MHz) δ = 23.3 (J = 7.3 Hz), 25.7, 27.0, 30.3 (J = 6.2 Hz), 53.1 (J = 6.1 Hz), 65.9 (J = 10.0 Hz), 94.7 (J = 186.1 Hz), 106.8 (J = 15.5 Hz), 202.3 (J = 5.1 Hz). ³¹P-NMR (242.9 MHz): δ 20.9. Anal. Calcd for C₁₂H₂₃O₄P (262.28): C 54.95, H 8.84. Found: C 55.02, H 8.78.

Dimethyl 1-(1-hydroxy-1-methylpropyl)-3-methylpenta-1,2-diene phosphonate (10g). Yellow oil, yield: 79%. Rf 0.60; IR (neat, cm⁻¹): 1250 (P=O), 1953 (C=C=C), 3398 (OH). ¹H-NMR (600.1 MHz): δ 1.11 (t, J = 7.6 Hz, 3H, Me-CH₂), 1.54 (d, J = 10.7 Hz, 3H, Me₂CO), 1.75 (d, J = 6.7 Hz, 3H, Me-C=),
2.04–2.13 (m, 2H, Me-CH$_2$), 2.93 (s, 1H, OH), 3.79 (d, J = 11.5 Hz, 3H, MeO). $^{13}$C-NMR (150.9 MHz) δ = 12.3, 18.2 (J = 6.5 Hz), 27.4 (J = 9.2 Hz), 31.0 (J = 8.2 Hz), 53.0 (J = 6.6 Hz), 68.2 (J = 10.2 Hz), 99.5 (J = 190.2 Hz), 104.3 (J = 15.4 Hz), 207.4 (J = 5.2 Hz). $^{31}$P-NMR (242.9 MHz): δ 22.4. Anal. Caled for C$_{11}$H$_{23}$O$_3$P (248.26): C 53.22, H 8.53. Found: C 53.15, H 8.44.

**Dimethyl 1-(1-hydroxy-1-methylethyl)-3-methylhepta-1,2-diene phosphonate (10h)**. Orange oil, yield: 78%. R$_f$ 0.57; IR (neat, cm$^{-1}$): 1255 (P=O), 1594 (C=C=C), 3416 (OH). $^1$H-NMR (600.1 MHz): δ 0.92 (t, J = 7.3 Hz, 3H, Me-CH$_2$), 1.28–1.40, 1.53–1.66, 2.05–2.13 (overlapping multiplets, 10H, Me-(CH$_2$)$_3$), 1.55 (d, J = 10.8 Hz, 3H, Me$_2$CO), 1.75 (d, J = 6.7 Hz, 3H, Me-C=), 2.95 (s, 1H, OH), 3.75 (d, J = 11.4 Hz, 3H, MeO). $^{13}$C-NMR (150.9 MHz) δ = 14.0, 19.0 (J = 6.7 Hz), 22.7, 29.8, 31.3 (J = 8.2 Hz), 33.1, 53.0 (J = 6.7 Hz), 66.6, 69.7 (J = 190.2 Hz), 104.1 (J = 15.7 Hz), 207.3 (J = 5.1 Hz). $^{31}$P-NMR (242.9 MHz): δ 22.8. Anal. Caled for C$_{13}$H$_{25}$O$_4$P (276.31): C 56.51, H 9.12. Found: C 56.59, H 9.06.

**2-Diphenylphosphinoyl-4-methylhexa-2,3-dien-1-ol (11a)**. Colourless oil, yield: 86%. R$_f$ 0.42; IR (neat, cm$^{-1}$): 1175 (P=O), 1440, 1489 (Ph), 1595 (C=C=C), 3378 (OH). $^1$H-NMR (600.1 MHz): δ 0.72 (t, J = 7.4 Hz, 3H, Me-CH$_2$), 1.54 (d, J = 6.0 Hz, 3H, Me-C=), 1.66–1.88 (m, 2H, Me-CH$_2$), 2.66 (s, 1H, OH), 4.41–4.47 (m, 2H, CH$_2$O), 7.28–7.82 (m, 10H, 2Ph). $^{13}$C-NMR (150.9 MHz) δ = 11.7, 17.6 (J = 5.6 Hz), 26.4, 64.2 (J = 7.5 Hz), 97.5 (J = 103.8 Hz), 105.3 (J = 13.6 Hz), 128.2–132.5 (2Ph), 206.3 (J = 7.2 Hz). $^{31}$P-NMR (242.9 MHz): δ 33.5. Anal. Caled for C$_{19}$H$_{25}$O$_4$P (312.34): C 73.06, H 6.78. Found: C 73.14, H 6.71.

**2-Diphenylphosphinoyl-4-methylocta-2,3-dien-1-ol (11b)**. Yellow oil, yield: 83%. R$_f$ 0.41; IR (neat, cm$^{-1}$): 1177 (P=O), 1436, 1492 (Ph), 1950 (C=C=C), 3374 (OH). $^1$H-NMR (600.1 MHz): δ 0.81 (t, J = 7.2 Hz, 3H, Me-CH$_2$), 1.04–1.17, 1.34–1.50, 1.67–1.84 (overlapping multiplets, 10H, Me-(CH$_2$)$_3$), 1.53 (d, J = 6.2 Hz, 3H, Me-C=), 2.65 (s, 1H, OH), 4.39–4.46 (m, 2H, CH$_2$O), 7.30–7.80 (m, 10H, 2Ph). $^{13}$C-NMR (150.9 MHz) δ = 13.8, 17.6 (J = 5.4 Hz), 18.8, 29.2, 32.9, 64.3 (J = 7.6 Hz), 96.7 (J = 103.9 Hz), 103.6 (J = 13.5 Hz), 128.7–132.5 (2Ph), 206.5 (J = 7.2 Hz). $^{31}$P-NMR (242.9 MHz): δ 32.9. Anal. Caled for C$_{21}$H$_{25}$O$_4$P (340.40): C 74.10, H 7.40. Found: C 74.17, H 7.32.

**3-Cyclohexylidene-2-diphenylphosphinoylprop-2-en-1-ol (11c)**. Pale yellow oil, yield: 81%. R$_f$ 0.41; IR (neat, cm$^{-1}$): 1170 (P=O), 1439, 1488 (Ph), 1947 (C=C=C), 3387 (OH). $^1$H-NMR (250.1 MHz): δ 0.97–1.04, 1.89–2.04, 3.38–3.54 (overlapping multiplets, 10H, (CH$_2$)$_3$), 2.64 (s, 1H, OH), 4.38–4.43 (m, 2H, CH$_2$O), 7.28–7.79 (m, 10H, 2Ph). $^{13}$C-NMR (62.9 MHz) δ = 25.4, 26.4, 30.0, 62.1 (J = 7.6 Hz), 95.6 (J = 104.1 Hz), 105.4 (J = 13.3 Hz), 128.8–132.5 (2Ph), 203.6 (J = 7.3 Hz). $^{31}$P-NMR (101.2 MHz): δ 33.3. Anal. Caled for C$_{21}$H$_{25}$O$_3$P (338.38): C 74.54, H 6.85. Found: C 74.62, H 6.79.

**3-Diphenylphosphinoyl-5-methiltheptha-3,4-dien-2-ol (11d)**. Light orange oil, yield: 87%. R$_f$ 0.59; IR (neat, cm$^{-1}$): 1174 (P=O), 1441, 1490 (Ph), 1951 (C=C=C), 3369 (OH). $^1$H-NMR (600.1 MHz): δ 0.86 (t, J = 7.4 Hz, 3H, Me-CH$_2$), 1.35 (dd, J = 6.2 Hz, J = 9.4 Hz, 3H, Me-CHO), 1.58 (d, J = 6.3 Hz, 3H, Me-C=), 1.78–1.90 (m, 2H, Me-CH$_2$), 2.70 (s, 1H, OH), 4.59–4.63 (m, 1H, Me-CHO), 7.35–7.90 (m, 10H, 2Ph). $^{13}$C-NMR (150.9 MHz) δ = 12.4, 18.5 (J = 5.4 Hz), 22.4 (J = 7.6 Hz), 26.7, 64.2 (J = 7.4 Hz), 96.5 (J = 104.2 Hz), 105.1 (J = 13.4 Hz), 129.1–132.4 (2Ph), 204.1 (J = 7.1 Hz). $^{31}$P-NMR (242.9 MHz): δ 34.2. Anal. Caled for C$_{20}$H$_{23}$O$_2$P (326.37): C 73.60, H 7.10. Found: C 73.67, H 7.05.
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3-Diphenylphosphinoyl-5-methylnona-3,4-dien-2-ol (11e). Yellow oil, yield: 85%. Rf 0.61; IR (neat, cm⁻¹): 1168 (P=O), 1438, 1487 (Ph), 1952 (C=C=C), 3379 (OH). ¹H-NMR (600.1 MHz): δ 0.92 (t, J = 7.3 Hz, 3H, Me-CH₂), 1.11–1.23, 1.29–1.47, 1.69–1.96 (overlapping multiplets, 10H, Me-(CH₂)₃), 1.37 (dd, J = 6.3 Hz, J = 9.6 Hz, 3H, Me-CHO), 1.56 (d, J = 6.4 Hz, 3H, Me-C=), 2.72 (s, 1H, OH), 4.61–4.67 (m, 1H, Me-CHO), 7.39–7.89 (m, 10H, 2Ph). ¹³C-NMR (150.9 MHz) δ = 13.7, 18.3 (J = 5.5 Hz), 18.9, 22.3 (J = 7.7 Hz), 29.5, 33.2, 65.4 (J = 7.6 Hz), 100.7 (J = 103.8 Hz), 104.8 (J = 13.5 Hz), 128.4–132.5 (2Ph), 205.3 (J = 7.3 Hz). ³¹P-NMR (242.9 MHz): δ 34.5. Anal. Calcd for C₂₂H₂₇O₂P (354.42): C 74.55, H 7.68. Found: C 74.61, H 7.60.

4-Cyclohexylidene-3-diphenylphosphinoylbut-3-en-2-ol (11f). Yellow oil, yield: 88%. Rf 0.58; IR (neat, cm⁻¹): 1168 (P=O), 1436, 1493 (Ph), 1948 (C=C=C), 3395 (OH). ¹H-NMR (600.1 MHz): δ 0.99–1.07, 1.84–2.01, 3.37–3.57 (overlapping multiplets, 10H, (CH₂)₅), 1.34 (dd, J = 6.2 Hz, J = 9.4 Hz, 3H, Me-CHO), 2.73 (s, 1H, OH), 4.64–4.69 (m, 1H, Me-CHO), 7.32–7.84 (m, 10H, 2Ph). ¹³C-NMR (150.9 MHz) δ = 22.2 (J = 7.5 Hz), 25.5, 26.5, 30.0, 66.2 (J = 7.3 Hz), 100.2 (J = 105.0 Hz), 106.6 (J = 13.6 Hz), 128.1–132.5 (2Ph), 202.6 (J = 7.4 Hz). ³¹P-NMR (242.9 MHz): δ 33.9. Anal. Calcd for C₂₂H₂₅O₂P (352.41): C 74.98, H 7.15. Found: C 75.05, H 7.09.

3-Diphenylphosphinoyl-2,5-dimethylhepta-3,4-dien-2-ol (11g). Orange oil, yield: 84%. Rf 0.60; IR (neat, cm⁻¹): 1171 (P=O), 1437, 1488 (Ph), 1954 (C=C=C), 3373 (OH). ¹H-NMR (600.1 MHz): δ 1.09 (t, J = 7.3 Hz, 3H, Me-CH₂), 1.49 (d, J = 10.1 Hz, 3H, Me₂CO), 1.53 (d, J = 6.4 Hz, 3H, Me-C=), 1.81–1.86 (m, 2H, Me-CH₂), 2.74 (s, 1H, OH), 7.28–7.88 (m, 10H, 2Ph). ¹³C-NMR (150.9 MHz) δ = 12.3, 18.4 (J = 5.6 Hz), 27.2, 31.4 (J = 8.1 Hz), 67.0 (J = 7.4 Hz), 98.3 (J = 104.8 Hz), 105.3 (J = 13.5 Hz), 128.3–132.4 (2Ph), 204.7 (J = 7.2 Hz). ³¹P-NMR (242.9 MHz): δ 33.8. Anal. Calcd for C₂₁H₂₅O₂P (340.40): C 74.10, H 7.40. Found: C 74.01, H 7.45.

4. Conclusions

In conclusion, a convenient and efficient method for regioselective synthesis of a new family of 1,1-bifunctionalized allenes has been explored. Phosphorylated α-hydroxyallenes prepared were derived from [2,3]-sigmatropic rearrangement of the intermediate propargyl phosphites or phosphinites formed in the reaction of protected alkynols with dimethylchloro phosphate or chlorodiphenyl phosphine in the presence of a base. Further investigations on this potentially important synthetic methodology are currently in progress. At the same time, the synthetic application of the prepared phosphorylated α-hydroxyallenes with protected or unprotected hydroxy group for synthesis of different heterocyclic compounds is now under investigation in our laboratory as a part of our general
synthetic strategy for investigation of the scope and limitations of the electrophilic cyclization and cycloisomerization reactions of bifunctionalized allenes. Results of these investigations will be reported in due course.

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Author Contributions

Valerij Ch. Christov proposed the subject, designed the study and offered necessary guidance to Ismail E. Ismailov and Ivaylo K. Ivanov. Valerij Ch. Christov and Ivaylo K. Ivanov conceived and designed the experiments. Ismail E. Ismailov and Ivaylo K. Ivanov performed the experiments under the supervision of the lead author Valerij Ch. Christov who analyzed the spectral data and wrote the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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*Sample Availability*: Samples of the compounds 7, 9, 10 and 11 are available from the authors.

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