

# Bifunctionalized Allenes, Part XI: Competitive Electrophilic Cyclization and Addition Reactions of 4-Phosphorylated Allenecarboxylates

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*Received 18 June 2013; revised 20 October 2013*

**ABSTRACT:** *The reaction of the 4-phosphorylated allenecarboxylates with different electrophilic reagents such as sulfur chloride, bromine, benzenesulfanyl, and benzeneselenanyl chlorides takes place with a 5-endo-trig cyclization or 2,3-addition reaction depending on the kind of the substituents in the phosphoryl group. Treatment of the 4-(dimethoxyphosphoryl)-allenoates with electrophiles gives a mixture of 2,5-dihydro-1,2-oxaphospholes and furan-2(5H)-ones in the ratio of about 1.7:1 as a result of the neighboring group participation of phosphonate and carboxylate groups in the cyclization. On the other hand, (3E)-4-(diphenylphosphoryl)-alk-3-enoates were prepared, in moderate yields, by chemo-, regio-, and stereoselective electrophilic addition to the C<sup>2</sup>–C<sup>3</sup>-double bond in the allenoate moiety. A possible mechanism involving cyclization and addition reactions of the 4-phosphorylated allenecarboxylates was proposed. © 2013 Wiley Periodicals, Inc. Heteroatom*

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Dedicated to Professor Toru Minami from Kyushu Institute of Technology, Kitakyushu, Japan, on the occasion of his 75th anniversary.

Contract grant sponsor: Research Fund of the Konstantin Preslavsky University of Shumen.

Contract grant number: RD-08-243/2013.

Contract grant sponsor: National Research Fund of Bulgaria.

Contract grant number: DRNF-02-13/2009.

Contract grant sponsor: Human Resources Development Operational Programme of the European Union.

Contract grant number: BG051PO001-3.3.06-0003/2012.

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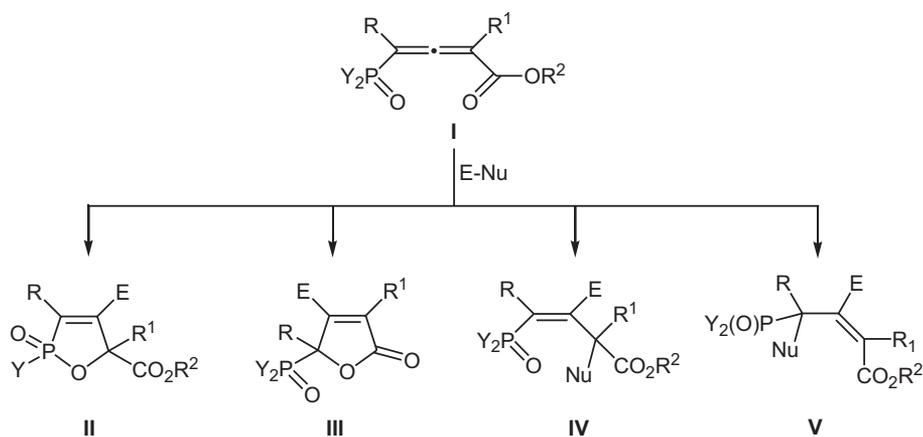
Chem. 25:60–71, 2014; View this article online at [wileyonlinelibrary.com](http://wileyonlinelibrary.com). DOI 10.1002/hc.21136

## INTRODUCTION

In the past four decades, synthesis and use of allene derivatives have been expanded in preparative organic chemistry. The presence of two  $\pi$  electron clouds separated by a single sp hybridized carbon atom is the identifying structural characteristic of allenes, and it is this unique structural and electronic arrangement that is responsible for the extraordinary reactivity profile displayed by allenic compounds [1].

Functionalized allenes have attracted a growing attention because of their versatility as key building blocks for organic synthesis. The synthetic potential of functionalized allenes has been explored extensively in recent years, and this has led to the development of novel methods for the construction of a variety of functionalized heterocyclic and carbocyclic systems [2]. An impressive number of heterocyclic systems have been prepared from allenic starting materials.

On the other hand, one of the characteristic reactions of the allenes is the electrophilic addition reactions in which the addition products of the reagent to the one and/or other double bond of the allenic system are usually obtained [3]. Functionalized allenes are very interesting substrates as a material of



SCHEME 1

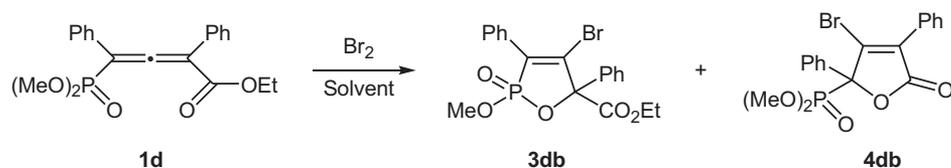
choice to study the electrophilic addition reactions on the carbon-carbon double bonds [4–6]. Unlike the allenic hydrocarbons, the presence of a functional group linked to the allenic system considerably changes the course of the reactions with electrophilic reagents. It has been shown [4–6] that the reactions proceeded with cyclization of the allenic system bearing a functional group to give heterocyclic compounds in most of cases. It makes the investigations on the functionalized allenes, more specifically in studying their reactions with electrophilic reagents, quite an interesting and topical task.

Furan-2(5*H*)-ones ( $\gamma$ -lactones) are important intermediates in organic synthesis due to the presence of the conjugated C=C bond as well as the five-membered lactone ring. Much attention has been paid to the development of efficient and diverse synthetic methods for construction of this five-membered ring system [7]. Among these, cyclization involving allenecarboxylic acids and their derivatives, the so-called lactonization reaction, is one of the most efficient pathways [8].  $\alpha$ -Allenecarboxylic acids and their esters, disubstituted on the  $\gamma$ -carbon atom, underwent electrophilic attack on the central atom and ring closure to furan-2(5*H*)-ones ( $\gamma$ -lactones) when treated with electrophile [8].

On the other hand, literature data on the reactions of phosphorylated allenes (phosphonates, phosphinates, and phosphine oxides) with electrophilic reagents show 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 [4–6]. Thus, the reaction of electrophilic reagents with dialkyl allenephosphonates [4–6] or allenyl phosphine oxides [9–11]

leads to 2,5-dihydro-1,2-oxaphospholes or/and 2,1- or/and 2,3-adducts or a mixture of them, depending on the degree of substitution at the C1 and C3 atoms of the allenic system, the nature of these substituents, and the type of the reagents. Recently, it was also observed by Ma and co-workers [12–14] that the electrophilic iodohydroxylation [12], fluorohydroxylation [13], and selenohydroxylation [14] reactions of allenyl phosphine oxides with iodine, Selectfluor, and benzeneselenyl chloride, affording 2-iodo(respectively, 2-fluoro or 2-phenylselenyl)-3-hydroxy-1(*E*)-alkenyl phosphine oxides with high regio- and stereoselectivities, which the authors [12–14] believed to be determined by the neighboring group participation effect of the diphenyl phosphine oxide functionality. More recently, we have reported the reactions of 1-vinyl- [15a] and 3-vinylallenyl [15b] phosphine oxides with electrophiles leading to formation of various heterocyclic or highly unsaturated compounds.

As a part of our long-standing studies directed toward the development of efficient electrophilic cyclization reactions of 1,1-bifunctionalized allenes [16], we became interested in 1,3-bifunctionalized allenes comprising a phosphoryl and an ester groups such as I (Scheme 1). Of particular interest are the applications of these groups as temporary transformers of chemical reactivity of the allenic system in the synthesis of eventually heterocyclic compounds. This molecule can be considered as a combination of an allenecarboxylate and an allenephosphonate or allenyl phosphine oxide and might have different reactivity profiles in electrophilic reactions. Recently, we presented a convenient and efficient method for regioselective synthesis of 4-phosphorylated allenecarboxylates, derived by an atom economical [2,3]-sigmatropic rearrangement of the mediated alkoxy-carbonyl-functionalized



## SCHEME 2

propargyl phosphites or phosphinites formed by a reaction of the alkyl 2-hydroxy-alk-3-ynoates with dimethylchlorophosphite or diphenylchlorophosphine, respectively, in the presence of a base [16i].

## RESULTS AND DISCUSSION

It should be pointed out that conceptually there exist two distinct modes of cyclization of the 4-phosphorylated 2,3-alkadienoates if the electrophilic atom forms a new bond with the central carbon of the allenic system, which seems likely [4–8]. It is evident that these pathways are closely connected with the intramolecular neighboring group participation of the phosphoryl and/or the ester groups as internal nucleophile(s) in the final step of the cyclization. Besides the 5-*endo-trig* cyclizations [17] to the 2,5-dihydro-1,2-oxaphosphole II or to the furan-2(5*H*)-one (butenolide,  $\gamma$ -lactone) III, electrophilic addition might afford the 3,2-adduct IV and/or the 3,4-adduct V (Scheme 1).

This paper is a part of our general synthetic strategy for investigation of the scope and limitations of the electrophilic cyclization reactions of 1,3-bifunctionalized allenes. Herein, we wish to report our recent results of these investigations.

We initiated this study with the electrophilic cyclization reaction of the ethyl 4-(dimethoxyphosphoryl)-2,4-diphenylbuta-2,3-dienoate **1d** with bromine (Scheme 2). We established that the reaction occurs with cyclization by neighboring group participation of the phosphonate and the carboxylate groups with formation of a mixture of the ethyl 4-bromo-2-methoxy-2-oxo-3,5-diphenyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate **3db** and the dimethyl (3-bromo-5-oxo-2,4-diphenyl-2,5-dihydrofuran-2-yl)phosphonate **4db**. We tried to optimize the reaction conditions to get a useful selectivity and the best total yield for the mixture of products by studying the electrophile equivalent, reaction temperature, time, and solvent effect. Note that when the reaction was conducted in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  at room temperature, thin-layer chromatography (TLC) showed that the two reactants still interacted and the reaction was completed within 4 h with the formation of the desired products. It is necessary to carry out this reaction under argon atmosphere since the electrophilic reagents are sensitive to the moisture in air. The desired products **3db** and **4db** were obtained in 50% total yield (see Table 1, entry 1). When the reaction was carried out at reflux, it was complete within 3 h

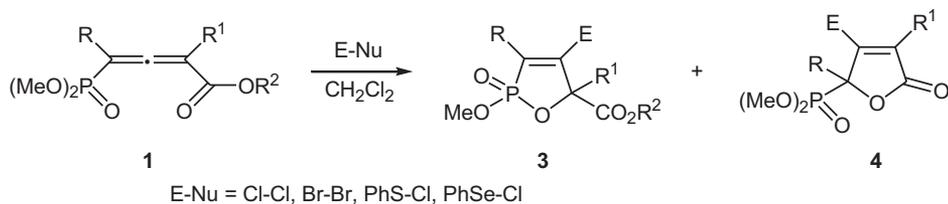
**TABLE 1** Screening of the Reaction Conditions for the Electrophilic Cyclization Reaction of the Ethyl 4-(Dimethoxyphosphoryl)-2,4-diphenylbuta-2,3-dienoate **1d** with Bromine

Entry	Bromine (Equiv.)	Solvent <sup>a</sup>	Reaction Temperature (°C)	Reaction Time (h)	Yield <sup>b</sup> (%)		
					3db	4db	3db:4db
1	1.0	$\text{ClCH}_2\text{CH}_2\text{Cl}$	rt	4	31	19	1.63:1
2	1.5	$\text{ClCH}_2\text{CH}_2\text{Cl}$	Reflux	3	24	15	1.60:1
3	1.5	$\text{ClCH}_2\text{CH}_2\text{Cl}$	-78	5	21	12	1.75:1
4	1.5	$\text{ClCH}_2\text{CH}_2\text{Cl}$	-20	5	20	11	1.81:1
5	1.5	$\text{CHCl}_3$	-20	4	22	13	1.69:1
6	1.2	EtOH	-30	6	18	10	1.80:1
7	1.2	MeCN	-20	8	19	11	1.73:1
8	1.2	$\text{MeNO}_2$	-20	7	17	10	1.70:1
9	1.2	Benzene	rt	8	15	9	1.67:1
10	1.0	$\text{CH}_2\text{Cl}_2$	rt	8	46	25	1.84:1
11	1.2	$\text{CH}_2\text{Cl}_2$	-20	5	50 <sup>c</sup>	28 <sup>c</sup>	1.79:1
12	1.5	$\text{CH}_2\text{Cl}_2$	-20	6	45	24	1.88:1
13	2.0	$\text{CH}_2\text{Cl}_2$	-20	7	39	22	1.77:1

<sup>a</sup>Reaction was carried out in the appropriate solvent (10 mL + 10 mL).

<sup>b</sup>Yields determined by  $^1\text{H}$  and  $^{31}\text{P}$  NMR analysis.

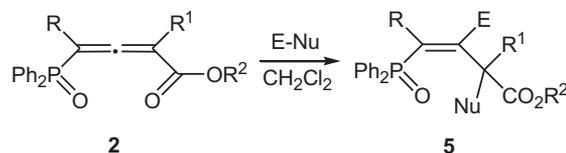
<sup>c</sup>Isolated yields by chromatographical purification on silica gel.



## SCHEME 3

and the yield was considerably lower (39%, entry 2). With 1.5 equiv. of bromine in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  and  $\text{CHCl}_3$ , the yield is lower (entries 3–5). Polar solvents such as ethanol, acetonitrile, and nitromethane gave low yields, even with longer reaction times (6–8 h) and mainly recovered starting materials (entries 6–8, respectively). Similar yield was obtained in benzene as a solvent (entries 9). Fortunately, when dichloromethane was used as a solvent at room temperature and minus temperatures for 5–8 h (entries 10–13), the yield improved to 78% when the temperature was  $-20^\circ\text{C}$  for 5 h (entry 11). It should be noted that temperature of  $-20^\circ\text{C}$  is the best and most convenient: When the temperature is higher or lower, the yield is worse (compare entries 1, 2, 9, and 10 with entries 3 and 6). When 1.2 equiv. of electrophilic reagent were used, the reaction was high yielding (entry 11). We therefore, conducted the remainder of the reactions in dichloromethane at  $-20^\circ\text{C}$  using 1.0 equiv. of the 4-phosphorylated allenates **1a–d** and 1.2 equiv. of the electrophilic reagent for 5 h. The ratio of the products **3db** and **4db** was 1.79:1, and the products were fully characterized by means of NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ), and IR spectroscopy.

Having determined the optimized reaction conditions, we explored the scope of the electrophilic cyclization reaction of the alkyl 4-(dimethoxyphosphoryl)-alka-2,3-dienoates **1a–d** (Scheme 3), and the results that we obtained are summarized in Table 2. It should be noted that



## SCHEME 4

the reaction under this set of standard reaction conditions in the favored 5-*endo-trig* mode affords mixtures of the 5-ethoxycarbonyl-2,5-dihydro-1,2-oxaphospholes **3** and the 5-(dimethoxyphosphoryl)-furan-2(5*H*)-ones **4** in the ratio from 1.59:1 to 1.82:1 as a result of the neighboring group participation of phosphonate and carboxylate groups in the cyclization in good to excellent yields irrespective of the nature of the substituents on the allenic system and the ester group. The reaction scope is wide: R can be propyl, butyl, or phenyl, R<sup>1</sup> can be methyl or phenyl, R<sup>2</sup> can be methyl or ethyl, and E can be Cl, Br, PhS, and PhSe.

To establish the generality of this methodology, the reaction of the 4-(diphenylphosphoryl)-allenecarboxylates **2a–d** with different electrophilic reagents such as sulfuryl chloride, bromine, benzenesulfanyl chloride, and benzeneselenanyl chloride was examined. To our surprise, when we applied the current standard conditions to the 1,3-bifunctionalized allenes comprising a phosphine oxide and alkoxy carbonyl groups such as **2** (Scheme 4), instead of the mixture of the

**TABLE 2** Synthesis of the 5-Ethoxycarbonyl-2,5-dihydro-1,2-oxaphospholes **3** and the 5-(Dimethoxyphosphoryl)-furan-2(5*H*)-ones **4** by Electrophilic Cyclization Reaction of the 4-(Dimethoxyphosphoryl)-allenecarboxylates **1a–d**

Entry	Allene	R	R <sup>1</sup>	R <sup>2</sup>	E	Nu	Time (h)	<b>3</b> , Yield <sup>a</sup> (%)	<b>4</b> , Yield <sup>a</sup> (%)	Ratio
1	<b>1a</b>	Pr	Me	Et	Cl	Cl	3	<b>3aa</b> , 50	<b>4aa</b> , 28	1.79:1
2	<b>1a</b>	Pr	Me	Et	SePh	Cl	5	<b>3ad</b> , 46	<b>4ad</b> , 28	1.64:1
3	<b>1b</b>	Pr	Ph	Me	Br	Br	6	<b>3bb</b> , 45	<b>4bb</b> , 28	1.61:1
4	<b>1b</b>	Pr	Ph	Me	SePh	Cl	4	<b>3bd</b> , 48	<b>4bd</b> , 29	1.66:1
5	<b>1c</b>	Bu	Me	Et	Br	Br	3.5	<b>3cb</b> , 51	<b>4cb</b> , 28	1.82:1
6	<b>1c</b>	Bu	Me	Et	SePh	Cl	5	<b>3cd</b> , 46	<b>4cd</b> , 29	1.59:1
7	<b>1d</b>	Ph	Ph	Et	Cl	Cl	4	<b>3da</b> , 49	<b>4da</b> , 27	1.81:1
8	<b>1d</b>	Ph	Ph	Et	Br	Br	5	<b>3db</b> , 50	<b>4db</b> , 28	1.79:1
9	<b>1d</b>	Ph	Ph	Et	SPh	Cl	9	<b>3dc</b> , 45	<b>4dc</b> , 28	1.61:1
10	<b>1d</b>	Ph	Ph	Et	SePh	Cl	7.5	<b>3dd</b> , 47	<b>4dd</b> , 27	1.74:1

<sup>a</sup>Isolated yields by chromatographical purification on silica gel.

**TABLE 3** Synthesis of the (3*E*)-4-(Diphenylphosphoryl)alk-3-enoates **4** by Electrophilic Addition Reaction of the 4-(Diphenylphosphoryl)-allene-carboxylates **2a–d**

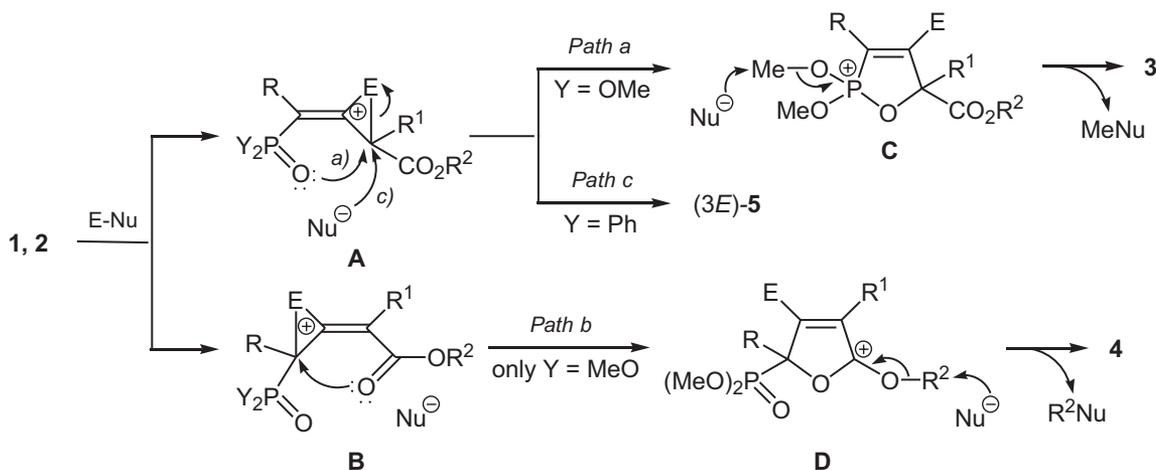
Entry	Allene	R	R <sup>1</sup>	R <sup>2</sup>	E	Nu	Time (h)	<b>5</b> , Yield <sup>a</sup> (%)
1	<b>2a</b>	Bu	Me	Et	Br	Br	4	<b>5ab</b> , 70
2	<b>2a</b>	Bu	Me	Et	SePh	Cl	6	<b>5ad</b> , 64
3	<b>2b</b>	Bu	Ph	Me	Br	Br	5	<b>5bb</b> , 73
4	<b>2b</b>	Bu	Ph	Me	SePh	Cl	7	<b>5bd</b> , 65
5	<b>2c</b>	Ph	Me	Et	Br	Br	6	<b>5cb</b> , 72
6	<b>2c</b>	Ph	Me	Et	SePh	Cl	6.5	<b>5cd</b> , 64
7	<b>2d</b>	Ph	Ph	Et	Cl	Cl	5.5	<b>5da</b> , 69
8	<b>2d</b>	Ph	Ph	Et	Br	Br	7	<b>5db</b> , 71
9	<b>2d</b>	Ph	Ph	Et	SPh	Cl	7.5	<b>5dc</b> , 66
10	<b>2d</b>	Ph	Ph	Et	SePh	Cl	8	<b>5dd</b> , 63

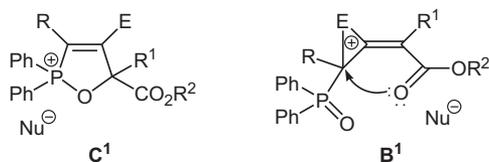
<sup>a</sup>Isolated yields by chromatographical purification on silica gel.

2,5-dihydro-1,2-oxaphospholes **3** and the furan-(5*H*)-ones **4**, the acyclic compounds **5** were isolated in 63–73% yield after stirring for several hours at –20°C and for 1 h to room temperature. The results are summarized in Table 3. Interestingly, this protocol can also be successfully applied to the electrophilic reaction of the 4-(diphenylphosphoryl)-allenoates **2a–d** which afforded the (3*E*)-4-(diphenylphosphoryl)alk-3-enoates **4** highly regio- and stereoselectively, indicating an addition reaction of electrophilic reagent to the C<sup>2</sup>–C<sup>3</sup>-double bond of the allenic system highly chemoselectively.

Thus, on the basis of the literature data [3–6, 8] and our previous results [16], a rationale for this reaction is depicted in Scheme 5. The initial act is the attack of the electrophile (Cl<sup>+</sup>, Br<sup>+</sup>, S<sup>+</sup>, or Se<sup>+</sup>) on the most nucleophilic atom of the allenic system of π bonds (C<sup>3</sup>) with the formation of the cyclic onium (chloronium, bromonium, thiiranium, or se-

leniranium) ion **A** after attack on the relatively more electron-rich C<sup>2</sup>–C<sup>3</sup>-double bond or the ion **B** after attack on the relatively more electron-deficient C<sup>3</sup>–C<sup>4</sup>-double bond. Subsequently, the ions **A** and **B** are easily transformed into the more stable five-membered cyclic ions **C** and **D** via the neighboring group participation of the oxygen atom of the phosphonate (*path a*) and carboxylate functionalities (*path b*), respectively. Furthermore, the intermediates **C** and **D** undergo nucleophilic attacks to MeO or R<sup>2</sup>O groups and elimination of methyl (MeNu) or alkyl halides (R<sup>2</sup>Nu) affording the final cyclic products **3** and **4** (*path a* and *path b*). On the other hand, in the case of 4-(diphenylphosphoryl)-allenoates **2a–d** (Y is Ph) as starting materials, the formation of the final (3*E*)-4-(diphenylphosphoryl)alk-3-enoates **5** can be considered in terms of the assumption for the nucleophilic attack on the cyclic three-membered onium ions **A** (*path c*) leading to the formation of the (3*E*)-2,3-adduct **5**. The stereoselectivity observed may be explained by the favorable *trans* arrangement of the electrophile and the phosphine oxide group and *anti*-attack of the external nucleophile Nu in the onium ions **A** (*path c*). These are presumed to arise from attack on the allenic C<sup>2</sup>–C<sup>3</sup> double bond *anti* to the functional groups, which assisted in the two cyclizations by neighboring groups participation as an internal nucleophiles. On the other hand, a possible explanation of the two types cyclization observed consists of the following. In the first case (Scheme 3), the reason for the predominant participation of the phosphonate group as an internal nucleophile is the higher nucleophilicity of the phosphoryl oxygen in comparison with carboxylic one, which is in connection with the more polarization of the phosphoryl group. In the second case (Scheme 4), this reaction pathway is probably

**SCHEME 5**



SCHEME 6

favorable from an energetic point of view. If the phosphine oxide group takes place as an internal nucleophile in the cyclization, the prepared cyclic compounds should be phosphonium salts [9–11] **C**<sup>1</sup> (Scheme 6), since in this case the stabilization by the elimination of phenyl halide (second stage of an Arbuzov-type rearrangement) and formation of stable products with tetracoordinated phosphorus is impossible. Moreover, the reason for the absence of as the cyclic products as well as the adducts on the C<sup>3</sup>–C<sup>4</sup>-double bond of the allenolate system obviously consists of the fact that the corresponding onium ions **B**<sup>1</sup> (Scheme 6) is not formed in the reaction of the 4-(diphenylphosphoryl)-allenates **2a–d** with electrophiles.

The above-mentioned explanation should be corroborated or refuted from the results on the study of the reactions of other four-functionalized allenecarboxylates with electrophilic reagents and specially their stereochemistry. Further work in this area is being focused on exploiting and extending the synthetic utility of the 1,3-bifunctionalized allenes for the preparation of different heterocyclic systems using the electrophilic cyclization methodology.

## CONCLUSIONS

In conclusion, we have developed a simple and convenient protocol for the reaction of the 4-phosphorylated allenecarboxylates with different electrophilic reagents, which takes place with 5-*endo-trig* cyclization or 2,3-addition reaction depending on the substituents on the phosphoryl group. Treatment of the 4-(dimethoxyphosphoryl)-allenates with electrophiles gives the mixture of 2,5-dihydro-1,2-oxaphospholes and furan-2(5*H*)-ones as a result of the competitive neighboring group participation of phosphonate and carboxylate groups in the cyclization. On the other hand, (3*E*)-4-(diphenylphosphoryl)-alk-3-enoates were prepared by the chemo-, regio, and stereoselective electrophilic addition to the C<sup>2</sup>–C<sup>3</sup>-double bond in the allene moiety. Owing to the easy availability of starting materials, the convenient operation and the usefulness of the 1,2-oxaphosphole and butenolide products, the reaction may show its potential use and will be useful in organic synthesis. Further

studies on the synthetic applications of this reaction and the physiological activity of selected cyclic and acyclic products are now under investigation in our laboratory. Furthermore, a continuation of these studies toward the synthesis and electrophilic cyclization reactions of other bifunctionalized allenes is currently in progress in our laboratory.

## EXPERIMENTAL

### General

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 (Bruker BioSpin, Karlsruhe, Germany) (<sup>1</sup>H at 250.1 MHz, <sup>13</sup>C at 62.9 MHz, <sup>31</sup>P at 101.2 MHz) and Bruker Avance II+600 (Bruker BioSpin GmbH, Karlsruhe, Germany) (<sup>1</sup>H at 600.1 MHz, <sup>13</sup>C at 150.9 MHz, <sup>31</sup>P at 242.9 MHz) spectrometers for solutions in CDCl<sub>3</sub>. Chemical shifts are in parts per million downfield from internal TMS. *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, Sofia, Bulgaria, using Vario EL3 CHNS(O) (Elementar Analysensysteme, Hanau, Germany). Column chromatography was performed on Kieselgel F<sub>254</sub>60 (70–230 mesh ASTM, 0.063–0.200 mm; Merck). The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. 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<sub>254</sub>60 (Merck).

### Starting Materials

Benzenesulfanyl chloride was prepared from diphenyl disulfide and sulfuryl chloride in dichloromethane and distilled in vacuo (bp 80–81°C/20 mmHg) before used [18]. Diphenyl disulfide, sulfuryl chloride, and benzeneselenanyl chloride were commercially available and used without purification.

### General Procedure for the Reactions of the 4-Phosphorylated Allenecarboxylates **1** and **2** with Electrophilic Reagents

To a solution of 4-phosphorylated-2,3-alkadienoates **1** or **2** (3 mmol) in dry dichloromethane (10 mL) at

–20°C, a solution of electrophilic reagent (sulfuryl chloride, bromine, benzenesulfanyl chloride, benzeneselenanyl chloride) (3.6 mmol) was added dropwise with stirring in the same solvent (10 mL). The reaction mixture was stirred at the same temperature for several hours (see Tables 2 and 3) and 1 h at room temperature. The solvent was removed using a rotatory evaporator, and the residue was purified by column chromatography on silica gel (Kieselgel Merck 60 F<sub>254</sub>) with ethyl acetate/hexane. The pure products **3** and **4** had the following properties.

*Ethyl 4-chloro-2-methoxy-5-methyl-2-oxo-3-propyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate (3aa)*. Light orange oil, yield: 0.45 g (1.50 mmol, 50%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.80; IR (neat,  $\text{cm}^{-1}$ ): 1013 (C—O—P), 1258 (P=O), 1434, 1492 (Ph), 1589 (C=C), 1718 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.84 (t,  $J$  7.4 Hz, 3H,  $\text{Me}-(\text{CH}_2)_2$ ), 1.29 (t,  $J$  7.0 Hz, 3H,  $\text{Me}-\text{CH}_2\text{O}$ ), 1.57 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 1.78 (s, 3H, Me), 2.11 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 3.66 (d,  $J$  11.5 Hz, 3H, MeO), 4.16 (m, 2H,  $\text{Me}-\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 14.2 (s,  $\text{CH}_3$ ), 14.9 (d,  $J$  5.0 Hz,  $\text{CH}_3$ ), 20.5 (d,  $J$  7.8 Hz,  $\text{CH}_2$ ), 22.1 (d,  $J$  7.4 Hz,  $\text{CH}_3$ ), 30.8 (d,  $J$  5.6 Hz,  $\text{CH}_2$ ), 50.9 (d,  $J$  7.0 Hz,  $\text{CH}_3$ ), 63.8 ( $\text{CH}_2$ ), 90.4 (d,  $J$  8.9 Hz, C), 130.6 (d,  $J$  98.4 Hz, C), 154.0 (d,  $J$  39.3 Hz, C), 173.7 (d,  $J$  2.8 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 29.8.  $\text{C}_{11}\text{H}_{18}\text{ClO}_5\text{P}$  (296.68). Calcd: C 44.53, H 6.12; found: C 44.46, H 6.06.

*Ethyl 4-benzeneselenanyl-2-methoxy-5-methyl-2-oxo-3-propyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate (3ad)*. Light orange oil, yield: 0.58 g (1.38 mmol, 46%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.79; IR (neat,  $\text{cm}^{-1}$ ): 1012 (C—O—P), 1259 (P=O), 1436, 1483 (Ph), 1585 (C=C), 1719 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.85 (t,  $J$  7.3 Hz, 3H,  $\text{Me}-(\text{CH}_2)_2$ ), 1.22 (t,  $J$  7.2 Hz, 3H,  $\text{Me}-\text{CH}_2\text{O}$ ), 1.50 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 1.77 (s, 3H, Me), 2.32 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 3.85 (d,  $J$  11.6 Hz, 3H, MeO), 4.05 (m, 2H,  $\text{Me}-\text{CH}_2\text{O}$ ), 7.28–7.49 (m, 5H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.9 (s,  $\text{CH}_3$ ), 14.0 (d,  $J$  4.5 Hz,  $\text{CH}_3$ ), 19.9 (d,  $J$  7.7 Hz,  $\text{CH}_2$ ), 20.9 (d,  $J$  7.1 Hz,  $\text{CH}_3$ ), 30.5 (d,  $J$  5.4 Hz,  $\text{CH}_2$ ), 53.9 (d,  $J$  6.9 Hz,  $\text{CH}_3$ ), 62.4 ( $\text{CH}_2$ ), 87.6 (d,  $J$  8.7 Hz, C), 128.4–139.9 (Ph), 131.8 (d,  $J$  106.5 Hz, C), 146.6 (d,  $J$  29.2 Hz, C), 168.2 (d,  $J$  2.9 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 34.4.  $\text{C}_{17}\text{H}_{23}\text{O}_5\text{PSe}$  (417.30). Calcd: C 48.93, H 5.56; found: C 49.02, H 5.52.

*Methyl 4-bromo-2-methoxy-2-oxo-5-phenyl-3-propyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate (3bb)*. Light yellow oil, yield: 0.53 g (1.35 mmol,

45%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.79; IR (neat,  $\text{cm}^{-1}$ ): 1014 (C—O—P), 1260 (P=O), 1441, 1486 (Ph), 1591 (C=C), 1721 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.99 (t,  $J$  7.4 Hz, 3H,  $\text{Me}-(\text{CH}_2)_2$ ), 1.69 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 2.43 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 3.87 (d,  $J$  11.4 Hz, 3H, MeO), 3.89 (s, 3H,  $\text{MeO}-\text{C}(\text{O})$ ), 7.39–7.53 (m, 5H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.9 (d,  $J$  4.3 Hz,  $\text{CH}_3$ ), 20.7 (d,  $J$  2.2 Hz,  $\text{CH}_2$ ), 29.9 (d,  $J$  9.9 Hz,  $\text{CH}_2$ ), 53.6 (d,  $J$  7.4 Hz,  $\text{CH}_3$ ), 54.1 ( $\text{CH}_3$ ), 88.8 (d,  $J$  5.1 Hz, C), 126.8–134.8 (Ph), 131.4 (d,  $J$  152.2 Hz, C), 134.1 (d,  $J$  50.3 Hz, C), 167.2 (d,  $J$  2.6 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 30.1.  $\text{C}_{15}\text{H}_{18}\text{BrO}_5\text{P}$  (389.18). Calcd: C 46.29, H 4.66; found: C 46.21, H 4.60.

*Methyl 4-benzeneselenanyl-2-methoxy-2-oxo-5-phenyl-3-propyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate (3bd)*. Yellow oil, yield: 0.67 g (1.44 mmol, 48%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.75; IR (neat,  $\text{cm}^{-1}$ ): 1013 (C—O—P), 1261 (P=O), 1443, 1493 (Ph), 1588 (C=C), 1720 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.74 (t,  $J$  7.3 Hz, 3H,  $\text{Me}-(\text{CH}_2)_2$ ), 1.36 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 2.18 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 3.83 (d,  $J$  11.8 Hz, 3H, MeO), 3.88 (s, 3H,  $\text{MeO}-\text{C}(\text{O})$ ), 6.96–7.66 (m, 10H, 2Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 14.1 ( $\text{CH}_3$ ), 20.3 (d,  $J$  2.6 Hz,  $\text{CH}_2$ ), 30.5 (d,  $J$  11.7 Hz,  $\text{CH}_2$ ), 53.5 ( $\text{CH}_3$ ), 53.8 (d,  $J$  6.9 Hz,  $\text{CH}_3$ ), 90.3 (d,  $J$  9.7 Hz, C), 126.7–135.9 (2Ph), 134.9 (d,  $J$  145.4 Hz, C), 148.5 (d,  $J$  26.5 Hz, C), 168.7 (d,  $J$  2.9 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 38.5.  $\text{C}_{21}\text{H}_{23}\text{O}_5\text{PSe}$  (465.34). Calcd: C 54.20, H 4.98; found: C 54.28, H 4.92.

*Ethyl 4-bromo-3-butyl-2-methoxy-5-methyl-2-oxo-2,5-dihydro-1,2-oxaphosphole-5-carboxylate (3cb)*. Light yellow oil, yield: 0.54 g (1.53 mmol, 51%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.77; IR (neat,  $\text{cm}^{-1}$ ): 1020 (C—O—P), 1263 (P=O), 1439, 1491 (Ph), 1584 (C=C), 1720 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.87 (t,  $J$  7.2 Hz, 3H,  $\text{Me}-(\text{CH}_2)_3$ ), 1.28 (t,  $J$  7.1 Hz, 3H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 1.32 (m, 4H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 1.91 (s, 3H, Me), 2.18 (m, 2H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 3.76 (d,  $J$  11.4 Hz, 3H, MeO), 4.21 (m, 2H,  $\text{Me}-\text{CH}_2-\text{O}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.5 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ), 21.1 (d,  $J$  4.2 Hz,  $\text{CH}_2$ ), 22.0 (d,  $J$  7.1 Hz,  $\text{CH}_3$ ), 29.1 (d,  $J$  7.1 Hz,  $\text{CH}_2$ ), 29.6 (d,  $J$  5.2 Hz,  $\text{CH}_2$ ), 52.3 (d,  $J$  7.1 Hz,  $\text{CH}_3$ ), 62.4 ( $\text{CH}_2$ ), 87.6 (d,  $J$  11.1 Hz, C), 128.3 (d,  $J$  125.4 Hz, C), 135.2 (d,  $J$  30.1 Hz, C), 174.1 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 29.6.  $\text{C}_{12}\text{H}_{20}\text{BrO}_5\text{P}$  (355.16). Calcd: C 40.58, H 5.68; found: C 40.63, H 5.62.

*Ethyl 4-benzeneselenanyl-3-butyl-2-methoxy-5-methyl-2-oxo-2,5-dihydro-1,2-oxaphosphole-5-carboxylate (3cd)*. Yellow oil, yield: 0.60 g (1.38 mmol,

46%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.73; IR (neat,  $\text{cm}^{-1}$ ): 1020 (C—O—P), 1264 (P=O), 1441, 1485 (Ph), 1590 (C=C), 1722 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.84 (t,  $J$  7.3 Hz, 3H,  $\text{Me}-(\text{CH}_2)_3$ ), 1.23 (t,  $J$  7.1 Hz, 3H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 1.41 (m, 2H,  $\text{Me}-\text{CH}_2-(\text{CH}_2)_2$ ), 1.49 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 1.72 (s, 3H, Me), 2.34 (m, 2H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 3.84 (d,  $J$  11.7 Hz, 3H, MeO), 4.07 (m, 2H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 7.27–7.45 (m, 5H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.7 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_2$ ), 22.7 (d,  $J$  8.1 Hz,  $\text{CH}_3$ ), 28.4 (d,  $J$  6.8 Hz,  $\text{CH}_2$ ), 29.5 (d,  $J$  5.0 Hz,  $\text{CH}_2$ ), 53.7 (d,  $J$  7.0 Hz,  $\text{CH}_3$ ), 62.6 ( $\text{CH}_2$ ), 87.6 (d,  $J$  12.3 Hz, C), 128.1–133.0 (Ph), 135.8 (d,  $J$  119.4 Hz, C), 146.5 (d,  $J$  27.6 Hz, C), 168.2 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 36.5.  $\text{C}_{18}\text{H}_{25}\text{O}_5\text{PSe}$  (431.32). Calcd: C 50.12, H 5.84; found: C 50.20, H 5.77.

*Ethyl 4-chloro-2-methoxy-2-oxo-3,5-diphenyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate* (**3da**). Light yellow oil, yield: 0.58 g (1.47 mmol, 49%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.76; IR (neat,  $\text{cm}^{-1}$ ): 1015 (C—O—P), 1259 (P=O), 1438, 1485 (Ph), 1586 (C=C), 1724 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz,  $\delta$ ): 1.39 (t,  $J$  7.1 Hz, 3H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 3.86 (d,  $J$  12.0 Hz, 3H, MeO), 4.34–4.45 (m, 2H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 7.41–7.83 (m, 10H, 2Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz,  $\delta$ ): 14.0 ( $\text{CH}_3$ ), 54.6 (d,  $J$  6.9 Hz,  $\text{CH}_3$ ), 63.3 ( $\text{CH}_2$ ), 78.8 (d,  $J$  13.9 Hz, C), 125.3 (d,  $J$  122.4 Hz, C), 127.2–129.9 (2Ph), 146.5 (d,  $J$  30.5 Hz, C), 166.9 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 101.2 MHz,  $\delta$ ): 31.9.  $\text{C}_{19}\text{H}_{18}\text{ClO}_5\text{P}$  (392.77). Calcd: C 58.10, H 4.62; found: C 58.03, H 4.70.

*Ethyl 4-bromo-2-methoxy-2-oxo-3,5-diphenyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate* (**3db**). Light yellow oil, yield: 0.66 g (1.5 mmol, 50%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.79; IR (neat,  $\text{cm}^{-1}$ ): 1012 (C—O—P), 1261 (P=O), 1439, 1490 (Ph), 1592 (C=C), 1724 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz,  $\delta$ ): 1.38 (t,  $J$  7.0 Hz, 3H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 3.85 (d,  $J$  11.8 Hz, 3H, MeO), 4.39–4.49 (m, 2H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 7.42–7.83 (m, 10H, 2Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz,  $\delta$ ): 13.9 ( $\text{CH}_3$ ), 54.5 (d,  $J$  6.8 Hz,  $\text{CH}_3$ ), 63.2 ( $\text{CH}_2$ ), 82.8 (d,  $J$  14.0 Hz, C), 127.1–129.7 (2Ph), 127.3 (d,  $J$  32.4 Hz, C), 128.6 (d,  $J$  117.1 Hz, C), 166.4 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 101.2 MHz,  $\delta$ ): 32.3.  $\text{C}_{19}\text{H}_{18}\text{BrO}_5\text{P}$  (437.22). Calcd: C 52.19, H 4.15; found: C 52.23, H 4.22.

*Ethyl 4-benzenesulfanyl-2-methoxy-2-oxo-3,5-diphenyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate* (**3dc**). Light orange oil, yield: 0.63 g (1.35 mmol, 45%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.77; IR (neat,  $\text{cm}^{-1}$ ): 1017 (C—O—P), 1257

(P=O), 1433, 1491 (Ph), 1594 (C=C), 1722 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 1.39 (t,  $J$  7.1 Hz, 3H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 3.75 (d,  $J$  12.2 Hz, 3H, MeO), 4.43 (m, 2H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 6.51–7.77 (m, 15H, 3Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 14.2 ( $\text{CH}_3$ ), 54.3 (d,  $J$  6.9 Hz,  $\text{CH}_3$ ), 63.1 ( $\text{CH}_2$ ), 89.9 (d,  $J$  7.7 Hz, C), 126.1–131.6 (3Ph), 131.4 (d,  $J$  114.3 Hz, C), 152.2 (d,  $J$  29.3 Hz, C), 167.8 (d,  $J$  3.1 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 36.4.  $\text{C}_{25}\text{H}_{23}\text{O}_5\text{PS}$  (466.49). Calcd: C 64.37, H 4.97; found: C 64.44, H 5.02.

*Ethyl 4-benzeneselenanyl-2-methoxy-2-oxo-3,5-diphenyl-2,5-dihydro-1,2-oxaphosphole-5-carboxylate* (**3dd**). Colourless oil, yield: 0.72 g (1.41 mmol, 47%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.75; IR (neat,  $\text{cm}^{-1}$ ): 1021 (C—O—P), 1262 (P=O), 1438, 1495 (Ph), 1589 (C=C), 1723 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 1.41 (t,  $J$  7.2 Hz, 3H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 3.71 (d,  $J$  12.1 Hz, 3H, MeO), 4.46 (m, 2H,  $\text{Me}-\text{CH}_2-\text{O}$ ), 6.59–7.72 (m, 15H, 3Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 14.5 ( $\text{CH}_3$ ), 54.5 (d,  $J$  6.8 Hz,  $\text{CH}_3$ ), 63.1 ( $\text{CH}_2$ ), 126.5–133.7 (3Ph), 126.7 (d,  $J$  105.6 Hz, C), 136.1 (d,  $J$  7.4 Hz, C), 151.0 (d,  $J$  25.6 Hz, C), 168.0 (d,  $J$  2.6 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 35.3.  $\text{C}_{25}\text{H}_{23}\text{O}_5\text{PSe}$  (513.38). Calcd: C 58.49, H 4.52; found: C 58.40, H 4.59.

*Dimethyl (3-chloro-4-methyl-5-oxo-2-propyl-2,5-dihydrofuran-2-yl)phosphonate* (**4aa**). Light yellow oil, yield: 0.24 g (0.84 mmol, 28%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.46; IR (neat,  $\text{cm}^{-1}$ ): 1124 (C—O—C), 1246 (P=O), 1437, 1494 (Ph), 1619 (C=C), 1751 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 1.18 (t,  $J$  7.1 Hz, 3H,  $\text{Me}-(\text{CH}_2)_2$ ), 1.72 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 2.17 (s, 3H, Me), 2.32 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 3.82 (d,  $J$  10.3 Hz, 6H, 2MeO).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 15.2 (d,  $J$  4.9 Hz,  $\text{CH}_3$ ), 15.5 (d,  $J$  4.7 Hz,  $\text{CH}_3$ ), 19.4 (d,  $J$  7.7 Hz,  $\text{CH}_2$ ), 35.3 (d,  $J$  5.7 Hz,  $\text{CH}_2$ ), 52.8 (d,  $J$  14.7 Hz,  $\text{CH}_3$ ), 99.9 (d,  $J$  126.4 Hz, C), 131.8 (d,  $J$  8.0 Hz, C), 159.4 (d,  $J$  40.1 Hz, C), 171.8 (d,  $J$  7.4 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 17.8.  $\text{C}_{10}\text{H}_{16}\text{ClO}_5\text{P}$  (282.66). Calcd: C 42.49, H 5.71; found: C 42.58, H 5.66.

*Dimethyl (3-benzeneselenanyl-4-methyl-5-oxo-2-propyl-2,5-dihydrofuran-2-yl)phosphonate* (**4ad**). Yellow oil, yield: 0.34 g (0.84 mmol, 28%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.44; IR (neat,  $\text{cm}^{-1}$ ): 1123 (C—O—C), 1245 (P=O), 1441, 1477 (Ph), 1622 (C=C), 1748 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.96 (t,  $J$  7.3 Hz, 3H,  $\text{Me}-(\text{CH}_2)_2$ ), 1.58 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 2.12 (s, 3H, Me), 2.38 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2$ ), 3.84 (d,  $J$  10.2 Hz, 6H, 2MeO), 7.38–7.57 (m, 5H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.0 (d,  $J$  5.2 Hz,  $\text{CH}_3$ ), 14.2 (d,  $J$  4.7 Hz,  $\text{CH}_3$ ),

15.8 (d,  $J$  7.4 Hz, CH<sub>2</sub>), 36.0 (d,  $J$  5.3 Hz, CH<sub>2</sub>), 52.8 (d,  $J$  15.2 Hz, CH<sub>3</sub>), 102.4 (d,  $J$  127.3 Hz, C), 128.0 (d,  $J$  7.8 Hz, C), 128.6–138.4 (Ph), 174.6 (d,  $J$  7.6 Hz, C), 177.1 (d,  $J$  50.8 Hz, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 242.9 MHz,  $\delta$ ): 20.2. C<sub>16</sub>H<sub>21</sub>O<sub>5</sub>PSe (403.27). Calcd: C 47.65, H 5.25; found: C 47.58, H 5.20.

*Dimethyl (3-bromo-2-oxo-4-phenyl-2-propyl-2,5-dihydrofuran-2-yl)phosphonate (4bb)*. Yellow oil, yield: 0.33 g (0.84 mmol, 28%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.46; IR (neat, cm<sup>-1</sup>): 1122 (C–O–C), 1248 (P=O), 1435, 1493 (Ph), 1616 (C=C), 1752 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600.1 MHz,  $\delta$ ): 1.09 (t,  $J$  7.1 Hz, 3H, Me-(CH<sub>2</sub>)<sub>2</sub>), 1.64 (m, 2H, Me-CH<sub>2</sub>-CH<sub>2</sub>), 2.26 (m, 2H, Me-CH<sub>2</sub>-CH<sub>2</sub>), 3.82 (d,  $J$  10.3 Hz, 6H, 2MeO), 7.45–7.78 (m, 5H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150.9 MHz,  $\delta$ ): 15.9 (d,  $J$  5.1 Hz, CH<sub>3</sub>), 17.8 (d,  $J$  7.2 Hz, CH<sub>2</sub>), 35.2 (d,  $J$  5.4 Hz, CH<sub>2</sub>), 53.1 (d,  $J$  15.0 Hz, CH<sub>3</sub>), 101.7 (d,  $J$  125.8 Hz, C), 126.8–129.0 (Ph), 141.5 (d,  $J$  51.4 Hz, C), 146.7 (d,  $J$  7.3 Hz, C), 170.5 (d,  $J$  7.8 Hz, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 242.9 MHz,  $\delta$ ): 18.2. C<sub>15</sub>H<sub>18</sub>BrO<sub>5</sub>P (389.18). Calcd: C 46.29, H 4.66; found: C 46.37, H 4.72.

*Dimethyl (3-benzeneselenanyl-5-oxo-4-phenyl-2-propyl-2,5-dihydrofuran-2-yl)phosphonate (4bd)*. Light orange oil, yield: 0.40 g (0.87 mmol, 29%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.41; IR (neat, cm<sup>-1</sup>): 1121 (C–O–C), 1246 (P=O), 1440, 1488 (Ph), 1622 (C=C), 1748 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600.1 MHz,  $\delta$ ): 1.14 (t,  $J$  7.4 Hz, 3H, Me-(CH<sub>2</sub>)<sub>2</sub>), 1.61 (m, 2H, Me-CH<sub>2</sub>-CH<sub>2</sub>), 2.35 (m, 2H, Me-CH<sub>2</sub>-CH<sub>2</sub>), 3.83 (d,  $J$  10.7 Hz, 6H, 2MeO), 7.33–7.96 (m, 10H, 2Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150.9 MHz,  $\delta$ ): 14.9 (CH<sub>3</sub>), 16.8 (d,  $J$  7.4 Hz, CH<sub>2</sub>), 34.7 (d,  $J$  5.6 Hz, CH<sub>2</sub>), 52.4 (CH<sub>3</sub>), 103.6 (d,  $J$  127.0 Hz, C), 127.4–138.2 (2Ph), 137.1 (d,  $J$  7.7 Hz, C), 170.4 (d,  $J$  7.9 Hz, C), 177.4 (d,  $J$  52.8 Hz, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 242.9 MHz,  $\delta$ ): 19.8. C<sub>21</sub>H<sub>23</sub>O<sub>5</sub>PSe (465.34). Calcd: C 54.20, H 4.98; found: C 54.13, H 5.02.

*Dimethyl (3-bromo-2-butyl-4-methyl-5-oxo-2,5-dihydrofuran-2-yl)phosphonate (4cb)*. Yellow oil, yield: 0.29 g (0.84 mmol, 28%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.47; IR (neat, cm<sup>-1</sup>): 1118 (C–O–C), 1239 (P=O), 1434, 1487 (Ph), 1621 (C=C), 1751 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600.1 MHz,  $\delta$ ): 0.90 (t,  $J$  7.2 Hz, 3H, Me-(CH<sub>2</sub>)<sub>3</sub>), 1.49 (m, 2H, Me-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>), 1.57 (m, 2H, Me-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 2.29 (s, 3H, Me), 2.48 (m, 2H, Me-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>), 3.83 (d,  $J$  10.8 Hz, 6H, 2MeO). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150.9 MHz,  $\delta$ ): 14.0 (CH<sub>3</sub>), 16.2 (CH<sub>3</sub>), 21.9 (d,  $J$  5.0 Hz, CH<sub>2</sub>), 27.0 (d,  $J$  7.4 Hz, CH<sub>2</sub>), 33.1 (d,  $J$  6.2 Hz, CH<sub>2</sub>), 54.3 (d,  $J$  14.1 Hz, CH<sub>3</sub>), 98.4 (d,  $J$  107.4 Hz, C), 130.2 (d,  $J$  7.8 Hz, C), 146.8 (d,  $J$  50.7 Hz, C), 176.0

(d,  $J$  7.8 Hz, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 242.9 MHz,  $\delta$ ): 18.8. C<sub>11</sub>H<sub>18</sub>BrO<sub>5</sub>P (341.14). Calcd: C 38.73, H 5.32; found: C 38.82, H 5.26.

*Dimethyl (3-benzeneselenanyl-2-butyl-4-methyl-5-oxo-2,5-dihydrofuran-2-yl)phosphonate (4cd)*. Pale yellow oil, yield: 0.36 g (0.87 mmol, 29%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.49; IR (neat, cm<sup>-1</sup>): 1125 (C–O–C), 1242 (P=O), 1436, 1490 (Ph), 1619 (C=C), 1748 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600.1 MHz,  $\delta$ ): 0.89 (t,  $J$  7.3 Hz, 3H, Me-(CH<sub>2</sub>)<sub>3</sub>), 1.46 (m, 2H, Me-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>), 1.51 (m, 2H, Me-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 2.17 (s, 3H, Me), 2.49 (m, 2H, Me-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>), 3.85 (d,  $J$  11.0 Hz, 6H, 2MeO), 7.38–7.51 (m, 5H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150.9 MHz,  $\delta$ ): 14.2 (CH<sub>3</sub>), 16.7 (CH<sub>3</sub>), 22.4 (d,  $J$  4.7 Hz, CH<sub>2</sub>), 26.1 (d,  $J$  7.2 Hz, CH<sub>3</sub>), 32.7 (d,  $J$  6.0 Hz, CH<sub>2</sub>), 53.9 (d,  $J$  13.9 Hz, CH<sub>3</sub>), 100.4 (d,  $J$  110.3 Hz, C), 127.4 (d,  $J$  7.7 Hz, C), 128.3–134.01 (Ph), 174.7 (d,  $J$  7.6 Hz, C), 177.6 (d,  $J$  51.2 Hz, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 242.9 MHz,  $\delta$ ): 17.9. C<sub>17</sub>H<sub>23</sub>O<sub>5</sub>PSe (417.30). Calcd: C 48.93, H 5.56; found: C 49.02, H 5.51.

*Dimethyl (3-chloro-5-oxo-2,4-diphenyl-2,5-dihydrofuran-2-yl)phosphonate (4da)*. Colorless oil, yield: 0.31 g (0.81 mmol, 27%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.47; IR (neat, cm<sup>-1</sup>): 1119 (C–O–C), 1243 (P=O), 1438, 1487 (Ph), 1621 (C=C), 1749 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz,  $\delta$ ): 3.71 (d,  $J$  11.2 Hz, 6H, 2MeO), 7.41–7.97 (m, 10H, 2Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz,  $\delta$ ): 53.4 (d,  $J$  15.2 Hz, CH<sub>3</sub>), 95.3 (d,  $J$  105.1 Hz, C), 122.4–131.9 (2Ph), 129.7 (d,  $J$  8.0 Hz, C), 147.5 (d,  $J$  45.2 Hz, C), 171.0 (d,  $J$  7.4 Hz, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 101.2 MHz,  $\delta$ ): 16.5. C<sub>18</sub>H<sub>16</sub>ClO<sub>5</sub>P (378.74). Calcd: C 57.08, H 4.26; found: C 57.13, H 4.22.

*Dimethyl (3-bromo-5-oxo-2,4-diphenyl-2,5-dihydrofuran-2-yl)phosphonate (4db)*. Yellow oil, yield: 0.36 g (0.84 mmol, 28%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.45; IR (neat, cm<sup>-1</sup>): 1121 (C–O–C), 1245 (P=O), 1443, 1492 (Ph), 1620 (C=C), 1752 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz,  $\delta$ ): 3.80 (d,  $J$  10.6 Hz, 6H, 2MeO), 7.45–7.98 (m, 10H, 2Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz,  $\delta$ ): 55.2 (d,  $J$  14.0 Hz, CH<sub>3</sub>), 91.4 (d,  $J$  102.4 Hz, C), 126.4–129.8 (2Ph), 132.0 (d,  $J$  7.7 Hz, C), 147.1 (d,  $J$  49.4 Hz, C), 170.9 (d,  $J$  7.1 Hz, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 101.2 MHz,  $\delta$ ): 14.3. C<sub>18</sub>H<sub>16</sub>BrO<sub>5</sub>P (423.19). Calcd: C 51.09, H 3.81; found: C 51.15, H 3.72.

*Dimethyl (3-benzenesulfanyl-5-oxo-2,4-diphenyl-2,5-dihydrofuran-2-yl)phosphonate (4dc)*. Orange oil, yield: 0.38 g (0.84 mmol, 28%). Eluent for TLC:

ethyl acetate-hexane = 1:1,  $R_f$  0.45; IR (neat,  $\text{cm}^{-1}$ ): 1114 (C–O–C), 1241 (P=O), 1435, 1490 (Ph), 1617 (C=C), 1750 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 3.77 (d,  $J$  10.9 Hz, 6H, 2MeO), 6.62–7.98 (m, 15H, 3Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 54.5 (d,  $J$  11.4 Hz,  $\text{CH}_3$ ), 92.4 (d,  $J$  110.5 Hz, C), 127.0–136.1 (3Ph), 128.7 (d,  $J$  7.1 Hz, C), 168.1 (d,  $J$  50.5 Hz, C), 170.6 (d,  $J$  7.1 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 16.5.  $\text{C}_{24}\text{H}_{21}\text{O}_5\text{PS}$  (452.46). Calcd: C 63.71, H 4.68; found: C 63.63, H 4.74.

*Dimethyl (3-benzeneselanyl-5-oxo-2,4-diphenyl-2,5-dihydrofuran-2-yl)phosphonate (4dd)*. Yellow oil, yield: 0.40 g (0.81 mmol, 27%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.48; IR (neat,  $\text{cm}^{-1}$ ): 1116 (C–O–C), 1244 (P=O), 1436, 1482 (Ph), 1616 (C=C), 1748 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 3.75 (d,  $J$  10.7 Hz, 6H, 2MeO), 6.79–7.93 (m, 15H, 3Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 55.3 (d,  $J$  12.4 Hz,  $\text{CH}_3$ ), 89.4 (d,  $J$  105.0 Hz, C), 126.1–134.4 (3Ph), 131.0 (d,  $J$  6.9 Hz, C), 157.6 (d,  $J$  7.4 Hz, C), 170.5 (d,  $J$  51.5 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 16.5.  $\text{C}_{24}\text{H}_{21}\text{O}_5\text{PSe}$  (499.35). Calcd: C 57.73, H 4.24; found: C 57.81, H 4.19.

*Ethyl (3E)-2,3-dibromo-4-(diphenylphosphoryl)-2-methyl-oct-3-enoate (5ab)*. Light orange oil, yield: 1.14 g (2.10 mmol, 70%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.73; IR (neat,  $\text{cm}^{-1}$ ): 1126 (P=O), 1436, 1493 (Ph), 1593 (C=C), 1719 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.82 (t,  $J$  7.0 Hz, 3H,  $\text{Me}-(\text{CH}_2)_3$ ), 1.21 (t,  $J$  7.1 Hz, 3H,  $\text{Me}-\text{CH}_2\text{O}$ ), 1.27 (m, 4H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 2.16 (m, 2H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 2.38 (s, 3H, Me), 4.13 (m, 2H,  $\text{Me}-\text{CH}_2\text{O}$ ), 7.54–8.05 (m, 10H, 2Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.7 ( $\text{CH}_3$ ), 14.3 ( $\text{CH}_3$ ), 21.7 ( $\text{CH}_2$ ), 30.5 ( $\text{CH}_2$ ), 33.1 (d,  $J$  6.3 Hz,  $\text{CH}_2$ ), 35.3 ( $\text{CH}_3$ ), 52.8 (d,  $J$  7.7 Hz, C), 80.0 ( $\text{CH}_2$ ), 129.3–135.6 (2Ph), 130.5 (d,  $J$  126.8 Hz, C), 138.4 (d,  $J$  30.4 Hz, C), 166.3 (d,  $J$  4.1 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 28.8.  $\text{C}_{23}\text{H}_{27}\text{Br}_2\text{O}_3\text{P}$  (542.24). Calcd: C 50.95, H 5.02; found: C 51.04, H 4.97.

*Ethyl (3E)-3-benzeneselanyl-2-chloro-4-(diphenylphosphoryl)-2-methyl-oct-3-enoate (5ad)*. Orange oil, yield: 1.10 g (1.92 mmol, 64%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.70; IR (neat,  $\text{cm}^{-1}$ ): 1117 (P=O), 1435, 1490 (Ph), 1589 (C=C), 1732 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.76 (t,  $J$  7.4 Hz, 3H,  $\text{Me}-(\text{CH}_2)_3$ ), 1.22 (m, 4H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 1.26 (t,  $J$  7.2 Hz, 3H,  $\text{Me}-\text{CH}_2\text{O}$ ), 1.95 (s, 3H, Me), 2.28 (m, 2H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 4.15 (m, 2H,  $\text{Me}-\text{CH}_2\text{O}$ ), 7.28–7.79 (m, 15H, 3Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 14.3 ( $\text{CH}_3$ ), 14.8 ( $\text{CH}_3$ ), 23.6 ( $\text{CH}_2$ ), 28.0 ( $\text{CH}_3$ ), 29.7 (d,  $J$  7.9 Hz,  $\text{CH}_2$ ), 37.6 (d,  $J$  13.6 Hz,

$\text{CH}_2$ ), 68.4 ( $\text{CH}_2$ ), 81.6 (d,  $J$  6.1 Hz, C), 128.9–139.5 (3Ph), 129.7 (d,  $J$  92.2 Hz, C), 147.0 (d,  $J$  34.8 Hz, C), 178.8 (d,  $J$  4.6 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 26.3.  $\text{C}_{29}\text{H}_{32}\text{ClO}_3\text{PSe}$  (573.95). Calcd: C 60.69, H 5.62; found: C 60.75, H 5.66.

*Methyl (3E)-2,3-dibromo-4-(diphenylphosphoryl)-2-phenyloct-3-enoate (5bb)*. Colorless oil, yield: 1.29 g (2.19 mmol, 73%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.79; IR (neat,  $\text{cm}^{-1}$ ): 1134 (P=O), 1440, 1488 (Ph), 1591 (C=C), 1724 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.75 (t,  $J$  7.0 Hz, 3H,  $\text{Me}-(\text{CH}_2)_3$ ), 1.25 (m, 4H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 2.17 (m, 2H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 3.73 (s, 3H, MeO), 7.42–8.08 (m, 15H, 3Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.4 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_2$ ), 28.1 ( $\text{CH}_2$ ), 38.2 (d,  $J$  11.7 Hz,  $\text{CH}_2$ ), 52.9 ( $\text{CH}_3$ ), 84.4 (d,  $J$  6.9 Hz, C), 127.4–142.7 (3Ph), 133.4 (d,  $J$  125.4 Hz, C), 137.0 (d,  $J$  29.3 Hz, C), 169.1 (d,  $J$  4.2 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 27.6.  $\text{C}_{27}\text{H}_{27}\text{Br}_2\text{O}_3\text{P}$  (590.28). Calcd: C 54.94, H 4.61; found: C 55.02, H 4.55.

*Methyl (3E)-3-benzeneselanyl-2-chloro-4-(diphenylphosphoryl)-2-phenyl-oct-3-enoate (5bd)*. Yellow oil, yield: 1.21 g (1.95 mmol, 65%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.74; IR (neat,  $\text{cm}^{-1}$ ): 1130 (P=O), 1436, 1494 (Ph), 1585 (C=C), 1732 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.79 (t,  $J$  7.2 Hz, 3H,  $\text{Me}-(\text{CH}_2)_3$ ), 1.18 (m, 2H,  $\text{Me}-\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 1.27 (m, 2H,  $\text{Me}-\text{CH}_2-(\text{CH}_2)_2$ ), 2.32 (m, 2H,  $\text{Me}-(\text{CH}_2)_2-\text{CH}_2$ ), 3.76 (s, 3H, MeO), 7.26–7.75 (m, 20H, 4Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.9 ( $\text{CH}_3$ ), 22.1 ( $\text{CH}_2$ ), 24.7 ( $\text{CH}_2$ ), 42.4 (d,  $J$  11.4 Hz,  $\text{CH}_2$ ), 52.4 ( $\text{CH}_3$ ), 92.1 (d,  $J$  7.1 Hz, C), 125.5–139.7 (4Ph), 134.2 (d,  $J$  112.8 Hz, C), 144.7 (d,  $J$  26.7 Hz, C), 169.4 (d,  $J$  4.0 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 26.8.  $\text{C}_{33}\text{H}_{32}\text{ClO}_3\text{PSe}$  (621.99). Calcd: C 63.73, H 5.19; found: C 63.80, H 5.12.

*Ethyl (3E)-2,3-dibromo-4-(diphenylphosphoryl)-2-methyl-4-phenylbut-3-enoate (5cb)*. Yellow oil, yield: 1.21 g (2.16 mmol, 72%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.78; IR (neat,  $\text{cm}^{-1}$ ): 1164 (P=O), 1432, 1485 (Ph), 1587 (C=C), 1719 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 1.20 (t,  $J$  7.1 Hz, 3H,  $\text{Me}-\text{CH}_2\text{O}$ ), 2.39 (s, 3H, Me), 4.14 (m, 2H,  $\text{Me}-\text{CH}_2\text{O}$ ), 7.40–8.06 (m, 15H, 3Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 14.0 ( $\text{CH}_3$ ), 35.1 ( $\text{CH}_3$ ), 55.6 (d,  $J$  7.5 Hz, C), 61.3 ( $\text{CH}_2$ ), 129.1–135.7 (3Ph), 134.1 (d,  $J$  128.4 Hz, C), 139.8 (d,  $J$  31.7 Hz, C), 167.2 (d,  $J$  3.9 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 26.2.  $\text{C}_{25}\text{H}_{23}\text{Br}_2\text{O}_3\text{P}$  (562.23). Calcd: C 53.41, H 4.12; found: C 53.50, H 4.05.

*Ethyl (3E)-3-benzenesulfonyl-2-chloro-4-(diphenylphosphoryl)-2-methyl-4-phenyl-but-3-enoate (5cd)*. Yellow oil, yield: 1.14 g (1.92 mmol, 64%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.73; IR (neat,  $\text{cm}^{-1}$ ): 1161 (P=O), 1439, 1477 (Ph), 1589 (C=C), 1732 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 1.18 (t,  $J$  7.0 Hz, 3H,  $\text{Me-CH}_2\text{O}$ ), 1.97 (s, 3H, Me), 4.17 (m, 2H,  $\text{Me-CH}_2\text{O}$ ), 7.27–8.10 (m, 20H, 4Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.7 ( $\text{CH}_3$ ), 25.2 ( $\text{CH}_3$ ), 61.3 ( $\text{CH}_2$ ), 81.4 (d,  $J$  7.3 Hz, C), 128.4–142.7 (4Ph), 131.9 (d,  $J$  96.4 Hz, C), 154.0 (d,  $J$  29.7 Hz, C), 180.4 (d,  $J$  4.1 Hz, C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 27.2.  $\text{C}_{31}\text{H}_{28}\text{ClO}_3\text{PSe}$  (593.94). Calcd: C 62.69, H 4.75; found: C 62.76, H 4.80.

*Ethyl (3E)-2,3-dichloro-4-(diphenylphosphoryl)-2,4-diphenylbut-3-enoate (5da)*. Colorless oil, yield: 1.11 g [2.07 mmol, 69%]. Eluent for TLC: ethyl acetate:hexane = 1:1,  $R_f$  0.78; IR (neat,  $\text{cm}^{-1}$ ): 1136 (P=O), 1439, 1483 (Ph), 1596 (C=C), 1727 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz,  $\delta$ ): 1.35 (t,  $J$  7.0 Hz, 3H,  $\text{Me-CH}_2\text{O}$ ), 4.35 (m, 2H,  $\text{Me-CH}_2\text{O}$ ), 7.03–7.69 (m, 20H, 4Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz,  $\delta$ ): 14.1 ( $\text{CH}_3$ ), 62.3 ( $\text{CH}_2$ ), 65.0 (d,  $J$  7.2 Hz, C), 127.5–133.2 (4Ph), 137.1 (d,  $J$  28.6 Hz, C), 140.1 (d,  $J$  122.4 Hz, C), 171.2 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 101.2 MHz,  $\delta$ ): 24.3.  $\text{C}_{30}\text{H}_{25}\text{Cl}_2\text{O}_3\text{P}$  (535.40). Calcd: C 67.30, H 4.71; found: C 67.23, H 4.77.

*Ethyl (3E)-2,3-dibromo-4-(diphenylphosphoryl)-2,4-diphenylbut-3-enoate (5db)*. Orange oil, yield: 1.33 g (2.13 mmol, 71%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.76; IR (neat,  $\text{cm}^{-1}$ ): 1131 (P=O), 1442, 1481 (Ph), 1598 (C=C), 1731 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz,  $\delta$ ): 1.25 (t,  $J$  7.1 Hz, 3H,  $\text{Me-CH}_2\text{O}$ ), 4.30 (m, 2H,  $\text{Me-CH}_2\text{O}$ ), 7.06–7.99 (m, 20H, 4Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz,  $\delta$ ): 14.6 ( $\text{CH}_3$ ), 62.9 ( $\text{CH}_2$ ), 63.8 (d,  $J$  7.4 Hz, C), 126.3–132.3 (4Ph), 134.0 (d,  $J$  30.0 Hz, C), 143.9 (d,  $J$  119.5 Hz, C), 168.1 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 101.2 MHz,  $\delta$ ): 23.8.  $\text{C}_{30}\text{H}_{25}\text{Br}_2\text{O}_3\text{P}$  (624.30). Calcd: C 57.72, H 4.04; found: C 57.78, H 4.11.

*Ethyl (3E)-3-benzenesulfonyl-2-chloro-4-(diphenylphosphoryl)-2,4-diphenylbut-3-enoate (5dc)*. Yellow oil, yield: 1.21 g (1.98 mmol, 66%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.71; IR (neat,  $\text{cm}^{-1}$ ): 1177 (P=O), 1441, 1491 (Ph), 1582 (C=C), 1735 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250.1 MHz,  $\delta$ ): 0.93 (t,  $J$  7.2 Hz, 3H,  $\text{Me-CH}_2\text{O}$ ), 3.97 (m, 2H,  $\text{Me-CH}_2\text{O}$ ), 6.70–7.53 (m, 25H, 5Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.9 MHz,  $\delta$ ): 18.3 ( $\text{CH}_3$ ), 60.8 ( $\text{CH}_2$ ), 68.4 (d,  $J$  7.8 Hz, C), 123.4–133.6 (5Ph), 147.2 (d,  $J$  123.5 Hz, C), 152.8 (d,  $J$  31.4 Hz, C), 172.4 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 101.2 MHz,

$\delta$ ): 24.8.  $\text{C}_{36}\text{H}_{30}\text{ClO}_3\text{PS}$  (609.11). Calcd: C 70.99, H 4.96; found: C 71.05, H 4.91.

*Ethyl (3E)-3-benzenesulfonyl-2-chloro-4-(diphenylphosphoryl)-2,4-diphenylbut-3-enoate (5dd)*. Light orange oil, yield: 1.24 g (1.89 mmol, 63%). Eluent for TLC: ethyl acetate-hexane = 1:1,  $R_f$  0.69; IR (neat,  $\text{cm}^{-1}$ ): 1177 (P=O), 1441, 1493 (Ph), 1599 (C=C), 1725 (C=O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600.1 MHz,  $\delta$ ): 0.91 (t,  $J$  7.1 Hz, 3H,  $\text{Me-CH}_2\text{O}$ ), 3.96 (m, 2H,  $\text{Me-CH}_2\text{O}$ ), 6.97–7.75 (m, 25H, 5Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150.9 MHz,  $\delta$ ): 13.5 ( $\text{CH}_3$ ), 61.8 ( $\text{CH}_2$ ), 70.5 (d,  $J$  7.6 Hz, C), 125.4–138.7 (5Ph), 147.8 (d,  $J$  122.4 Hz, C), 153.3 (d,  $J$  32.0 Hz, C), 172.1 (C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 242.9 MHz,  $\delta$ ): 26.8.  $\text{C}_{36}\text{H}_{30}\text{ClO}_3\text{PSe}$  (656.01). Calcd: C 65.91, H 4.61; found: C 65.85, H 4.57.

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