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A new approach to 2,2-disubstituted 1-(methylsulfanyl)vinyl phosphonates via an intermediate thiocarbonyl ylide

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Dedicated to Professor Marek Zaidlewicz on the occasion of his 70th birthday

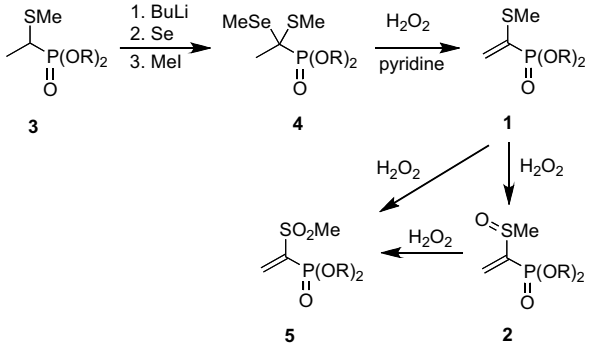
ABSTRACT

The reaction of methyl (diethylphosphoryl)dithioformate (**6**) with diaryldiazomethanes **7a–d** in THF at −60 °C to room temperature followed by desulfurization is shown to be a convenient method for the preparation of 2,2-disubstituted 1-(methylsulfanyl)vinyl phosphonates **8a–d**. The analogous reactions with 2-diazoacenaphthen-1-one (**7f**) or 2-diazocamphor (**7g**) in refluxing THF yield selectively the corresponding (*Z*)- and (*E*)-vinyl phosphonates **8f** and **8g**, respectively. These products can be easily oxidized to the vinylsulfoxides **13** and vinylsulfones **14**. On the other hand, methyl (diethylphosphoryl)-dithioformate (**6**) and 2-diazo-1,2-diphenylethanone (**7e**) in boiling THF react to give the 1,3-oxathiole **12**. All these reactions occur via an intermediate thiocarbonyl ylide **11** followed by 1,3-dipolar electrocyclization and sulfur extrusion or 1,5-dipolar electrocyclization.

1. Introduction

The activation of C,C-double bonds by phosphorus and sulfur functional groups is widely explored in organic synthesis.[1–3] The most important applications relate to their use as dipolarophiles dienophiles, and Michael acceptors. In the case of 1-(alkylsulfanyl)-vinyl phosphonates **1**, the activation is of the 'capto-dative' type.[4] The selective oxidation to 1-sulfinylvinyl phosphonates **2** opens access to highly activated electron-deficient alkenes, which can also be prepared in enantiomerically pure form. In this case, the stereogenic center located at the *S*-atom governs the stereochemical outcome of the reaction.[5] The most frequently applied method for the preparation of vinyl phosphonates **1** is based on the selenylation/oxidation sequence of reactions starting with α-(methylsulfanyl)phosphonates **3** (Scheme 1).[1,2]

A well-known and general method for the synthesis of substituted alkenes, especially suitable for sterically congested systems, is the so-called 'twofold extrusion' method developed by Barton.[6–9] In this case, a thiocarbonyl compound is used as a dipolarophile in the reaction with a diazo compound, the subsequent elimination of N_2 leads to a thiirane, which in turn is desulfurized to give the alkene. The key intermediate in this sequence is a reactive thiocarbonyl ylide, the precursor of the thiirane.



Scheme 1.

In a series of recent papers, methyl (dialkylphosphoryl)dithioformates were shown to react smoothly as dipolarophiles, e.g., with diazomethane and thiocarbonyl ylides.[10–13]

The [2+3] cycloaddition with diazomethane leads to the unstable 1,3,4-thiadiazoline, which extrudes N_2 already at −35 °C, and in the absence of an intercepting agent, the intermediate thiocarbonyl ylide undergoes a head-to-head dimerization.[11] On the other hand, it is well established that tetrasubstituted thiocarbonyl ylides do not dimerize but form thiiranes as products of a 1,3-dipolar electrocyclization.[14,15] Based on these results, we decided to test the reactivity of methyl (diethylphosphoryl)dithioformate **6** toward disubstituted diazomethanes **7** with the aim of obtaining the corresponding thiiranes, which by elimination of sulfur could

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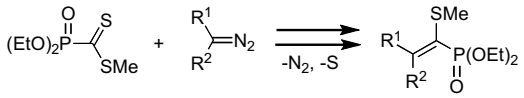
be converted to the corresponding 1-(methylsulfanyl)vinyl phosphonates **8** (Scheme 2).



Scheme 2.

To the best of our knowledge, vinyl phosphonates of type **8** with R^1, R^2=alkyl or aryl are hitherto only little known.[16,17]

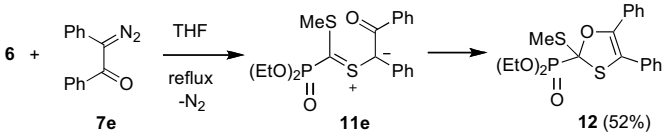
2. Results and discussion

2.1. Reactions of 6 with diazo compounds

The reactions of diaryldiazomethanes **7a–d** with **6** are significantly slower than with the parent diazomethane and the decoloration of the reaction mixture at −60 °C was observed only after ca. 30 min. The evolution of N_2 started after warming of the mixture to room temperature. In the case of diphenyldiazomethane (**7a**), the crude product was identified as a mixture of thiirane **9a** and the vinyl phosphonate **8a**, formed after spontaneous desulfurization (Scheme 3). The attempted chromatographic separation of **8a** and **9a** was in vain and, therefore, the mixture was treated with tris-(diethylamino)phosphine in boiling THF yielding **8a** exclusively (65%). The reactions with the diaryldiazomethanes **7b–d** were carried out in an analogous manner to give the corresponding vinyl phosphonates **8b–d** in satisfactory yields.

α-Oxodiazo compounds were frequently used in reactions with thiocarbonyl derivatives. In these systems, the intermediate thiocarbonyl ylides enter two competitive electrocyclizations leading to either thiiranes (1,3-dipolar electrocyclization) or 1,3-oxathioles (1,5-dipolar electrocyclization). The reaction course strongly depends on the type of the C=S dipolarophile as well as on the substitution pattern of the α-oxodiazo compounds.[14,18–22]

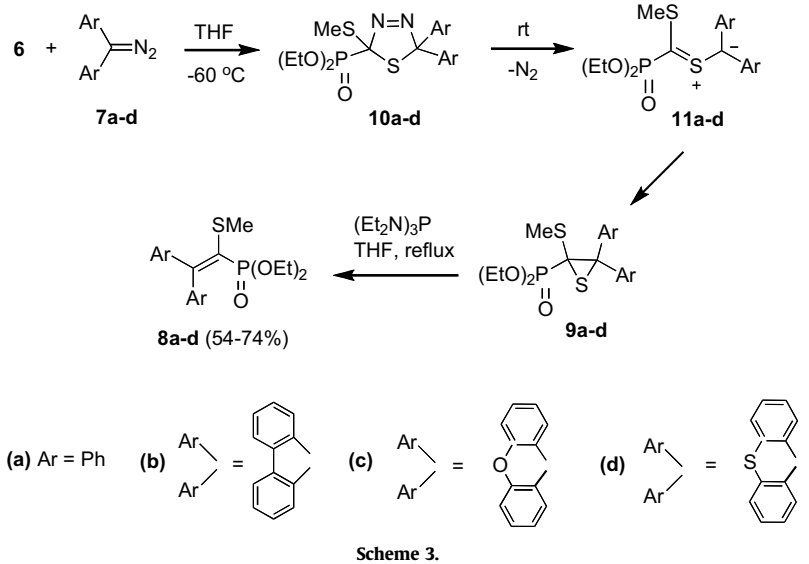
Due to the low reactivity of α-oxodiazo compounds, the reaction of **6** with 2-diazo-1,2-diphenylethanone ('azibenzil') **7e** was carried out in boiling THF. The product isolated after typical workup displayed in the ^{1}H NMR spectrum signals of the MeS and the EtO groups as well as for two Ph groups, indicating that a '1:1-adduct' was formed. Furthermore, the IR spectrum (neat) of the oily substance evidenced the absence of a C=O group. Based on this information and supported by additional data (^{13}C NMR, MS, elemental analysis), the structure of the 1,3-oxathiole **12** was assigned to the product (Scheme 4). The formation of **12** is the result of the 1,5-dipolar electrocyclization of the intermediate thiocarbonyl ylide **11e**. This result fits well into the observed formation of 1,3-oxathiols from **7e** and thiobenzophenone as well as cycloaliphatic thioketones.[20]



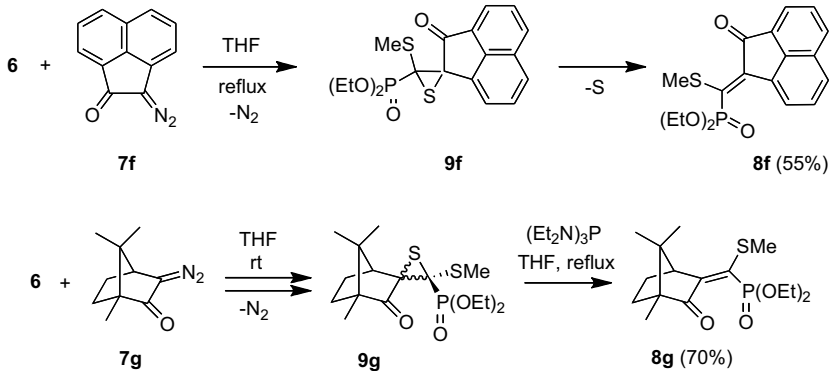
Scheme 4.

As another α-oxodiazo compound with an aromatic skeleton, 2-diazoacenaphthen-1-one (**7f**) was used in the reaction with **6**. Under comparable conditions, the reaction was complete after 2 h, and the single product formed (^{1}H NMR) was isolated after chromatography. The IR spectrum (KBr) showed a strong C=O absorption at 1713 cm^{-1}, and the ESI-MS as well as the elemental analysis confirmed that in this case the vinyl phosphonate **8f** was obtained (Scheme 5). Apparently, the intermediate thiocarbonyl ylide **11f**, in contrast to **11e**, undergoes the 1,3-dipolar electrocyclization to give the thiirane **9f**, which spontaneously extrudes sulfur yielding the isolated product. An explanation of this observation may be the significantly higher ring strain in the case of the 1,3-oxathiole with the acenaphthene skeleton. The configuration of **8f** presented in Scheme 5 was confirmed by the X-ray crystal-structure determination of the corresponding sulfoxide **13f** (see below).

α-Diazocamphor (**7g**) belongs to a class of relatively reactive α-oxodiazo compounds, and its reactions with aromatic thioketones **7a–d** leading to an *endo*/*exo* mixture of the corresponding thiiranes were carried out at room temperature.[23] Similarly, the reaction of **7g** with **6** occurred smoothly at room temperature with evolution of N_2. After 1 h, the reaction was completed, and the ^{1}H NMR spectrum of the crude product indicated that a mixture of two stereoisomeric thiiranes, **9g**, was formed, which, without separation, was desulfurized by treatment with tris(diethylamino)phosphine in boiling THF. The sole product obtained thereafter showed in the ^{1}H NMR spectrum the characteristic absorption of the MeS group at 2.49 ppm.



Scheme 3.



Scheme 5.

The formation of the expected vinyl phosphonate **8g** was confirmed by the CIMS (*m*/*z* 347, $[M+1]^+$), elemental analysis, and ^{13}C NMR data (Scheme 5). The given (*E*)-configuration of **8g** was confirmed by the X-ray crystal structure of the corresponding sulfone **14g** (see below).[24]

2.2. Oxidation of 1-(methylsulfanyl)vinyl phosphonates 8

As already mentioned in the Introduction, vinyl phosphonates bearing a sulfoxide moiety at C(1) are especially attractive building blocks in organic synthesis. Furthermore, the sulfoxide group further activates the vinyl group and, on the other hand, the presence of a stereogenic center enables their applications for stereoselective transformations.[5] Further oxidation leads to highly activated vinyl phosphonates with a sulfonyl group at C(1), which have been used as dienophiles,[25] as Michael acceptors,[26] and for cyclopropanation reactions.[27] The diaryl-substituted vinyl phosphonates **8a**,**b** were sequentially oxidized with *m*CPBA in dichloromethane. The experiment carried out with **8a** and 1 equiv of the oxidizing reagent yielded exclusively the sulfoxide **13a** (Scheme 6).

A similar reaction with 2.2 equiv of *m*CPBA led to the corresponding sulfone **14a**, which after chromatographic separation and crystallization delivered crystals suitable for an X-ray crystal-structure determination (Fig. 1).

The fluorenylidene derivatives **13b** and **14b** were obtained analogously. The same oxidation procedure with 1 equiv of

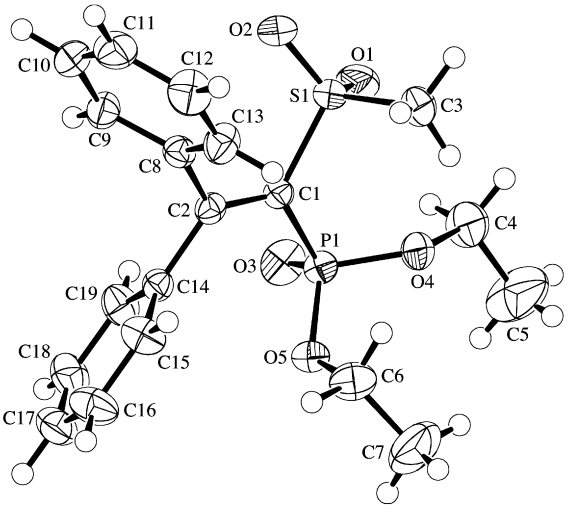
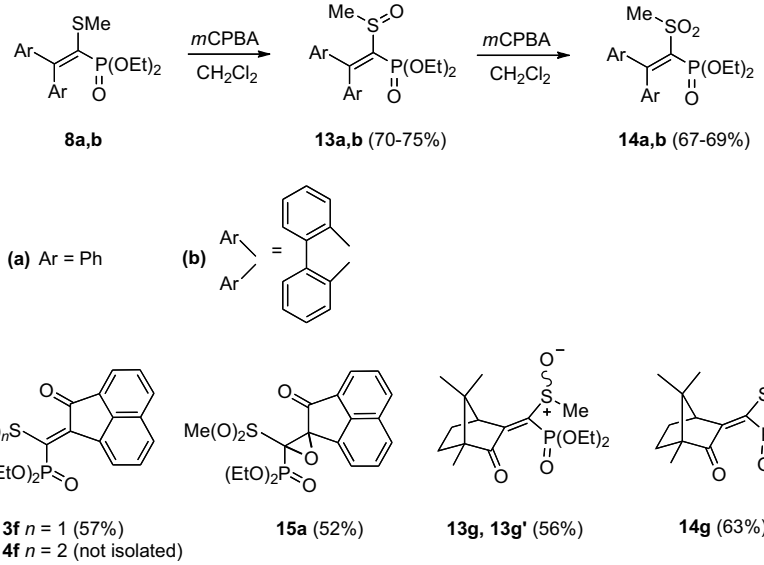


Figure 1. ORTEP plot[28] of the molecular structure of **14a** (arbitrary numbering of the atoms; 50% probability ellipsoids).

*m*CPBA was applied in order to prepare the sulfoxide of the non-symmetric vinyl phosphonate **8f**. The structure of the crystalline product **13f** was also determined by X-ray crystallography (Fig. 2), which showed unambiguously that the



Scheme 6.

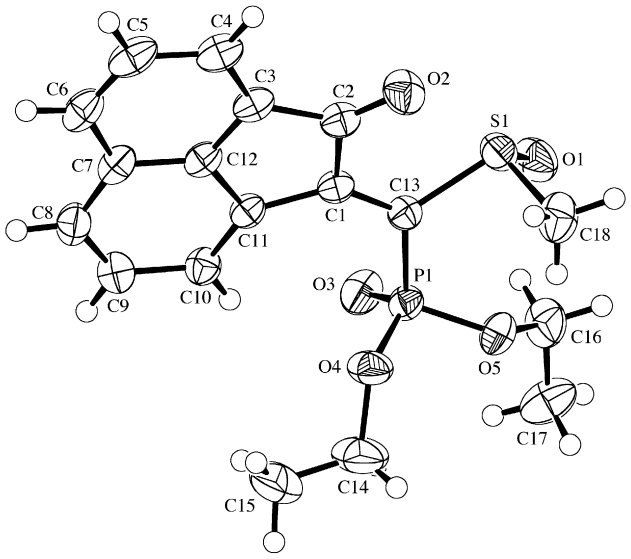


Figure 2. ORTEP plot[28] of the molecular structure of **13f** (arbitrary numbering of the atoms; 50% probability ellipsoids).

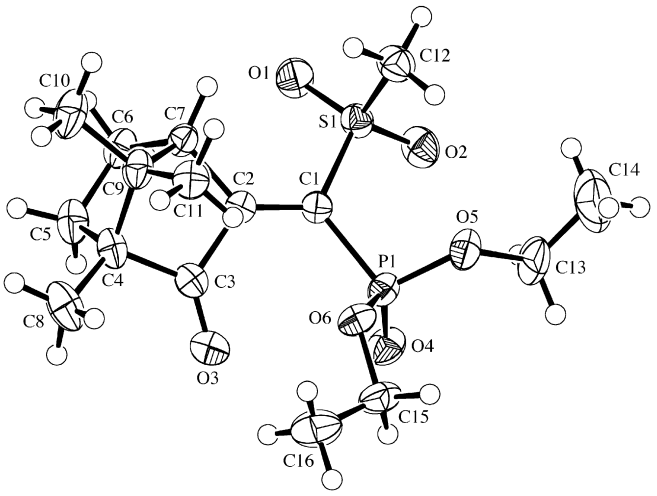


Figure 3. ORTEP plot[28] of the molecular structure of **14g** (arbitrary numbering of the atoms; 50% probability ellipsoids).

sulfoxide group and the C=O group are *cis*-oriented. Therefore, this configuration was also assigned to **8f**. The attempted oxidation of **8f** with ca. 2 equiv of *m*CPBA in CH_2Cl_2 solution at room temperature, instead of affording the expected sulfone **14f**, led to a mixture of products, which could be separated neither by crystallization, nor by chromatography (PLC plates, SiO_2). Therefore, the amount of the oxidizing agent was increased to ca. 3 equiv. Under these conditions, oxidation of both reactive centers, i.e., the sulfur atom (to give a SO_2 unit) and the C=C bond (to yield the oxirane ring) was achieved, and product **15a** was isolated by simple crystallization from MeOH in quite good yield (52%). The IR spectrum (KBr) of **15a** showed no absorption band at ca. 1550 cm^{-1}, which was present in **13a**, **13f**, and **14a**. Apparently, the reactivities of the S=O group and the C=C bond in **13f** are comparable, in contrast to other sulfoxides of type **13** described in this study, and therefore, the oxidation does not occur chemoselectively. Oxiranes possessing a substitution pattern similar to **15a** are rather rare; however, similar derivatives, prepared by threefold oxidation of the corresponding vinylsulfanes via a one-pot procedure, were reported in a recent paper.[29]

The oxidation of the camphor derivative **8g** at room temperature with 2.5 equiv of *m*CPBA led to the sulfone **14g**. The ^1H NMR analysis showed that only one product was formed in the reaction, and the determination of the structure by means of X-ray crystallography proved that in contrast to the acenaphthen-1-one derivatives (e.g., **13f**), the C=O group and the phosphonate group are *cis*-oriented (Fig. 3). The compound in the crystal is enantiomerically pure and the absolute configuration of the molecule was determined independently by the diffraction experiment. The molecule has the expected 4*R*,7*S*-configuration. The $[\alpha]_D$-value of the enantiomerically pure product **14g** was determined to +157.5 (CH_2Cl_2).

On the other hand, the oxidation of **8g** at room temperature with 1 equiv of *m*CPBA afforded a different product, which was identified as a ca. 3:2 mixture of two stereoisomeric sulfoxides **13g**/**13g′**. Apparently, the oxidation reaction occurs in a non-stereoselective manner. An explanation of this result may be the *trans* location of the MeS group with regard to the C=O group and, therefore, the discrimination caused by the camphor skeleton can be neglected. Further oxidation of the mixture **13g**/**13g′** yielded the sulfone **14g** as the sole product.

3. Conclusion

The described results show that the reaction of methyl (diethylphosphoryl)dithioformate with disubstituted diazomethanes opens a convenient access to 2,2-disubstituted 1-(methylsulfanyl)vinyl phosphonates. These products can be easily oxidized to give the corresponding sulfoxides and sulfones. All of the prepared vinyl phosphonates are attractive Michael acceptors and reagents for cycloaddition reactions. The enantiomerically pure camphor derivative **14g** can potentially be used as a catalyst in asymmetric synthesis. Unexpectedly, the products obtained from 2-diazoacenaphthen-1-one and 2-diazocamphor show different configurations of the new C=C bond, which is (*Z*) in the first case, but (*E*) in the camphor derivative. Remarkably, the acenaphthen-1-one derived sulfoxide **13f** does not undergo chemoselective oxidation to the expected sulfone **14f**, and with an increased amount of *m*CPBA, it was converted to **15a**, a very rare 2-phosphoryl-2-sulfonyl-substituted oxirane.

4. Experimental

4.1. General comments

The ^1H and ^{13}C NMR spectra were recorded with a Bruker AC-300 (^1H at 300.1 MHz, ^{13}C at 75.5 MHz, ^{31}P at 121.5 MHz) or Bruker Avance II Plus 700 (^1H at 700 MHz, ^{13}C at 176 MHz, ^{31}P at 283.6 MHz) or Varian Gemini 200 (^1H at 200 MHz, ^{13}C at 50 MHz, ^{31}P at 81 MHz) spectrometer using $CDCl_3$ as a solvent. Chemical shifts (δ) are reported in parts per million downfield from internal TMS. The multiplicities of the ^{13}C signals were assigned with the aid of DEPT spectra. IR spectra were recorded in KBr pellets or as films on a Nexus FTIR spectrometer. CI and ESI mass spectra were taken on an LKB-2091, Finnigan MAT-90 or Finnigan MAT-95 instrument. Elemental analyses were performed in the Analytical Laboratory of the University of Zürich or the Polish Academy of Science in Łódź. Melting points were determined in capillaries on a Mel-Temp. II apparatus (Aldrich) and are uncorrected. Column chromatography was carried out using silica gel (Merck 60, 0.063–0.200 μm). Thin layer chromatography (TLC) was performed on Merck 5554 aluminum backed SiO_2 plates; products were visualized by UV light. THF was distilled from the blue solution of sodium benzophenone ketyl.

Diphenyldiazomethane (**7a**), 9-diazo-9*H*-fluorene (**7b**), 9-diazo-9*H*-xanthene (**7c**), 9-diazo-9*H*-thioxanthene (**7d**), α-diazobenzil (**7e**), 2-diazoacenaphthen-1-one (**7f**), and α-diazocamphor (**7g**) were prepared by oxidation of the corresponding hydrazone with

nickel peroxide or yellow mercury oxide according to the literature procedure.[30,31] Methyl (diethylphosphoryl)dithioformate (**6**) was prepared from diethyl phosphite and carbon disulfide following a known protocol.[32]

4.2. Reaction of diazo compounds 7a–d with ethyl (diethylphosphoryl)dithioformate (6)

To a solution of 228.3 mg (1 mmol) of dithioformate **6** in 1 mL of dry THF at −65 °C, 1 mmol of the corresponding diazo compound **7** was added. After 30 min, complete decoloration of the reaction mixture was observed. The mixture was allowed to warm to room temperature while stirring. The solvent was evaporated and the residue, after chromatographic purification, was desulfurized by treatment with tris(diethylamino)phosphine in boiling THF (1–1.5 h). After evaporation of the solvent, the crude mixture was purified by column chromatography or by preparative layer chromatography on plates precoated with silica gel using hexane/ethyl acetate 3:2 (for **8a**,**b**,**d**) or 4:1 (for **8c**). Analytically pure products **8a–d** were obtained by crystallization from hexane at 0–5 °C.

*4.2.1. [1-(Methylsulfanyl)-2,2-diphenylvinyl]phosphonic acid diethyl ester (**8a**).* Yield: 235 mg (65%). Colorless crystals. Mp 56–58 °C. ^{1}H NMR: δ 1.11 (t, J_{HH}=7.0 Hz, 2 CH_3CH$_2$O), 2.14 (s, CH$_3$S), 3.80–3.90 (m, CH$_3$CH_2O), 3.93–4.06 (m, CH$_3$CH_2O), 7.23–7.36 (m, 10 CH$_{arom}$). ^{13}C NMR: δ 16.0 (d, $^3J_{CP}$=6.8 Hz, 2 CH_3CH$_2$O), 19.4 (CH$_3$S), 62.4 (d, $^2J_{CP}$=6.8 Hz, 2 CH$_3$CH_2O), 125.0 (d, $^1J_{CP}$=190.0 Hz, P–C=C), 127.7, 128.1, 128.3, 128.4, 129.4, 129.7 (10 CH$_{arom}$), 142.2, 142.3, 142.4 (2 C$_{arom}$), 160.4 (d, $^2J_{CP}$=ca. 15 Hz, P–C=C). ^{31}P NMR: δ 13.71. IR (KBr, cm^{-1}): 2982m, 2959m, 1553m, 1489m, 1443m, 1389m, 1239vs (P=O), 1167m, 1055vs and 1027vs (P–O–C), 971s, 941s, 705s, 562s. ESI-MS, *m*/*z* (%): 385 (100, [M+Na]$^+$). Anal. Calcd for $C_{19}H_{23}O_3PS$ (362.43): C 62.97, H 6.40, S 8.85; found: C 62.99, H 5.86, S 8.84.

*4.2.2. [(Fluoren-9-ylidene)(methylsulfanyl)methyl]phosphonic acid diethyl ester (**8b**).* Yield: 210 mg (58%). Yellow crystals. Mp 62–64 °C. ^{1}H NMR: δ 1.29 (t, J_{HH}=7.0 Hz, 2 CH_3CH$_2$O), 2.47 (d, $^4J_{HP}$=1.0 Hz, CH$_3$S), 4.15–4.29 (m, 2 CH$_3$CH_2O), 7.21–7.39 (m, 4 CH$_{arom}$), 7.57–7.65 (m, 2 CH$_{arom}$), 8.43 (d, J_{HH}=7.8 Hz, 1 CH$_{arom}$), 8.59 (d, J_{HH}=7.7 Hz, 1 CH$_{arom}$). ^{13}C NMR: δ 16.2 (d, $^3J_{CP}$=6.2 Hz, 2 CH_3CH$_2$O), 21.8 (CH$_3$S), 63.4 (d, $^2J_{CP}$=6.6 Hz, 2 CH$_3$CH_2O), 118.9, 119.6, 127.2, 127.7, 127.8, 127.9, 129.7, 129.9 (8 CH$_{arom}$), 130.3, 136.7, 136.8, 137.8, 140.8, 141.9, 149.5, 151.0 (4 C$_{arom}$, P–C=C). ^{31}P NMR: δ 12.43. IR (KBr, cm^{-1}): 2981m, 2925m, 1599w, 1525w, 1474w, 1447s, 1244s (P=O), 1051vs and 1025vs (P–O–C), 970s, 782s, 735s. CIMS (NH$_3$), *m*/*z* (%): 363 (7), 362 (20), 361 (100, [M+1]$^+$), 315 (9). Anal. Calcd for $C_{19}H_{21}O_3PS$ (360.42): C 63.32, H 5.87, S 8.90; found: C 63.09, H 5.65, S 8.83.

*4.2.3. [(Methylsulfanyl)(xanthen-9-ylidene)methyl]phosphonic acid diethyl ester (**8c**).* Yield: 280 mg (74%). Yellow crystals. Mp 57–59 °C. ^{1}H NMR: δ 1.11, 1.12 (2t, J_{HH}=7.1 Hz, 2 CH_3CH$_2$O), 2.24 (d, $^4J_{HP}$=0.9 Hz, CH$_3$S), 3.94–4.03 (m, 2 CH$_3$CH_2O), 7.17–7.38 (m, 6 CH$_{arom}$), 8.15 (dd, J_{HH}=7.9 Hz, $^5J_{HP}$=1.5 Hz, 1 CH$_{arom}$), 8.46 (d, J_{HH}=8.0 Hz, 1 CH$_{arom}$). ^{13}C NMR: δ 16.0 (d, $^3J_{CP}$=6.9 Hz, 2 CH_3CH$_2$O), 19.8 (CH$_3$S), 62.6 (d, $^2J_{CP}$=6.9 Hz, 2 CH$_3$CH_2O), 115.6, 116.2, 122.3, 122.7, 129.5, 129.8, 129.9, 130.3 (8 CH$_{arom}$), 119.8 (d, $^1J_{CP}$=192.5 Hz, P–C=C), 123.7, 123.9, 124.5, 124.6, 147.2, 147.4, 152.9, 153.3 (4C$_{q\ arom}$, P–C=C). ^{31}P NMR: δ 16.55. IR (KBr, cm^{-1}): 2984m, 2923m, 1596s, 1590s, 1529m, 1445vs, 1320m, 1251vs (P=O), 1055vs and 1031vs (P–O–C), 970s, 774s, 577m, 549m. CIMS (NH$_3$), *m*/*z* (%): 379 (8), 378 (24), 377 (100, [M+1]$^+$), 333 (8), 331 (16). Anal. Calcd for $C_{19}H_{21}O_4PS$ (376.41): C 60.63, H 5.62, S 8.52; found: C 60.52, H 5.50, S 8.27.

*4.2.4. [(Methylsulfanyl)(thioxanthen-9-ylidene)methyl]phosphonic acid diethyl ester (**8d**).* Yield: 212 mg (54%). Pale yellow crystals. Mp 58–60 °C. ^{1}H NMR: δ 1.10 (t, J_{HH}=7.2 Hz, 2 CH_3CH$_2$O), 2.16 (d, $^4J_{HP}$=0.7 Hz, CH$_3$S), 3.70–4.15 (m, 2 CH$_3$CH_2O), 7.25–7.28 (m, 4 CH$_{arom}$), 7.50–7.60 (m, 2 CH$_{arom}$), 7.85–8.05 (m, 2 CH$_{arom}$). ^{13}C NMR: δ 16.1 (2 CH_3CH$_2$O), 19.4 (CH$_3$S), 62.0 (2 CH$_3$CH_2O), 125.3, 125.9, 126.4, 126.7, 127.5, 127.9, 129.6, 130.1 (8 CH$_{arom}$), 133.9, 135.6, 136.3, 151.0, 151.2, 155.4, 155.8 (4 C$_{arom}$, P–C=C). ^{31}P NMR: δ 15.05. IR (KBr, cm^{-1}): 2980m, 2924m, 1571w, 1534w, 1456m, 1438m, 1238s (P=O), 1053vs and 1026vs (P–O–C), 969s, 745s, 562m. CIMS (NH$_3$), *m*/*z* (%): 393 (100, [M+1]$^+$), 350 (6), 349 (28), 348 (7), 347 (30). Anal. Calcd for $C_{19}H_{21}O_3PS_2$ (392.48): C 58.15, H 5.39, S 16.34; found: C 58.17, H 5.28, S 16.04.

4.3. Reaction of α-oxodiazo compounds 7e,f,g with methyl (diethylphosphoryl)dithioformate (6)

To a solution of 228.3 mg (1 mmol) of **6** in 1 mL of boiling THF, 1 mmol of the corresponding diazo compound **7** was added. The mixture was heated under reflux for 1.5 h. The reaction with **7g** was carried out at room temperature for 1 h. After this time, complete decoloration of the reaction mixtures was observed. The solvent was evaporated and the residue was purified chromatographically (SiO_2) using dichloromethane (for **12**), ethyl acetate (for **8f**), and a mixture of methanol and dichloromethane 2:98 (for **8g**) as the eluent. Analytically pure **8f** was obtained by crystallization from hexane at 0–5 °C. The products **12** and **8g** were obtained as yellowish oils.

*4.3.1. [2-(Methylsulfanyl)-4,5-diphenyl-[1,3]oxathiol-2-yl]phosphonic acid diethyl ester (**12**).* Yield: 220 mg (52%). Pale yellow oil. ^{1}H NMR: δ 1.40 (t, J_{HH}=7.1 Hz, 2 CH_3CH$_2$O), 2.50 (d, $^4J_{HP}$=0.9 Hz, CH$_3$S), 4.36–4.42 (m, 2 CH$_3$CH_2O), 7.21–7.36 (m, 10 CH$_{arom}$). ^{13}C NMR: δ 13.5 (CH$_3$S), 16.5 (d, $^3J_{CP}$=4.7 Hz, 2 CH_3CH$_2$O), 64.8 (d, $^2J_{CP}$=6.9 Hz, CH$_3$CH_2O), 65.2 (d, $^2J_{CP}$=7.0 Hz, CH$_3$CH_2O), 98.3 (d, $^1J_{CP}$=196.6 Hz, P–C$_q$), 127.5, 128.2, 128.3, 128.7, 128.8, 129.1 (10 CH$_{arom}$), 112.3, 129.8, 130.9 (3 C$_q$), 141.9 (d, $^3J_{CP}$=8.8 Hz, C$_q$). ^{31}P NMR: δ 10.8. IR (film, cm^{-1}): 2980m, 2927m, 2867m, 1636m, 1599m, 1496m, 1444m, 1260s (P=O), 1051vs and 1025vs (P–O–C), 976s, 953s, 754s, 695s. CIMS (NH$_3$), *m*/*z* (%): 423 (35, [M+1]$^+$), 391 (27), 375 (100), 271 (13), 240 (12), 239 (63), 214 (33), 197 (17), 156 (14). Anal. Calcd for $C_{20}H_{23}O_4PS_2$ (422.51): C 56.86, H 5.49, S 15.18; found: C 56.85, H 5.70, S 14.97.

*4.3.2. (Z)-[(Methylsulfanyl)(2-oxoacenaphthen-1-ylidene)methyl]phosphonic acid diethyl ester (**8f**).* Yield: 200 mg (55%). Yellow crystals. Mp 67–70 °C. ^{1}H NMR: δ 1.39, 1.40 (2t, J_{HH}=7.1 Hz, 2 CH_3CH$_2$O), 2.63 (d, J_{HP}=0.8 Hz, CH$_3$S), 4.33–4.41 (m, 2 CH$_3$CH_2O), 7.56–8.17 (m, 5 CH$_{arom}$), 8.45–8.63 (m, 1 CH$_{arom}$). ^{13}C NMR: δ 16.4 (d, $^3J_{CP}$=6.5 Hz, 2 CH_3CH$_2$O), 20.1 (CH$_3$S), 63.6 (d, $^2J_{CP}$=6.6 Hz, 2 CH$_3$CH$_2$O), 121.7, 124.9, 127.1, 128.0, 128.3, 131.1 (6 CH$_{arom}$), 130.4, 131.2, 132.1, 133.7, 140.8, 145.3 (4 C$_{arom}$, P–C=C), 190.0 (C=O). ^{31}P NMR: δ 11.7. IR (KBr, cm^{-1}): 2984m, 2928m, 2906m, 1717s (C=O), 1541m, 1491m, 1442m, 1256m, 1241s (P=O), 1051s and 1030s (P–O–C), 966s, 837m, 771s, 568s. ESI-MS, *m*/*z* (%): 401 [M+K]$^+$, 385 [M+Na]$^+$. Anal. Calcd for $C_{18}H_{19}O_4PS$ (362.39): C 59.66, H 5.28, S 8.85; found: C 59.44, H 5.35, S 8.63.

*4.3.3. (E)-[(Methylsulfanyl)(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phosphonic acid diethyl ester (**8g**).* Yield: 244 mg (70%). Pale yellow oil. ^{1}H NMR: δ 0.84, 0.97, 0.98 (3s, 3 CH$_3$), 1.23–1.33 (m, 2 CH_3CH$_2$O), 1.35–2.13 (m, 2 CH$_2$), 2.49 (s, CH$_3$S), 3.19–3.22 (m, CH), 4.19–4.29 (m, 2 CH$_3$CH_2O). ^{13}C NMR: δ 9.6 (CH$_3$), 16.2 (d, $^3J_{CP}$=7.1 Hz, CH_3CH$_2$O), 16.3 (d, $^3J_{CP}$=7.2 Hz, CH_3CH$_2$O), 18.2 (CH$_3$), 18.8 (broad, CH$_3$), 20.7 (CH$_3$), 25.6, 30.6 (2 CH$_2$), 45.6 (C$_q$), 54.3 (d, $^3J_{CP}$=11.4 Hz, CH), 60.4 (C$_q$), 63.0, 63.1 (2d, $^2J_{CP}$=6.7 Hz, 2 CH$_3$CH$_2$O), 130.8 (d, $^1J_{CP}$=185.3 Hz, P–C=C), 158.4 (d, $^2J_{CP}$=10.7 Hz, P–C=C), 201.8 (d, $^3J_{CP}$=6.3 Hz, C=O). ^{31}P NMR: δ 10.38. IR (film, cm^{-1}):

2960s, 2928s, 2827m, 1734s (C=O), 1574m, 1475m, 1443m, 1252 (P=O), 1164m, 1062vs and 1027vs (P–O–C), 964s, 744m. CIMS (NH_3), *m*/*z* (%): 347 (100, $[M+1]^+$). Anal. Calcd for $C_{16}H_{27}O_4PS$ (346.43): C 55.47, H 7.85, S 9.26; found: C 55.44, H 6.96, S 8.92.

4.4. Oxidation of 1-(methylsulfanyl)vinylphosphonates 8a,b,f,g with *m*CPBA

A solution of 1 mmol of the corresponding vinyl phosphonate **8a**,**b**,**f**,**g** in 20 mL of dichloromethane was placed in a flask equipped with a magnetic stirring bar and cooled in a ice bath to −5 °C. While stirring, a corresponding amount (2.5 mmol in reactions with **8a**, **8b**, and **8g** and 3.5 mmol in the reaction with **8f**) of commercial (77%) *m*CPBA was added portion-wise and stirring was continued for 0.5–1 h. After this time, the mixture was shaken with a saturated aqueous solution of $NaHCO_3$, then with a 5% solution of NaOH, and with brine. The organic layer was dried with $MgSO_4$ and the solvent was evaporated in vacuo. The residue was purified chromatographically (SiO_2) (except **15a**), and analytically pure products were obtained by crystallization from a mixture of petroleum ether with a small amount of dichloromethane (for **13a**, **14a**, **13f**, and **14g**), from diethyl ether (for **13b** and **14b**), and from methanol at 0–5 °C (for **15a**). The product **13g** was obtained as a yellowish oil.

*4.4.1. [1-(Methanesulfinyl)-2,2-diphenylvinyl]phosphonic acid diethyl ester (**13a**).* Yield: 265 mg (70%). Colorless crystals. Mp 93–96 °C. ^{1}H NMR: δ 0.98, 1.29 (2 t, J_{HH}=7.0 Hz, 2 C*H*$_3$CH$_2$O), 3.16 (s, CH_3SO), 3.76–4.25 (m, 2 CH_3CH_2O), 7.11–7.13 (m, 2 CH_{arom}), 7.32–7.41 (m, 8 CH_{arom}). ^{13}C NMR: δ 15.8, 16.2 (2d, $^3J_{CP}$=7.0 Hz, 2 *C*H$_3$CH$_2$O), 39.4 (s, CH_3SO), 62.4, 62.5 (2d, $^2J_{CP}$=5.3 Hz, 2 CH_3CH_2O), 127.8, 128.2, 129.4, 129.5, 129.9 (10 CH_{arom}), 135.4 (d, $^1J_{CP}$=170.7 Hz, P–*C*=C), 140.2 (d, $^3J_{CP}$=15.8 Hz, C_{arom}), 140.5 (d, $^3J_{CP}$=7.0 Hz, C_{arom}), 166.4 (d, $^2J_{CP}$=8.8 Hz, P–C=*C*). ^{31}P NMR: δ 10.80. IR (KBr, cm^{-1}): 3059m, 2980m, 1550m, 1490m, 1444m, 1251s (P=O), 1050vs and 1028vs (P–O–C), 1005m, 958m, 705m. CIMS (isobutane), *m*/*z* (%): 379 (100, $[M+1]^+$). Anal. Calcd for $C_{19}H_{23}O_4PS$ (378.43): C 60.30, H 6.13, S 8.47; found: C 60.33, H 6.11, S 8.21.

*4.4.2. [1-(Methanesulfonyl)-2,2-diphenylvinyl]phosphonic acid diethyl ester (**14a**).* Yield: 272 mg (69%). Colorless crystals. Mp 122–124 °C. ^{1}H NMR: δ 1.15 (t, J_{HH}=7.2 Hz, 2 C*H*$_3$CH$_2$O), 3.19 (s, CH_3SO_2), 3.80–4.20 (m, 2 CH_3CH_2O), 7.22–7.45 (m, 10 CH_{arom}). ^{13}C NMR: δ 16.0 (d, $^3J_{CP}$=7.0 Hz, 2 *C*H$_3$CH$_2$O), 45.5 (s, CH_3SO_2), 63.2 (d, $^2J_{CP}$=7.0 Hz, 2 CH_3CH_2O), 127.9, 128.1, 129.5, 130.1, 130.3, 130.5 (10 CH_{arom}), 133.4 (d, $^1J_{CP}$=184.8 Hz, P–*C*=C), 140.7 (d, $^3J_{CP}$=15.8 Hz, C_{arom}), 141.3 (d, $^3J_{CP}$=5.3 Hz, C_{arom}), 169.4 (d, $^2J_{CP}$=5.2 Hz, P–C=*C*). ^{31}P NMR: δ 9.41. IR (KBr, cm^{-1}): 3000m, 2980m, 1556m, 1488m, 1446m, 1311vs, 1258s (P=O), 1142vs, 1050vs and 1027vs (P–O–C), 966s, 828s, 704s, 554s, 520s. CIMS (isobutane), *m*/*z* (%): 395 (100, $[M+1]^+$). Anal. Calcd for $C_{19}H_{23}O_5PS$ (394.43): C 57.86, H 5.88, S 8.13; found: C 57.78, H 5.86, S 8.17.

*4.4.3. [(Fluoren-9-ylidene)(methanesulfinyl)methyl]phosphonic acid diethyl ester (**13b**).* Yield: 283 mg (75%). Yellow crystals. Mp 66–68 °C. ^{1}H NMR: δ 1.29, 1.36 (2t, J_{HH}=7.0 Hz, 2 C*H*$_3$CH$_2$O), 3.26 (s, CH_3SO), 4.22–4.35 (m, 2 CH_3CH_2O), 7.24–7.27 (m, 2 CH_{arom}), 7.38–7.40 (m, 2 CH_{arom}), 7.54 (d, J_{HH}=7.7 Hz, 2 CH_{arom}), 7.79 (d, J_{HH}=8.4 Hz, 1 CH_{arom}), 8.54 (d, J_{HH}=7.7 Hz, 1 CH_{arom}). ^{13}C NMR: δ 16.2 (d, $^3J_{CP}$=7.0 Hz, 2 *C*H$_3$CH$_2$O), 38.2 (s, CH_3SO), 62.5, 63.5 (2d, $^2J_{CP}$=5.3 Hz, 2 CH_3CH_2O), 119.4, 119.9, 127.7, 127.8, 129.7, 130.7, 131.6, 131.8 (8 CH_{arom}), 134.9 (d, $^1J_{CP}$=167.2 Hz, P–*C*=C), 135.7 (d, $^3J_{CP}$=7.0 Hz, C_{arom}), 137.1 (d, $^3J_{CP}$=17.6 Hz, C_{arom}), 142.4, 142.5 (2 C_{arom}), 155.1 (d, $^2J_{CP}$=7.0 Hz, P–C=*C*). ^{31}P NMR: δ 10.32. IR (KBr, cm^{-1}): 2982m, 2927w, 1602m, 1534m, 1447s, 1250s (P=O), 1096 m, 1059vs, 1043vs, 1015vs (P–O–C), 980s, 788s, 731s, 565s. CIMS (isobutane), *m*/*z* (%): 377 (100, $[M+1]^+$). Anal. Calcd for $C_{19}H_{21}O_4PS$ (376.41): C 60.63, H 5.62, S 8.52; found: C 60.71, H 5.83, S 8.57.

*4.4.4. [(Fluoren-9-ylidene)(methanesulfonyl)methyl]phosphonic acid diethyl ester (**14b**).* Yield: 262 mg (67%). Orange crystals. Mp 110–112 °C. ^{1}H NMR: δ 1.26 (t, J_{HH}=7.0 Hz, 2 C*H*$_3$CH$_2$O), 3.49 (s, CH_3SO_2), 4.16–4.28 (m, 2 CH_3CH_2O), 7.18–7.24 (m, 2 CH_{arom}), 7.36–7.38 (m, 2 CH_{arom}), 7.47, 7.50, 8.25, 8.35 (4d, J_{HH}=7.7 Hz, 4 CH_{arom}). ^{13}C NMR: δ 15.9 (d, $^3J_{CP}$=5.3 Hz, 2 *C*H$_3$CH$_2$O), 43.6 (s, CH_3SO_2), 63.7 (d, $^2J_{CP}$=5.3 Hz, 2 CH_3CH_2O), 119.5, 120.0, 127.6, 128.2, 130.5, 131.3, 132.8, 133.1 (8 CH_{arom}), 129.9 (d, $^1J_{CP}$=180.3 Hz, P–*C*=C), 136.2 (d, $^3J_{CP}$=15.9 Hz, C_{arom}), 136.8 (d, $^3J_{CP}$=7.0 Hz, C_{arom}), 142.6, 143.4 (2 C_{arom}), 160.6 (d, $^2J_{CP}$=3.5 Hz, P–C=*C*). ^{31}P NMR: δ 9.01. IR (KBr, cm^{-1}): 2983m, 2910w, 1600w, 1523s, 1448m, 1316vs, 1251vs (P=O), 1142vs, 1040vs, 1013s (P–O–C), 989s, 976s, 767s, 740s, 570s. CIMS (isobutane), *m*/*z* (%): 393 (100, $[M+1]^+$). Anal. Calcd for $C_{19}H_{21}O_5PS$ (392.41): C 58.16, H 5.39, S 8.17; found: C 58.21, H 5.27, S 8.20.

*4.4.5. (Z)-[(Methanesulfinyl)(2-oxoacenaphthen-1-ylidene)methyl]phosphonic acid diethyl ester (**13f**).* Yield: 215 mg (57%). Orange crystals. Mp 138–140 °C. ^{1}H NMR: δ 1.36, 1.37 (2t, J_{HH}=7.0 Hz, 2 C*H*$_3$CH$_2$O), 3.25 (s, CH_3SO), 4.32–4.36 (m, 2 CH_3CH_2O), 7.75–7.77 (m, 2 CH_{arom}), 7.98 (d, J_{HH}=7.0 Hz, 1 CH_{arom}), 8.02 (d, J_{HH}=8.4 Hz, 1 CH_{arom}), 8.16 (d, J_{HH}=7.7 Hz, 1 CH_{arom}), 8.78 (d, J_{HH}=7.7 Hz, 1 CH_{arom}). ^{13}C NMR: δ 16.2, 16.3 (2d, $^3J_{CP}$=6.4 Hz, 2 *C*H$_3$CH$_2$O), 39.8 (CH_3SO), 62.8 (d, $^2J_{CP}$=6.2 Hz, CH_3CH_2O), 64.0 (d, $^2J_{CP}$=5.4 Hz, CH_3CH_2O), 122.2, 127.6, 127.9, 128.7, 128.8, 132.3 (6 CH_{arom}), 129.6 (d, $^3J_{CP}$=6.5 Hz, 1 C_{arom}), 129.8 (d, $^4J_{CP}$=2.8 Hz, 1 C_{arom}), 130.5, 142.9 (2 C_{arom}), 145.1 (d, $^2J_{CP}$=5.0 Hz, P–C=*C*), 146.9 (d, $^1J_{CP}$=163.3 Hz, P–*C*=C), 192.5 (d, $^3J_{CP}$=19.4 Hz, C=O). ^{31}P NMR: δ 9.26. IR (KBr, cm^{-1}): 2983m, 2926w, 1703s (C=O), 1624m, 1553m, 1435m, 1246s (P=O), 1063vs and 1033vs (P–O–C), 964s, 949s, 566m. CIMS (isobutane), *m*/*z* (%): 379 (100, $[M+1]^+$). Anal. Calcd for $C_{18}H_{19}O_5PS$ (378.39): C 57.14, H 5.06, S 8.47; found: C 57.11, H 5.03, S 8.41.

*4.4.6. (Z)-[3′-Methanesulfonyl-2-oxo(acenaphthen-2-spiro-2′-oxiran)-3′-yl]phosphonic acid diethyl ester (**15a**).* Yield: 205 mg (52%). Pale yellow crystals. Mp 148–150 °C. ^{1}H NMR: δ 1.22, 1.42 (2t, J_{HH}=7.0 Hz, 2 C*H*$_3$CH$_2$O), 3.51 (s, CH_3SO_2), 4.14, 4.42 (2dq, $^2J_{H,H}$=7.0 Hz, $^3J_{H,P}$=7.5 Hz, 2 CH_3CH_2O), 7.60–7.82 (m, 2 CH_{arom}), 7.92–8.10 (m, 2 CH_{arom}), 8.15 (d, J_{HH}=8.2 Hz, 1 CH_{arom}), 8.55 (d, J_{HH}=7.1 Hz, 1 CH_{arom}). ^{13}C NMR: δ 16.0 (d, $^3J_{CP}$=5.7 Hz, *C*H$_3$CH$_2$O), 16.5 (d, $^3J_{CP}$=5.2 Hz, *C*H$_3$CH$_2$O), 29.5 (d, $^2J_{C,P}$=42.0 Hz, C(3′)-oxiran), 42.3 (CH_3SO_2), 43.5 (d, $^1J_{C,P}$=408.0 Hz, C(2′)-oxiran), 64.8, 65.0 (2d, $^2J_{CP}$=6.8 Hz, 2 CH_3CH_2O), 122.7, 125.8, 127.5, 128.1, 128.5, 132.3 (6 CH_{arom}), 126.5, 129.9, 130.3, 143.0 (4 C_{arom}), 193.3 (C=O). ^{31}P NMR: δ 8.00. IR (KBr, cm^{-1}): 3000m, 2986m, 1745vs (C=O), 1605m, 1493m, 1441m, 1321vs, 1273s (P=O), 1149vs, 1051vs and 1020vs (P–O–C), 971s, 780s, 520s. ESI-MS, *m*/*z* (%): 433 (100, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{19}O_7PS$ (410.39)·0.5H_2O: C 51.55, H 4.81, S 7.65; found: C 51.69, H 4.67, S 7.57.

*4.4.7. (E)-[(Methanesulfinyl)(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phosphonic acid diethyl ester (**13g**).* Yield: 204 mg (56%). Yellowish oil. The product was obtained as a mixture of two diastereoisomers A and B. ^{1}H NMR: δ 0.82, 0.88 (2s, CH_3, A+B), 1.00, 1.03 (2s, 2 CH_3, A+B), 1.31 (t, J_{HH}=7.2 Hz, 2 C*H*$_3$CH$_2$O, A+B), 1.50–2.40 (m, 2 CH_2, A+B), 2.95 (s, CH_3SO, A+B), 4.05–4.48 (m, 2 CH_3CH_2O, CH, A+B). ^{13}C NMR: δ 9.1 (CH_3SO, A+B), 16.0, 16.1 (CH_3, A+B), 17.8 (CH_3, A+B), 20.9, 21.0 (2 *C*H$_3$CH$_2$O, A+B), 25.2, 26.9 (CH_2, A+B), 29.4, 29.7 (CH_2, A+B), 41.1, 41.4 (CH_3SO, A+B), 44.8, 45.6 (C_q, A+B), 47.4 (d, $^4J_{CP}$=11.1 Hz, CH, A), 48.7 (d, $^4J_{CP}$=11.8 Hz, CH, B), 56.1, 56.2 (C_q, A+B), 63.0, 63.2, 63.4, 63.5 (4d, 2 CH_3CH_2O, A+B), 137.6 (d, $^1J_{CP}$=172.8 Hz, P–*C*=C, A), 137.8 (d, $^1J_{CP}$=173.9 Hz, P–*C*=C, B), 159.7 (P–C=*C*, A+B), 203.2 (d, $^3J_{CP}$=8.2 Hz, C=O, A), 203.4 (d, $^3J_{CP}$=8.9 Hz, C=O, B). ^{31}P NMR: δ 7.33, 7.61. IR (film, cm^{-1}): 2983s, 2960s, 2930s,

2872s, 1743s (C=O), 1644m, 1595m, 1477m, 1392m, 1254s (P=O), 1162m, 1054s and 1015s (P–O–C), 962s, 877m, 830m, 756m. ESI-MS, *m*/*z* (%): 385 (100, $[M+Na]^+$), 311 (6). Anal. Calcd for $C_{16}H_{27}O_5PS$ (362.43): C 53.02, H 7.51, S 8.85; found: C 52.78, H 7.35, S 8.73.

*4.4.8. (E)-[(Methanesulfonyl)(4,7,7-trimethyl-3-oxobicyclo[2.2.1]-hept-2-ylidene)methyl]phosphonic acid diethyl ester (**14g**).* Yield: 240 mg (63%). Yellowish crystals. Mp 128–130 °C. $[\alpha]_D^{20}=+157.5$ (CH_2Cl_2). ^{1}H NMR: δ 0.88, 0.98, 1.01 (3s, 3 CH_3), 1.32 (t, J_{HH}=7.1 Hz, 2 CH_3CH_2O), 1.45–2.50 (m, 2 CH_2), 3.30 (s, CH_3SO_2), 3.88–4.02 (m, CH), 4.05–4.52 (m, 2 CH_3CH_2O). ^{13}C NMR: δ 9.7 (CH_3), 16.4 (broad, CH_3), 18.2 (CH_3), 21.2 (2 CH_3CH_2O), 25.7, 30.8 (2 CH_2), 44.7 (CH_3SO_2), 45.6 (C_q), 53.9 (d, $^3J_{CP}$=10.5 Hz, CH), 57.9 (C_q), 64.07, 64.14 (2d, $^2J_{CP}$=6.5, 6.0 Hz, 2 CH_3CH_2O), 134.1 (d, $^1J_{CP}$=181.5 Hz, P–C=C), 166.5 (P–C=C), 204.8 (d, $^3J_{CP}$=7.5 Hz, C=O). ^{31}P NMR: δ 5.07. IR (KBr, cm^{-1}): 2987m, 2972m, 2920m, 1747s (C=O), 1592m, 1323vs, 1254vs (P=O), 1143s, 1052s and 1021s (P–O–C), 994s, 984s, 960s, 780m, 568m. ESI-MS, *m*/*z* (%): 401 (100, $[M+Na]^+$). Anal. Calcd for $C_{16}H_{27}O_6PS$ (378.43): C 50.78, H 7.19, S 8.47; found: C 50.75, H 7.25, S 8.41.

4.5. X-ray crystal-structure determination of 14a, 13f, and 14g

All measurements for **14a** were performed on a Bruker SMART-CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ 0.71073 Å). Data reduction was performed with the Bruker SAINT software.[33] The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method[34] was applied. All measurements for **13f** and **14g** were made on a Nonius KappaCCD area-detector diffractometer[35] using graphite-monochromated Mo Kα radiation (λ 0.71073 Å) and, in the case of **14g**, an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack.[36] The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method[37] was applied. Equivalent reflections were merged in all cases, except for the Friedel pairs in **14g**. The data collection and refinement parameters are given below[38] and views of the molecules are shown in Figures 1–3. The structures were solved by direct methods using SIR92,[39] which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the methyl groups). The refinement of the structures was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2-F_c^2)^2$. A correction for secondary extinction was applied in the case of **14a**. In the cases of **14a** and **13f**, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. Refinement of the absolute structure parameter[40] in the case of **14g** yielded a value of 0.04(7), which confidently confirms that the refined model corresponds with the true enantiomorph. Neutral atom scattering factors for non-H-atoms were taken from Ref. 41, and the scattering factors for H-atoms were taken from Ref. 42. Anomalous dispersion effects were included in F_c;[43] the values for f' and f'' were those of Ref. 44. The values of the mass attenuation coefficients are those of Ref. 45. All calculations were performed using the *SHELXL97*[46] program.

*Crystal data for **14a***: $C_{19}H_{23}O_5PS$, M=394.42, crystallized from CH_2Cl_2/hexane, colorless, needle, crystal dimensions 0.12×0.20×0.84 mm, monoclinic, space group $P2_1/c$, Z=4, reflections for cell determination 935, 2θ range for cell determination 5–58°, a=6.4748(6) Å, b=32.713(3) Å, c=9.3989(9) Å, β=94.854(3), V=1983.6(3) Å^3, T=233(1) K, D_X=1.321 g cm^{-3}, μ(MoKα)=0.270mm^{-1}, scan type ω, $2\theta_{(max)}$=61°, transmission factors (min; max) 0.834; 1.000, total reflections measured 26,908, symmetry independent reflections 6054, reflections with $I>2\sigma(I)$ 4346, reflections used in refinement 6053, parameters refined 239; $R(F)$ [$I>2\sigma(I)$ reflections]=0.0555, $wR(F^2)$ [all data]=0.1206 ($w=[\sigma^2(F_o^2)+(0.0437P)^2+0.8184P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$), goodness of fit 1.094, final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min)=0.29; −0.30 e Å^{-3}, secondary extinction coefficient=0.0042(7).

*Crystal data for **13f***: $C_{18}H_{19}O_5PS$, M=378.38, crystallized from CH_2Cl_2/hexane, orange, prism, crystal dimensions 0.12×0.15×0.25 mm, monoclinic, space group $P2_1/c$, Z=4, reflections for cell determination 27,091, 2θ range for cell determination 4–60°, a=15.1731(2) Å, b=7.8235(1) Å, c=15.6336(3) Å, β=109.9740(9), V=1744.18(5) Å^3, T=250(1) K, D_X=1.441 g cm^{-3}, μ(MoKα)=0.303 mm^{-1}, scan type ϕ and ω, $2\theta_{(max)}$=60°, transmission factors (min; max) 0.819; 0.964, total reflections measured 49,825, symmetry independent reflections 5085, reflections with $I>2\sigma(I)$ 3462, reflections used in refinement 5084, parameters refined 229; $R(F)$ [$I>2\sigma(I)$ reflections]=0.0473, $wR(F^2)$ [all data]=0.1347 ($w=[\sigma^2(F_o^2)+(0.0658P)^2+0.5114P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$), goodness of fit 1.046, final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min)=0.57; −0.53 e Å^{-3}.

*Crystal data for **14g***: $C_{16}H_{27}O_6PS$, M=378.42, crystallized from CH_2Cl_2/hexane, pale yellow, prism, crystal dimensions 0.17×0.20×0.30 mm, tetragonal, space group $P4_3$, Z=4, reflections for cell determination 33,269, 2θ range for cell determination 4–55°, a=10.2390(2) Å, c=18.7150(5) Å, V=1962.03(8) Å^3, T=160(1) K, D_X=1.281 g cm^{-3}, μ(MoKα)=0.273 mm^{-1}, scan type ϕ and ω, $2\theta_{(max)}$=55°, transmission factors (min; max) 0.883; 0.956, total reflections measured 25,655, symmetry independent reflections 4453, reflections with $I>2\sigma(I)$ 3783, reflections used in refinement 4453, parameters refined 223; restraints 1, $R(F)$ [$I>2\sigma(I)$ reflections]=0.0369, $wR(F^2)$ [all data]=0.0866 ($w=[\sigma^2(F_o^2)+(0.0422P)^2+0.4138P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$), goodness of fit 1.036, final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min)=0.20; −0.23 e Å^{-3}.

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