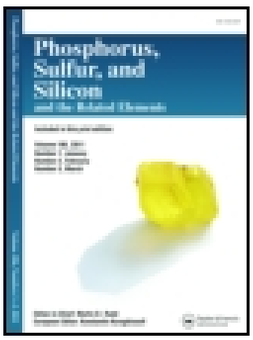

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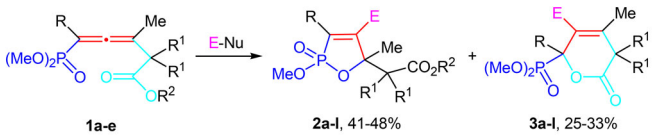
ABSTRACT

We report herein a study on the competitive electrophilic cyclization of 5-(dimethoxyphosphoryl)-alka-3,4-dienoates involving 5-*endo-trig* and 6-*endo-trig* mode cyclizations. Reaction with electrophiles produces mixtures of the 2-(2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-alkanoates and (6-oxo-5,6-dihydro-2*H*-pyran-2-yl)-phosphonates by competitive electrophilic cyclization due to the participation of the neighboring phosphonate and carboxylate groups.

GRAPHICAL ABSTRACT



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Introduction

In recent years, allenes have atracted the interest of scientists due to their unique cumulene structure and atypical biological activities. They are adaptable building blocks with broad applications in modern synthetic chemistry.[1] Allenes are key subunits in a variety of natural products and pharmaceutical molecules.[1b,e,2] Allenyl phosphonates are an important class of allene-containing, extremely versatile reagents in organic chemistry, especially for the preparation of structurally diverse organo-phosphorus compounds and phosphorus containing heterocyclic compounds.[3]

Several recent articles on allenyl phosphonates and phosphine oxides concerning synthesis[4a–e] and various cyclization reactions[4e–o] have appeared and demonstrate, that the resulting allenes are very attractive synthetic building blocks due to their versatile reactivity. Acyclic analogs of nucleotides containing an allenic skeleton were prepared by Brel and coworkers[5] directly from alcohols by Horner-Mark [2,3]-sigmatropic rearrangement of unstable propargylic phosphites.

A literature survey on the reactions of allenyl phosphonates with electrophilic reagents showed that depending on the structure of the starting allenic compound as well as the type of the electrophile, the reactions proceed with cyclization of the allenic system bearing phosphoryl group (O = P-C = C=C) to give heterocyclic compounds in most cases.[6] The reactions lead to 2,5-dihydro-1,2-oxaphospholes (Scheme 1, as products **I**) or/and 4,3- (as products **III**) or/and 4,5-adducts (as products **IV**) or a mixture of them, depending on the degree of substitution at the C^1 and C^3 atoms of the allenic system, the nature of these substituents, and the type of the reagents.[6]

The electrophilic cyclization involving α-allenic acids and their derivatives, disubstituted on the γ-carbon atom, the so-called lactonization reaction, leads through an electrophilic attack on the central atom of the allenic structure and ring closure to furan-2(5*H*)-ones (γ-lactones).[7]

Dihydropyrans are important intermediates in organic synthesis due to the presence of the C = C bond as well as the six-membered ring. Consequently, much attention has been paid to the development of efficient and diverse synthetic methods for the construction of this six-membered ring system.[8] Dihydropyrans and their derivatives are structural subunits frequently found in a wide variety of natural products which find application as flavor and fragrance compounds and pharmaceuticals.[9] Dihydropyrans represent an important structural motif featured in bioactive molecules and natural products,[10] and they are also versatile intermediates in organic synthesis.[11] It was observed by Wan and Nelson[12a] that the Ag(I)-catalyzed cyclization of a β-allenic acid, accelerated by a substoichiometric quantity of amine base (iPr$_2$NEt), resulted in rapid formation of δ-lactone (Scheme 1, as products **II**). Related δ-lactone was

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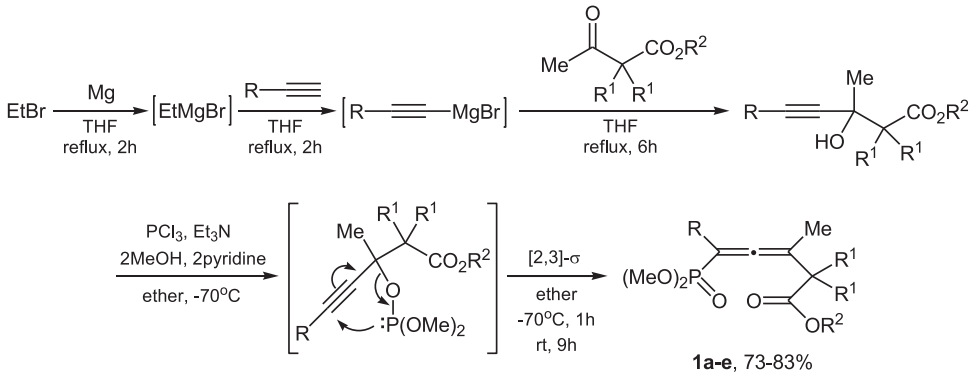
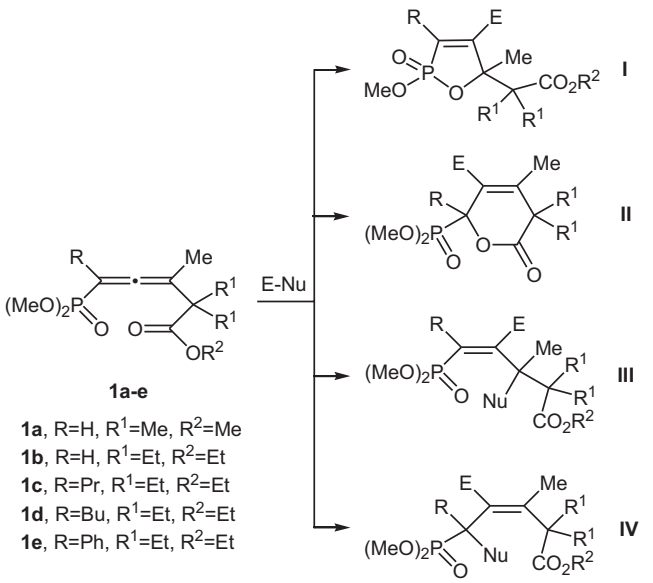


Entry	Product	R	R^1	R^2
1	**1a**	H	Me	Me
2	**1b**	H	Et	Et
3	**1c**	Pr	Et	Et
4	**1d**	Bu	Et	Et
5	**1e**	Ph	Et	Et

Scheme 1. Synthesis of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates 1a-e.[14]



Scheme 2. Possible products of the electrophilic reaction of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates 1a-e.[14]

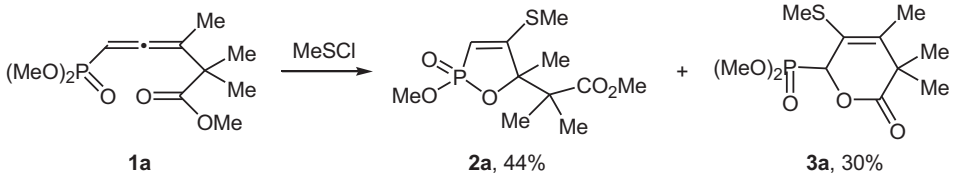
the product of bromination of 1-bromoallenyl ethyl ester (*β*-allenic ester) the formation of which can be explained by a reaction cascade, starting with the electrophilic addition to the central allenic carbon atom followed by intramolecular cyclization accompanied by elimination of ethyl bromide.[12b] On the other hand, intramolecular cyclization of the diethylphosphono-substituted α-allenic alcohols in the presence of $AgNO_3$[13a] and $CuCl_2$[13b] yielded 3,6-dihydro-2*H*-pyran-4-yl-[5] and 4,5-dihydro-3-furanyl-phosphonates.

With this in mind, and in continuation of our long-standing program directed toward the synthesis[14] and the development of efficient protocols for the synthesis of heterocyclic compounds by electrophilic cyclization reactions[15] of bifunctionalized allenes, our attention is drawn to the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a**-**e** as 1,3-bifunctionalized allenes, that comprise an 1-(α-phosphonate) and a 3-(*β*-alkoxycarbonyl) group in the allenic system of double bonds (Schemes 1 and 2). The applications of these groups as temporary transformers of chemical reactivity of the allenic system in the synthesis of heterocyclic compounds are of particular interest. These molecules can be considered a combination of an allenephosphonate and an allenecarboxylate and they are supposed to have different reactivity profiles in cyclization reactions. In continuation of our communications[15] on the synthesis and cyclization reactions of the bifunctionalized allenes, in this paper, we present recent results of our studies dedicated toward the competitive electrophilic cyclization reaction of a library of 5-(dimethoxyphosphoryl)-alka-3,4-dienoates, which improve the scope of this method for the synthesis of heterocyclic compounds.

Results and discussion

Synthesis of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates 1a-e

We applied a convenient, efficient, atom economical and regioselective four-step method to prepare a range of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a**-**e**.[14] Our strategy for the synthesis of **1a**-**e**, using our experience on the preparation of other bifunctionalized allenes,[16] relies on the well-precedented 2,3-sigmatropic shift of propargylic phosphites to allenephosphonates. In order to assess this approach toward the target 5-phosphorylated allenecarboxylates **1a**-**e**, a range of propargylic alcohols was prepared by the reaction of metallated acetylenes with commercialy available alkyl 3-oxoalkanoates (Scheme 2). With the required alkyl 3-hydroxy-alk-4-ynoates in hand, we were then able to investigate the proposed reaction with dimethyl chlorophosphite and subsequent atom economical [2,3]-sigmatropic



1a **2a**, 44% **3a**, 30%

Scheme 3. Synthesis of **2a** and **3a** by competitive electrophilic cyclization of 5-(dimethoxyphosphoryl)-2,2,3-trimethylpenta-3,4-dienoates **1a**. *Reagents and Conditions*: E = MeSCl (1.2 eq.), CH_2Cl_2, −20 °C, 2 h, rt, 3 h, stirring, column chromatography.

rearrangement of the mediated 5-(dimethoxyphosphanyloxy)-alk-4-ynoates.[14]

The allenylphosphonates **1a**-**e** were isolated in preparative amounts, which allowed us to study their chemical behavior in the reaction with electrophilic reagents. The present paper is a recent part of our long-term objective to investigate both the scope and the limitations of the electrophilic cyclization reaction of bifunctionalized allenes, namely the 5-(dimethoxyphosphoryl)-*β*-allenecarboxylates.

Competitive electrophilic cyclization of 5-(dimethoxyphosphoryl)-alka-3,4-dienoates 1a-e

It is necessary to draw the attention to the fact, that conceptually three distinct modes of cyclization of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a**-**e** are possible. They depend on the electrophilic atom that forms a new bond with the central carbon atom of the allenic system, which seems likely.[6,7,15,17] It is evident that these pathways are closely connected with the participation of the competitive intramolecular neighboring phosphonate and/or alkoxycarbonyl groups as internal nucleophiles in the final step of the cyclization. Besides the 5-*endo-trig* cyclization[18] to the 2-(2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-alkanoates **I**, and the 6-*endo-trig* cyclization[18] to the (6-oxo-5,6-dihydro-2*H*-pyran-2-yl)-phosphonates (*δ*-lactones) **II**, the electrophilic addition might afford the 4,3-adducts **III** and/or the 4,5-adducts **IV** (Scheme 1).

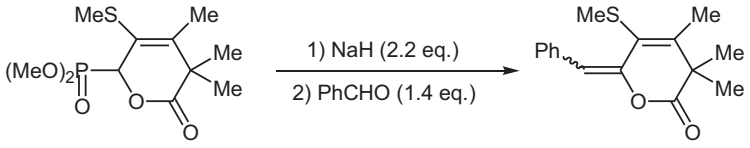
We started the present study with the reaction of the methyl 5-(dimethoxyphosphoryl)-2,2,3-trimethylpenta-3,4-dienoate **1a** with methanesulfenyl chloride (Scheme 3). We conducted the reaction under the optimized reaction conditions determined in similar reactions of bifunctionalized allenes[15]—solvent CH_2Cl_2 at −20 °C using 1.0 equiv. of the allenephosphonate and 1.2 equiv. of the electrophilic reagent. Using spectral methods we established that the reaction under this set of standard reaction conditions in the favored 5-*endo-trig* and 6-*endo-trig* mode afforded a mixture of methyl 2-(2-methoxy-5-methyl-4-methylsulfenyl-2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-methylpropanoate **2a** and dimethyl (4,5,5-tri-methyl-3-methylsulfenyl-6-oxo-5,6-dihydro-2*H*-pyran-2-yl)-phosphonate **3a** (Scheme 3) in the ratio of 1.47:1. Obviously the reaction proceeds by competitive electrophilic cyclization of the allenephosphonate **1a** with the neighboring group participation of phosphonate and carboxylate groups in the cyclization in very good overall isolated yield (74%).

In order to confirm the structure of the cyclic product **3a** we carried out a Horner–Wadsworth–Emmons reaction[19] by the treatment of 5,6-dihydro-2*H*-pyran-2-ylphosphonate **3a** with 2.2. eq. of NaH followed by reaction with PhCHO in THF (Scheme 4). We established that the reaction under these reaction conditions led to the formation of the 6-benzylidene-3,6-dihydro-2*H*-pyran-2-one **4** as a mixture of (6*E*)- and (6*Z*)-isomer in a ratio of *E:Z* = 6.4:1 in overall yield of 63%.

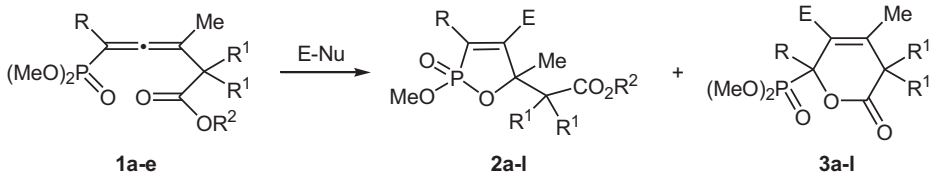
To outline the general terms of this methodology, the reactions of other 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1b**-**e** with different electrophilic reagents such as sulfuryl chloride, bromine, methane- and benzene-sulfenyl chloride, and benzeneselenenyl chloride were investigated. In all cases (Scheme 5), the interaction afforded mixtures of the 2-(2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-alkanoates **2b**-**l** and (6-oxo-5,6-dihydro-2*H*-pyran-2-yl)-phosphonates **3b**-**l** in overall yields of 66–81% in the ratio from 1.26:1 to 1.68:1. These reaction pathways may be interpreted as the result of competitive electrophilic cyclization of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a**-**e** with participation of the neighboring phosphonate and alkoxycarbonyl groups as internal nucleophiles in the favored 5-*endo-trig* and 6-*endo-trig* mode cyclizations.

Thus, on the basis of the available literature data[6,7,17] and our previous results,[15] a rationale for this reaction is depicted in Scheme 6. The starting point is the attack of the electrophile (Cl^+, Br^+, S^+, or Se^+) on both C^3-C^4- and C^4-C^5-double bonds with formation of the cyclic onium (chloronium, bromonium, thiiranium, or seleniranium) ions **A** and **B**. Then, the ions **A** and **B** are easily transformed into the more stable five-membered cyclic ions **C** and **D** *via* the attachment of the oxygen atom of the phosphonate and carboxylate functionality. Further, the intermediates **C** undergo nucleophilic attack on the MeO group of the phosphonate group and elimination of methyl halide (MeNu) affording the final cyclic products **2a**-**l**. Similarly, the ions **D** transform to the 5,6-dihydro-2*H*-pyrans **3a**-**l** after nucleophilic attack on the R^2O group of the carboxylate group and elimination of alkyl halide (R^2Nu). The electronic difference of the two double bonds due to the presence of two electron-withdrawing groups at the terminal carbon atoms as well as the steric effect resulting from the substitutions may both contribute to the observed regioselectivity.

Formation of the cyclic products **2a**-**l** and **3a**-**l** can be considered in terms of the assumption of concurrent attacks of the internal nucleophiles (phosphonate and carboxylate groups) on the cyclic three-membered onium ion **A** and **B**. Obviously, this mechanistic rationale could be explained by the assumption of favorable *trans* arrangement of the electrophile and the internal nucleophile (phosphonate or



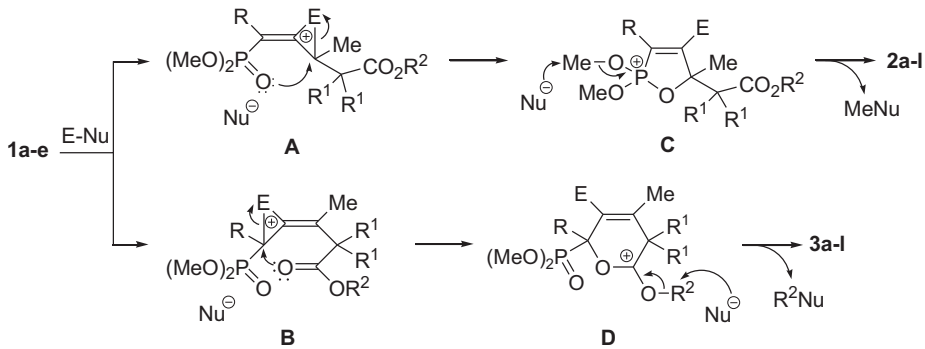
Scheme 4. Synthesis of the (6*E*)-**4** and (6*Z*)-**4** by Horner-Wadsworth-Emmons reaction of **3a**. *Reagents and Conditions*: NaH (2.2 eq.), THF, rt, 30 min, PhCHO (1.4 eq.) THF, 40–50 °C, 120 min, column chromatography.



Entry	R	R^1	R^2	E	Nu	**2**, yield,[a] %	**3**, yield,[a] %	Ratio **2**:**3**
1	H	Me	Me	MeS	Cl	**2a**, 44	**3a**, 30	1.47
2	H	Me	Me	Cl	Cl	**2b**, 48	**3b**, 33	1.45
3	H	Et	Et	Br	Br	**2c**, 45	**3c**, 32	1.40
4	H	Et	Et	PhSe	Cl	**2d**, 43	**3d**, 28	1.54
5	Pr	Et	Et	Cl	Cl	**2e**, 48	**3e**, 31	1.26
6	Pr	Et	Et	PhSe	Cl	**2f**, 42	**3f**, 27	1.56
7	Pr	Et	Et	PhS	Cl	**2g**, 44	**3g**, 28	1.57
8	Bu	Et	Et	Br	Br	**2h**, 45	**3h**, 28	1.61
9	Bu	Et	Et	PhSe	Cl	**2i**, 41	**3i**, 25	1.64
10	Bu	Et	Et	PhS	Cl	**2j**, 42	**3j**, 25	1.68
11	Ph	Et	Et	Br	Br	**2k**, 46	**3k**, 30	1.53
12	Ph	Et	Et	PhS	Cl	**2l**, 43	**3l**, 29	1.48

[a] Isolated yields.

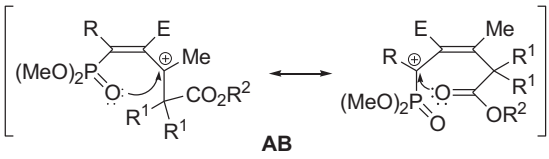
Scheme 5. Synthesis of the 2-(2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-alkanoates **2a-l** and (6-oxo-5,6-dihydro-2*H*-pyran-2-yl)-phosphonates **3a-l** by competitive electrophilic cyclization of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a-e**. *Reagents and Conditions*: E = Cl, Br, MeS, PhS, PhSe; Nu = Cl, Br (1.2 eq.), CH_2Cl_2, −20 °C, 2 h, rt, 3 h, stirring, column chromatography.



Scheme 6. A rationale for the reaction of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a-e** with electrophilic reagents.

carboxylate groups) and *anti*-attack of the internal nucleophiles on the onium ions **A** and **B**. This is supposed to arise from attacks on the allenic C^3-C^4- and C^4-C^5-double bonds *anti* to the phosphonate and carboxylate groups, respectively, which assisted in the two types cyclization by the neighboring groups participation of the internal nucleophiles. On the other hand, a possible explanation of the two types cyclization observed consists of the following: In the first case, it is possible that the cyclic onium ions **A** and **B** further transform to the non-cyclic allylic cations **AB** (Scheme 7), the predominant formation of the 2,5-dihydro-1,2-oxaphospholes **2a-j** could be explained by charge distribution in allylic resonance form. Larger positive charge should be located in this cation on the carbon atom, which is located far from the acceptor P = O group:

In the second case, another probable reason for the predominant participation of the phosphonate group as an internal nucleophile is the higher nucleophilicity of the



Scheme 7. Non-cyclic allylic cations **AB**.

phosphonate oxygen atom in comparison with the carboxylic one, which is in connection with the larger polarization of the phosphoryl group.

The above mentioned explanation should account for the results on the study of the reactions of other bifunctionalized allenes with electrophilic reagents. Further work in this area shall focus on exploiting and extending the synthetic utility of the bifunctionalized allenes for the preparation of different heterocyclic systems by application of the electrophilic cyclization methodology.

Experimental

General information

All synthesized compounds were purified by column chromatography and characterized by NMR, IR, MS and microanalytical data. NMR spectra were recorded with Brucker Avance II + 600 (^{1}H at 600.1 MHz, ^{13}C at 150.9 MHz, ^{31}P at 242.9 MHz) spectrometer in $CDCl_3$ solutions. All ^{1}H and ^{13}C NMR experiments were measured referring to the signal of internal TMS and the ^{31}P NMR experiments were measured referring to the signal of external 85% H_3PO_4. *J* values are given in hertz. IR spectra were recorded with an FT-IR Afinity-1 Shimadzu spectrophotometer. Elemental analyses were carried out by the Microanalytical Service Laboratory using Vario EL*3* CHNS(O). HRMS were recorded with a Thermo Scientific Q Exactive hybrid quadrupole-orbitrap mass spectrometer. Column chromatography was performed on Kieselgel F_{254}60 (70–230 mesh ASTM, 0.063–0.200 nm, Merck). CH_2Cl_2 was distilled over CaH_2. 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 F_{254} 60 (Merck).

Starting materials

Dimethyl and diphenyl disulfide and sulfuryl chloride in dichloromethane were used to prepare methane- and benzene-sulfenyl chloride. All other chemicals used in this study were commercially available and were used without additional purification unless otherwise noted. The starting 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a**-**e** were prepared according to earlier reported procedure.[14]

General procedure for the reactions of the alkyl 5-(dimethoxyphosphoryl)-alka-3,4-dienoates 1a-e with electrophilic reagents

To a solution of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates **1a**-**e** (3.0 mmol) in dry dichloromethane (10 mL) at −20 °C was added dropwise with stirring a solution of electrophilic reagent (sulfuryl chloride, bromine, methane- or benzenesulfenyl chloride, or benzeneselenenyl chloride) (3.6 mmol) in the same solvent (10 mL). The reaction mixture was stirred at the same temperature for 2 h and then at room temperature for 3 h (reactions were monitored by TLC). After evaporation of the solvent, the residue was purified by column chromatography on a silica gel with ethyl acetate/hexane. The pure products **2a**-**l** and **3a**-**l** had the following properties.

Methyl 2-(2-methoxy-5-methyl-4-methylsulfenyl-2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-methyl-propanoate 2a

Yellow oil, yield: 44%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.69; IR (neat, cm^{-1}): 1017 (C-O-P), 1251 (P = O), 1586 (C = C), 1731 (C = O). ^{1}H NMR (600.1 MHz): δ = 1.27 (s, 3H, MeCMe), 1.35 (s, 3H, MeCMe), 1.67 (s, 3H, MeC), 2.41 (s, 3H, MeS), 3.59 (s, 3H, MeOC(O)), 3.69 (d, J = 9.1 Hz, 3H, MeOP(O)), 5.88 (d, J = 24.6 Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): δ = 16.7 (J = 4.5 Hz, CH_3), 19.4 (J = 1.5 Hz, CH_3), 20.8 (J = 1.4 Hz, CH_3), 23.3 (J = 4.9 Hz, CH_3), 48.8 (J = 7.8, C), 52.5 (CH_3), 52.7 (J = 15.0 Hz, CH_3), 96.1 (J = 10.5 Hz, C), 110.6 (J = 71.9 Hz, CH), 164.7 (J = 15.2 Hz, C), 178.1 (J = 4.0 Hz, C). ^{31}P NMR (242.9 MHz): δ = 33.2. HRMS (ESI): *m/z* calcd for $C_{11}H_{20}O_5PS$ $[M+H]^+$ 295.3133, found 295.3127. Anal. Calcd for $C_{11}H_{19}O_5PS$: C 44.89, H 6.51. Found: C 44.97, H 6.55%.

Dimethyl (4,5,5-trimethyl-3-methylsulfenyl-6-oxo-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3a

Yellow oil, yield: 30%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.40; IR (neat, cm^{-1}): 1118 (C–O–C), 1259 (P = O), 1621 (C = C), 1752 (C = O). ^{1}H NMR (600.1 MHz): δ = 1.36 (s, 3H, MeCMe), 1.51 (s, 3H, MeCMe), 1.60 (s, 3H, MeC=) 2.00 (s, 3H, MeS), 3.92 (d, J = 11.1 Hz, 6H, MeO), 6.01 (d, J = 15.2 Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): δ = 16.0 (J = 4.4 Hz, CH_3), 15.7 (J = 4.6 Hz, CH_3), 23.2 (CH_3), 25.4 (CH_3), 41.4 (J = 5.0 Hz, C), 52.7 (J = 14.6 Hz, CH_3), 76.1 (J = 112.7 Hz, CH), 128.6 (J = 15.0 Hz, C), 134.9 (J = 8.1 Hz, C), 174.5 (J = 7.8 Hz, C). ^{31}P NMR (242.9 MHz): δ = 25.3. HRMS (ESI): *m/z* calcd for $C_{11}H_{20}O_5PS$ $[M+H]^+$ 295.3133, found 295.3156. Anal. Calcd for $C_{11}H_{19}O_5PS$: C 44.89, H 6.51. Found: C 44.83, H 6.43%.

Methyl 2-(4-chloro-2-methoxy-5-methyl-2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-methyl-propanoate 2b

Pale yellow oil, yield: 48%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.75; IR (neat, cm^{-1}): 1023 (C-O-P), 1249 (P = O), 1580 (C = C), 1730 (C = O). ^{1}H NMR (600.1 MHz): δ = 1.22 (s, 3H, MeCMe), 1.41 (s, 3H, MeCMe), 1.66 (s, 3H, MeC), 3.61 (s, 3H, MeOC(O)), 3.78 (d, J = 11.4 Hz, 3H, MeOP(O)), 6.14 (d, J = 25.3 Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): δ = 20.4 (J = 7.9 Hz, CH_3), 20.9 (J = 4.8 Hz,

CH_3), 23.1 ($J = 4.9$ Hz, CH_3), 46.5 ($J = 8.1$ Hz, C), 50.9 (CH_3), 52.8 ($J = 15.0$ Hz, CH_3), 98.1 ($J = 9.7$ Hz, C), 112.9 ($J = 75.0$ Hz, CH), 162.7 ($J = 39.6$ Hz, C), 173.5 ($J = 4.5$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 34.1$. HRMS (ESI): *m/z* calcd for $C_{10}H_{17}ClO_5P$ $[M + H]^+$ 283.6654, found 283.6647. Anal. Calcd for $C_{10}H_{16}ClO_5P$: C 42.49, H 5.71. Found: C 42.56, H 5.65%.

Dimethyl (3-chloro-4,5,5-trimethyl-6-oxo-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3b

Yellow oil, yield: 33%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.41; IR (neat, cm^{-1}): 1121 (C–O–C), 1257 (P = O), 1619 (C = C), 1751 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 1.41$ (s, 3H, MeCMe), 1.56 (s, 3H, MeCMe), 2.11 (s, 3H, Me-C=), 3.88 (d, $J = 10.5$ Hz, 6H, MeO), 5.40 (d, $J = 15.0$ Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): $\delta = 12.0$ ($J = 4.7$ Hz, CH_3), 23.4 (CH_3), 25.0 (CH_3), 40.9 ($J = 5.0$ Hz, C), 52.8 ($J = 14.5$ Hz, CH_3), 80.5 ($J = 112.9$ Hz, CH), 117.7 ($J = 39.2$ Hz, C), 135.0 ($J = 8.2$ Hz, C), 168.5 ($J = 8.1$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 26.2$. HRMS (ESI): *m/z* calcd for $C_{10}H_{17}ClO_5P$ $[M + H]^+$ 283.6654, found 283.6661. Anal. Calcd for $C_{10}H_{16}ClO_5P$: C 42.49, H 5.71. Found: C 42.42, H 5.63%.

Ethyl 2-(4-bromo-2-methoxy-5-methyl-2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-ethyl-butanoate 2c

Pale yellow oil, yield: 45%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.71; IR (neat, cm^{-1}): 1018 (C-O-P), 1260 (P = O), 1582 (C = C), 1733 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.91$ (t, $J = 6.8$ Hz, 6H, $MeCH_2$), 1.21 (t, $J = 7.0$ Hz, 3H, $MeCH_2O$), 1.74 (s, 3H, MeC), 1.78 (m, 4H, $MeCH_2$), 3.70 (d, $J = 11.4$ Hz, 3H, MeO), 4.03 (m, 2H, $MeCH_2O$), 6.51 (d, $J = 25.4$ Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): $\delta = 10.9$ (CH_3), 14.3 (CH_3), 19.0 ($J = 4.6$ Hz, CH_2), 21.1 ($J = 4.6$ Hz, CH_2), 22.3 ($J = 4.7$ Hz, CH_3), 50.9 ($J = 7.9$ Hz, C), 52.7 ($J = 14.4$ Hz, CH_3), 60.4 (CH_2), 90.9 ($J = 9.8$ Hz, C), 109.5 ($J = 74.8$ Hz, CH), 143.9 ($J = 32.8$ Hz, C), 173.8 ($J = 5.0$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 35.2$. HRMS (ESI): *m/z* calcd for $C_{13}H_{23}BrO_5P$ $[M + H]^+$ 370.1965, found 370.1954. Anal. Calcd for $C_{13}H_{22}BrO_5P$: C 42.29, H 6.01. Found: C 42.37, H 5.96%.

Dimethyl (3-bromo-5,5-diethyl-4-methyl-6-oxo-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3c

Yellow oil, yield: 32%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.38; IR (neat, cm^{-1}): 1123 (C–O–C), 1259 (P = O), 1619 (C = C), 1753 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.76$ (t, $J = 7.4$ Hz, 6H, $MeCH_2$), 1.52 (m, 4H, $MeCH_2$), 2.18 (s, 3H, Me-C=), 3.89 (d, $J = 10.4$ Hz, 6H, MeO), 6.03 (d, $J = 15.5$ Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): $\delta = 11.1$ (CH_3), 16.1 ($J = 5.1$, CH_3), 18.6 (CH_2), 20.4 (CH_2), 48.7 ($J = 4.9$ Hz, C), 52.9 ($J = 14.5$, CH_3), 80.2 ($J = 114.8$ Hz, CH), 111.8 ($J = 48.8$ Hz, C), 143.7 ($J = 8.0$ Hz, C), 168.3 ($J = 7.8$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 25.7$. HRMS (ESI): *m/z* calcd for $C_{12}H_{21}BrO_5P$ $[M + H]^+$ 356.1699, found 356.1706. Anal. Calcd for $C_{12}H_{20}BrO_5P$: C 40.58, H 5.68. Found: C 40.51, H 5.62%.

Ethyl 2-ethyl-2-(2-methoxy-5-methyl-2-oxo-4-phenylselenenyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-butanoate 2d

Yellow oil, yield: 43%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.73; IR (neat, cm^{-1}): 1024 (C-O-P), 1254 (P = O), 1437, 1489 (Ph), 1579 (C = C), 1729 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.91$ (t, $J = 6.8$ Hz, 6H, $MeCH_2$), 1.21 (t, $J = 7.0$ Hz, 3H, $MeCH_2O$), 1.61 (s, 3H, MeC), 1.78 (m, 4H, $MeCH_2$), 3.66 (d, $J = 11.5$ Hz, 3H, MeO), 4.03 (m, 2H, $MeCH_2O$), 6.39 (d, $J = 27.9$ Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): $\delta = 10.5$ (CH_3), 14.4 (CH_3), 18.1 ($J = 4.6$ Hz, CH_2), 20.1 ($J = 4.7$ Hz, CH_2), 20.3 ($J = 7.9$ Hz, CH_3), 53.0 ($J = 15.0$ Hz, CH_3), 58.1 ($J = 7.8$ Hz, C), 61.8 (CH_2), 96.2 ($J = 9.8$ Hz, C), 111.1 ($J = 72.4$ Hz, CH), 129.1 (CH), 129.3 (CH), 131.1 (C), 138.1 (CH), 174.3 ($J = 4.6$ Hz, C), 175.8 ($J = 14.3$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 36.0$. HRMS (ESI): *m/z* calcd for $C_{19}H_{28}O_5PSe$ $[M + H]^+$ 446.3564, found 446.3571. Anal. Calcd for $C_{19}H_{27}O_5PSe$: C 51.24, H 6.11. Found: C 51.17, H 6.05%.

Dimethyl (5,5-diethyl-4-methyl-6-oxo-3-phenylselenenyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3d

Yellow oil, yield: 28%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.41; IR (neat, cm^{-1}): 1122 (C–O–C), 1261 (P = O), 1439, 1492 (Ph), 1621 (C = C), 1749 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.78$ (t, $J = 7.4$ Hz, 6H, $MeCH_2$), 1.48 (m, 4H, $MeCH_2$), 1.94 (s, 3H, Me-C=), 3.91 (d, $J = 10.5$ Hz, 6H, MeO), 6.07 (d, $J = 15.0$ Hz, 1H, PCH=). ^{13}C NMR (150.9 MHz): $\delta = 11.2$ (CH_3), 15.4 ($J = 5.1$, CH_3), 17.8 (CH_2), 19.7 (CH_2), 52.7 ($J = 14.4$ Hz, CH_3), 53.9 ($J = 5.0$, C), 82.4 ($J = 114.1$ Hz, CH), 105.1 ($J = 14.6$ Hz, C), 128.4 ($J = 43.2$ Hz, C), 128.7 ($J = 9.9$ Hz, CH), 129.4 (CH), 136.31 $J = 4.9$ Hz, (CH), 138.4 ($J = 7.9$ Hz, C), 171.9 ($J = 8.1$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 24.4$. HRMS (ESI): *m/z* calcd for $C_{18}H_{26}O_5PSe$ $[M + H]^+$ 432.3298, found 632.3289. Anal. Calcd for $C_{18}H_{25}O_5PSe$: C 50.12, H 5.84. Found: C 50.20, H 5.89%.

Ethyl 2-(4-chloro-2-methoxy-5-methyl-2-oxo-3-propyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-ethyl-butanoate 2e

Pale yellow oil, yield: 48%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.73; IR (neat, cm^{-1}): 1021 (C-O-P), 1260 (P = O), 1584 (C = C), 1726 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.81$ (t, $J = 7.0$ Hz, 3H, $MeCH_2CH_2$), 0.90 (t, $J = 6.8$ Hz, 6H, $MeCH_2$), 1.21 (t, $J = 7.0$ Hz, 3H, $MeCH_2O$), 1.54 (m, 2H, $MeCH_2CH_2$), 1.65 (s, 3H, MeC), 1.70–1.88 (m, 4H, $MeCH_2$), 1.96 (m, 2H, $MeCH_2CH_2$), 3.68 (d, $J = 11.3$ Hz, 3H, MeO), 4.14 (m, 2H, $MeCH_2O$). ^{13}C NMR (150.9 MHz): $\delta = 10.1$ (CH_3), 14.6 (CH_3), 15.4 ($J = 4.6$ Hz, CH_3), 20.0 ($J = 4.9$ Hz, CH_2), 20.7 ($J = 8.2$ Hz, CH_2), 20.9 ($J = 7.8$ Hz, CH_3), 21.7 ($J = 4.7$ Hz, CH_2), 31.5 ($J = 6.3$ Hz, CH_2), 49.9 ($J = 15.0$ Hz, CH_3), 51.3 ($J = 8.0$ Hz, C), 61.7 (CH_2), 94.9

($J = 10.2$ Hz, C), 127.9 ($J = 98.8$ Hz, C), 156.0 ($J = 39.3$ Hz, C), 176.1 ($J = 5.0$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 22.8$. HRMS (ESI): *m/z* calcd for $C_{16}H_{29}ClO_5P$ $[M+H]^+$ 367.8249, found 367.8260. Anal. Calcd for $C_{16}H_{28}ClO_5P$: C 52.39, H 7.69. Found: C 52.46, H 7.77%.

Dimethyl (3-chloro-5,5-diethyl-4-methyl-6-oxo-2-propyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3e

Yellow oil, yield: 31%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.42; IR (neat, cm^{-1}): 1119 (C–O–C), 1265 (P = O), 1620 (C = C), 1749 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.79$ (t, $J = 7.4$ Hz, 6H, $MeCH_2$), 1.09 (t, $J = 7.1$ Hz, 3H, $MeCH_2CH_2$), 1.52–1.77 (m, 4H, $MeCH_2$), 1.76 (m, 2H, $MeCH_2CH_2$), 2.03 (s, 3H, Me-C=), 2.27 (m, 2H, $MeCH_2CH_2$), 3.83 (d, $J = 10.5$ Hz, 6H, MeO). ^{13}C NMR (150.9 MHz): $\delta = 10.9$ (CH_3), 11.8 (CH_3), 15.2 ($J = 4.9$ Hz, CH_3), 19.1 ($J = 8.1$ Hz, CH_2), 19.2 (CH_2), 20.8 (CH_2), 36.2 ($J = 6.2$ Hz, CH_2), 48.3 ($J = 4.5$ Hz, C), 53.1 ($J = 14.7$, CH_3), 88.9 ($J = 124.6$ Hz, C), 127.1 ($J = 40.2$ Hz, C), 138.5 ($J = 7.7$ Hz, C), 169.4 ($J = 7.8$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 23.1$. HRMS (ESI): *m/z* calcd for $C_{15}H_{27}ClO_5P$ $[M+H]^+$ 353.7983, found 353.7989. Anal. Calcd for $C_{15}H_{26}ClO_5P$: C 51.07, H 7.43. Found: C 51.12, H 7.50%.

Ethyl 2-ethyl-2-(2-methoxy-5-methyl-2-oxo-4-phenylselenenyl-3-propyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-butanoate 2f

Yellow oil, yield: 42%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.70; IR (neat, cm^{-1}): 1020 (C-O-P), 1258 (P = O), 1437, 1489 (Ph), 1582 (C = C), 1730 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.82$ (t, $J = 7.1$ Hz, 3H, $MeCH_2CH_2$), 0.90 (t, $J = 6.8$ Hz, 6H, $MeCH_2$), 1.21 (t, $J = 7.0$ Hz, 3H, $MeCH_2O$), 1.42 (m, 2H, $MeCH_2CH_2$), 1.60 (s, 3H, MeC), 1.66–1.77 (m, 4H, $MeCH_2$), 2.09 (m, 2H, $MeCH_2CH_2$), 3.69 (d, $J = 11.0$ Hz, 3H, MeO), 4.07 (m, 2H, $MeCH_2O$), 7.32–7.45 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): $\delta = 10.0$ (CH_3), 14.6 (CH_3), 15.0 ($J = 4.7$ Hz, CH_3), 17.9 ($J = 4.7$ Hz, CH_2), 19.2 ($J = 8.1$ Hz, CH_2), 19.9 ($J = 7.9$ Hz, CH_3), 20.1 ($J = 4.6$ Hz, CH_2), 32.0 ($J = 5.7$ Hz, CH_2), 51.2 ($J = 14.5$ Hz, CH_3), 57.4 ($J = 8.0$ Hz, C), 61.5 (CH_2), 96.1 ($J = 9.9$ Hz, C), 129.0 (CH), 129.2 (CH), 129.7 (C), 128.4 ($J = 97.7$ Hz, C), 138.2 (CH), 171.7 ($J = 15.0$ Hz, C), 176.9 ($J = 5.0$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 26.6$. HRMS (ESI): *m/z* calcd for $C_{22}H_{34}O_5PSe$ $[M+H]^+$ 488.4361, found 488.4369. Anal. Calcd for $C_{22}H_{33}O_5PSe$: C 54.21, H 6.82. Found: C 54.15, H 6.75%.

Dimethyl (5,5-diethyl-4-methyl-6-oxo-3-phenylselenenyl-2-propyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3f

Yellow oil, yield: 27%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.40; IR (neat, cm^{-1}): 1118 (C–O–C), 1262 (P = O), 1440, 1488 (Ph), 1622 (C = C), 1752 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.76$ (t, $J = 7.3$ Hz, 6H, $MeCH_2$), 1.09 (t, $J = 7.1$ Hz, 3H, $MeCH_2CH_2$), 1.46–1.68 (m, 4H, $MeCH_2$), 1.61 (m, 2H, $MeCH_2CH_2$), 1.95 (s, 3H, Me-C=), 2.27–2.45 (m, 2H, $MeCH_2CH_2$), 3.85 (d, $J = 10.5$ Hz, 6H, MeO), 7.41–7.50 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): $\delta = 10.9$ (CH_3), 15.3 ($J = 4.8$ Hz, CH_3), 16.1 ($J = 4.8$ Hz, CH_3), 17.3 ($J = 8.1$ Hz, CH_2), 17.5 (CH_2), 19.5 (CH_2), 35.2 ($J = 5.7$ Hz, CH_2), 53.1 ($J = 14.6$ Hz, CH_3), 53.4 ($J = 4.7$, C), 90.5 ($J = 125.4$ Hz, C), 110.5 ($J = 14.0$ Hz, C), 128.5 (CH), 128.8 (C), 129.6 (CH), 138.6 (CH), 138.9 ($J = 8.1$ Hz, C), 174.7 ($J = 7.8$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 23.9$. HRMS (ESI): *m/z* calcd for $C_{21}H_{32}O_5PSe$ $[M+H]^+$ 374.4095, found 374.4089. Anal. Calcd for $C_{21}H_{31}O_5PSe$: C 53.28, H 6.60. Found: C 53.22, H 6.64%.

Ethyl 2-ethyl-2-(2-methoxy-5-methyl-2-oxo-4-phenylsulfenyl-3-propyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-butanoate 2g

Yellow oil, yield: 44%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.73; IR (neat, cm^{-1}): 1023 (C-O-P), 1256 (P = O), 1438, 1492 (Ph), 1580 (C = C), 1733 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.83$ (t, $J = 7.0$ Hz, 3H, $MeCH_2CH_2$), 0.90 (t, $J = 6.8$ Hz, 6H, $MeCH_2$), 1.22 (t, $J = 7.1$ Hz, 3H, $MeCH_2O$), 1.66 (m, 2H, $MeCH_2CH_2$), 1.69 (s, 3H, MeC), 1.88–1.97 (m, 4H, $MeCH_2$), 2.19 (m, 2H, $MeCH_2CH_2$), 3.74 (d, $J = 11.4$ Hz, 3H, MeO), 4.11 (m, 2H, $MeCH_2O$), 7.19–7.43 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): $\delta = 10.2$ (CH_3), 13.8 (CH_3), 14.8 ($J = 4.6$ Hz, CH_3), 20.3 ($J = 5.1$ Hz, CH_2), 21.4 ($J = 8.0$ Hz, CH_2), 22.6 ($J = 5.0$ Hz, CH_2), 24.9 ($J = 7.9$ Hz, CH_3), 32.4 ($J = 5.8$ Hz, CH_2), 51.8 ($J = 14.2$ Hz, CH_3), 53.8 ($J = 7.8$ Hz, C), 61.6 (CH_2), 91.9 ($J = 9.8$ Hz, C), 125.9 (CH), 127.0 (CH), 129.1 (CH), 130.7 ($J = 98.5$ Hz, C), 140.1 ($J = 5.0$ Hz, C), 160.1 ($J = 15.0$ Hz, C), 177.5 ($J = 4.8$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 26.7$. HRMS (ESI): *m/z* calcd for $C_{22}H_{34}O_5PS$ $[M+H]^+$ 441.5421, found 441.5416. Anal. Calcd for $C_{22}H_{33}O_5PS$: C 59.98, H 7.55. Found: C 60.06, H 7.61%.

Dimethyl (5,5-diethyl-4-methyl-6-oxo-3-phenylsulfenyl-2-propyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3g

Yellow oil, yield: 28%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.39; IR (neat, cm^{-1}): 1117 (C–O–C), 1260 (P = O), 1439, 1493 (Ph), 1623 (C = C), 1750 (C = O). ^{1}H NMR (600.1 MHz): $\delta = 0.75$ (t, $J = 7.3$ Hz, 6H, $MeCH_2$), 1.13 (t, $J = 7.2$ Hz, 3H, $MeCH_2CH_2$), 1.66–1.87 (m, 4H, $MeCH_2$), 1.90 (m, 2H, $MeCH_2CH_2$), 1.96 (s, 3H, Me-C=), 2.39–2.50 (m, 2H, $MeCH_2CH_2$), 3.86 (d, $J = 10.6$ Hz, 6H, MeO), 7.22–7.47 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): $\delta = 10.7$ (CH_3), 15.2 ($J = 4.7$ Hz, CH_3), 19.4 ($J = 7.8$ Hz, CH_2), 20.0 ($J = 4.6$ Hz, CH_3), 20.3 (CH_2), 21.6 (CH_2), 36.4 ($J = 5.7$ Hz, CH_2), 50.4 ($J = 5.0$ Hz, C), 52.9 ($J = 5.1$ Hz, CH_3), 84.7 ($J = 125.5$ Hz, C), 125.8 (CH), 127.3 (CH), 129.2 (CH), 129.5 ($J = 14.5$ Hz, C), 135.0 (C), 141.7 ($J = 8.2$ Hz, C), 174.7 ($J = 7.9$ Hz, C). ^{31}P NMR (242.9 MHz): $\delta = 23.9$. HRMS (ESI): *m/z* calcd for $C_{21}H_{32}O_5PS$ $[M+H]^+$ 427.5155, found 427.5149. Anal. Calcd for $C_{21}H_{31}O_5PS$: C 59.14, H 7.33. Found: C 59.20, H 7.37%.

Ethyl 2-(4-bromo-3-butyl-2-methoxy-5-methyl-2-oxo-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-ethyl-butanoate 2h

Pale yellow oil, yield: 45%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.76; IR (neat, cm^{-1}): 1017 (C-O-P), 1255 (P = O), 1581 (C = C), 1732 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.82 (m, 3H, Me$(CH_2)_3$, 0.93 (t, J = 6.8 Hz, 6H, $MeCH_2$), 1.22 (t, J = 7.0 Hz, 3H, $MeCH_2O$), 1.27–1.37 (m, 4H, Me$(CH_2)_2CH_2$), 1.71–1.90 (m, 4H, $MeCH_2$), 1.74 (s, 3H, MeC), 2.07–2.14 (m, 2H, Me$(CH_2)_2CH_2$), 3.79 (d, J = 11.4 Hz, 3H, MeO), 4.06–4.13 (m, 2H, $MeCH_2O$). ^{13}C NMR (150.9 MHz): δ = 10.0 (CH_3), 14.2 (CH_3), 14.4 (CH_3), 19.1 (J = 4.7 Hz, CH_2), 20.9 (J = 4.7 Hz, CH_2), 22.0 (J = 5.1 Hz, CH_2), 22.5 (J = 8.1 Hz, CH_3), 29.7 (J = 8.0 Hz, CH_2), 30.1 (J = 5.8 Hz, CH_2), 51.0 (J = 7.8 Hz, C), 52.4 (J = 15.0 Hz, CH_3), 61.3 (CH_2), 93.8 (J = 9.7 Hz, C), 126.4 (J = 147.4 Hz, C), 139.9 (J = 50.5 Hz, C), 176.7 (J = 5.0 Hz, C). ^{31}P NMR (242.9 MHz): δ = 27.2. HRMS (ESI): m/z calcd for $C_{17}H_{31}BrO_5P$ $[M+H]^+$ 426.3028, found 426.3037. Anal. Calcd for $C_{17}H_{30}BrO_5P$: C 48.01, H 7.11. Found: C 47.94, H 7.06%.

Dimethyl (3-bromo-2-butyl-5,5-diethyl-4-methyl-6-oxo-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3h

Yellow oil, yield: 28%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.44; IR (neat, cm^{-1}): 1121 (C–O–C), 1260 (P = O), 1622 (C = C), 1749 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.79 (t, J = 7.3 Hz, 6H, $MeCH_2$), 0.90 (m, 3H, Me$(CH_2)_3$, 1.42–1.78 (m, 8H, $MeCH_2$, Me$(CH_2)_2CH_2$), 2.15 (s, 3H, Me-C=), 2.27–2.50 (m, 2H, Me$(CH_2)_2CH_2$), 3.88 (d, J = 10.6 Hz, 6H, MeO). ^{13}C NMR (150.9 MHz): δ = 10.9 (CH_3), 14.5 (CH_3), 16.7 (J = 5.0 Hz, CH_3), 18.4 (CH_2), 20.6 (CH_2), 21.7 (J = 5.0 Hz, CH_2), 27.4 (J = 7.7 Hz, CH_2), 33.8 (J = 5.7 Hz, CH_2), 49.2 (J = 4.7 Hz, C), 53.5 (J = 14.6 Hz, CH_3), 87.4 (J = 124.8 Hz, C), 115.8 (J = 50.4 Hz, C), 141.9 (J = 8.0 Hz, C), 170.9 (J = 7.8 Hz, C). ^{31}P NMR (242.9 MHz): δ = 26.7. HRMS (ESI): m/z calcd for $C_{16}H_{29}BrO_5P$ $[M+H]^+$ 412.2762, found 412.2748. Anal. Calcd for $C_{16}H_{28}BrO_5P$: C 46.73, H 6.86. Found: C 46.78, H 6.90%.

Ethyl 2-(3-butyl-2-methoxy-5-methyl-2-oxo-4-phenylselenenyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-ethyl-butanoate 2i

Yellow oil, yield: 41%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.72; IR (neat, cm^{-1}): 1022 (C-O-P), 1257 (P = O), 1437, 1487 (Ph), 1580 (C = C), 1727 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.79 (t, J = 6.6 Hz, 3H, Me$(CH_2)_3$, 0.90 (t, J = 7.1 Hz, 6H, $MeCH_2$), 1.21 (t, J = 7.2 Hz, 3H, $MeCH_2O$), 1.24–1.34 (m, 4H, Me$(CH_2)_2CH_2$), 1.62 (s, 3H, MeC), 1.74–1.83 (m, 4H, $MeCH_2$), 2.15–2.24 (m, 2H, Me$(CH_2)_2CH_2$), 3.73 (d, J = 11.1 Hz, 3H, MeO), 4.03–4.10 (m, 2H, $MeCH_2O$), 7.32–7.46 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ = 10.2 (CH_3), 14.0 (CH_3), 14.4 (CH_3), 18.0 (J = 4.7 Hz, CH_2), 20.1 (J = 4.6 Hz, CH_2), 20.7 (J = 7.8 Hz, CH_3), 21.6 (J = 4.6 Hz, CH_2), 28.7 (J = 7.6 Hz, CH_2), 30.3 (J = 8.0 Hz, CH_2), 51.8 (J = 14.6 Hz, CH_3), 57.0 (J = 7.8 Hz, C), 61.8 (CH_2), 96.7 (J = 10.1 Hz, C), 128.6 (J = 100.1 Hz, C), 129.0 (J = 4.7 Hz, C), 129.2 (CH), 129.4 (CH), 137.4 (CH), 172.6 (J = 14.9 Hz, C), 176.8 (J = 5.0 Hz, C). ^{31}P NMR (242.9 MHz): δ = 28.0. HRMS (ESI): m/z calcd for $C_{23}H_{36}O_5PSe$ $[M+H]^+$ 502.4627, found 502.4641. Anal. Calcd for $C_{23}H_{35}O_5PSe$: C 55.09, H 7.04. Found: C 55.16, H 6.99%.

Dimethyl (2-butyl-5,5-diethyl-4-methyl-6-oxo-3-phenylselenenyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3i

Yellow oil, yield: 25%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.44; IR (neat, cm^{-1}): 1117 (C–O–C), 1265 (P = O), 1441, 1491 (Ph), 1624 (C = C), 1748 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.76 (t, J = 7.3 Hz, 6H, $MeCH_2$), 0.89 (t, J = 6.0 Hz, 3H, Me$(CH_2)_3$, 1.41–1.72 (m, 8H, $MeCH_2$, Me$(CH_2)_2CH_2$), 1.93 (s, 3H, Me-C=), 2.36–2.60 (m, 2H, Me$(CH_2)_2CH_2$), 3.69 (d, J = 11.1 Hz, 6H, MeO), 7.47–7.53 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ = 10.9 (CH_3), 14.5 (CH_3), 16.5 (J = 5.1 Hz, CH_3), 17.3 (CH_2), 19.5 (CH_2), 22.2 (J = 4.8 Hz, CH_2), 26.5 (J = 7.9 Hz, CH_2), 33.2 (J = 5.8 Hz, CH_2), 53.4 (J = 9.8 Hz, C), 53.9 (J = 14.6 Hz, CH_3), 90.4 (J = 126.0 Hz, C), 110.6 (J = 15.0 Hz, C), 128.0 (J = 4.7 Hz, C), 128.7 (CH), 129.0 (CH), 134.7 (J = 7.9 Hz, C), 137.4 (CH), 174.5 (J = 7.8 Hz, C). ^{31}P NMR (242.9 MHz): δ = 25.9. HRMS (ESI): m/z calcd for $C_{22}H_{34}O_5PSe$ $[M+H]^+$ 488.4361, found 488.4377. Anal. Calcd for $C_{22}H_{33}O_5PSe$: C 54.21, H 6.82. Found: C 54.14, H 6.74%.

Ethyl 2-(3-butyl-2-methoxy-5-methyl-2-oxo-4-phenylsulfenyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-ethyl-butanoate 2j

Yellow oil, yield: 42%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.71; IR (neat, cm^{-1}): 1021 (C-O-P), 1254 (P = O), 1439, 1490 (Ph), 1586 (C = C), 1729 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.83 (t, J = 6.7 Hz, 3H, Me$(CH_2)_3$, 0.91 (t, J = 7.0 Hz, 6H, $MeCH_2$), 1.20 (t, J = 7.2 Hz, 3H, $MeCH_2O$), 1.25–1.50 (m, 4H, Me$(CH_2)_2CH_2$), 1.64 (s, 3H, MeC), 1.83–2.00 (m, 4H, 2x$MeCH_2$), 2.20–2.29 (m, 2H, Me$(CH_2)_2CH_2$), 3.75 (d, J = 11.4 Hz, 3H, MeO), 4.07–4.12 (m, 2H, $MeCH_2O$), 7.14–7.40 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ = 10.0 (CH_3), 14.1 (CH_3), 14.4 (CH_3), 20.2 (CH_2), 21.3 (J = 5.1 Hz, CH_2), 22.5 (J = 5.1 Hz, CH_2), 25.3 (J = 8.1 Hz, CH_3), 30.2 (J = 7.9 Hz, CH_2), 30.6 (J = 7.9 Hz, CH_2), 52.4 (J = 15.1 Hz, CH_3), 53.4 (J = 7.8 Hz, C), 61.8 (CH_2), 91.4 (J = 10.1 Hz, C), 125.1 (J = 5.1 Hz, C), 126.7 (CH), 129.2 (CH), 130.0 (J = 99.4 Hz, C), 136.1 (CH), 160.2 (J = 14.7 Hz, C), 177.5 (J = 5.0 Hz, C). ^{31}P NMR (242.9 MHz): δ = 26.9. HRMS (ESI): m/z calcd for $C_{23}H_{36}O_5PS$ $[M+H]^+$ 455.5687, found 455.5661. Anal. Calcd for $C_{23}H_{35}O_5PS$: C 60.77, H 7.76. Found: C 60.84, H 7.82%.

Dimethyl (2-butyl-5,5-diethyl-4-methyl-6-oxo-3-phenylsulfenyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3j

Yellow oil, yield: 25%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.42; IR (neat, cm^{-1}): 1122 (C–O–C), 1266 (P = O), 1438, 1486 (Ph), 1620 (C = C), 1751 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.78 (t, J = 7.5 Hz, 6H, MeCH$_2$), 0.89 (t, J = 6.1 Hz, 3H, Me(CH$_2$)$_3$, 1.44–1.55 (m, 2H, MeCH$_2$(CH$_2$)$_2$), 1.60–1.90 (m, 2H, MeCH$_2$), 1.70–1.80 (m, 2H, MeCH$_2$CH$_2$CH$_2$), 1.96 (s, 3H, Me-C=), 2.40–2.63 (m, 2H, Me(CH$_2$)$_2$CH$_2$), 3.87 (d, J = 10.6 Hz, 6H, (MeO)$_2$), 7.15–7.47 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ = 10.7 (CH$_3$), 14.4 (CH$_3$), 19.9 (CH$_2$), 20.1 (J = 4.7 Hz, CH$_3$), 21.7 (CH$_2$), 22.4 (J = 5.0 Hz, CH$_2$), 28.9 (J = 7.8 Hz, CH$_2$), 33.6 (J = 5.8 Hz, CH$_2$), 50.3 (J = 5.0 Hz, C), 53.7 (J = 15.2 Hz, CH$_3$), 84.9 (J = 124.9 Hz, C), 125.9 (C), 127.1 (CH), 129.4 (CH), 129.7 (J = 14.6 Hz, C), 134.8 (CH), 140.1 (J = 8.0 Hz, C), 175.5 (J = 7.9 Hz, C). ^{31}P NMR (242.9 MHz): δ = 24.8. HRMS (ESI): m/z calcd for $C_{22}H_{34}O_5PS$ $[M+H]^+$ 441.5421, found 441.5445. Anal. Calcd for $C_{22}H_{33}O_5PS$: C 59.98, H 7.55. Found: C 59.92, H 7.62%.

Ethyl 2-(4-bromo-2-methoxy-5-methyl-2-oxo-3-phenyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-2-ethyl-butanoate 2k

Pale yellow oil, yield: 46%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.74; IR (neat, cm^{-1}): 1019 (C-O-P), 1257 (P = O), 1444, 1491 (Ph), 1586 (C = C), 1728 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.92 (t, J = 6.8 Hz, 6H, MeCH$_2$), 1.22 (t, J = 7.0 Hz, 3H, MeCH$_2$O), 1.74 (s, 3H, MeC), 1.63–1.80 (m, 4H, MeCH$_2$), 3.71 (d, J = 11.4 Hz, 3H, MeO), 4.00–4.09 (m, 2H, MeCH$_2$O), 7.38–7.88 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ = 10.2 (CH$_3$), 13.8 (CH$_3$), 19.1 (J = 4.6 Hz, CH$_2$), 21.1 (J = 4.6 Hz, CH$_2$), 22.6 (J = 8.1 Hz, CH$_3$), 51.4 (J = 8.0 Hz, C), 52.9 (J = 15.0 Hz, CH$_3$), 61.2 (CH$_2$), 95.1 (J = 9.9 Hz, C), 125.2 (J = 9.4 Hz, CH), 128.7 (J = 153.9 Hz, C), 129.6 (J = 4.8 Hz, C), 130.4 (J = 5.0 Hz, CH), 130.8 (CH), 140.5 (J = 48.8 Hz, C), 174.9 (J = 4.6 Hz, C). ^{31}P NMR (242.9 MHz): δ = 27.0. HRMS (ESI): m/z calcd for $C_{19}H_{27}BrO_5P$ $[M+H]^+$ 446.2924, found 446.2908. Anal. Calcd for $C_{19}H_{26}BrO_5P$: C 51.25, H 5.89. Found: C 51.31, H 5.93%.

Dimethyl (3-bromo-5,5-diethyl-4-methyl-6-oxo-2-phenyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3k

Yellow oil, yield: 30%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.43; IR (neat, cm^{-1}): 1122 (C–O–C), 1263 (P = O), 1440, 1494 (Ph), 1618 (C = C), 1750 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.79 (t, J = 7.5 Hz, 6H, MeCH$_2$), 1.40–1.69 (m, 2H, MeCH$_2$), 2.09 (s, 3H, Me-C=), 3.81 (d, J = 10.5 Hz, 6H, MeO), 7.47–7.85 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ = 10.7 (CH$_3$), 16.9 (CH$_3$), 18.3 (CH$_2$), 20.4 (CH$_2$), 48.6 (J = 4.6 Hz, C), 53.9 (J = 5.1 Hz, CH$_3$), 86.6 (J = 126.8 Hz, C), 114.8 (J = 48.7 Hz, C), 122.9 (J = 7.8 Hz, CH), 127.9 (J = 5.0 Hz, CH), 131.9 (CH), 135.3 (J = 10.1 Hz, C), 143.7 (J = 8.0 Hz, C), 171.4 (J = 5.9 Hz, C). ^{31}P NMR (242.9 MHz): δ = 24.1. HRMS (ESI): m/z calcd for $C_{18}H_{25}BrO_5P$ $[M+H]^+$ 432.2659, found 432.2644. Anal. Calcd for $C_{18}H_{24}BrO_5P$: C 50.13, H 5.61. Found: C 50.20, H 5.57%.

Ethyl 2-ethyl-2-(2-methoxy-5-methyl-2-oxo-3-phenyl-4-phenylsulfenyl-2,5-dihydro-1,2-oxaphosphol-5-yl)-butanoate 2l

Yellow oil, yield: 43%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.75; IR (neat, cm^{-1}): 1021 (C-O-P), 1254 (P = O), 1441, 1492 (Ph), 1583 (C = C), 1730 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.92 (t, J = 6.9 Hz, 6H, MeCH$_2$), 1.20 (t, J = 7.1 Hz, 3H, MeCH$_2$O), 1.65 (s, 3H, MeC), 1.80–2.01 (m, 4H, MeCH$_2$), 3.69 (d, J = 11.4 Hz, 3H, MeO), 4.07–4.11 (m, 2H, MeCH$_2$O), 7.16–7.79 (m, 10H, Ph). ^{13}C NMR (150.9 MHz): δ = 10.3 (CH$_3$), 14.4 (CH$_3$), 20.4 (J = 5.1 Hz, CH$_2$), 22.5 (J = 5.0 Hz, CH$_2$), 25.4 (J = 7.8 Hz, CH$_3$), 53.2 (J = 15.0 Hz, CH$_3$), 53.7 (J = 7.7 Hz, C), 61.3 (CH$_2$), 93.2 (J = 10.1 Hz, C), 125.4 (J = 7.7 Hz, CH), 125.9 (CH), 127.0 (CH), 128.9 (J = 100.1 Hz, C), 129.1 (J = 4.6 Hz, CH), 129.9 (CH), 130.0 (J = 9.7 Hz, C), 130.2 (CH), 139.1 (J = 5.0 Hz, C), 161.0 (J = 4.7 Hz, C), 177.3 (J = 5.0 Hz, C). ^{31}P NMR (242.9 MHz): δ = 27.7. HRMS (ESI): m/z calcd for $C_{25}H_{32}O_5PS$ $[M+H]^+$ 475.5583, found 475.5597. Anal. Calcd for $C_{25}H_{31}O_5PS$: C 63.27, H 6.58. Found: C 63.19, H 6.66%.

Dimethyl (5,5-diethyl-4-methyl-6-oxo-2-phenyl-3-phenylsulfenyl-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3l

Yellow oil, yield: 29%. Eluent for TLC: ethyl acetate:hexane = 1:2, R_f 0.41; IR (neat, cm^{-1}): 1119 (C–O–C), 1266 (P = O), 1439, 1490 (Ph), 1622 (C = C), 1752 (C = O). ^{1}H NMR (600.1 MHz): δ = 0.80 (t, J = 7.5 Hz, 6H, MeCH$_2$), 1.60–1.86 (m, 2H, MeCH$_2$), 1.98 (s, 3H, Me-C=), 3.89 (d, J = 10.4 Hz, 6H, MeO), 7.13–7.75 (m, 10H, Ph). ^{13}C NMR (150.9 MHz): δ = 11.0 (CH$_3$), 19.7 (CH$_2$), 20.7 (J = 4.7 Hz, CH$_3$), 21.9 (CH), 49.9 (J = 4.8 Hz, C), 54.1 (J = 5.0 Hz, CH$_3$), 84.9 (J = 126.6 Hz, C), 125.3 (CH), 126.7 (J = 4.6 Hz, CH), 127.0 (CH), 127.5 (J = 14.6 Hz, C), 129.9 (J = 7.8 Hz, CH), 130.0 (CH), 131.3 (CH), 135.6 (J = 5.0 Hz, C), 135.7 (J = 9.9 Hz, C), 141.7 (J = 9.8 Hz, C), 174.3 (J = 4.8 Hz, C). ^{31}P NMR (242.9 MHz): δ = 25.5. HRMS (ESI): m/z calcd for $C_{24}H_{30}O_5PS$ $[M+H]^+$ 461.5318, found 461.5326. Anal. Calcd for $C_{24}H_{29}O_5PS$: C 62.59, H 6.35. Found: C 62.64, H 6.42%.

Procedure for the synthesis of the (6E)- and (6Z)-benzylidene-3,3,4-trimethyl-5-methylsulfenyl-3,6-dihydro-2H-pyran-2-one 4 by the Horner-Wadsworth-Emmons reaction of the dimethyl (4,5,5-trimethyl-3-methylsulfenyl-6-oxo-5,6-dihydro-2H-pyran-2-yl)-phosphonate 3a

To a suspension of sodium hydride (NaH) (60% dispersion in mineral oil, 2.2 eq. 1.8 mmol) in THF (3 mL) was added a

solution of the dimethyl **3a** (460 mg, 0.8 mmol) in dry THF (3 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. After the addition of a solution of 1.4 eq. PhCHO (1.1 mmol) in 6 mL THF to the mixture, the reaction mixture was heated at 40–50 °C for 120 min (reaction was monitored by TLC). After that the mixture was quenched with 2 N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography on a silica gel using hexane: ethylacetate (4:1) as an eluent to give the pure product **4**, which had the following properties.

(6E)- and (6Z)-benzylidene-3,3,4-trimethyl-5-methylsulfenyl-3,6-dihydro-2H-pyran-2-one 4

Pale yellow oil, yield: 63%. *E*:*Z* = 6.4:1 (87:13). Eluent for TLC: hexane:ethyl acetate = 4:1, R_f 0.49; IR (neat, cm^{-1}): 1112 (C–O–C), 1443, 1487 (Ph), 1602, 1625 (C = C), 1748 (C = O). ^{1}H NMR (600.1 MHz): δ = 1.38 (s, 3H, Me_2C), 1.59 (s, 3H, Me_2C), 1.99 (s, 3H, Me-C = C), 2.25 (s, 3H, MeS), 6.67 (s, 1H, (*E*)-HC = C), 6.17 (s, 1H, (*Z*)-HC = C), 7.17–7.89 (m, 5H, Ph). ^{13}C NMR (150.9 MHz): δ = 15.4 (CH_3), 15.9 (CH_3), 22.8 (CH_3), 25.3 (CH_3), 43.9 (C), 112.6 (*E*)-CH), 114.8 (*Z*)-CH), 126.3 (*E*)-CH), 127.1 (*Z*)-CH), 127.6 (*E*)-CH), 128.3 (*Z*)-CH), 128.8 (Z)-C), 129.7 (E)-C), 130.3 (*E*)-CH), 131.0 (*Z*)-CH), 134.4 (*Z*)-C), 135.1 (*E*)-C), 136.2 (C), 152.4 (C), 175.0 (C). HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_2S$ $[M+H]^+$ 275.3869, found 275.3895. Anal. Calcd for $C_{16}H_{18}O_2S$: C 70.04, H 6.61. Found: C 69.86, H 6.43%.

Conclusions

In conclusion, the reaction of the 5-(dimethoxyphosphoryl)-alka-3,4-dienoates with electrophilic reagents occur *via* competitive 5-*endo-trig* and 6-*endo-trig* cyclization giving mixtures of the 2,5-dihydro-1,2-oxaphosphol-2-ones and the 5,6-dihydro-2*H*-pyran-6-ones because of the participation of the phosphonate and carboxylate neighboring group in the cyclizations. Due to the easy availability of the starting materials, the convenient operation and mild conditions, the good yields and the usefulness of the heterocyclic compounds prepared, the cyclization reactions may show potential and will be useful in organic synthesis as well as in their application in target-oriented synthesis. Further investigation on the chemistry of other bifunctionalized allenes for the synthesis of different heterocyclic systems is being intensively carried out in our laboratory. Moreover, results of an initial investigation of the biological activity of the compounds prepared were encouraging, and the antibacterial and antifungal activities of selected compounds as well as potential precursors of effective anticancer drugs are now under investigation in our university and the results will be reported in due course.

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