Studies on an Oxidative 1,4-Addition to *s-trans*-1,3-Dienes, a Key Reaction in a Strigol Total Synthesis

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Dedicated to Professor Wolfgang Steglich on the occasion of his 70th birthday

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Oxidation of 4,6-heptadienoic acid systems with hydrogen peroxide in the presence of a catalytic amount of diphenyl diselenide leads to 5-(3-hydroxypropenyl)dihydrofuran-2-one systems with defined relative configuration at the 4 and 7 positions (carboxylic acid numbering). A system having a six-membered ring as part of the *s-trans*-diene system was an intermediate in a strigol total synthesis; a second system lacking the six-membered ring is the subject of the present publication. We accomplished a stereoselective synthesis of the diene system by (i) trapping a π-allyl palladium complex with lithium diphenylphosphinite to give an allylic diphenylphosphane oxide and (ii) a subsequent Horner–Wittig reaction. The species that brings about the oxidative 1,4-addition is benzeneperoxyseleninic acid. We also report observations that shed some light on the mechanism.

Introduction

Root parasitic flowering plants of the general *Striga*, *Alectra* (*Scrophulariaceae*), and *Orobanche* (*Orobanchaceae*) and their respective host plants use a very interesting system of chemical communication. It has long been known that germination of the seeds of the parasites is stimulated by compounds exuded from the roots of their host plant into the soil.[1] Well-known stimulants are strigol and its acetate (isolated from *Striga* hosts[2] and from cotton, *Gossypium hirsutum*,[3] a non-host), as well as sorgolactone, isolated from the root exudates of *Sorghum vulgare*,[4] a host for *Striga*). Recently, orobanchol, an isomer of strigol, was isolated by Yokota et al. from root exudates of its host, *Trifolium pratense*.[4,5] Finally, a compound, alectrol, has been isolated from the root exudates of *Vigna unguiculata*[6] (host for *Striga* and *Alectra*). A structure has been proposed for this compound that was recently rejected (Figure 1).[7]

The exchange of chemical information indicated above raises basic questions, such as (i) which structural features of the stimulants are essential to elicit a high seed germination potency, (ii) how is the chemical signal that is released from the host recognized by the seed, and (iii) how does the primary chemical signal initiate the biochemical processes that are involved in germination?

It has been determined that both the absolute and relative configurations at the individual stereogenic units of strigol-type compounds have a strong influence on their biological activity.[8]

Results

Strigolactones are available from the root exudates of the host plants only under extreme difficulty. The chemical synthesis is, therefore, indispensable for gaining access to these compounds. A number of synthetic routes have been developed for strigol that involve the reduction of a keto group at C-5 (strigol numbering), which leads to a 1:1 mixture of epimeric 5-alcohols.[8,9] We have developed a synthesis in which diene **3** is a key intermediate (Scheme 1).[10–12] An oxidative 1,4-addition furnished the desired hydroxylactone. When the oxidizing agent was a peracid, hydrogen peroxide (slow reaction), or *N*-phenyloxaziridine, a 1:1 mixture of 5-alcohols **2a** and **2b** resulted. We have speculated that the reaction proceeds via the epimeric allylic epoxides **4** that

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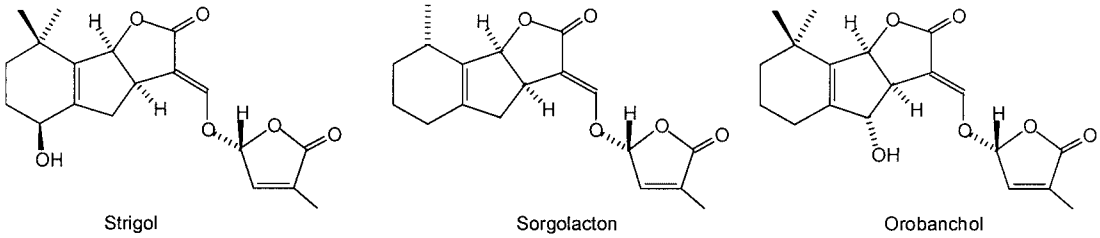


Figure 1. Naturally occurring strigolactones

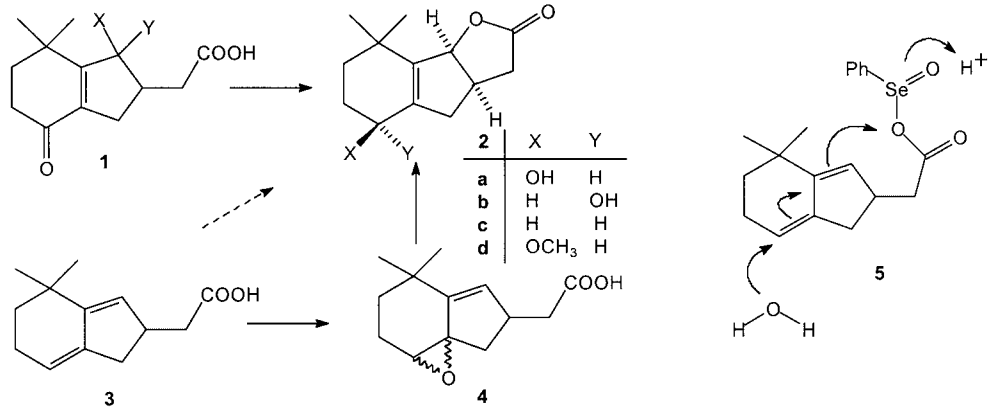
are attacked intramolecularly by the carboxylic acid group. On the other hand, treatment of diene **3** with 30 % H_2O_2 and a catalytic amount of diphenyl diselenide in CH_2Cl_2 proceeded stereoselectively with the exclusive formation of the desired stereoisomer **2a**, which was isolated in 70 % yield. The result was taken as a hint that the formation of **2a** under these conditions takes a course other than that of the oxidation reactions leading to the 1:1 mixture of **2a** and **2b**. We reasoned that an anhydride intermediate of type **5**, formed from **3** with benzeneseleninic acid (the oxidation product of diphenyl diselenide[13]), reacts as indicated to give **2a** and benzeneselenenic acid, which could be reoxidized to benzeneseleninic acid (Scheme 1). It was also adumbrated that the peracid anhydride version of **5** would result directly in the formation of benzeneseleninic acid. The *s-trans* diene system in **3** is incorporated into a system containing a six-membered ring. To exclude specific effects in such systems, such as in the reduction of cyclohexanones[14] or in S_N2' reactions,[15] we tried to prepare dienes **7** and **10** (Figure 2) and to submit these compounds to the oxidative cyclization reaction. Each isomer should lead to a single hydroxy lactone (**8** and **11**, respectively).

Attempted Synthesis of Dienes *rac*-7 and *rac*-10 via Hydroxysulfones *rac*-6 and *rac*-9

The synthesis of the four racemic hydroxysulfones *rac*-**6a/b** and *rac*-**9a/b** (R = α-H and β-H) has been described.[16] We wanted to convert them into the desired dienes making use of a Julia-type reductive elimination.[17] Thus, the hydroxysulfones were converted into the corresponding *m*-trifluoromethylbenzoates. Our idea was to use the Saito photochemical deoxygenation method[18] for the reductive formation of the double bond; these experiments were unsuccessful, however.[19] We were also unable to achieve the olefin formation with samarium diiodide or zinc−copper couple.[19] Finally, treatment of *rac*-**6c**, *rac*-**6d**, and *rac*-**9c** with sodium amalgam[20] brought about the desired reductive β-elimination. Unfortunately, in all cases we obtained a mixture of the isomeric dienes *rac*-**7a** and *rac*-**10a** (GC analysis, ratio ca. 1.5:1). A NOESY cross peak between the proton at the exocyclic double bond and 3-H revealed that *rac*-**10a** was the major isomer. Since we were unable to separate *rac*-**7a** and *rac*-**10a**, it made no sense to perform the oxidative cyclization because no information on the stereoselectivity could be expected.

Synthesis of Diphenylphosphane Oxides *rac*-13b and *rac*-14b

Phosphane oxide-mediated olefin synthesis, i.e., reaction of lithium derivatives of alkyl diphenylphosphane oxides with aldehydes to give β-hydroxyphosphane oxides followed by separation of the stereoisomers, and stereospecific elimination of Ph_2PO^- with a sodium or a lithium base (Horner−Wittig olefin synthesis[21,22]) seemed to offer a way out of the difficulties experienced with the non-stereoselective formation of the trisubstituted olefins *rac*-**7** and *rac*-**10** during the Julia-type reactions described above. Our concept was to convert the unsaturated lactone *rac*-**12** into a π-allyl−palladium complex and to trap this intermediate with a nucleophilic precursor of the diphenylphosphane ox-



Scheme 1

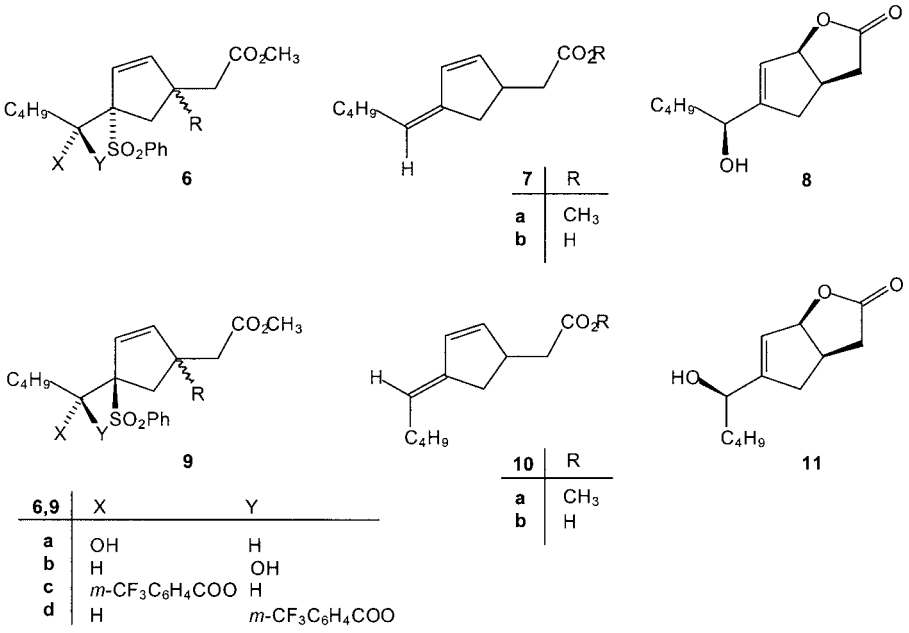
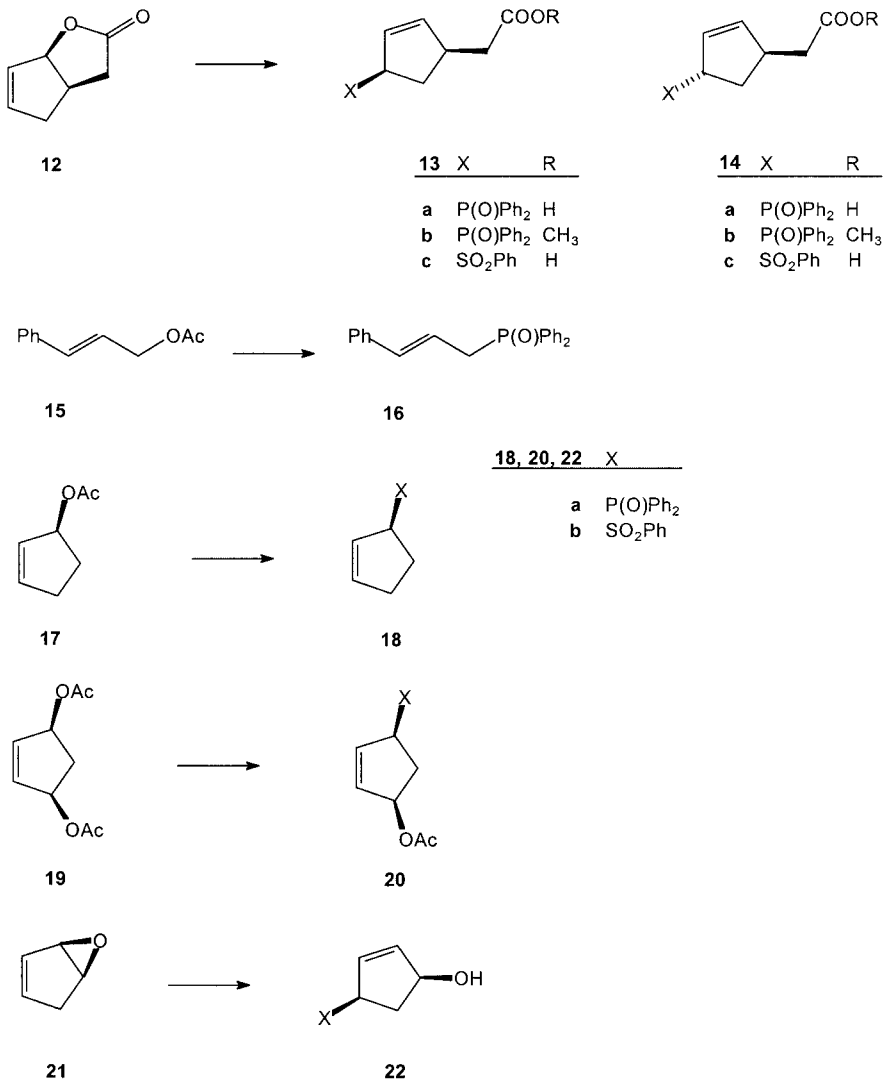


Figure 2. Structures of compounds **6**−**11**

ide substituent. Our investigations started on the basis of a report by Mañas et al.[23] who disclosed that cinnamyl acetate (**15**) in a Pd-mediated reaction with methyl diphenylphosphinite [$Pd(acac)_2$ in dioxane at 150 °C (pressure vessel)] furnished the allylic diphenylphosphane oxide **16** in a yield of 49 %. By repeating these experiments we found that the reaction proceeds equally well in acetonitrile (at 101 °C) or MeOH solution (at 60 °C) to give **16** in yields of 53 and 68 %, respectively. The use of a pressure vessel is, therefore, not required. Unfortunately lactone *rac*-**12** did not react with methyl diphenylphosphinite under the conditions used for the conversion of **15** into **16**, neither in dioxane, acetonitrile, or MeOH solution. We reasoned that an external nucleophile that would attack the methoxy group could improve the reaction. Thus, the reaction was performed in MeOH at 60 °C in the presence of LiCl, NaOAc, and $(Bu)_4N^+Cl^-$, respectively, but without success. At this point we decided to include model compounds 2-cyclopentenyl acetate (*rac*-**17**), *cis*-3,5-diacetoxycyclopent-1-ene (**19**), and 3,4-epoxycyclopent-1-ene (*rac*-**21**) into the investigations (Scheme 2) and to use also other nucleophilic diphenylphosphane oxide precursors. The results, summarized in Table 1, demonstrate that only lithium diphenylphosphinite was of any use for our purpose. The phosphinite, upon reaction with lactone *rac*-**12** in the presence of $Pd(PPh_3)_4$ (−80 °C, 1 h), provided the desired diphenylphosphane oxide in 67 % yield as a 3:1 mixture (^{31}P NMR) of the two (racemic) diastereoisomers *rac*-**13a** and *rac*-**14a**; we isolated *rac*-**24** as a side product. Prolonging the reaction time from 1 to 2 h increased the yield to 78 %. To exclude the possibility that the intermediate π-allyl-palladium complexes were not formed during the unsuccessful trials, *rac*-**12**, **19**, and *rac*-**21** were treated with sodium benzenesulfinate in the presence of either $Pd(acac)_2$ or $Pd(PPh_3)_4$. In all cases the corresponding sulfones (*rac*-**13c**, *rac*-**20b**, *rac*-**22b**, respectively) were formed.

Another method for the preparation of **13a** might be the oxidation of *rac*-**23**, which was obtained by Pd^0-mediated reaction of *rac*-**12** with lithium diphenylthiophosphinite[24] in a yield of 61 % (Scheme 3).

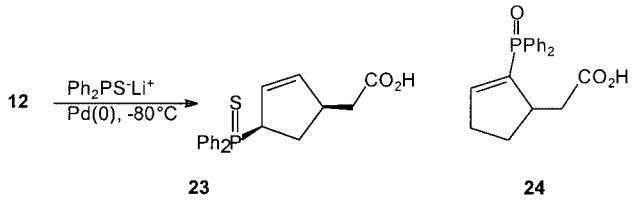
The diastereoisomeric acids *rac*-**13a**/*rac*-**14a** were converted ($MeOH/H^+$) into their methyl esters, which were separated by crystallization to give a crystalline and an oily stereoisomer, respectively. Their configurational assignments were far from trivial; Figures 3 and 4 display the ^1H NMR spectra of the two compounds. The protons at C-5 of one stereosiomer give rise to two multiplets at δ = 1.79 and 2.45 ppm. Interpreting these multiplets is complicated because of ^{31}P-^1H coupling. Upon ^{31}P decoupling, the multiplets collapse to six lines from which, by spin simulation, we derived coupling constants of $J_{1,5a} = J_{4,5a} = 4.8$ Hz, $J_{1,5b} = J_{4,5b} = 6.0$ Hz, and $J_{5a,5b} = 9.0$ Hz. We conclude from the values of $J_{1,5a}/J_{4,5a}$ and $J_{1,5b}/J_{4,5b}$, respectively, that this isomer has the cis configuration, as indicated in *rac*-**13b**. We determined both one- and two-dimensional NOEs. In addition to the NOEs summarized in Figure 5, we found a structurally important NOE contact between 5-H_a and CH_2-COOMe. These NOEs allowed us to assign the signals of 2-H and 3-H, as well as those of 5-H_a and 5-H_b. We believe that the unexpected small chemical shift of 5-H_a is the result of a shielding effect of the ester CO group and/or an aromatic ring. We observed no NOE contact between 1-H and 4-H. The chemical shift difference for the olefinic protons at C-2 and C-3 is ca. 0.3 ppm for one isomer (*rac*-**13b**) and 0.6 ppm for the other (*rac*-**14b**). This fea-



Scheme 2

Table 1. Pd-mediated reaction of *rac*-**12**, *rac*-**21**, **15**, and **19** with nucleophilic diphenylphosphane oxide precursors

Substrate	Nucleophiles			
	$Ph_2P(O)Me$	$Ph_2POSiMe_3$[25]	$Ph_2POMgCl$[26,27]	$Ph_2PO^-Li^+$ [28,29]
15	**16**, 68 %		**16**, 24 %	**16**, 78 %
rac-**17**	*rac*-**18a**, 68 %		*rac*-**18a**, 28 %	
19	no reaction[30]		*rac*-**20a**, 0 %[30]	*rac*-**20a**, 45 %
rac-**21**	decomposition[30]		*rac*-**22a**, 7 %	*rac*-**22a**, 28 %
rac-**12**	no reaction[30]	*rac*-**13a**/*rac*-**14a**, 0 %[30]	no reaction[30]	*rac*-**13a**/*rac*-**14a**, 78 %



Scheme 3

ture, which we cannot explain at present, is of high diagnostic value.

The multiplets of the protons in the 5-position of the other stereoisomer remain complex, even in the ^{31}P-decoupled spectra, which is a situation that indicates that this compound is the trans isomer, *rac*-**14b**. In the NOESY spectra of *rac*-**14b**, the following structurally important NOEs, summarized in Figure 5, were observed, and in addition to those between 5-H_a and CH_2-COOMe.

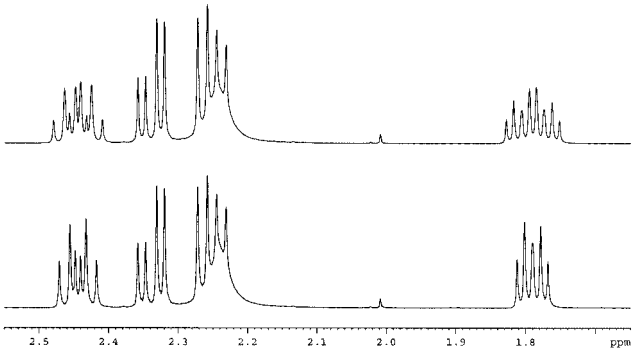


Figure 3. ^{1}H NMR signals of CH_2-5 of *rac*-**13b** (top: normal spectrum; bottom: ^{31}P-decoupled spectrum)

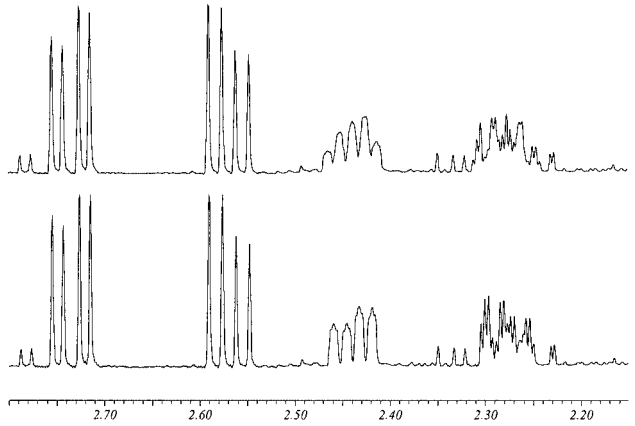


Figure 4. ^{1}H NMR signals of CH_2-5 of *rac*-**14b** (top: normal spectrum; bottom: ^{31}P-decoupled spectrum)

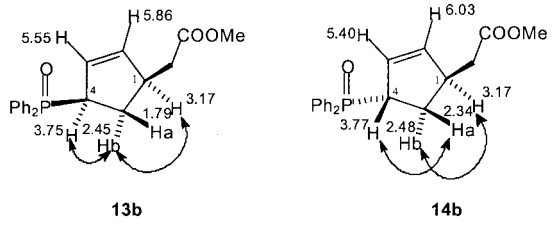


Figure 5. Selected NOE contacts of *rac*-**13b** and *rac*-**14b** (also see text)

The NOEs again allowed us to assign the signals of 5-H_a, 5-H_b, 2-H, and 3-H. Interestingly, we observed a 1-H/4-H cross peak in the NOESY spectrum of *rac*-**14b** that originates from a relay process (proven by an NOE building-up experiment).

Compound *rac*-**13b** constitutes the major component isolated from the reaction mixture formed from *rac*-**12** and lithium diphenylphosphinite. If the product ratio reflects kinetic control, and if the normal *anti* course for formation of the palladium complex is followed, the preferred formation of the *cis* product means that the incoming diphenylphosphinite behaves as a soft nucleophile attacking C-4 directly. On equilibration with sodium methoxide in MeOH, *rac*-**13b** rearranged into *rac*-**14b**.

The ^{1}H NMR spectra of *rac*-**23** were analysed less rigorously. They resemble, however, those of *rac*-**13b**. We assume, therefore, that the two substituents at the five-membered ring of *rac*-**23** are also in a *cis* relation.[31]

Synthesis of β-Hydroxyphosphane Oxides *rac*-31 and *rac*-32

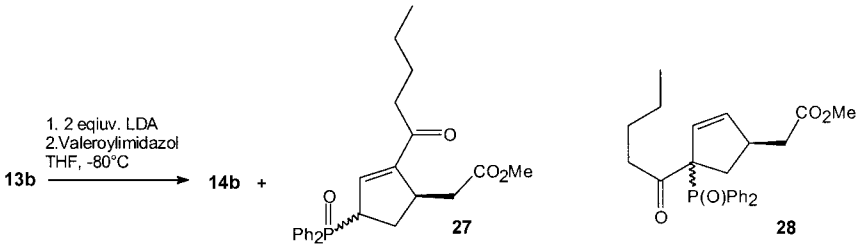
An array of methods exist for the formation of β-hydroxyphosphane oxides, including the addition of lithiated alkyldiphenylphosphane oxides to carbonyl compounds[32] and their acylation followed by reduction of the resulting β-oxophosphane oxides.[21,33] We tried the latter approach first. Compound *rac*-**13b** was deprotonated with LDA and the anion treated at −80 °C with an excess of valeroylimidazole. After workup, we isolated only the *trans* isomer *rac*-**14b**; *rac*-**28** was not formed (Scheme 4). Sequential treatment of phosphane oxide *rac*-**13b** with LDA and valeroyl chloride and valeraldehyde, respectively, also proved fruitless.[30] Deprotonation of *rac*-**13b** with 2 equiv. of LDA and subsequent quenching with valeroylimidazole at −80 °C led to the formation of the γ-substituted product, *rac*-**27** (24 %). Again, the recovered material (22 %) was the *trans* isomer, *rac*-**14b**.

The ^{1}H NMR spectrum of *rac*-**27** displays the 3-H signal at δ = 6.47 ppm, which is indicative of an α,β-unsaturated ketone. In *rac*-**13b**, this signal appears at δ = 5.55 ppm. We tried to avoid γ attack by protecting the γ position with a trimethylsilyl substituent. Thus, deprotonation of *rac*-**13b** and subsequent treatment with trimethylsilyl chloride furnished the silyl derivative *rac*-**29** in 78 % yield.[34] The structure agrees well with the ^{1}H NMR spectrum (no 4-H signal and the signal of 2-H at δ = 1.93 ppm). A trans relationship between the trimethylsilyl unit and the acetic acid side chain seems reasonable, but has not been proven.

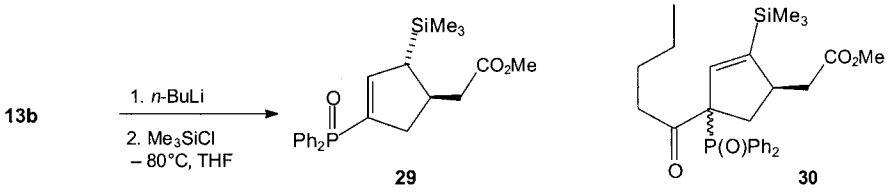
The reaction of *rac*-**29** with LDA and valeroylimidazole led to the formation of a multitude of reaction products, but the desired product, *rac*-**30**, could not be detected (Scheme 5).[30] When *rac*-**29** was treated sequentially with LDA and valeraldehyde, *rac*-**13b** was isolated.

It is known that the problem of α vs. γ attack in substituted allylic anions can be mastered by a sequence of two S_E' reactions.[35−38] Thus, following a report by Murray and co-workers,[38] *rac*-**13b** was deprotonated with LDA in THF at −80 °C and then dichlorotitanium diisopropoxide was added; after keeping this mixture at −80 °C for 2 h, the product was trapped with an excess of valeraldehyde.

This protocol led to two of the four possible (racemic) diastereoisomeric α products, *rac*-**31** and *rac*-**32**, in a ratio of 74:26 (HPLC) and a combined yield of 73 % (Scheme 6). The oily β-hydroxyphosphane oxides were separated by preparative HPLC. Their spectra are in agreement with their proposed structures, but there are characteristic differences between these ^{1}H NMR spectra. The chemical shift of 1-H of *rac*-**31** is δ = 3.17 ppm, but for *rac*-**32** this signal is found at δ = 2.39 ppm. The signals of the olefinic protons at C-2 and C-3 appear at δ = 6.12/5.81 and 5.85/5.40 ppm, respectively. The assignment of the relative configuration at C-4 and the carbinol carbon atom rests on the outcome of the Horner−Wittig elimination; the relative configuration at C-



Scheme 4

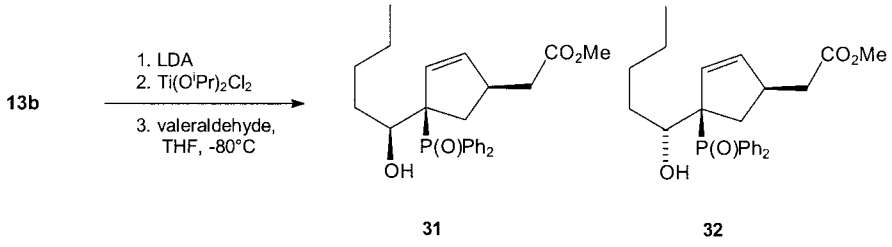


Scheme 5

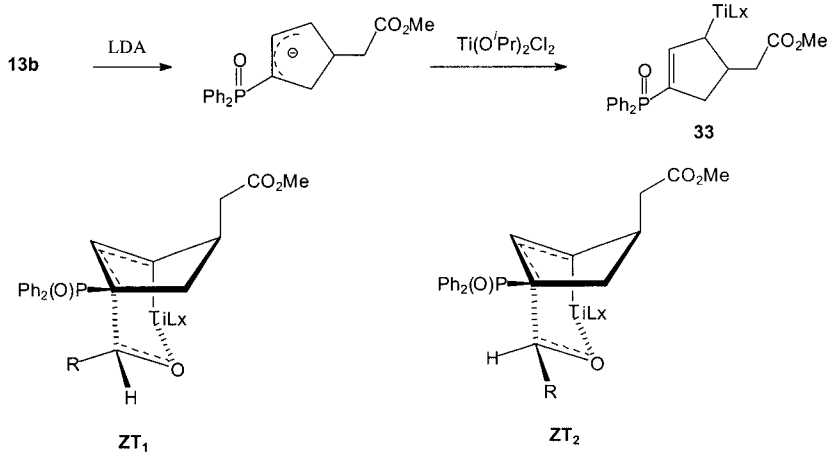
1 is not relevant. If the reasonable assumption is made that the side chain at C-1 and the titanium ligand are *trans* to one another, the relative configurations of *rac*-**31** and *rac*-**32** should be as indicated in the formulae. The formation of the β-hydroxyphosphane oxides may proceed as indicated in Scheme 7 by (i) attack of the titanium reagent at the γ position and (ii) reaction of the allylic titanium species with the aldehyde via a Zimmerman−Traxler transition state.

Horner−Wittig Elimination

Compounds *rac*-**31** and *rac*-**32** were treated individually with with KO*t*Bu in THF. Each reaction gave a single (racemic) diene in a yield of 95 %. The compounds were highly volatile and were purified by flash chromatography (FC) using pentane/diethyl ether as eluent. The NOEDIF spectra of *rac*-**10a** displayed unequivocally an NOE contact between 1′-H and 3-H, whereas *rac*-**7a** showed weak NOE



Scheme 6



Scheme 7

signals between 1′-H, 5-H_a, and 5-H_b. From this information, we deduced the *Z* configuration of *rac*-**7a** and the *E* configuration of *rac*-**10a** and, thereby, the relative configurations of *rac*-**31** and *rac*-**32**, respectively. Hydrolysis of esters *rac*-**7a** and *rac*-**10a** was accomplished under mild conditions using barium hydroxide in MeOH at 20 °C. The very sensitive dienecarboxylic acids formed, *rac*-**7b** and *rac*-**10b**, respectively, were used directly in the next step.

Oxidative Cyclization of *rac*-7b and *rac*-10b

The oxidative cyclization was performed with H_2O_2 and cat. diphenyl diselenide in CH_2Cl_2 solution at 0 °C, i.e., exactly under the conditions used for the conversion of *rac*-**3** into *rac*-**2a**. TLC control revealed that *rac*-**7b** and *rac*-**10b** reacted completely stereospecifically with each giving a single oxidation product, which, by analogy with the results obtained for the oxidative cyclization of **3**, we assume to be *rac*-**8** and *rac*-**11**, respectively. The constitutions of both compounds are agree well with the spectroscopic data. The ^{1}H NMR spectra of both compounds exhibit signals of the 1′-H, 6-H, and 6a-H protons in the range $\delta = 4-6$ ppm (Table 2).

Table 2. Selected ^{1}H NMR spectroscopic chemical shifts of **8** and **11**

	1′-H	6-H	6a-H
8	4.48	5.70	4.70
11	4.20	5.68	5.41

Unfortunately, *rac*-**8** and *rac*-**11** are oily compounds. We tried to obtain crystalline derivatives by ester formation with anthracene-2-carboxylic acid, 4-nitro-, and 3,5-dinitrobenzoic acid (Figure 6). Several simple crystalline esters are known to derive from anthracene-2-carboxylic acid.[39−41] As expected, the isopropyl ester of anthracene-2-carboxylic acid, which we prepared as a model compound, was a crystalline solid.[30] We were unable, however, to get suitable crystals from esters *rac*-**34a** and *rac*-**35a**, which we prepared from *rac*-**8** and *rac*-**11** by reaction with 2-anthracenecarboxylic acid, *N*′-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide, and Steglich's base in CH_2Cl_2. Similarly, esters *rac*-**35b** and *rac*-**35c** were oily compounds.[30] Attempts to solve the structures by low-temperature X-ray crystallography remained unsuccessful.

Some Observations That May Help to Explain the Stereochemistry of the Oxidative Cyclization

At first we wanted to identify the selenium species that brings about the oxidative cyclization. Compound **3** was treated with benzeneseleninic acid, benzeneseleninic peracid, and benzeneselenonic acid in stoichiometric amounts. In the absence of hydrogen peroxide, benzeneseleninic acid did not effect the oxidative cyclization, i.e., **3** was stable under the reaction conditions. On the other hand, the benzeneseleninic acid/hydrogen peroxide combination converted **3** with high stereoselectivity into hydroxylactone **2a** when the reaction was performed in CH_2Cl_2 solution. Finally, benzeneselenonic acid behaved as a strong acid and induced cyclization to lactone **2c**, a compound that was previously obtained from **3** upon camphorsulfonic acid-mediated cyclization.[12] We conclude from these results that benzeneseleninic peracid[42] is the species that is responsible for the conversion of **3** into **2a**. All electrophilic reagents that attack the distal double bond of **3** lead to mixtures of stereoisomeric 5-substituted bicyclic lactones (vide supra). Interestingly, reaction of **3** with benzeneseleninic peracid in a polar solvent, such as MeOH, also gives a 1:1 mixture of **2a** and **2b**, which indicates that the reaction follows the normal attack of the peracid onto the distal double bond leading to the two epoxides **4** that are then opened as described above. Thus, the mechanism as formulated in **5** (Scheme 1) seems to offer an explanation. This mechanism implies that, after electrophilic attack of a selenium species, the 5-OH group originates from the solvent. This mechanism is, however, not compatible with the following experiment. When **3** was treated with benzeneseleninic acid in CH_2Cl_2 in the presence of one equiv. of H_2O_2 and one equiv. of MeOH, the stereoselectivity was still high, although slightly reduced (4:1 ratio). No methoxy lactone **2d**[12] was detected from this experiment. Thus, it seems reasonable to assume that an anhydride of type **5**[43] is formed from **3** and the peracid,

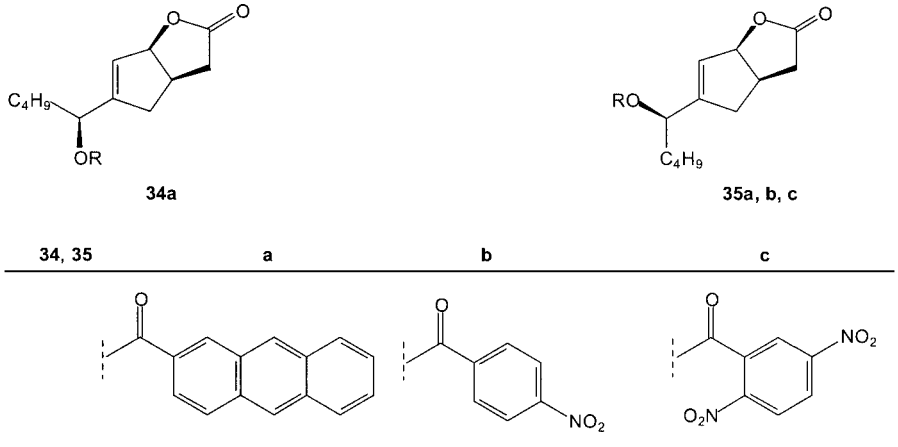
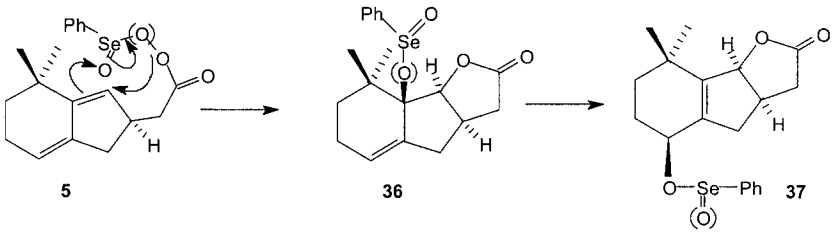


Figure 6. Esters *rac*-**34a** and *rac*-**35a**



Scheme 8

which then undergoes a cycloaddition to give **36**. A sigmatropic rearrangement would then lead to **37**, from which **2a** is formed by hydrolysis (Scheme 8). The rearrangement of allylic selenoxides to selenenates is, of course, well known.[44]

In conclusion, we have found a new oxidation reaction that converts *s-trans*-4,6-heptadienoic acid systems stereoselectively into 5-(3-hydroxypropenyl)dihydrofuran-2-one systems. We stress that this reaction is complementary to Bäckvall's palladium-mediated oxidative cyclizations of the corresponding *s-cis*-systems.[45] We were unable to achieve the oxidative cyclization of **3** under the Bäckvall conditions.[46]

Experimental Section

Thin-layer chromatography (TLC) was carried out using pre-coated aluminium plates (Kieselgel 60 F_{254}, Merck) that were visualized using a phosphomolybdate−ceric sulfate reagent.[47] Flash column chromatography (FC) was performed on silica gel (Kieselgel 60, Merck 40−63 μm). Melting points were determined in capillary tubes using a Büchi (B-540) apparatus. IR spectra were determined on an FTIR spectrometer (ATI Mattson, Genesis series). ^{1}H and ^{13}C NMR spectra were obtained on Varian Gemini 200, Gemini 2000, and Gemini 300 and Bruker DRX-400 and DRX-600 spectrometers, with $CDCl_3$ as the solvent unless otherwise stated. The signals of $CHCl_3$ (δ = 7.26 ppm) and $CDCl_3$ (δ = 77.16 ppm) were used as internal references. *J* values are given in Hz. Signals were assigned by means of 2D proton−proton (COSY) and proton−carbon (HMQC, HMBC) shift-correlation spectra. Mass spectra were recorded on a VG ZAB-HSQ (VG Analytics) using 3-nitrobenzyl alcohol as the matrix (FAB MS) and by FT ICR (MS, 7 T APEX II, Bruker-Daltonics) in a positive or negative mode (ESI MS). Analytical HPLC was performed on a HPLC system containing a pump PU-980 (Jasco), a multiwave UV detector MD-910 (Jasco), and a solvent mixing system LG 980−02 (Uniflows). Preparative HPLC was performed on an HPLC system containing a pump PU-987 (Jasco) and a multiwave UV detector 875-UV (Jasco).

(1*S,4*S**,1′*S**)-1-[4-(Methoxycarbonylmethyl)-1-(phenylsulfonyl)-cyclopent-2-enyl]pentyl 3-Trifluoromethylbenzoate (*rac*-6d):** A solution of DMAP (27.1 mg, 0.239 mmol) in pyridine (1 mL) and 3-(trifluoromethyl)benzoyl chloride (135 μL, 0.888 mmol) were added to a solution of β-hydroxysulfone *rac*-**6b** (81.4 mg, 0.222 mmol) in pyridine (1 mL). The mixture was stirred at 20 °C for 19 h. Saturated aqueous NH_4Cl was added. Usual workup (CH_2Cl_2), solvent evaporation and FC (petroleum ether/EtOAc, 7:1) provided *rac*-**6d** (118.6 mg, 99 %). IR ($CHCl_3$): ṽ = 3020, 2970, 1735, 1445, 1325, 1300, 1245, 1170, 1140 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, H,H COSY): δ = 0.77 (t, 3 H, 5′-CH_3), 1.29−1.50 (m, 4 H, 4-CH_2, 3′-CH_2), 1.42−1.58 (m, 2 H, 2′-CH_2), 1.98 (dd, 1 H, 5-H_a), 2.27−2.43 (m, 2 H, CH_2CO$_2$CH$_3$, AB part of an ABX system, J_{AB} = 15.3 Hz), 2.90−3.04 (m, 2 H, 4-H and dd at 2.95, 5-H_b), 3.62 (s, 3 H, OCH_3), 5.39 (dd, 1 H, 2-H), 5.84 (dd, 1 H, 1′-H), 6.04 (dd, 1 H, 3-H), 7.37−7.59 (m, 4 H, Ar-H), 7.71−7.88 (m, 3 H, Ar-H), 8.06−8.18 (m, 2 H, Ar-H) ppm; $J_{2,3}$ = 5.6 Hz; $J_{2,4}$ = 1.7 Hz; $J_{3,4}$ = 2.1 Hz; $J_{4,5\text{-H}a}$ = 6.2 Hz; $J_{4,5\text{-H}b}$ = 8.1 Hz; J_{5gem} = 14.2 Hz; $J_{4',5'}$ = 7.1 Hz; $J_{1',2'}$ = 9.6, $J_{1',2'}$ = 3.6 Hz. $C_{27}H_{29}F_3O_6S$ (538.58, 538.1637). EI MS: *m*/*z* (%) = 397 (23) [M − $C_6H_5O_2S$]$^+$, 366 (4), 208 (17), 207 (100), 173 (47), 147 (29), 145 (17), 91 (16), 77 (13).

(1*S,4*S**,1′*R**)-1-[4-(Methoxycarbonylmethyl)-1-(phenylsulfonyl)-cyclopent-2-enyl]pentyl 3-Trifluoromethylbenzoate (*rac*-6c):** β-Hydroxysulfone *rac*-**6a** was converted into *rac*-**6c** as described for **6d**. Quantitative yield. IR ($CHCl_3$): ṽ = 3020, 2950, 1735, 1445, 1325, 1300, 1245, 1170, 1140, 1070 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, H,H COSY): δ = 0.88 (t, 3 H, 5′-CH_3), 1.20−1.50 (m, 4 H, 4′-CH_2, 3′-CH_2), 1.66−1.99 (m, 2 H, 2′-H_a and dd at 1.93, 5-H_a), 2.12−2.43 (m, 3 H, 2′-H_b and AB part of an ABX system, J_{AB} = 15.8 Hz, CH_2CO$_2$CH$_3$), 2.65−2.83 (m, 1 H, 4-H), 2.94 (dd, 1 H, 5-H_b), 3.65 (s, 3 H, OCH_3), 5.63 (dd, 1 H, 3-H), 5.84 (dd, 1 H, 2-H), 5.87 (dd, 1 H, 1′-H), 7.42−7.70 (m, 4 H, Ar-H), 7.77−7.93 (m, 3 H, Ar-H), 8.10−8.40 (m, 2 H, Ar-H) ppm; $J_{2,3}$ = 5.9 Hz; $J_{2,4}$ = 1.8 Hz; $J_{3,4}$ = 2.2 Hz; $J_{4,5\text{-H}a}$ = 7.0 Hz; $J_{4,5\text{-H}b}$ = 8.0 Hz; J_{5gem} = 15.0 Hz; $J_{4',5'}$ = 7.0 Hz; $J_{1',2'}$ = 10.6, $J_{1',2'}$ = 2.6 Hz. $C_{27}H_{29}F_3O_6S$ (538.58, 538.1637), EI MS: *m*/*z* (%) = 397 (21) [M − $C_6H_5O_2S$]$^+$, 366 (5) [397 − OCH_3], 208 (15), 207 (100), 173 (47), 147 (25), 145 (20), 91 (17), 77 (12).

(1*R,4*S**,1′*R**)-1-[4-(Methoxycarbonylmethyl)-1-(phenylsulfonyl)-cyclopent-2-enyl]pentyl 3-Trifluoromethylbenzoate (*rac*-9c):** *rac*-**9a** was converted into *rac*-**9c** as described for *rac*-**6d**. Yield: quantitative. IR ($CHCl_3$): ṽ =1735, 1440, 1330, 1300, 1250, 1160, 1130 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, HH COSY): δ = 0.84 (t, 3 H, 5′-CH_3), 1.18−1.40 (m, 4 H, 4′-CH_2, 3′-CH_2), 1.50−1.67 (m, 2 H, 2′-CH_2), 2.27−2.44 (m, 3 H, containing dd of 5-H_a and AB of ABX, CH_2CO$_2$CH$_3$), 2.82 (dd, 1 H, 5-H_b), 3.20−3.40 (m, 1 H, 4-H), 3.71 (s, 3 H, OCH_3), 5.51 (dd, 1 H, 3-H), 5.86 (dd, 1 H, 1′-H), 6.11 (dd, 1 H, 2-H), 7.41−7.63 (m, 4 H, Ar-H), 7.77−7.93 (m, 3 H, Ar-H), 8.08−8.21 (m, 2 H, Ar-H) ppm; $J_{2,3}$ = 5.9 Hz; $J_{2,4}$ = 2.2 Hz; $J_{3,4}$ = 2.2 Hz; $J_{4,5\text{-H}b}$ = 9.2 Hz; J_{5gem} = 15.8 Hz; $J_{4',5'}$ = 6.6 Hz; $J_{1',2'}$ = 8.2, $J_{1',2'}$ = 5.0 Hz. $C_{27}H_{29}F_3O_6S$ (538.58, 538.1637), EI MS: *m*/*z* (%) = 397 (4) [M − $C_6H_5O_2S$]$^+$, 381 (22), 311(12), 208 (20), 207 (100), 173 (71), 147 (33), 145 (25), 91 (28), 77 (19).

(1*R,4*S**,1′*S**)-1-[4-(Methoxycarbonylmethyl)-1-(phenylsulfonyl)-cyclopent-2-enyl]pentyl 3-Trifluoromethylbenzoate (*rac*-9d):** *rac*-**9b** was converted into *rac*-**9d** as described for *rac*-**6d**. Yield: quantitative. IR ($CHCl_3$): ṽ = 3020, 2920, 1735, 1440, 1325, 1300, 1250, 1160, 1130 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, H,H COSY): δ = 0.87 (t, 3 H, 5′-CH_3), 1.16−1.45 (m, 4 H, 4′-CH_2, 3′-CH_2),

1.60−1.90 (m, 1 H, 2′-H_a), 1.95-2.32 (m, 4 H, containing AB of ABX, CH_2CO$_2$CH$_3$, 2′-H_b and dd at 2.21, 5-H_a), 2.57 (dd, 1 H, 5-H_b), 3.10−3.30 (m, 1 H, 4-H), 3.68 (s, 3 H, OCH$_3$), 5.77 (dd, 1 H, 3-H), 5.81 (dd, 1 H, 1′-H), 5.94 (dd, 1 H, 2-H), 7.41−7.60 (m, 4 H, Ar-H), 7.72−7.87 (m, 3 H, Ar-H), 8.04−8.13 (m, 2 H, Ar-H) ppm; $J_{2,3}$ = 5.5 Hz; $J_{2,4}$ = 2.2 Hz; $J_{3,4}$ = 2.2 Hz; $J_{4,5\text{-H}a}$ = 5.9 Hz; $J_{4,5\text{-H}b}$ = 8.8 Hz; J_{5gem} = 15.8 Hz; $J_{4',5'}$ = 6.8 Hz; $J_{1',2'}$ = 9.5, $J_{1',2}$ = 1.8 Hz. $C_{27}H_{29}F_3O_6S$ (538.58, 538.1637), EI MS: *m*/*z* (%) = 397 (20) [M − $C_6H_5O_2S$]$^+$, 381 (14), 311 (27), 208 (93), 207 (100), 173 (59), 147 (29), 145 (20), 91 (14), 77 (14).

Reaction of *rac*-9c, *rac*-6c, *rac*-6d with Sodium Amalgam: a) Sodium amalgam (2 % sodium, 76.3 mg) in MeOH (0.5 mL) was cooled to −20 °C. A solution of *rac*-**9c** (15.2 mg, 0.028 mmol) in THF (1.5 mL) was added and the mixture was stirred for 22 h at −20 °C and then for 8 h at 0 °C. Water was added. The usual workup (CH_2Cl_2) gave a solution of a 1:1.6 mixture (determined by GC) of the very volatile dienes *rac*-**7b** and *rac*-**10b**. b) Compound *rac*-**6c** (101.8 mg) was treated with sodium amalgam (1.087 g) as described above. According to GC, *rac*-**7a** and *rac*-**10a** were formed in a 1:1.7 ratio. The reaction products were purified by FC (pentane). The spectroscopic data were obtained from this sample. c) Compound *rac*-**6d** (118.6 mg) was treated with sodium amalgam (1.282 g) as described above to give a 1:2.2 mixture of *rac*-**7a** and *rac*-**10a** (GC).

Methyl (*Z*)- and (*E*)-(1*R)-(4-Pentylidenecyclopent-2-enyl)acetate (*rac*-7a and *rac*-10a):** $C_{13}H_{20}O$ (208.30, 208.1463), GC MS: *m*/*z* (%) = 208 (33), 165 (38) [M − $CH_3CH_2CH_2$]$^+$, 135 (38), 134 (45), 105 (100), 91 (53), 79 (45). ^{1}H NMR of the *E* isomer (200 MHz, $CDCl_3$, H,H COSY, NOESY): δ = 0.90 (t, 3 H, 5′-CH_3), 1.22−1.43 (m, 4 H, 4′-CH_2, 3′-CH_2), 1.94−2.22 (m, 3 H, 2′-CH_2, 5-H_a), 2.24−2.52 (m, 2 H, CH_2CO$_2$CH$_3$, AB of ABX, J_{AB} ≈ 15 Hz), 2.66−2.86 (m, 1 H, 5-H_b), 3.11−3.34 (m, 1 H, 1-H), 3.69 (s, 3 H, OCH$_3$), 5.26−5.39 (m, 1 H, 1′-H), 5.88 (dd, 1 H, 2-H), 6.11 (dd, 1 H, 5-H) ppm; $J_{1,2}$ = 2.4 Hz; $J_{1,3}$ = 1.8 Hz; $J_{2,3}$ = 5.5 Hz. NOESY cross peak between 1′-H and 3-H. ^{1}H NMR of the *Z* isomer (200 MHz, $CDCl_3$, H,H COSY, NOESY): δ = 0.88 (t, 3 H, 5′-CH_3), 1.22−1.43 (m, 4 H, 4′-CH_2, 3′-CH_2), 1.94−2.22 (m, 3 H, 2′-CH_2 and 5-H_a), 2.24−2.52 (m, 2 H, CH_2CO$_2$CH$_3$, AB of ABX, J_{AB} ≈ 15 Hz), 2.66−2.86 (m, 1 H, 5-H_b), 3.11−3.34 (m, 1 H, 1-H), 3.68 (s, 3 H, OCH$_3$), 5.10−5.22 (m, 1 H, 1′-H), 5.96−6.03 (m, 1 H, 2-H), 6.37−6.44 (m, 1 H, 3-H).

Pd-Mediated Conversion of Cinnamyl Acetate and Methyl Diphenylphosphinite into 3-(Diphenylphosphanoyl)-1-phenylprop-1-ene (*rac*-16). a) Reaction in Dioxane: Cinnamyl acetate (2.07 mL, 0.12 mol), $Pd(acac)_2$ (0.15 g, 0.05 mol), and methyl diphenylphosphinite (1.15 mL, 0.10 mol) were added in that order under Ar to anhydrous dioxane (100 mL). The mixture was heated at 150 °C in a pressure reactor for 22 h. The precipitate that formed was filtered off and the solvent was evaporated. The residue was purified by FC (EtOAc) to provide *rac*-**16** (1.69 g, 49 %).

b) Reaction in MeCN: Cinnamyl acetate (0.095 mL, 0.57 mmol), $Pd(acac)_2$ (0.008 g, 0.027 mmol), and methyl diphenylphosphinite (0.280 mL, 1.420 mmol) were added in that order and under Ar to MeCN (10 mL). The mixture was heated at 101 °C in a pressure reactor (Büchi mini clave) for 22 h. The precipitate that formed was filtered off and the solvent was evaporated. FC (EtOAc) provided *rac*-**16** (0.096 g, 53 %).

c) In MeOH: Cinnamyl acetate (0.047 mL, 0.280 mmol), $Pd(acac)_2$ (4.0 mg, 0.013 mmol) and methyl diphenylphosphinite (0.14 mL, 0.71 mmol) were added in that order under Ar to MeOH (10 mL). The mixture was heated at 60 °C for 22 h. The precipitate that formed was filtered off and the solvent was evaporated. FC (EtOAc) provided *rac*-**16** (0.056 g, 68 %). The spectroscopic data (^{1}H and ^{31}P NMR) were in agreement with ref.[48]

Treatment of *rac*-12 with Methyl Diphenylphosphinite in the Presence of Cat. Pd(acac)$_2$: The reactions were performed in dioxane, MeCN, and MeOH solution exactly as described for the formation of *rac*-**16** and also in MeOH in the presence of LiCl, NaOAc, or $(Bu)_4NCl$. According to TLC and NMR spectra, *rac*-**13** did not form.

1-(Diphenylphosphanoyl)cyclopent-2-ene (*rac*-18a): Methyl diphenylphosphinite (0.316 mL, 1.6 mmol) and $Pd(acac)_2$ (12 mg, 0.04 mmol) were added under Ar to a stirred solution of 2-cyclopentene-1-yl acetate (**17**; 100 mg, 0.8 mmol) in MeOH (2 mL). The mixture was heated at 60 °C for 24 h. After cooling to room temperature, water was added. The aqueous suspension was extracted with CH_2Cl_2 (3 ×). The combined organic fractions were dried (Na_2SO_4), evaporated under reduced pressure, and then purified by FC ($CHCl_3$/MeOH, 9:1) to give **18a** (146 mg, 68 %). M.p.: 126−128 °C (EtOAc/petroleum ether). IR (KBr): $\tilde{\nu}$ = 1714, 1436, 1170, 1116, 752 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, HMQC, HMBC): δ = 2.41 (m, 4 H, 4-H, 5-H), 3.72 (m, 1 H, 1-H), 5.55 (m, 1 H, 3-H), 5.95 (m, 1 H, 2-H), 7.47 (m, 6 H, Ar-H), 7.84 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.96 (C-5), 32.80 (C-4, d, $^4J_{C,P}$ = 3 Hz), 46.37 (C-1, d, $^1J_{C,P}$ = 72 Hz), 125.56 (C-2, d, $^3J_{C,P}$ = 6 Hz), 136.14 (C-3, d, $^2J_{C,P}$ = 11 Hz), 128.43−131.83 (Ar-C) ppm. ^{31}P NMR (80.9 MHz, $CDCl_3$): δ = 35.15 ppm. $C_{17}H_{17}OP$ (268.30, 268.1017), FAB MS: *m*/*z* = 269.1 [M + H]$^+$, 283.1 [M + Na]$^+$.

Conversion of *rac*-12 into [4-(Phenylsulfonyl)cyclopent-2-enyl]acetic Acid (*rac*-13c and *rac*-14c): A solution of *rac*-**12** (100 mg, 0.81 mmol) in THF (1 mL) and a solution of $Pd(acac)_2$ (12 mg, 0.004 mmol) in THF (1 mL) were added under Ar to a suspension of sodium benzenesulfinate (330 mg, 2.01 mmol) in THF (2 mL). After stirring for 5 h at 60 °C, the mixture was cooled to room temperature, and 5 % HCl was added until pH 3. The aqueous suspension was extracted with CH_2Cl_2 (3 ×). The combined organic fractions were dried (Na_2SO_4), evaporated under reduced pressure and purified by FC (petroleum ether/EtOAc, 1:2) to give a mixture of *rac*-**13c** and *rac*-**14c** (117 mg, 55 %). ^{1}H NMR and ^{13}C NMR spectroscopic data agreed with that of ref.[49]

Conversion of 17 into 3-(Phenylsulfonyl)cyclopent-1-ene (18b): The reaction was performed as described for *rac*-**13c** and *rac*-**14c**. FC (petroleum ether/EtOAc, 1:2) provided **18b** (55 %) as a colourless oil. IR (KBr): $\tilde{\nu}$ = 1301, 1141 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.23 (m, 4 H, 4-CH_2, 5-CH_2), 4.26 (m, 1 H, 1-H), 5.66 (m, 1 H, 3-H), 6.09 (m, 1 H, 2-H), 7.56 (m, 3 H, Ar-H), 7.88 (m, 2 H, Ar-H) ppm. ^{13}C NMR, (50 MHz, $CDCl_3$): δ = 24.55 (+, C-4), 31.97 (+, C-5), 72.46 (−, C-1), 77.25 (+, C-4), 123.82 (−, C-2), 133.64 (−, C-3), 128.98, 129.15, 131.66, 140.26 (Ar-C) ppm. $C_{11}H_{12}O_2S$ (208.28, 208.0558), MS (EI): *m*/*z* (%) = 208.0 (5) [M$^+$], 143.0 (25) [PhO_2S^+].

Conversion of 21 into 4-(Phenylsulfonyl)cyclopent-2-en-1-ol (*rac*-22b): The reaction was performed as described above. FC (petroleum ether/EtOAc, 1:2) provided *rac*-**22b** (57 %) as a colourless oil. IR (KBr): $\tilde{\nu}$ = 3492, 1306, 1165, 783 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, H,H COSY): δ = 2.21 (m, 1 H, 5-H_a), 2.40 (m, 1 H, 5-H_b), 4.15 (m, 1 H, 1-H), 4.71 (m, 1 H, 4-H), 5.75 (m, 1 H, 2-H), 6.36 (m, 1 H, 3-H), 7.65 (m, 3 H, Ar-H), 7.90 (m, 2 H, Ar-H). $C_{11}H_{12}O_3S$ (224.27, 224.0507) MS (FAB): *m*/*z* = 225.0 [M + H]$^+$, 247.0 [M + Na]$^+$.

Conversion of *cis*-3,5-Diacetoxycyclopent-1-ene (19) into 4-(Phenylsulfonyl)cyclopent-2-ene-1-yl Acetate (*rac*-20b): The reaction was

performed as described above. FC (petroleum ether/EtOAc, 1:2) provided *rac*-**20b** (63 %) as a colourless oil. IR (KBr): $\tilde{\nu}$ = 3056, 1255, 1160, 750 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 1.89 (s, 3 H, CH_3), 2.17 (m, 1 H, 5-H_a), 2.64 (m, 1 H, 5-H_b), 4.24 (m, 1 H, 4-H), 5.54 (m, 1 H, 1-H), 6.09 (m, 2 H, 3-H, 4-H), 7.63 (m, 3 H, Ar-H), 7.86 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 21.00 (−, CH_3), 31.03 (+, C-5), 70.43 (−, C-4), 77.52 (−, C-1), 129.83 (−, C-3), 137.00 (−, C-2), 129.11, 129.50, 134.01, 136.89 (−, Ar-C), 170.58 (+, CO) ppm. $C_{13}H_{14}O_4S$ (266.31, 266.0612), MS (EI): *m*/*z* (%) = 266.0 (ca. 1) [$M^{+\cdot}$], 124.9 (20) [PhOS]$^+$, 83.1 (100).

Pd-Mediated Reaction of Cinnamyl Acetate with Chloromagnesium Diphenylphosphinite: Cinnamyl acetate (0.1 mL, 0.27 mmol), Pd(acac)$_2$ (8.0 mg, 0.03 mmol) and a solution of chloromagnesuim diphenylphosphinite (78 mg, 0.30 mmol) in THF (2 mL) was stirred at 50 °C for 24 h under Ar. The mixture was cooled to room temperature and water was added. The aqueous suspension was extracted with CH_2Cl_2 (3 ×). The combined organic fractions were dried (Na_2SO_4), evaporated under reduced pressure and purified by FC (EtOAc then EtOAc/MeOH, 6:1) to give of *rac*-**16** (20 mg, 24 %).

Pd-Mediated Reaction of Cinnamyl Acetate with Lithium Diphenylphosphinite: A mixture of cinnamyl acetate (0.20 mL, 0.57 mmol) and Pd(acac)$_2$ (17 mg, 0.06 mmol) in THF (2 mL) was cooled to 0 °C under Ar. A solution of freshly prepared lithium diphenylphosphinite (0.57 mmol) in THF was added slowly and the mixture was then stirred for 1 h at 0 °C followed by 6 h at room temperature. The mixture was neutralized with 5 % HCl and extracted with CH_2Cl_2. The combined organic layers were dried and the solvent was evaporated. Pure *rac*-**16** (110 mg, 78 %) was obtained upon crystallisation from EtOAc. M.p.: 192−193 °C (ref.[50] 193−193.5 °C)

Pd-Mediated Reaction of 2-Cyclopentene-1-yl Acetate (*rac*-17) with Chloromagnesium Diphenylphosphinite: The reaction was performed as described above. FC (EtOAc/MeOH, 6:1) gave of *rac*-**18a** (7 %).

Pd-Mediated Reaction of *rac*-17 with Lithium Diphenylphosphinite: The reaction was performed as described above. FC ($CHCl_3$/EtOAc, 4:1, then $CHCl_3$/MeOH, 10:1) gave *rac*-**18a** (28 %).

Pd-Mediated Reaction of *rac*-12 with Lithium Diphenylphosphinite: A solution of lithium diphenylphosphinite (0.5 mmol) was added slowly to a solution of *rac*-**12** (58 mg, 0.5 mmol) and Pd(acac)$_2$ (10 mg, 0.09 mmol) in THF (2 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and then for 6 h at room temperature. The mixture was neutralised with 1 M NaOH and extracted with CH_2Cl_2 (3 ×). The aqueous phase was acidified with 5 % HCl and again extracted with CH_2Cl_2. These organic layers were dried and the solvent was evaporated. FC ($CHCl_3$/EtOAc, 4:1, then $CHCl_3$/MeOH, 10:1) provided a mixture of *rac*-**13a** and *rac*-**14a** (110 mg, 67 %) and *rac*-**24** (13 mg, 8 %) as a by-product.

[4-(Diphenylphosphanoyl)cyclopent-2-enyl]acetic Acid (*rac*-13a and *rac*-14a): M.p.: 178−180 °C (EtOAc/petroleum ether). IR (KBr): $\tilde{\nu}$ = 3365, 2954, 1737, 1257 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$,): δ = 1.83 (m, 1 H, 5-H_a), 2.40 (m, 3 H, 5-H_b, CH_2COOMe), 3.20 (m, 1 H, 1-H), 3.67 (m, 1 H, 4-H), 5.39 (m, 1 H, 3-H), 5.84 (m, 1 H, 2-H), 7.41 (m, 6 H, Ar-H), 7.67 (m, 4 H, Ar-H) ppm. ^{13}C NMR of the main isomer (50 MHz, $CDCl_3$): δ = 29.72 (C-5, d, $^4J_{C,P}$ = 3 Hz), 40.31 (*C*H_2COOMe), 42.60 (C-1, d, $^2J_{C,P}$ = 3 Hz), 46.17 (C-4, d, $^1J_{C,P}$ = 72 Hz), 125.41 (C-2, d, $^3J_{C,P}$ = 6 Hz), 139.41 (C-3, d, $^2J_{C,P}$ = 11 Hz), 128.74−132.97 (C-Ar), 175.06 (CO) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 33.19 (75 %), 31.25 (25 %). $C_{17}H_{17}O_3P$ (326.33, 326.1071). FAB MS: *m*/*z* = 327.1 [M + H]$^+$.

[2-(Diphenylphosphanoyl)cyclopent-2-enyl]acetic Acid (*rac*-24): ^1H NMR (300 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 2.19 (m, 4 H, 5-CH_2, CH_2COOMe), 3.09 (m, 3 H, 4-CH_2, 1-H), 3.76 (m, 1 H, 4-H), 5.39 (m, 1 H, 3-H), 7.48 (m, 6 H, Ar-H), 7.74 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 24.31 (+, C-5), 35.33 (+, *C*H_2COOMe, d, $^2J_{C,P}$ = 2 Hz), 36.73 (+, C-4, d, $^2J_{C,P}$ = 2 Hz), 46.37 (−, C-1, d, $^1J_{C,P}$ = 72 Hz), 123.48 (−, C-2, d, $J_{C,P}$ = 3 Hz), 128.83−132.21 (C-Ar), 141.83 (+, C-3, d, $^2J_{C,P}$ = 11 Hz), 171.02 (CO) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 32.65 ppm. $C_{17}H_{17}O_3P$ (326.33, 326.1071), FAB MS: *m*/*z* = 327.1 [M + H]$^+$.

(Diphenylphosphanoyl)-2-cyclopenten-4-ol (*rac*-22a) by Pd-Mediated Reaction of 3,4-epoxycyclopent-1-ene (*rac*-21) with Lithium Diphenylphosphinite: A solution of freshly prepared lithium diphenylphosphinite (1.2 mmol) was slowly added to a solution of *rac*-**21** (100 mg, 1.2 mmol) and Pd(acac)$_2$ (8.0 mg, 0.12 mmol) in THF (2 mL) at 0 °C. The mixture was stirred for 1 h at 0°C and then for 8 h at room temperature. The mixture was acidified with 5 % HCl and extracted with CH_2Cl_2. The combined organic layers were dried and the solvent was evaporated. FC ($CHCl_3$/EtOAc, 4:1, then $CHCl_3$/MeOH, 10:1) gave *rac*-**22a** (95 mg, 28 %). IR (KBr): $\tilde{\nu}$ = 3313, 1295, 1120 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 2.01 (m, 1 H, 5-H_a), 2.79 (m, 1 H, 5-H_b), 5.28 (m, 1 H, 1-H), 5.47 (m, 1 H, 4-H), 6.04 (m, 2 H, 2-H, 3-H), 7.46 (m, 6 H, Ar-H), 7.91 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.04 (C-5, d, $^2J_{C,P}$ = 4 Hz), 77.35 (C-1), 77.54 (C-4, d, $^4J_{C,P}$ = 6 Hz), 128.53−131.83 (Ar-C), 134.31 (C-3), 135.93 (C-2, d, $^1J_{C,P}$ = 2 Hz) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 30.95 ppm. $C_{17}H_{17}O_2P$ (284.29, 284.0966). FAB MS: *m*/*z* = 285.1 [M + H]$^+$.

Pd-Mediated Reaction of *rac*-21 with Chloromagnesium Diphenylphosphinite: A solution of $Ph_2POMgCl$ (337 mg, 1.2 mmol) was added to a solution of *rac*-**21** (100 mg, 1.2 mmol) and Pd(acac)$_2$ (8.0 mg, 0.12 mmol) in THF (2 mL). The mixture was stirred for 24 h at 50 °C. Water was added and the aqueous suspension was extracted with CH_2Cl_2 (3 ×). The combined organic fractions were dried, evaporated under reduced pressure and purified by FC (EtOAc/MeOH, 6:1) to give *rac*-**22a** (26 mg, 7 %).

4-(Diphenylphosphanoyl)-2-cyclopentene-1-yl Acetate (*rac*-20a) by Pd-Mediated Reaction of 19 with Lithium Diphenylphosphinite: A solution of freshly prepared lithium diphenylphosphinite (0.54 mmol) was slowly added at 0 °C under Ar to a solution of **19** (100 mg, 0.54 mmol) and Pd(acac)$_2$ (16 mg, 0.05 mmol) in THF (2 mL). The mixture was stirred for 1 h at 0 °C and then for 8 h at room temperature. A usual workup (CH_2Cl_2) followed by FC ($CHCl_3$/EtOAc, 4:1, then $CHCl_3$/MeOH, 10:1) gave *rac*-**20a** (80 mg, 45 %). IR (KBr): $\tilde{\nu}$ = 1731, 1245, 1120 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 2.01 (m, 1 H, 5-H_a), 2.06 (s, 3 H, CH_3), 2.79 (m, 1 H, 5-H_b), 5.28 (m, 1 H, 1-H), 5.47 (m, 1 H, 4-H), 6.04 (m, 2 H, 2-H, 3-H), 7.46 (m, 6 H, Ar-H), 7.91 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.25 (CH_3), 39.04 (C-5, d, $^2J_{C,P}$ = 4 Hz), 77.35 (C-1), 77.54 (C-4, d, $^4J_{C,P}$ = 6 Hz), 128.53−131.83 (C-Ar), 134.31 (C-2), 135.93 (C-3, d, $^1J_{C,P}$ = 2 Hz), 170.79 (CO) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 30.95. $C_{19}H_{19}O_3P$ (326.33, 326.1071). FAB MS: *m*/*z* = 327.1 [M + H]$^+$.

[4-(Diphenylthiophosphanoyl)cyclopent-2-enyl]acetic Acid (*rac*-23) by Pd-Mediated Reaction of *rac*-12 with Lithium Diphenylthiophosphinite: The reaction was performed as described above. FC

($CHCl_3$/MeOH, 10:1) gave *rac*-**23** (120 mg, 61 %). M.p.: 101−103 °C (EtOAc/petroleum ether). IR (KBr): $\tilde{\nu}$ = 1764, 1706 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.90 (m, 1 H, 5-H_a), 2.45 (m, 3 H, 5-H_b, CH_2COOMe), 3.25 (m, 1 H, 1-H), 4.10 (m, 1 H, 4-H), 5.43 (m, 1 H, 3-H), 5.90 (m, 1 H, 2-H), 7.45 (m, 6 H, Ar-H), 7.88 (m, 4 H, Ar-H) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 48.55 ppm. $C_{19}H_{19}O_2PS$ (342.39, 342.0843). EI MS: *m*/*z* (%) = 341.9 (40) [M^+], 234.9 (40), 218.0 (100).

Esterification of *rac*-13a and *rac*-14a: A drop of thionyl chloride was added to a solution of *rac*-**13a** and *rac*-**14a** (220 mg, 0.68 mmol) in MeOH (5 mL). The mixture was stirred for 1 h. Workup (CH_2Cl_2) and subsequent recrystallisation from EtOAc/petroleum ether yielded solid *rac*-**13b** and, from the filtrate, *rac*-**14b** as a colourless oil in quantitative yield.

Methyl *cis*-[4-(Diphenylphosphanoyl)cyclopent-2-enyl]acetate (*rac*-13b): M.p.: 124−125 °C (EtOAc/petroleum ether). IR (KBr): $\tilde{\nu}$ = 1727, 1174 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 1.79 (1 H, 5-H_a, for *J* values, see general part), 2.30−2.40 (AB of ABX, J_{AX} = 7, J_{BX} = 8, J_{AB} = 16 Hz, m, 2 H, CH_2COOMe), 2.45 (1 H, 5-H_b, for *J* values, see general part), 3.17 (m, 1 H, 1-H), 3.67 (s, OCH_3), 3.75 (m, 1 H, 4-H), 5.55 (m, 1 H, 3-H), 5.86 (m, 1 H, 2-H), 7.41 (m, 6 H, Ar-H), 7.67 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.92 (C-5, d, $^2J_{C,P}$ = 2 Hz), 39.68 (*C*H_2COOMe, d, $^4J_{C,P}$ = 2 Hz), 42.48 (C-1, d, $^2J_{C,P}$ = 3 Hz), 45.03 (C-4, d, $^1J_{C,P}$ = 72 Hz), 51.52 (OCH_3), 126.25 (C-3, d, $^3J_{C,P}$ = 6 Hz), 138.40 (C-2, d, $^2J_{C,P}$ = 11 Hz), 128.44−131.83 (C-Ar), 173.20 (CO) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 30.45. $C_{20}H_{21}O_3P$ (340.36, 340.1228). FAB MS: *m*/*z* = 341.1 $[M + H]^+$, 363.1 $[M + Na]^+$.

Methyl *trans*-[4-(Diphenylphosphanoyl)cyclopent-2-enyl]acetate (*rac*-14b): ^1H NMR (300 MHz, $CDCl_3$): δ = 2.34 and 2.48 (2 m, 2 H, 5-CH_2), 2.62−2.80 (AB of ABX, J_{AX} = 7, J_{BX} = 8, J_{AB} = 17.0 Hz m, 2 H, CH_2COOMe), 3.17 (m, 1 H, 1-H), 3.42 (s, OCH_3), 3.77 (m, 1 H, 4-H), 5.40 (m, 1 H, 3-H), 6.03 (m, 1 H, 2-H), 7.46 (m, 6 H, Ar-H), 7.78 (m, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.94 (C-5, d, $^2J_{C,P}$ = 2 Hz), 35.72 (*C*H_2COOMe, d, $^4J_{C,P}$ = 2 Hz), 38.63 (C-1, d, $^2J_{C,P}$ = 3 Hz), 47.67 (C-4, d, $^1J_{C,P}$ = 70 Hz), 51.38 (CH_3), 126.80 (C-3, d, $^3J_{C,P}$ = 6 Hz), 128.52−131.07 (C-Ar), 135.87 (C-2, d, $^2J_{C,P}$ = 11 Hz), 173.21 (CO) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 26.93. $C_{20}H_{21}O_3P$ (340.36, 340.1228). FAB MS: *m*/*z* = 341.1 $[M + H]^+$, 363.1$[M + Na]^+$.

Treatment of *rac*-13b with Pentanoyl-1*H*-imidazole: A solution of freshly prepared LDA [−80 °C, 0.29 mmol in THF/hexane (1 mL)] and pentanoyl-1*H*-imidazole (221 mg, 1.45 mmol) was added to a solution of *rac*-**13b** (100 mg, 0.29 mmol) in THF (2 mL) cooled to −80 °C. The mixture was stirred for 1 h at −80 °C before the cooling bath was removed and sat. aq. NH_4Cl was added. Usual workup (CH_2Cl_2) followed by FC (EtOAc) furnished *rac*-**14b** (53 mg, 53 %).

Methyl [4-(Diphenylphosphonyl)-2-pentanoylcyclopent-2-enyl]acetate (*rac*-27) by Treatment of *rac*-14b with Pentanoyl-1*H*-imidazole in the Presence of 2 Equiv. of LDA: A solution of freshly prepared LDA [−80 °C, 0.58 mmol in THF/hexane (1 mL)] and pentanoyl-1*H*-imidazole (221 mg, 1.45 mmol) was added to a solution of *rac*-**13b** (100 mg, 0.29 mmol) in THF (2 mL) at −80 °C. The mixture was stirred and after 1 h the cooling bath was removed and sat. aq. NH_4Cl (2 mL) was added. Usual workup (CH_2Cl_2) followed by FC (EtOAc) furnished *rac*-**27** (29 mg, 22 %) and *rac*-**14b** (23 mg, 22 %). IR (film): $\tilde{\nu}$ = 2921, 1735, 1442, 1247, 1143 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 0.88 (t, 3 H, 5′-CH_3), 1.26 (m, 2 H, 4′-CH_2), 1.53 (m, 2 H, 3′-CH_2), 1.95 (m, 1 H, 5-H_a), 2.56 (m, 3 H, 2′-CH_2, 5-H_a), 2.82 (m, 2 H, CH_2COOMe) 3.51 (m, 1 H, 1-H), 3.60 (s, 3 H, CH_3), 3.84 (m, 1 H, 4-H), 6.47 (m, 1 H, 3-H), 7.47 (m, 6 H, Ar-H), 7.73 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.01 (C-5′), 22.51 (C-4′), 26.66 (C-3′), 30.68 (C-2′), 38.02 (C-5, d, $^1J_{C,P}$ = 6 Hz), 39.33 (*C*H_2COOMe), 41.25 (C-1, d, $^4J_{C,P}$ = 3 Hz), 47.64 (C-4, d, $^1J_{C,P}$ = 67 Hz), 51.49 (CH_3), 76.30 (C-OH), 127.17 (C-2, d, $^3J_{C,P}$ = 6 Hz), 132.30 (C-3, d, $^2J_{C,P}$ = 11 Hz), 128.83−131.49 (C-Ar), 173.35 (C-1′) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 29.97 ppm. $C_{24}H_{27}O_4P$ (424.48, 424.1803). FAB MS: *m*/*z* = 425.1 $[M + H]^+$.

Conversion of *rac*-13b into Methyl [4-(Diphenylphosphanoyl)-2-trimethylsilylcyclopent-3-enyl]acetate (*rac*-29): A solution of *n*BuLi (1.6 M in hexane, 0.230 mL, 0.32 mmol) and trimethylchlorosilane (0.04 mL, 0.33 mmol) were added to a solution of *rac*-**13b** (100 mg, 0.29 mmol) cooled to −80 °C in THF (2 mL). The mixture was warmed and water was added. Usual workup (CH_2Cl_2) followed by FC (EtOAc) furnished *rac*-**29** (93 mg, 78 %) as a colourless oil. IR (KBr): $\tilde{\nu}$ = 2948, 1733, 1172 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, H,H COSY, HMBC, HMQC): δ = 0.00 (s, 9 H, Si-CH_3), 1.93 (m, 1 H, 2-H), 2.31 (m, 3 H, 5-H_a, CH_2COOMe), 2.78 (m, 2 H, 5-H_b, 1-H), 3.60 (s, 3 H, CH_3), 6.35 (m, 1 H, 3-H), 7.45 (m, 6 H, Ar-H), 7.67 (m, 4 H, Ar-H) ppm. ^{13}C NMR (APT, 75 MHz, $CDCl_3$): δ = −2.87 (−, CH_3-Si), 36.91 (+, C-1, d, $^2J_{C,P}$ = 3 Hz), 39.95 (+, C-5, d, $^2J_{C,P}$ = 2 Hz), 41.68 (+, *C*H_2COOMe), 45.10 (−, C-2, d, $^3J_{C,P}$ = 6 Hz), 51.38 (−, CH_3), 128.29−131.62 (−, Ar-C), 149.73 (−, C-3, d, $^2J_{C,P}$ = 11 Hz), 172.56 (+, CO) ppm. ^{31}P NMR (80.9 MHz, $CDCl_3$): δ = 21.87 ppm. $C_{23}H_{29}O_3PSi$ (412.54, 412.16). EI MS: *m*/*z* (%) = 412.0 (20, $[M]^{+\cdot}$), 339 (100, $[M - Me_3Si]^+$).

Treatment of *rac*-29 with Valeraldehyde: A freshly prepared solution of LDA (0.23 mmol) in THF and valeraldehyde (1.17 mL, 1.1 mmol) were added to a solution of *rac*-**29** (93 mg, 0.22 mmol) cooled to −80 °C in THF (2 mL). The mixture was stirred 1 h at −80 °C. Usual workup (CH_2Cl_2) followed by FC (EtOAc) furnished *rac*-**13b** (21 mg, 23 %).

Conversion of *rac*-13b into *rac*-31 and *rac*-32 with Valeraldehyde in the Presence of Dichlorotitanium Diisopropoxide: A freshly prepared solution of LDA (0.48 mmol) in THF was added slowly to a solution of *rac*-**13b** (137 mg, 0.40 mmol) in THF (2 mL) cooled to −80 °C. The mixture was stirred at −80 °C for 0.5 h and then a solution of [Ti(*i*OPr)$_2$Cl$_2$] (0.48 mmol) in THF was added. After stirring for 2 h at −80 °C, valeraldehyde (0.128 mL, 1.206 mmol) was added. After stirring for 1 h the mixture was slowly warmed to 20 °C. Sat. aq. NH_4Cl−KF (5 mL) was added. A usual workup (CH_2Cl_2) followed by FC (EtOAc) and HPLC (EtOAc/pentane, 2:1; flow rate: 10 mL/min) furnished *rac*-**31** (70 mg, 52 %) and *rac*-**32** (36 mg, 21 %) as colourless oils and the starting material *rac*-**13b** (7 mg).

(1*S, 4*R**, 1′S*)-[4-(Diphenylphosphanoyl)-4-(1-hydroxypentyl)-cyclopent-2-enyl]acetic Acid (*rac*-31):** IR (KBr): $\tilde{\nu}$ = 3543, 1754, 1227, 1116 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, H,H COSY): δ = 0.81 (t, 3 H, CH_3-5′), 1.21 (m, 2 H, CH_2-4′), 1.28 (m, 3 H, CH_2-3′, 2′-H_a), 1.51 (m, 1 H, 2′-H_b), 1.58 and 1.92 (AB of ABX, J_{AX} = 7, J_{BX} = 8, J_{AB} = 17.0 Hz, m, 2 H, CH_2COOMe), 1.52 (m, 1 H, 5-H_a), 2.26 (m, 1 H, 5-H_b), 3.17 (m, 1 H, 1-H), 3.61 (m, 3 H, CH_3), 3.92 (dt, $J_{H,H}$ = 10, J_{P-H} = 3 Hz, 1 H, 1′-H), 5.90 (m, 1 H, 3-H), 6.19 (m, 1 H, 2-H), 7.67 (m, 5 H, Ar-H), 7.74 (m, 2 H, Ar-H), 7.92 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.18 (C-5′), 22.86 (C-4′), 28.51 (C-3′), 31.74 (C-2′, d, $^2J_{C,P}$ = 9.5 Hz), 35.13 (C-5, d, $^2J_{C,P}$ = 6 Hz), 39.46 (*C*H_2COOMe, d, $^3J_{C,P}$ = 3 Hz), 42.74 (C-1, d, $^3J_{C,P}$ = 2 Hz), 51.73 (CH_3), 61.58 (C-4), 76.05 (C-1′), 129.24 (C-3, d, $^3J_{C,P}$ = 7.5 Hz), 138.24 (C-3, d, $^2J_{C,P}$ = 11 Hz), 128.15−132.24 (C-Ar), 172.66 (CO) ppm. ^{31}P NMR (80.96 MHz,

$CDCl_3$): δ = 35.57 ppm. $C_{25}H_{31}O_4P$ (426.49, 426.1803). ESI MS: *m/z* = $[C_{25}H_{31}O_4P + H]^+$ calcd. 427.2033, found 427.2037.

(1*S,4*R**,1′*R**)-[4-(Diphenylphosphanoyl)-4-(1-hydroxypentyl)cyclopent-2-enyl]acetic Acid (*rac*-32):** IR (KBr): ṽ = 3543, 1756, 1227, 1117 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 0.82 (t, 3 H, 5′-CH_3), 1.20 (m, 2 H, 4′-CH_2), 1.24 (m, 3 H, 3′-CH_2, 2′-H_a), 1.51 (m, 1 H, 2′-H_b), 1.58 and 1.92 (AB of ABX, J_{AX} = 7, J_{BX} = 8, J_{AB} = 17.0 Hz, m, 2 H, CH_2COOMe), 1.52 (m, 1 H, 5-H_a), 2.24 (m, 1 H, 5-H_b), 3.17 (m, 1 H, 1-H), 3.61 (m, 3 H, CH_3), 3.90 (dt, $J_{H,H}$ = 10, J_{P-H} = 3 Hz, 1 H, 1′-H), 5.97 (m, 1 H, 3-H), 6.19 (m, 1 H, 2-H), 7.67 (m, 5 H, Ar-H), 7.74 (m, 2 H, Ar-H), 7.92 (m, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.14 (C-5′), 22.67 (C-4′), 28.61 (C-2′), 32.00 (C-3′), 35.26 (C-5), 39.52 (*C*H_2COOMe), 42.83 (C-1), 51.65 (CH_3), 76.18 (C-1′, d, $^1J_{C,P}$ = 32 Hz), 128.93 (C-3, d, $^3J_{C,P}$ = 7.5 Hz), 138.17 (C-3, d, $^2J_{C,P}$ = 11 Hz), 128.15−132.24 (C-Ar), 172.60 (CO) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 34.51 ppm. $C_{25}H_{31}O_4P$ (426.49, 426.1803). ESI MS: *m/z* = $[C_{25}H_{31}O_4P + H]^+$ calcd. 427.2033, found 427.2037.

Reaction of *rac*-13b with Valeraldehyde in the Presence of Chlorotitanium Triisopropoxide: A freshly prepared solution of LDA (0.43 mmol) in THF was added slowly to a solution of *rac*-**13b** (450 mg, 0.40 mmol) in THF (2 mL) cooled to −80 °C. The mixture was stirred at −80 °C for 0.5 h and a solution of [Ti(*i*OPr)$_3$Cl] (3.44 mL, 0.48 mmol, THF) was added. After stirring for 2 h at −80 °C, valeraldehyde (0.13 mL, 1.2 mmol) was added. After stirring for 1 h, the mixture was warmed slowly to room temp. Sat. aq. NH_4Cl−KF (5 mL) was added. Usual workup (CH_2Cl_2) followed by FC (EtOAc) and HPLC (EtOAc/pentane, 2:1; flow rate: 10 mL/min) furnished *rac*-**31** (53 mg, 33 %, based on consumed *rac*-**13b**) and *rac*-**32** (46 mg, 38 %, based on consumed *rac*-**13b**) as colourless oils and starting material *rac*-**13b** (287 mg).

(1*S,4*R**,1′*R**)-[4-(Diphenylphosphanoyl)-4-(1-hydroxypentyl)-cyclopent-2-enyl]acetic Acid (*rac*-31):** IR (KBr): ṽ = 3543, 1754, 1227, 1116 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 0.81 (t, 3 H, CH_3-5′), 1.23 (m, 6 H, 4′-CH_2, 3′-CH_2, 2′-CH_2), 1.93 (m, 1 H, 5-H_a), 2.21 (m, 2 H, CH_2COOMe), 2.39 (m, 2 H, 5-H_b, 1′-H), 3.61 (s, 3 H, CH_3), 4.13 (dt, $J_{C,H}$ = 10, J_{P-H} = 3 Hz, 1 H, 1′-H), 5.47 (m, 1 H, 3-H), 5.88 (m, 1 H, 2-H), 7.44 (m, 6 H, Ar-H), 7.90 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.14 (C-5′), 22.91 (C-4′), 28.48 (C-3′), 31.17 (C-5, d, $^2J_{C,P}$ = 6 Hz), 32.22 (C-2′, d, $^2J_{C,P}$ = 9.5 Hz), 39.81 (*C*H_2COOMe, d, $^3J_{C,P}$ = 3 Hz), 41.82 (C-1, d, $^3J_{C,P}$ = 2 Hz), 51.63 (CH_3), 61.60 (C-4, d, $^1J_{C,P}$ = 68 Hz), 71.92 (C-1′), 129.91 (C-3, d, $^3J_{C,P}$ = 7.5 Hz), 138.72 (C-3, d, $^2J_{C,P}$ = 11 Hz), 128.15−132.24 (C-Ar), 172.46 (CO) ppm. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ = 21.00 ppm. $C_{25}H_{31}O_4P$ (426.49, 426.1803). FAB MS: *m/z* = 427.0 $[M + H]^+$, 448.7 $[M + Na]^+$.

(1*S,4*R**,1′*R**)-[4-(Diphenylphosphanoyl)-4-(1-hydroxypentyl)-cyclopent-2-enyl]acetic Acid (*rac*-32):** IR (KBr): ṽ = 3543, 1754, 1227, 1116 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 0.83 (t, 3 H, 5′-CH_3), 1.18 (m, 6 H, 4′-CH_2, 3′-CH_2, 2′-H_a), 1.47 (m, 2 H, 5-H_a and probably 2′-H_b), 1.73 (m, 2 H, CH_2COOMe), 2.71 (m, 1 H, 5-H_b), 3.14 (m, 1 H, 1-H), 3.61 (s, 3 H, CH_3), 3.99 (dt, $J_{C,H}$ = 10, J_{P-H} = 3 Hz, 1 H, 1′-H), 5.45 (m, 1 H, 3-H), 5.85 (m, 1 H, 2-H), 7.44 (m, 6 H, Ar-H), 7.90 (m, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.13 (C-5′), 22.87 (C-4′), 28.53 (C-3′), 30.84 (C-2′), 31.74 (C-5, d, $^2J_{C,P}$ = 9.5 Hz), 39.24 (*C*H_2COOMe,), 43.14 (C-1, d, $^3J_{C,P}$ = 4 Hz), 51.61 (CH_3), 61.56 (C-4, d, $^3J_{C,P}$ = 72 Hz), 72.44 (C-1′), 129.84 (C-3, d, $^3J_{C,P}$ = 7.5 Hz), 138.77 (C-2, d, $^2J_{C,P}$ = 11 Hz), 128.15−132.24 (C-Ar), 172.54 (CO) ppm. ^{31}P NMR (80 MHz, $CDCl_3$): δ = 29.93 ppm. $C_{25}H_{31}O_4P$ (426.49, 426.1803). FAB MS: *m/z* = 427.1 $[M + H]^+$, 449.0 $[M + Na]^+$.

Methyl (*Z*)-(1*R)-(4-Pentylidenecyclopent-2-enyl)acetate (*rac*-7a):** A solution of KO*t*Bu (9 mg, 0.07 mmol) in THF (1 mL) was added slowly under Ar to a solution of *rac*-**31** (26 mg, 0.06 mmol) in THF (3 mL). The mixture was stirred for 0.5 h and then water was added. A usual workup (Et_2O) followed by FC (pentane/Et_2O,1:1) furnished *rac*-**7a** (11 mg, 95 %). ^1H NMR (400 MHz, CD_3OD, H,H COSY, NOEDIF): δ = 0.90 (t, 3 H, 5′-CH_3), 1.34 (m, 4 H, 4′-CH_2, 3′-CH_2), 2.14 (m, 3 H, 2′-CH_2, 5-H_a), 2.26 and 2.39 (AB of ABX, J_{AX} = 6, J_{BX} = 7, J_{AB} = 16 Hz, m, 2 H, CH_2COOMe) 2.73 (m, 1 H, 5-H_b), 3.12 (m, 1 H, 1-H), 3.66 (s, 3 H, CH_3), 5.14 (t, 1 H, 1′-H), 6.00 (m, 1 H, 2-H), 6.41 (m, 1 H, 3-H) ppm. $C_{13}H_2O_2$ (208.30, 208.1463).

Methyl (*E*)-(1*R)-(4-Pentylidenecyclopent-2-enyl)acetate (*rac*-10a):** *rac*-**32a** was converted into *rac*-**10c** as described for **7a**. Yield: 11 mg, (95 %). ^1H NMR (300 MHz, $CDCl_3$/CD_3OD, H,H COSY, NOEDIF): δ = 0.86 (t, 3 H, 5′-CH_3), 1.28 (m, 4 H, 4′-CH_2, 3′-CH_2), 2.00 (m, 3 H, 2′-CH_2, 5-H_a), 2.28 and 2.39 (AB of ABX, J_{AX} = 6, J_{BX} = 7, J_{AB} = 16 Hz, m, 2 H, CH_2COOMe), 2.71 (m, 1 H, 5-H_b), 3.20 (m, 1 H, 1-H), 3.66 (s, 3 H, CH_3), 5.28 (t, 1 H, 1′-H), 5.82 (dd, 1 H, 2-H), 6.06 (dd, 1 H, 3-H) ppm. $C_{13}H_2O_2$ (208.30, 208.1463).

Saponification of *rac*-7a: A solution of barium hydroxide (143 mg, 0.52 mmol) in MeOH (1 mL) was added under Ar to a solution of *rac*-**7a** (11 mg, 0.052 mmol) in MeOH (2 mL). The mixture was stirred for 3 h and then 0.1 M HCl (3 mL) was added. A usual workup (Et_2O) and concentration under vacuum under Ar gave the crude product *rac*-**7b** (7.4 mg, 85 %), which was used in the next step without purification. Compound *rac*-**10a** was converted into *rac*-**10b** as described for **7b**. Yield: 80 % (7.5 mg).

(3*aR,6*aS**,1′*S**)-5-(1-Hydroxypentyl)-3,3a,4,6a-tetrahydrocyclopenta[*b*]furan-2-one (*rac*-8) by Oxidation of *rac*-7b with H_2O_2/Diphenyl Diselenide:** A solution of diphenyl diselenide (1 mg, 3.8 μmol) in CH_2Cl_2 (1 mL) and aq. 50 % H_2O_2 (4 μL) were added under Ar to a solution of *rac*-**7b** (7.5 mg, 38 μmol) in CH_2Cl_2 (0.5 mL) at 0 °C. The mixture was stirred at 0 °C for 4 h and then extracted with Et_2O. The organic phase was washed with aq. 5 % $NaHCO_3$ (2 ×), dried (Na_2SO_4), filtered, and the solvents were evaporated. FC (EtOAc) gave *rac*-**8** (5 mg, 61 %). ^1H NMR (400 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 0.91 (t, 3 H, CH_3), 1.36 (m, 4 H, 4′-CH_2, 3′-CH_2), 1.84 (m, 2 H, 4′-CH_2), 2.20 (m, 2 H, 2-H_a, 4-H_a), 2.86 (m, 2 H, 2-H_b, 4-H_b), 3.20 (m, 1 H, 3a-H), 4.48 (br. s, 1 H, 1′-H), 4.70 (dd, *J* = 1, *J* = 6 Hz, H, 6a-H), 5.70 (m, 1 H, 6-H). $C_{12}H_{18}O_3$ (210.27, 210.1255), FAB MS: *m/z* = 211.2 $[M + H]^+$.

(3*aR,6*aS**,1′*R**)-5-(1-Hydroxypentyl)-3,3a,4,6a-tetrahydrocyclopenta[*b*]furan-2-one (*rac*-11) by Oxidation of *rac*-10b with H_2O_2/Diphenyl Diselenide:** *rac*-**10b** was converted into *rac*-**11** as described for *rac*-**8**. Yield: 5 mg (61 %). ^1H NMR (400 MHz, $CDCl_3$, H,H COSY, HMQC, HMBC): δ = 0.84 (t, 3 H, CH_3), 1.28 (m, 4 H, 4′-CH_2, 3′-CH_2), 1.51 (m, 2 H, 4′-CH_2), 2.28 (m, 2 H, 2-H_a, 4-H_a), 2.76 (m, 2 H, 2-H_b, 4-H_b), 3.11 (m, 1 H, 3a-H), 4.20 (t, 1 H, 1′-H), 5.41 (m, 1 H, 6a-H), 5.68 (m, 1 H, 6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.95 (C-5′), 21.51 (C-4′), 26.47 (C-3′), 34.07 (C-2′), 34.46 (C-3a), 35.15 (C-2), 37.11 (C-4), 69.90 (C-1′), 88.28 (C-6a), 121.94 (C-6), 158.96 (CO) ppm. $C_{12}H_{18}O_3$ (210.27, 210.1255). FAB MS: *m/z* = 211.2 $[M + H]^+$, 193.1 $[C_{12}H_8O_2]$.

Oxidative Cyclization of *rac*-3 with a Catalytic Amount of Diphenyl Diselenide and Hydrogen Peroxide: A solution of diphenyl diselen-

ide (3.4 mg, 0.01 mmol) in CH_2Cl_2 (2 mL) was added at 0 °C to a solution of *rac*-**3** (21.8 mg, 0.11 mmol) in CH_2Cl_2 (1 mL). After slow addition of hydrogen peroxide (45 μL, 31 wt.% solution in water), the mixture was stirred for 1 h and then warmed to room temperature. After dilution with CH_2Cl_2 (5 mL), the solution was extracted with 10 % aq. $NaHCO_3$ (10 mL). A usual workup (CH_2Cl_2) and LC (petroleum ether/EtOAc, 1:1) yielded *rac*-**2a** (18.3 mg, 78 % yield) containing a trace of the corresponding *trans*-diastereoisomer *rac*-**2b**.

Oxidative Cyclization of *rac*-3 with a Stoichiometric Amount of Benzeneseleninic Acid and Hydrogen Peroxide in CH_2Cl_2: Benzeneseleninic acid (24.8 mg, 0.13 mmol) in CH_2Cl_2 (1 mL) was added to a solution of *rac*-**3** (26.4 mg, 0.13 mmol) in CH_2Cl_2 (1 mL). Hydrogen peroxide (13 μL, 31 wt.% solution in water) was then added slowly at 0 °C under vigorous stirring. The mixture was stirred for 2 h. A usual workup (aq. $NaHCO_3$ and CH_2Cl_2), followed by LC (petroleum ether/EtOAc, 1:1) yielded an 8:1 mixture (determined by ^{1}H NMR spectroscopy) of **2a** (major component) and **2b** (65 % total yield).

Oxidative Cyclization of *rac*-3 Acid with a Stoichiometric Amount of Benzeneselenonic Acid in CH_2Cl_2: *rac*-**3** (15.3 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at 0 °C to benzeneselenonic acid (16.7 mg, 0.08 mmol) as a suspension in CH_2Cl_2 (1 mL). Water (3 μL) was added and the mixture was stirred for 3 h. A usual workup (CH_2Cl_2) and LC (petroleum ether/EtOAc, 1:1) yielded the cyclization product *rac*-**2c** (11.3 mg, 74 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3 H), 1.08 (s, 3 H), 1.31−1.39 (ddd, 1 H), 1.43−1.49 (ddd, 1 H), 1.58−1.74 (m, 2 H), 1.85−2.03 (m, 2 H), 2.08−2.16 (d, 1 H), 2.27−2.35 (dd, 1 H), 2.53−2.62 (dd, 1 H), 2.72−2.82 (dd, 1 H), 2.94−3.04 (m, 1 H), 5.42−5.47 (d, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.54, 26.68, 28.03, 28.35, 32.16, 34.75, 36.49, 39.21, 42.56, 90.46, 140.21, 141.76, 177.90 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1760, 1170 cm^{-1}. HR MS: calcd. for $C_{13}H_{18}O_2$ 206.1307, found 206.1308.

Oxidative Cyclization of *rac*-3 with Benzeneseleninic Acid, Hydrogen Peroxide and MeOH in CH_2Cl_2: Benzeneseleninic acid (23.0 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) was added to a solution containing *rac*-**3** (24.9 mg, 0.12 mmol) and MeOH (5 μL) in CH_2Cl_2 (1 mL). Hydrogen peroxide (12.2 μL, 31 wt.% solution in water) was added at 0 °C and the mixture was stirred for 1 h. A usual workup (aq. $NaHCO_3$ and CH_2Cl_2) followed by LC (petroleum ether/EtOAc, 1:1) yielded a 4:1 mixture (^{1}H NMR) of *rac*-**2a** and *rac*-**2b** (68 % total yield), with *rac*-**2a** as the major diastereoisomer. The corresponding methoxylactones (*rac*-**2d** and its diastereoisomer) were not observed.

Oxidative Cyclization of *rac*-3 with Benzeneseleninic Acid, Hydrogen Peroxide in MeOH: A mixture of benzeneseleninic acid (20.9 mg, 0.11 mmol), *rac*-**3** (22.6 mg, 0.11 mmol), and hydrogen peroxide (11.1 μL, 31 wt.% solution in water) in MeOH (1 mL) was stirred for 1 h at 0 °C. Usual workup (aq. $NaHCO_3$ and CH_2Cl_2) followed by LC (petroleum ether/EtOAc, 1:1) yielded a 1.2:1 mixture (^{1}H NMR) of *rac*-**2a** and *rac*-**2b** (35 % total yield). The methoxylactone **2d** and its stereoisomer were not observed.

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