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Fully regio- and *endo*-stereoselective synthesis of new polycyclic allylic sulfides via a Diels–Alder reaction. Synthetically useful transformations of these sulfides

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Abstract—Thermal and Lewis acid catalyzed cycloadditions of (*Z*)-1,2-diheterosubstituted-1,3-dienes to a variety of dienophiles are described. Both *endo*/*exo* and regioselectivity have been investigated. In all cases cycloaddition reactions exhibited full regio- and *endo*-stereoselectivity. The obtained cycloadducts are new polycyclic allylic sulfides carrying much structural and stereochemical informations. Work on transformation of the adducts, mainly to the corresponding new 1,3-dienes and aromatic compounds, is also presented.

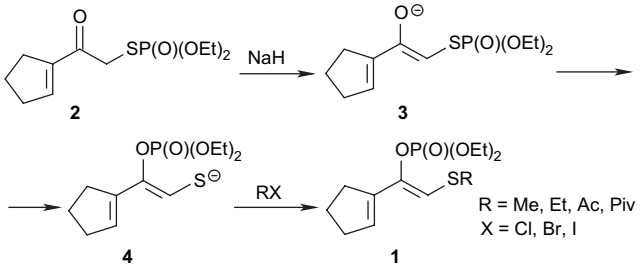
1. Introduction

The Diels–Alder reaction is amongst the most powerful and versatile of synthetic methods and continues to attract considerable attention.[1] In particular, great effort has been directed toward understanding the factors governing facial stereochemistry, regiochemical and absolute stereochemical controls. 1,3-Dienes with hetero substituents have proven to be versatile reactants for the synthesis of functionalized ring systems including natural products via the Diels–Alder reaction.[2,3] In addition heteroatoms in the substituent groups of the 1,3-dienes are known to enhance the regio- and stereoselectivity of Diels–Alder reactions. PhS as a substituent in dienes is even more powerful than RO in determining the orientation of Diels–Alder addition.[4,5] On the other hand, 2-dialkoxyphosphoryloxy-1,3-butadiene and its adducts have been found to be unusually stable under the acidic conditions of Lewis acid catalyzed cycloaddition reactions, compared with other oxygen substituted dienes containing alkoxy or silyloxy functionality.[6]

We wish to present a full account of our work utilizing the new and versatile (*Z*)-1,2-diheterosubstituted-1,3-dienes[7] in fully regio- and stereoselective Diels–Alder reactions.[8] The obtained cycloadducts are versatile synthons carrying much structural and stereochemical informations. The attractiveness of these adducts lies in the facility with which they can be transformed with full stereoselectivity into novel functionalized polycyclic allylic alcohols and α-hydroxy ketones[9] as well as into 1,3-dienes and aromatic compounds.[10]

2. Results and discussion

We have already described the simple and efficient one-pot synthesis of novel (*Z*)-1,3-dienes **1** containing both an alkylthio (acylthio, dialkoxyphosphorylthio) substituent in position 1 and a diethoxyphosphoryloxy substituent in position 2.[7] Our methodology is outlined in Scheme 1. Treatment of thiophosphates **2** prepared in situ with sodium hydride results in the formation of enolate anions **3**. The latter undergo rearrangement involving migration of a phosphoryl group from



Scheme 1. A fully stereoselective synthesis of 1,2-diheterosubstituted-1,3-dienes **1**.

Keywords: Diels–Alder reaction; Stereoselectivity; 1,2-Diheterosubstituted 1,3-dienes; Polycyclic allylic sulfides; 1,3-Diene aromatic systems.
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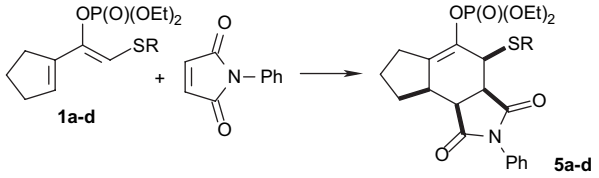
sulfur to oxygen affording thiolate anions **4**. These react very easily with a number of electrophiles producing the desired dienes **1** in high yield. They are stable at 0 °C for several weeks. All dienes **1** have *Z*-oriented RS and $(EtO)_2P(O)O$ substituents. The assignment of the *Z* configuration is based on the characteristics (>1) of the $^4J_{PH}$ coupling constant.

We wished to explore the potential of substituents located in positions 1 and 2 of the dienes to control the regio- and *endo*-stereoselectivity of associated Diels–Alder reactions. We have investigated the Diels–Alder reaction of dienes **1** with a number of dienophiles in toluene solution under reflux or with Lewis acid catalysis.

2.1. Diels–Alder cycloadditions of (*Z*)-1,3-dienes 1a–d with symmetrical dienophiles

We studied the reactions between **1a–d** and *N*-phenylmaleimide. They were run under experimental conditions already described providing *endo*-cycloadducts **5a–d** (Scheme 2). The yield of the reactions was generally high (Table 1).



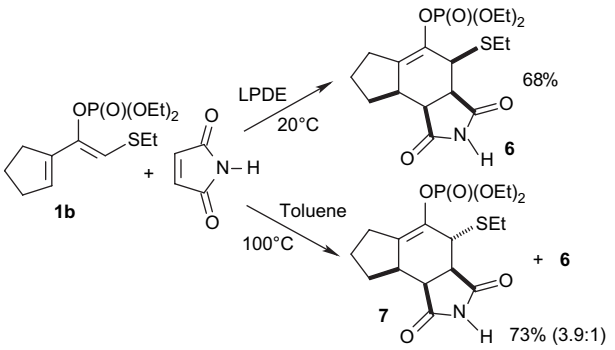
Scheme 2. Cycloaddition of dienes **1** with *N*-phenylmaleimide.

Table 1. Diels–Alder reactions of **1a–d** with *N*-phenylmaleimide

Diene	R	Cat. method, temperature, time	Adduct	Yield[a] (%)
1a	Me	Toluene, 100 °C, 5 h	**5a**	78
1a	Me	LPDE,[b] 20 °C, 48 h	**5a**	72
1b	Et	Toluene, 100 °C, 5 h	**5b**	86
1b	Et	LPDE,[b] 20 °C, 48 h	**5b**	68
1c	Ac	Toluene, 100 °C, 4 h	**5c**	80
1c	Ac	LPDE,[b] 20 °C, 72 h	**5c**	83
1d	Piv	Toluene, 100 °C, 8 h	**5d**	85

[a] All yields refer to analytically pure compounds.
[b] LPDE=5 M solution of $LiClO_4$ in Et_2O.

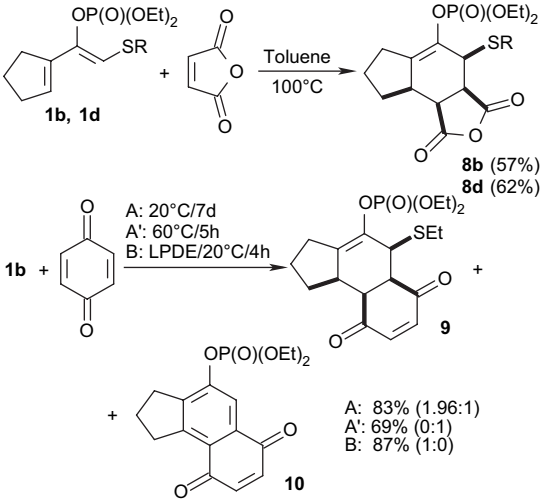
The reaction of diene **1b** with an excess of maleimide catalyzed by LPDE at 20 °C afforded cycloadduct **6** with *endo*-configuration as the unique product. However, the same reaction performed under thermal conditions provided a mixture of *endo*-adduct **6** and its epimer **7** in the ratio 3.9:1 (Scheme 3).



Scheme 3. Cycloaddition of diene **1b** with maleimide.

The configuration of these adducts was established on the basis of NMR data in particular on the coupling constant values. It seems reasonable to assume that in the thermal reaction the primary *endo*-adduct **6** is formed initially. Then epimerization takes place under the influence of the base and temperature giving epimeric adduct **7**.

We have found that dienes **1b** and **1d** react with maleic anhydride and **1b** with *p*-benzoquinone providing the corresponding *endo*-adducts **8b**, **8d** and **9**, respectively. Compound **9** is not stable. It undergoes spontaneous aromatization to compound **10** via elimination of EtSH (Scheme 4).



Scheme 4. Cycloaddition of dienes **1b** and **1d** with maleic anhydride and diene **1b** with *p*-benzoquinone.

The suitable crystals of the cycloadduct **8d** we obtained for an X-ray structure determination to establish the stereochemistry. The X-ray analysis confirmed its *endo*-configuration and revealed deformed boat conformation of cyclohexene ring (Figs. 1 and 2).

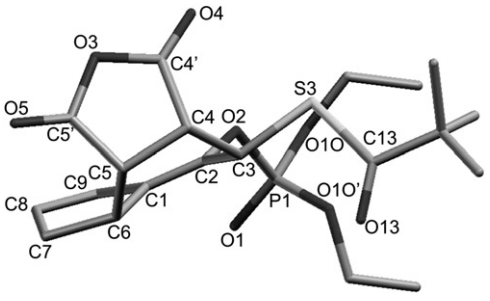


Figure 1. Boat conformation of the cyclohexene ring and orientations of its substituents.

Dienes **1b** and **1c** underwent Diels–Alder reaction with dimethyl acetylene dicarboxylate (10% of excess) at 100 °C giving cis adducts **11b** and **11c** (Scheme 5). The resultant adduct **11b** was treated with *m*CPBA to afford a 56% of aromatic system **37** (Scheme 16).

Cycloaddition of fumaronitrile to diene **1b** was performed using both catalysts $ZnBr_2$ at 80 °C and $LiClO_4$–THF at

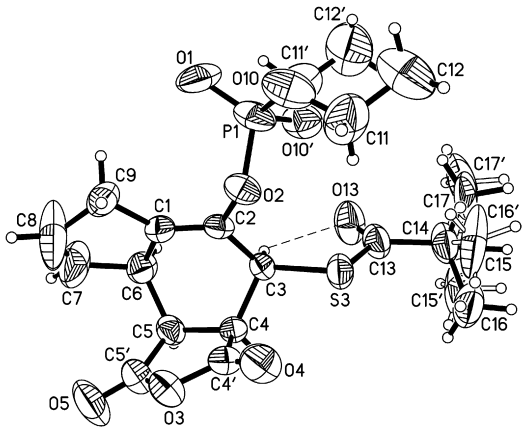
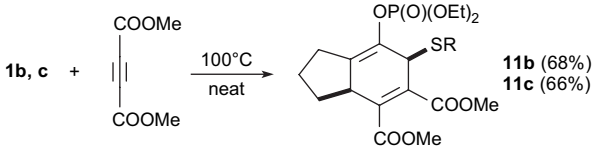
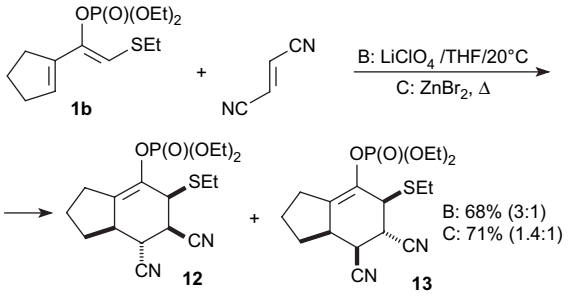


Figure 2. General view of compound **8d**. Thermal ellipsoids are drawn at 50% probability level. The shortest intramolecular hydrogen contact C3–H···O13 also shown.



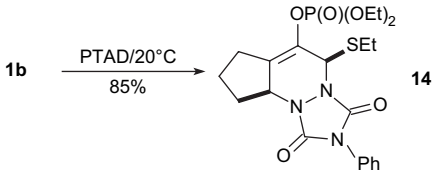
Scheme 5. Cycloaddition of dienes **1b** and **1c** with dimethyl acetylene dicarboxylate.

room temperature affording mixture of diastereoisomers **12** and **13** as shown by ^{1}H and ^{31}P NMR. The diastereoisomers could be separated by column chromatography (Scheme 6).



Scheme 6. Cycloaddition of diene **1b** with fumaronitrile in the presence of $ZnBr_2$ or LPDE.

Reaction of diene **1b** with the highly reactive hetero-dienophile 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (PTAD) took place almost instantaneously (the red dienophile solution added to the diene in dichloromethane lost its color immediately) at ambient temperature, affording cycloadduct **14** in almost quantitative yield (Scheme 7).



Scheme 7. Cycloaddition of diene **1b** with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione.

Examining the stereochemical course of the investigated reactions, we detected only one adduct in the crude reaction mixture by NMR spectroscopy. The all-cis configuration of the adducts, consistent with the reaction via an *endo*-transition state, was established on the basis of: (a) X-ray analysis of cycloadduct **8d**; (b) the coupling constant values (in the range 4.4–5.5) between the protons of the sulfur-bearing carbon atom and the proton of the carbon atom of adjacent ring derived from the dienophiles; (c) determination that the latter proton is also coupled to the proton on the other neighboring carbon atom in the range 8.0–9.2. The best examples are the data of the isomeric pair of adducts **6**, **7** and **43**, **44**. Thus for the *endo*-adducts **6** and **43** we found $^{3}J_{HH}$ 5.5 and ≈5.0 for the C*H*SEt or C*H*SO_2Me, respectively, whereas for isomeric adducts **7** and **44** we found $^{3}J_{HH}$ 1.2 and <0.5 for the C*H*SEt or C*H*SO_2Me, respectively; (d) close similarity of NMR data of cycloadduct **8d** (for which X-ray analysis revealed *endo*-configuration) with those of other obtained cycloadducts; (e) comparing all these NMR data with those related compounds described.

2.2. Diels–Alder cycloadditions of (*Z*)-1,3-dienes 1a–d with unsymmetrical dienophiles

We wanted to determine the regioselectivity of cycloadditions of the dienes **1**. Therefore, we extended our investigation to the reaction of **1** with unsymmetrical dienophiles such as cyclohex-2-enone, methyl vinyl ketone (MVK), acrylonitrile, ethyl acrylate, acrolein, and methacrolein.

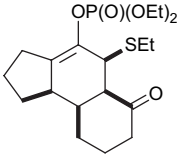
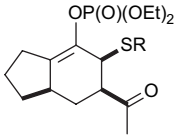
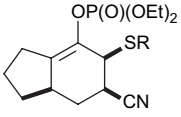
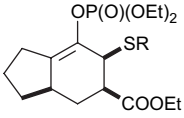
The best results were obtained using thermal conditions at 100 °C or the following Lewis acid catalysts: $EtAlCl_2$, $ZnBr_2$, and LPDE (Table 2). Other catalysts such as $SnCl_4$, $TiCl_4$, and BF_3 were not effective.

We have found that LPDE at 20 °C is also a very useful catalyst for the introduction of an aldehyde function into adducts during the Diels–Alder reaction. Cycloaddition of **1b** and acrolein was markedly accelerated by this catalyst (Scheme 8). The *endo*-adduct **19b** was obtained in high yield. In contrast, the same reaction performed under thermal conditions and with excess of acrolein (5 equiv) provided the new 1,3-diene **20** as final product. There appears to be no doubt that adduct **19** is formed in the first step of this reaction. Subsequent oxidation of the thioalkyl substituent to sulfoxide or sulfone (**21**) and then elimination, facilitated by high temperature, gave the 1,3-dienes **20**. Cycloaddition of **1b** with the less reactive dienophile methacrolein catalyzed by LPDE completed after 3 days afforded *endo*-adduct **22** in good yield (Scheme 9).

The results depicted in Tables 1 and 2 and in Schemes 8 and 9 showed that $LiClO_4$ in Et_2O (LPDE) or in THF at ambient temperature is an excellent catalyst for the cycloaddition reactions of (*Z*)-1,3-dienes **1** and particularly good for less reactive dienophiles. In addition LPDE does not oxidize either thioalkyl or aldehyde group.

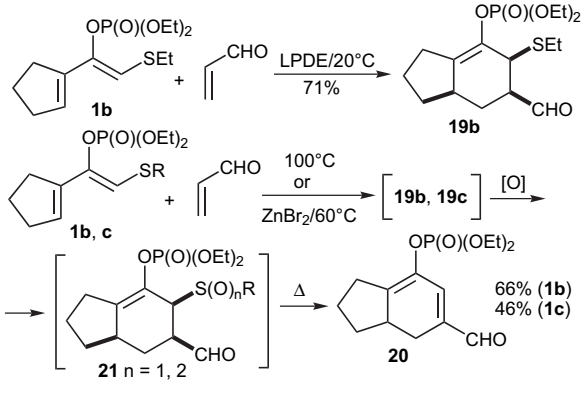
All cycloaddition reactions of **1** with unsymmetrical dienophiles presented here were fully '*ortho*' regioselective and occurred with *endo*-addition. The NMR spectra of isomeric cycloadducts **12** and **13**: coupling constant values between protons C*H*S and C*H*CN (4.0 and 1.2, respectively) clearly

Table 2. Cycloaddition of (*Z*)-1,3-dienes **1** with unsymmetrical dienophiles

Entry	Diene	Dienophile	Conditions[a]	Adducts	Yield[b] (%)
1	**1b**	Cyclohex-2-enone[c]	$LiClO_4$–THF, 100 °C, 8 h	 **15b**	38
2	**1a**	Methyl vinyl ketone[d]	$EtAlCl_2$, −78 °C→0 °C, 14 h	 **16a** (R=Me)	52
3	**1b**	Methyl vinyl ketone[d]	$EtAlCl_2$, −78 °C→0 °C, 14 h	**16b** (R=Et)	56
4	**1b**	Methyl vinyl ketone[d]	LPDE, Et_2O, 20 °C, 20 h	**16b** (R=Et)	62
5	**1c**	Methyl vinyl ketone[d]	$EtAlCl_2$, −78 °C→0 °C, 14 h	**16c** (R=Ac)	84
6	**1c**	Methyl vinyl ketone[d]	LPDE, Et_2O, 20 °C, 48 h	**16c** (R=Ac)	81
7	**1d**	Methyl vinyl ketone[d]	$EtAlCl_2$, −78 °C→0 °C, 14 h	**16d** (R=Piv)	77
8	**1a**	Acrylonitrile[e]	$ZnBr_2$, 60 °C, 4 h	 **17a** (R=Me)	46
9	**1b**	Acrylonitrile[e]	$LiClO_4$–THF, 80 °C, 8 h	**17b** (R=Et)	51
10	**1b**	Acrylonitrile[e]	$ZnBr_2$, 60 °C, 4 h	**17b** (R=Et)	47
11	**1c**	Acrylonitrile[e]	$ZnBr_2$, 60 °C, 4 h	**17c** (R=Ac)	51
12	**1c**	Acrylonitrile[e]	$LiClO_4$–THF, 80 °C, 8 h	**17c** (R=Ac)	59
13	**1d**	Acrylonitrile[e]	$ZnBr_2$, 60 °C, 6 h	**17d** (R=Piv)	55
14	**1b**	Ethyl acrylate[c]	$ZnBr_2$, 80 °C, 5 h	 **18b** (R=Et)	24
15	**1b**	Ethyl acrylate[c]	$LiClO_4$–THF, 100 °C, 5 h	**18b** (R=Et)	55
16	**1c**	Ethyl acrylate[c]	$ZnBr_2$, 80 °C, 8 h	**18c** (R=Ac)	38

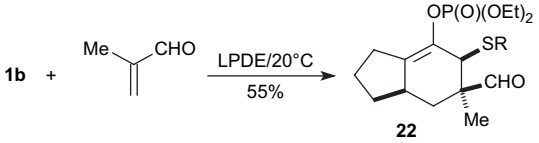
[a] LPDE=5 M solution of $LiClO_4$ in Et_2O or in THF.
[b] All yields refer to analytically pure compounds.
[c] Dienophile (10 equiv).
[d] Dienophile (2 equiv).
[e] Dienophile (5 equiv).

established regio- and stereochemistry of all obtained adducts. The best evidence for '*ortho*' regioselectivity is also the elimination reaction affording the corresponding 1,3-dienes **20**, **27**, and **33** (elimination reactions presented in Schemes 8, 12, 14 and 15). Their structures were established based on the ^1H NMR data and in particular on the characteristic doublet of one vinyl proton at 6.81 ($^4J_{PH}$ 2.8), 6.69 ($^4J_{PH}$ 3.1), and 6.91 ($^4J_{PH}$ 2.9), respectively. The NMR data found for allylic alcohols derived from the transformation of cycloadducts strongly supported the conclusions about regioselectivity.[9] The stereochemistry of the elimination reaction also confirmed the *endo*-configuration of the adducts.

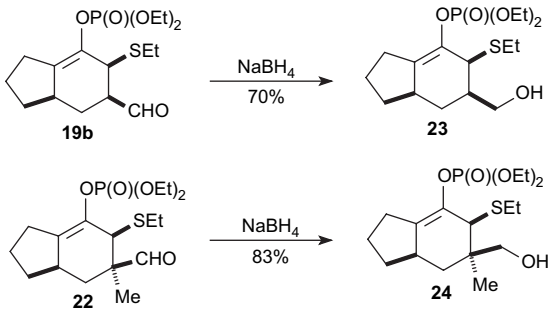


Scheme 8. Cycloaddition of dienes **1b** and **1c** with acrolein in the presence of LPDE or $ZnBr_2$.

The complete regiocontrol exercised by the SR substituent demonstrates the excellent regio-directing ability of these



Scheme 9. Cycloaddition of diene **1b** with methacrolein.



Scheme 10. Reduction of formyl function in **19b** and **22**.

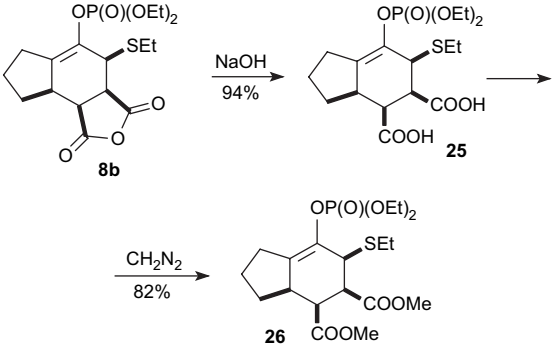
sulfur groups. There is no regiocompetition between sulfur and dialkoxyphosphoryloxy substituents. The regiochemistry observed here complements the regiochemistry described with 2-dialkoxyphosphoryloxy-butadiene.[6]

2.3. Transformations of cycloadducts

In our program to expand the horizons of these cycloadducts, we have investigated some important transformations by using their functional groups. In the previous paper, we described a stereospecific entry to novel functionalized bi- and tricyclic allylic alcohols and the corresponding α-hydroxy ketones.[9] In this paper, we want to describe in detail transformations of adducts mainly into the corresponding 1,3-dienes and aromatic compounds. In performing these transformations we had a second goal: providing supporting evidence for the regio- and stereochemistry of the initial cycloadducts.

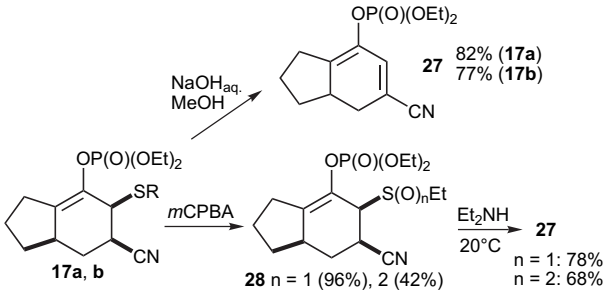
We have found that the aldehyde function in both adducts **19b** and **22** is easily converted to a hydroxyl group using sodium boron hydride (Scheme 10).

Base catalyzed hydrolysis of adduct **8b** bearing a maleic anhydride ring provided the new adduct **25** containing two carboxylic acid functions, both of which undergo efficient esterification to **26** with diazomethane at ambient temperature (Scheme 11).



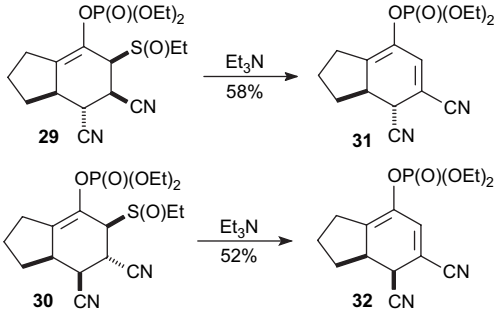
Scheme 11. Hydrolysis of maleic anhydride ring in **8b** and subsequent esterification of dicarboxylic function.

The base catalyzed elimination of the sulfur substituent in adducts provided new class of bicyclic conjugated dienes. In the course of these reactions it was necessary to use a quite strong base, like an aqueous solution of sodium hydroxide at ambient temperature, because the SR group is a poor leaving group. In contrast, oxidation of the sulfide moiety using *m*CPBA to the better leaving group sulfoxide or sulfone **28** allowed the use of diethylamine to give the 1,3-diene **27** (Scheme 12).



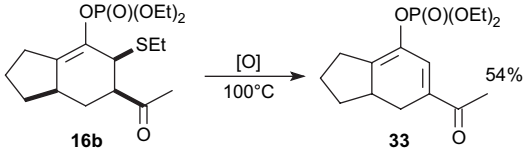
Scheme 12. Elimination reactions of sulfide, sulfinyl, and sulfonyl groups promoted by bases.

In similar manner, the diastereoisomeric sulfoxides **29** and **30** were converted to 1,3-dienes **31** and **32** (Scheme 13).



Scheme 13. Elimination reactions of sulfinyl group promoted by base.

Oxidation of adduct **16b**, which has a quite acidic hydrogen in the α-position to the sulfur substituent, at 100 °C provided 1,3-diene **33** without the help of amine (Scheme 14).

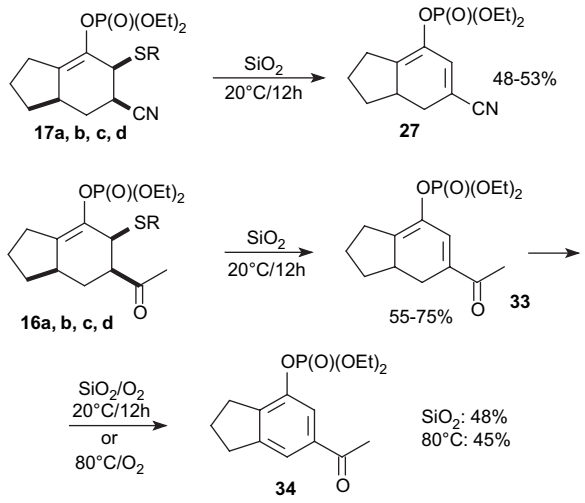


Scheme 14. Thermal elimination reaction of sulfur substituent group.

An efficient way to catalyze the elimination of a sulfur substituent is to deposit the adducts **16** and **17** in benzene–AcOEt 2:1 solution on silica gel at ambient temperature overnight. After a further 12 h the 1,3-diene **33** aromatizes to the aromatic phosphate **34** (Scheme 15). Aromatization involves oxidation of **33** on silica gel.

A control experiment revealed that dienes **33** and **20** in benzene solution at 80 °C undergo oxidation by oxygen in air to the aromatic compounds **34** and **35**.

We have also obtained aromatic phosphates **35**, **37**, **40**, and **42** by the action of ammonium fluoride or by warming **39** and **41** containing a sulfoxide function at 60 °C for 1 h in an aqueous solution of sodium hydroxide. It is well known that the fluoride anion is not only a strong base but also an



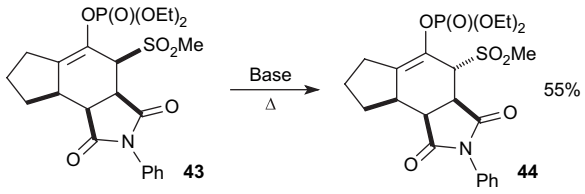
Scheme 15. Elimination reactions on silica gel and subsequent aromatization.

excellent nucleophile toward a phosphoryl phosphorus atom. Indeed, e.g., aromatic phosphates **35** and **37** were easily converted into hydroxy arene derivatives **36** and **38** in good yield by treatment with fluoride anion (Scheme 16).

We have found that *endo*-cycloadduct bearing sulfonyl functional group **43** undergoes epimerization to cycloadduct **44** by treating with triethylamine or imidazole at 50 °C for 3 h (Scheme 17).

3. Conclusion

(*Z*)-1,2-Diheterosubstituted-1,3-dienes reacted with several dienophiles to provide access to a variety of new functionalized polycyclic allylic sulfides. The most significant feature for the synthetic application of these dienes is the fully regio- and *endo*-selectivity observed in their thermal and Lewis acid catalyzed cycloaddition reactions. The regiochemistry of these Diels–Alder reactions is completely controlled by the sulfur substituent. We have also demonstrated that the



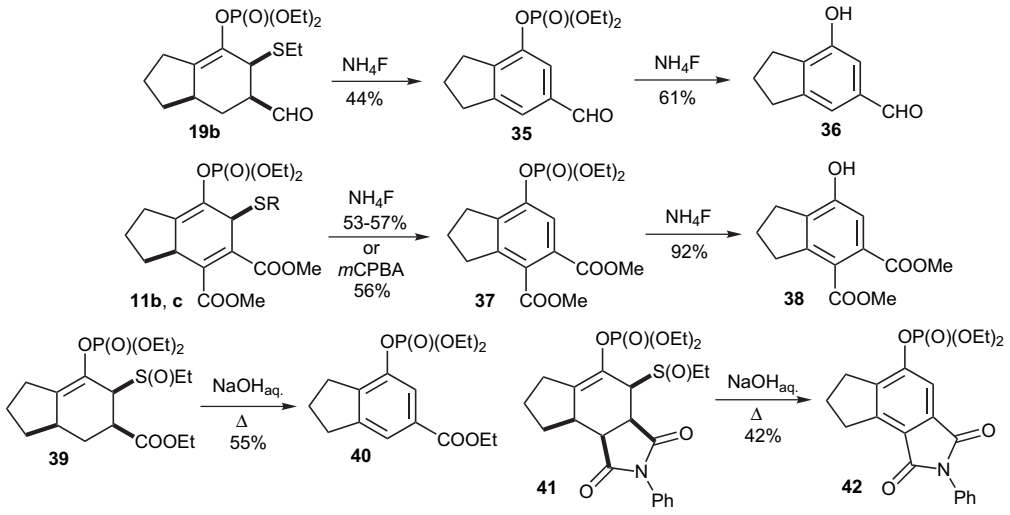
Scheme 17. Epimerization of sulfonyl substituent in **43** promoted by bases.

obtained cycloadducts are functionalized versatile synthons with fixed stereochemistry: all substituents can be easily transformed in different ways to an important class of new compounds, e.g., functionalized cyclic 1,3-dienes and aromatic phosphates and hydroxy arenes.

4. Experimental

4.1. General

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Brucker AV 200, DSX 300, or DRX 500 spectrometers at the indicated frequency (using $CDCl_3$ as solvent). Coupling constants *J* are given in hertz. MS spectra were recorded on LKB2091 and on a Finnigan MAT 95 spectrometer. Microanalyses were carried out on EA1108 apparatus. Melting points were measured with a PHMK Boetius (VEB Analytik Dresden) apparatus. All reactions were performed using anhydrous conditions and under an atmosphere of argon, unless otherwise noted. Yields refer to materials purified by column chromatography. Chromatographic purification was performed on silica gel columns (Merck, Kieselgel 70–230 mesh or silanized Kieselgel) with benzene–ethyl acetate as eluant, unless otherwise noted. TLC was carried out on silica gel plates (Merck F_{254}) with benzene–ethyl acetate (1:1, v/v) as eluant, unless otherwise noted. Chemicals and solvents were obtained from commercial sources and distilled or dried according to standard methods. All (*Z*)-1,2-diheterosubstituted 1,3-dienes **1** were prepared according to the published procedure.[7]



Scheme 16. Elimination reactions promoted by bases and dephosphorylation reactions.

4.2. Crystallography

Compound **8d** crystallizes in the orthorhombic system in space group *Pbca* with the unit cell consisting of eight molecules. In the compound, the six-membered ring adopts a deformed boat conformation with the flap position atoms being C3 and C6 (Fig. 1). The overall view of the molecule with the atom numbering scheme are shown in Figure 2. Selected bond lengths, bond and torsion angles are listed in Tables S1, S2, and S3 (Electronic supplementary information, ESI), respectively. Molecules of **8d** are rather loosely packed in the crystal and there are only three weak C–H···O hydrogen contacts present, one intramolecular C3–H···O13 shown in Figure 2, and two intermolecular ones (Table S4, ESI), in which the most acidic hydrogen atoms H4 and H5 attached to C4 and C5 are engaged in the contacts.

The crystal and molecular structures of the compound were determined using the data collected at room temperature on an Oxford Diffraction KM4CCD diffractometer[11,12] with graphite-monochromated Mo Kα radiation. Crystal data and experimental details are given in Table 3. The lattice constants were refined by least-squares fits of 1610 reflections in the θ range 2.8°–14.6°. A total of 51,644 collected reflections were used to solve the crystal structure by direct methods and to refine it by full-matrix least-squares methods using F^2.[12,13] Hydrogen atoms were placed geometrically at idealized positions, and set as riding with fixed thermal parameters equal to 1.5 times the equivalent isotropic thermal parameter of the parent atom. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The final R was 0.071 for 307 refined parameters and 5293 observed reflections with $I>2\sigma(I)$.

The conformation of the six-membered ring was determined on the basis of the torsion angles, asymmetry parameters,[14,15] puckering parameters,[16] and also by dihedral angles between the selected least-square planes[17] (Tables S5, S6, and S7 in Supplementary data).

Table 3. Crystal data and experimental details

Molecular formula	$C_{20}H_{27}O_8PS$
Formula weight	458.45
Diffractometer	KM4CCD
Crystallographic system	Orthorhombic
Space group	*Pbca*
a (Å)	11.2777(5)
b (Å)	17.5367(4)
c (Å)	23.6976(5)
V (Å^3)	4686.8(3)
Z	8
μ (mm^{-1})	0.247
λ (Å)	0.71073
T (K)	293(2)
Reflections collected	51644
Unique reflections	5293
Observed reflect. [$I>2\sigma(I)$]	2953
No. parameters	307
R_{int}	0.1232
R_{obs}	0.0710
wR_{obs} [a]	0.2075

[a] Weighting scheme $w=[\sigma^2(F_o^2)+(0.1212P)^2+2.41P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$.

Data reduction was carried out with CrysAlis CCD, Oxford Diffraction[11] crystallographic computing package, structure solution with SHELXS,[12] and structure refinement with SHELXL.[13]

4.3. Syntheses

4.3.1. Cycloaddition of dienes 1 with dienophiles: preparation of allylic sulfides. *General procedure (A):* a mixture of diene **1** (3 mmol), hydroquinone (1 mol %), and 1.1 equiv of dienophile was dissolved in toluene (5 mL) and stirred at 100 °C for 4–15 h (depending on substrates) in Schlenk tube. The reaction mixture was concentrated in vacuo (0.1 mmHg) and purified by column chromatography to give pure cycloadduct.

General procedure (B): diene **1** (3 mmol) and 1.1 equiv of dienophile were dissolved in 5 M solution of $LiClO_4$–Et_2O (LPDE) or THF and stirred at room temperature for 48–72 h. The reaction mixture was diluted with $CHCl_3$ (50 mL) and washed with water (2×10 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was purified by column chromatography using benzene–ethyl acetate (1:1) as eluant to give pure cycloadduct.

General procedure (C): diene **1** (1 mmol), 1 equiv of $ZnBr_2$, hydroquinone (1 mol %), and 5 equiv of acrylonitrile were dissolved in toluene (10 mL) and stirred at 60 °C for 4–8 h. The reaction mixture was diluted with $CHCl_3$ (50 mL) and washed with water (2×10 mL). The organic layer was dried ($MgSO_4$) and solvent was removed in vacuo. Analytically pure adduct was obtained after purification by column chromatography using benzene–ethyl acetate (1:1) as eluant.

General procedure (D): a solution of diene **1** (1 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise at −78 °C to a mixture of 2 equiv of methyl vinyl ketone (MVK) and 2 equiv of $EtAlCl_2$ (1.6 M in hexane) in anhydrous CH_2Cl_2 (10 mL) prepared at the same temperature. The reaction mixture in Schlenk tube was stirred at −78 °C for 1 h and at −15 °C for 20 h. Then cooled again to −78 °C and quenched by the addition of satd NH_4Cl (10 mL). The reaction mixture was diluted with $CHCl_3$ (100 mL). The organic layer was washed with satd NH_4Cl (2×10 mL) and water (3×10 mL) to neutral pH, dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by column chromatography using benzene–ethyl acetate (1:1) as eluant to provide pure cycloadduct.

4.3.2. Reactions with *N*-phenylmaleimide. Reactions of dienes **1** with *N*-phenylmaleimide were performed according to procedures A and B for 4–8 h and 48–72 h, respectively.

4.3.2.1. Phosphoric acid diethyl ester 4-methylsulfanyl-1,3-dioxo-2-phenyl-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-5-yl ester 5a. Yield: 78% (A) or 72% (B)—pale yellow dense oil. R_f 0.38; δ_P (80.96 MHz, $CDCl_3$) −5.38; δ_C (50.32 MHz, $CDCl_3$) 16.00 (d, J_{PC} 6.6, 2×OCH_2CH_3), 17.78, 25.68, 28.15, 28.54, 40.82, 41.71, 46.07 (d, J_{PC} 6.0, CHS), 47.79, 64.36 (d, J_{PC} 6.6, OCH_2), 64.49 (d, J_{PC} 6.6, OCH_2), 126.55 (s, *o*-C_6H_5), 128.39 (s, *p*-C_6H_5), 128.88 (s, *m*-C_6H_5), 130.15 (d, J_{PC} 5.8, =COP), 131.77 (s, *ipso*-C_6H_5), 135.59 (d, J_{PC} 6.1), 174.78 (s, C=O), 175.59 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.32

(3H, dq, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.33 (3H, dq, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.55–1.88 (3H, m), 2.21 (3H, s, SCH_3), 2.23–2.40 (2H, m), 2.43–2.57 (2H, m), 3.36 (1H, dd, J_{HH} 8.0 and 8.4, CHC(O)), 3.68 (1H, dd, J_{HH} 8.0 and 5.8, CHC(O)), 3.69–3.78 (1H, m, CHS), 4.11–4.32 (4H, m, 2×OCH_2), 7.16–7.48 (5H, m, C_6H_5); *m/z* (15 eV) 465 (M^+, 6%), 418 (10, M^+−SMe), 155 (29, $(H+HOP(O)(OEt)_2)^+$). Found: C, 56.8; H, 6.0; N, 3.0; P, 6.7. Calcd for $C_{22}H_{28}NO_6PS$: C, 56.8; H, 6.1; N, 3.0; P, 6.7%.

4.3.2.2. Phosphoric acid diethyl ester 4-ethylsulfanyl-1,3-dioxo-2-phenyl-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-5-yl ester 5b. Yield: 86% (A) or 68% (B)—pale yellow dense oil. R_f 0.47; δ_P (80.96 MHz, $CDCl_3$) −5.52; δ_C (50.32 MHz, $CDCl_3$) 14.04 (s, SCH_2CH_3), 15.84 (d, J_{PC} 7.0, 2×OCH_2CH_3), 25.67, 28.18, 28.31, 38.32, 40.74, 41.76, 43.99, 48.07, 64.14 (d, J_{PC} 6.9, OCH_2), 64.28 (d, J_{PC} 6.9, OCH_2), 126.42 (s, *o*-C_6H_5), 128.16 (s, *p*-C_6H_5), 128.67 (s, *m*-C_6H_5), 129.44 (d, J_{PC} 5.6, =COP), 131.69 (s, *ipso*-C_6H_5), 135.72 (d, J_{PC} 8.9), 174.75 (s, C=O), 175.45 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.26 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.32 (3H, dt, J_{PH} 1.1, J_{HH} 7.0, OCH_2CH_3), 1.33 (3H, dt, J_{PH} 1.1, J_{HH} 7.0, OCH_2CH_3), 1.58–1.85 (2H, m), 2.01–2.42 (2H, m), 2.43–2.55 (2H, m), 2.68 (1H, q, J_{HH} 7.4, SCH_2), 2.71 (1H, q, J_{HH} 7.4, SCH_2), 2.69–2.83 (1H, m), 3.36 (1H, dd, J_{HH} 8.3 and 8.4, CHC(O)), 3.66 (1H, dd, J_{HH} 5.5 and 8.3, CHC(O)), 3.74–3.78 (1H, m, CHS), 4.10–4.32 (4H, m, 2×OCH_2), 7.26–7.48 (5H, m, C_6H_5); *m/z* (15 eV) 479 (M^+, 4%), 419 (95, M^+(−SEt, +H)), 418 (47, M^+−SEt), 417 (100, M^+−HSEt), 265 (28, M^+(−HSEt, −HOP(O)$(OEt)_2$)), 155 (33, (H+HOP(O)$(OEt)_2)^+$); *m/z* (CI) (Finnigan MAT 95) 480 (M^+(+H), 100%), 418 (37, M^+−SEt), 264 (4, M^+(−SEt, −HOP(O)$(OEt)_2$)), 155 (5, $(H+HOP(O)(OEt)_2)^+$). HRMS (CI) calcd for $C_{23}H_{30}NO_6PS$+H (M^++H): 480.160974. Found: 480.158900.

4.3.2.3. Thioacetic acid *S*-[5-(diethoxyphosphoryloxy)-1,3-dioxo-2-phenyl-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-4-yl] ester 5c. Yield: 80% (A) or 83% (B)—pale yellow dense oil. R_f 0.41; δ_P (80.96 MHz, $CDCl_3$) −5.59; δ_C (50.32 MHz, $CDCl_3$) 15.94 (d, J_{PC} 6.6, 2×OCH_2CH_3), 26.50, 28.42, 29.14, 30.03, 40.80, 41.32, 42.79, 47.65, 64.41 (d, J_{PC} 5.7, 2×OCH_2), 126.48 (s, *o*-C_6H_5), 128.50 (s, *p*-C_6H_5), 128.91 (s, *m*-C_6H_5), 129.70 (d, J_{PC} 5.5, =COP), 131.58 (s, *ipso*-C_6H_5), 134.24 (d, J_{PC} 9.7), 175.45 (s, NC=O), 175.48 (s, NC=O), 194.57 (s, SC=O); δ_H (200.13 MHz, $CDCl_3$) 1.29 (3H, dt, J_{PH} 1.9, J_{HH} 7.0, OCH_2CH_3), 1.30 (3H, dt, J_{PH} 1.9, J_{HH} 7.0, OCH_2CH_3), 1.61–1.80 (3H, m), 1.95–2.17 (1H, m), 2.17–2.39 (1H, m), 2.41 (3H, s, $SC(O)CH_3$), 2.42–2.63 (1H, m), 2.84–3.02 (1H, m), 3.42 (1H, dd_{AB}, J_{HH} 8.0, J_{HH}(AB) 8.5, CHC(O)), 3.47 (1H, dd_{AB}, J_{HH} 4.4, J_{HH}(AB) 8.5, CHC(O)), 4.04–4.29 (4H, m, 2×OCH_2), 4.65–4.73 (1H, m, CHS), 7.23–7.58 (5H, m, C_6H_5); *m/z* (15 eV) 493 (M^+, 1%), 450 (4, M^+−Ac), 418 (5, M^+−SAc). Found: C, 56.1; H, 5.6; N, 2.8; P, 6.3. Calcd for $C_{23}H_{28}NO_7PS$: C, 56.0; H, 5.7; N, 2.8; P, 6.3%.

4.3.2.4. 2,2-Dimethyl thiopropionic acid *S*-[5-(diethoxyphosphoryloxy)-1,3-dioxo-2-phenyl-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-4-yl] ester 5d. Yield: 85% (A)—deep yellow dense oil. R_f 0.74; δ_P (80.96 MHz, $CDCl_3$) −5.76; δ_C (50.32 MHz, $CDCl_3$) 15.85 (d, J_{PC} 6.6, 2×OCH_2CH_3), 26.43, 27.14 (s, $C(CH_3)_3$), 28.31, 29.06, 40.46, 41.33, 42.71, 46.23 (s, $C(CH_3)_3$), 47.44, 64.25 (d, J_{PC} 4.6, 2×OCH_2), 126.49 (s, *o*-C_6H_5), 128.35 (s, *p*-C_6H_5), 128.76 (s, *m*-C_6H_5), 129.21 (d, J_{PC} 5.2, =COP), 131.58 (s, *ipso*-C_6H_5), 134.43 (d, J_{PC} 9.5), 175.32 (s, C=O), 175.45 (s, C=O), 205.36 (s, SC=O); δ_H (200.13 MHz, $CDCl_3$) 1.28 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.29 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.29 (9H, s, $C(CH_3)_3$), 1.57–1.84 (2H, m), 1.87–2.17 (2H, m), 2.18–2.45 (1H, m), 2.46–2.63 (1H, m), 2.85–3.01 (1H, m), 3.40 (1H, dd_{AB}, J_{HH} 7.8, J_{HH}(AB) 8.5, CHC(O)), 3.47 (1H, dd_{AB}, J_{HH} 4.5, J_{HH}(AB) 8.5, CHC(O)), 4.04–4.22 (4H, m, 2×OCH_2), 4.58–4.63 (1H, m, CHS), 7.25–7.47 (5H, m, C_6H_5); *m/z* (70 eV) (Finnigan MAT 95) 535 (M^+, 3%), 450 (94, M^+−Piv), 418 (14, M^+−SPiv), 85 (21, Piv^+), 57 (100, t-Bu^+). Found: C, 58.4; H, 6.4; N, 2.6; P, 5.8. Calcd for $C_{26}H_{34}NO_7PS$: C, 58.3; H, 6.4; N, 2.6; P, 5.8%.

4.3.3. Reactions with maleimide. Reactions of diene **1b** with maleimide were performed according to procedures A and B for 10 and 48 h, respectively.

4.3.3.1. (3ar,4c,8ac,8bc)-Phosphoric acid diethyl ester 4-ethylsulfanyl-1,3-dioxo-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-5-yl ester 6. Yield: 58% (A) or 68% (B)—deep yellow dense oil. R_f 0.35; δ_P (80.96 MHz, $CDCl_3$) −6.06; δ_C (50.32 MHz, $CDCl_3$) 13.85 (s, SCH_2CH_3), 15.68 (d, J_{PC} 7.2, 2×OCH_2CH_3), 26.00 (s, CH_2), 27.78 (s, CH_2), 28.15 (s, CH_2), 28.40 (s, CH_2), 40.78 (s, CH), 43.26 (s, CH), 43.86 (s, CH), 48.94 (s, CH), 64.15 (d, J_{PC} 6.5, OCH_2), 64.29 (d, J_{PC} 6.5, OCH_2), 129.34 (d, J_{PC} 5.3, =COP), 135.53 (d, J_{PC} 10.0, C=COP), 176.70 (s, C=O), 177.67 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.25 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.33 (3H, dt, J_{PH} 1.3, J_{HH} 7.1, OCH_2CH_3), 1.34 (3H, dt, J_{PH} 1.3, J_{HH} 7.1, OCH_2CH_3), 1.51–2.09 (4H, m), 2.22–2.48 (3H, m), 2.62 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 14.9, SCH_2), 2.67 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 14.9, SCH_2), 3.18 (1H, dd, J_{HH} 8.1 and 8.3, CHC(O)), 3.45 (1H, dd, J_{HH} 5.5 and 8.3, CHC(O)), 3.53–3.59 (1H, m, CHS), 4.05–4.33 (4H, m, 2×OCH_2), 9.04 (1H, s, N–H); *m/z* (15 eV) 402 (M^+(−H), 1%), 374 (3, M^+−Et), 343 (94, M^+(−SEt, +H)), 342 (29, M^+−SEt), 188 (20, M^+(−SEt, −HOP(O)$(OEt)_2$)), 187 (15, M^+(−HSEt, −HOP(O)$(OEt)_2$)), 155 (100, $(H+HOP(O)(OEt)_2)^+$). Found: C, 50.7; H, 6.5; N, 3.5; P, 7.6. Calcd for $C_{17}H_{26}NO_6PS$: C, 50.6; H, 6.5; N, 3.5; P, 7.7%.

4.3.3.2. (3ar,4t,8ac,8bc)-Phosphoric acid diethyl ester 4-ethylsulfanyl-1,3-dioxo-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-5-yl ester 7. Yield: 15% (A) and 0% (B)—pale yellow dense oil. R_f 0.52; δ_P (80.96 MHz, $CDCl_3$) −5.05; δ_C (50.32 MHz, $CDCl_3$) 14.20 (s, SCH_2CH_3), 15.96 (d, J_{PC} 6.9, 2×OCH_2CH_3), 23.52 (s, CH_2), 24.68 (s, CH_2), 27.04 (s, CH_2), 33.45 (s, CH_2), 38.38 (s, CH), 42.50 (s, CH), 43.95 (s, CH), 52.78 (s, CH), 64.46 (d, J_{PC} 8.2, OCH_2), 64.62 (d, J_{PC} 8.2, OCH_2), 131.48 (d, J_{PC} 6.8, =COP), 134.82 (d, J_{PC} 8.4), 177.09 (s, C=O), 178.75 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.28 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.2, J_{HH} 7.0, OCH_2CH_3), 1.38 (3H, dt, J_{PH} 1.2, J_{HH} 7.0, OCH_2CH_3), 1.52–1.95 (4H, m), 2.08–2.35 (3H, m), 2.61 (2H, q, J_{HH} 7.4, SCH_2), 2.65 (1H, dd, J_{HH} 7.6 and 9.6, CHC(O)), 3.62 (1H, dd, J_{HH} 1.9 and 7.6, CHC(O)), 4.05–4.15 (1H, m, CHS), 4.10–4.37

(4H, m, 2×OCH_2), 9.04 (1H, s, N–H); *m/z* (15 eV) 403 (M^+, 0.2%), 374 (6, M^+−Et), 343 (100, M^+(−SEt, +H)), 342 (16, M^+−SEt), 188 (50, M^+(−SEt, −HOP(O)$(OEt)_2$)), 155 (72, (H+HOP(O)$(OEt)_2$)$^+$). Found: C, 50.5; H, 6.5; P, 7.5. Calcd for $C_{17}H_{26}NO_6PS$: C, 50.6; H, 6.5; P, 7.7%.

4.3.4. Reactions with maleic anhydride. Reactions of dienes **1b** and **1d** with maleic anhydride were performed according to procedure A for 10 h. Crude product **8b** was purified by column chromatography on silanized silica gel and then **8d** was recrystallized from Et_2O–pentane (1:2, v/v) to give pure adduct as colorless needles.

4.3.4.1. Phosphoric acid diethyl ester 4-ethylsulfanyl-1,3-dioxo-3,3a,4,6,7,8,8a,8b-octahydro-1*H*-indeno[4,5-*c*]-furan-5-yl ester 8b. Yield: 57%—pale yellow dense oil. R_f 0.84 (TLC, silanized gel, benzene); δ_P (80.96 MHz, $CDCl_3$) −5.36; δ_C (50.32 MHz, $CDCl_3$) 13.58 (s, SCH_2CH_3), 15.39 (d, J_{PC} 6.6, 2×OCH_2CH_3), 24.68, 27.42, 27.45, 27.78, 39.22, 41.61, 42.18, 48.48, 63.94 (d, J_{PC} 5.8, OCH_2), 64.06 (d, J_{PC} 5.8, OCH_2), 129.95 (d, J_{PC} 6.0, =COP), 135.02 (d, J_{PC} 8.9), 169.54 (s, C=O), 170.48 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.26 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.37 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.52–1.95 (3H, m), 2.00–2.28 (2H, m), 2.42–2.54 (2H, m), 2.68 (1H, q, J_{HH} 7.4, SCH_2), 2.70 (1H, q, J_{HH} 7.4, SCH_2), 3.40–3.54 (1H, m, CHC(O)), 3.76–3.83 (1H, m, CHC(O)), 4.07–4.59 (5H, m, 2×OCH_2, CHS); *m/z* (15 eV) 404 (M^+, 3%), 375 (4, M^+−Et), 344 (100, M^+(−SEt, +H)), 343 (19, M^+−SEt), 271 (5, M^+(−SEt, −$(CO)_2$O)), 270 (7, M^+(−HSEt, −$(CO)_2$O)). Found: C, 50.6; H, 6.1; P, 7.5. Calcd for $C_{17}H_{25}O_7PS$: C, 50.5; H, 6.2; P, 7.7%.

4.3.4.2. 2,2-Dimethyl thiopropionic acid *S*-[5-(diethoxyphosphoryloxy)-1,3-dioxo-3,3a,4,6,7,8,8a,8b-octahydro-1*H*-indeno[4,5-*c*]furan-4-yl] ester 8d. Yield: 68%—colorless needles. R_f 0.47; mp 124–126 °C (from Et_2O–pentane); δ_P (80.96 MHz, $CDCl_3$) −5.66; δ_C 16.04 (d, J_{PC} 6.4, 2×OCH_2CH_3), 25.97, 27.27 (s, $C(CH_3)_3$), 28.55, 28.94, 46.30 (s, $C(CH_3)_3$), 40.15, 40.53, 43.37, 48.37, 64.57 (d, J_{PC} 5.8, 2×OCH_2), 130.40 (d, J_{PC} 6.4, =COP), 134.90 (d, J_{PC} 8.0), 170.30 (s, OC=O), 170.35 (s, OC=O), 205.01 (s, SC=O); δ_H (200.13 MHz, $CDCl_3$) 1.29 (9H, s, $C(O)C(CH_3)_3$), 1.33 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.34 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.58–1.97 (3H, m), 1.98–2.28 (2H, m), 2.35–2.67 (1H, m), 2.75–2.95 (1H, m), 3.51 (1H, dd_{AB}, J_{HH}(AB) 9.2, J_{HH} 8.0, CHC(O)), 3.62 (1H, dd_{AB}, J_{HH}(AB) 9.2, J_{HH} 5.3, CHC(O)), 4.07–4.25 (4H, m, 2×OCH_2), 4.54–4.61 (1H, m, CHS); *m/z* 460 (15 eV) (M^+, 9%), 375 (100, M^+−Piv), 343 (27, M^+−SPiv). Found: C, 52.0; H, 6.3; P, 6.6. Calcd for $C_{20}H_{29}O_8PS$: C, 52.0; H, 6.4; P, 6.7%.

4.3.5. Reactions with *p*-benzoquinone. Reaction of diene **1b** with *p*-benzoquinone was performed according to procedure A at room temperature for 7 days to give mixture of adducts **9** and **10**. The same reaction was carried out at 60 °C for 5 h to provide adduct **10** exclusively, whereas the reaction performed according to procedure B at room temperature for 4 h gave adduct **9** exclusively. Pure adducts **9** and **10** were obtained after purification by column chromatography.

4.3.5.1. Phosphoric acid diethyl ester 5-ethylsulfanyl-6,9,-dioxo-2,3,5,5a,9,9a-hexahydro-1*H*-cyclopenta[*a*]naphthalen-4-yl ester 9. Yield: 55% (A) or 87% (B)—deep orange crystals. R_f 0.48; mp 177–180 °C (from benzene–pentane); δ_P (80.96 MHz, $CDCl_3$) −4.27; δ_C (50.32 MHz, $CDCl_3$) 14.54 (s, SCH_2CH_3), 15.23 (d, J_{PC} 6.1, 2×OCH_2CH_3), 27.95, 28.13, 31.37, 34.78, 41.05, 44.31, 49.52, 50.34, 64.18 (d, J_{PC} 6.6, 2×OCH_2), 125.83 (d, J_{PC} 7.5), 139.73 (s, =CH), 140.41 (s, =CH), 143.83 (d, J_{PC} 5.0, =COP), 196.29 (s, C=O), 198.62 (s, C=O); δ_H (300.13 MHz, $CDCl_3$) 0.98 (3H, t, J_{HH} 7.5, SCH_2CH_3), 1.43 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.45 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.66–1.81 (3H, m), 1.81–2.05 (1H, m), 2.00 (1H, d_{AB}q, J_{HH}(AB) 12.4, J_{HH} 7.5, SCH_2), 2.11–2.30 (3H, m), 2.16 (1H, d_{AB}q, J_{HH}(AB) 12.4, J_{HH} 7.5, SCH_2), 2.48–2.62 (1H, m, CHC(O)), 4.21–4.82 (6H, m, 2×OCH_2, CHC(O), CHS), 6.61 (1H, d_{AB}, J_{HH} 8.6, =CHC(O)), 6.63 (1H, d_{AB}, J_{HH} 8.6, =CHC=O); *m/z* (15 eV) 413 (M^+−H, 1%), 411 (1, M^+(−H, −H_2)), 353 (15, M^+−SEt), 352 (74, M^+−HSEt), 350 (90, M^+(−SEt, −H_2)), 324 (20, M^+(−SEt, −Et)), 323 (15, M^+(−HSEt, −Et)), 322 (35, M^+(−HSEt, −C_2H_6)), 295 (30, M^+(−SEt, −Et_2)), 294 (47, M^+(−HSEt, −Et_2)), 293 (33, M^+(−HSEt, −Et, −C_2H_6)), 270 (3, M^+(−HSEt, −$(C{=}O)_2CH{=}CH$)), 198 (30, M^+(−HOP(O)$(OEt)_2$, −HSEt)), 155 (22, (H+HOP(O)$(OEt)_2$)$^+$). Found: C, 55.0; H, 6.6; P, 7.5. Calcd for $C_{19}H_{27}O_6PS$: C, 55.1; H, 6.6; P, 7.5%.

4.3.5.2. Phosphoric acid diethyl ester 6,9-dioxo-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-4-yl ester 10. Yield: 69% (A, 60 °C) or 28% (A, 20 °C)—orange dense oil. R_f 0.77; δ_P (80.96 MHz, $CDCl_3$) −6.19; δ_C (50.32 MHz, $CDCl_3$) 15.96 (d, J_{PC} 6.3, 2×OCH_2CH_3), 24.49, 29.26, 34.08, 64.96 (d, J_{PC} 6.0, 2×OCH_2), 115.69, 116.52, 124.85 (s, =CH), 133.25, 137.65 (s, =CH), 139.16 (s, =CH), 143.48 (d, J_{PC} 6.8, =COP), 150.41, 184.23 (s, C=O), 185.45 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.40 (6H, dt, J_{PH} 0.8, J_{HH} 7.1, 2×OCH_2CH_3), 2.20 (2H, quint, J_{HH} 7.6), 3.04 (2H, t, J_{HH} 7.6, CH_2–C=), 3.42 (2H, t, J_{HH} 7.6, CH_2–C=), 4.25 (2H, q, J_{HH} 7.1, OCH_2), 4.28 (2H, q, J_{HH} 7.1, OCH_2), 6.88 (1H, d_{AB}, J_{HH} 10.3, =CHC(O)), 6.90 (1H, d_{AB}, J_{HH} 10.3, =CHC(O)), 7.82 (1H, s, POC=CH); *m/z* (15 eV) 350 (M^+, 72%), 322 (27, M^+−CO), 294 (37, M^+−$(CO)_2$), 198 (19, M^+(−OP(O)$(OEt)_2$, +H)), 196 (13, M^+−HOP(O)$(OEt)_2$), 168 (8, M^+(−CO, −HOP(O)$(OEt)_2$)), 155 (9, (H+HOP(O)$(OEt)_2$)$^+$), 138 (54, M^+(−$(HCO)_2$, −HOP(O)$(OEt)_2$)). Found: C, 58.4; H, 5.4; P, 8.8. Calcd for $C_{17}H_{19}O_6P$: C, 58.3; H, 5.5; P, 8.8%.

4.3.6. Reactions with dimethyl acetylene dicarboxylate. Cycloadducts **11b** and **11c** were obtained according to procedure A by heating at 100 °C without toluene for 4 h.

4.3.6.1. Dimethyl 7-(diethoxyphosphoryloxy)-6-ethylsulfanyl-2,3,3a,6-tetrahydro-1*H*-indene-4,5-dicarboxylate 11b. Yield: 68%—orange dense oil. R_f 0.75; δ_P (80.96 MHz, $CDCl_3$) −4.49; δ_C (50.32 MHz, $CDCl_3$) 13.73 (s, SCH_2CH_3), 15.92 (d, J_{PC} 6.4, 2×OCH_2CH_3), 21.72, 22.54, 24.43, 31.81, 44.40 (s, OCH_3), 44.42 (s, OCH_3), 52.00, 52.11, 64.44 (d, J_{PC} 5.4, 2×OCH_2), 129.73 (d, J_{PC} 5.7, =COP), 131.42, 132.35 (d, J_{PC} 8.1), 135.32, 165.95 (s, C=O), 167.90 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.15 (3H, t, J_{HH} 7.5, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.1, J_{HH} 7.0, OCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.1, J_{HH} 7.0,

OCH_2CH_3), 1.63–2.01 (2H, m), 2.02–2.67 (3H, m), 2.28 (1H, q, J_{HH} 7.5, SCH_2), 2.29 (1H, q, J_{HH} 7.5, SCH_2), 2.94–3.08 (1H, m), 3.16–3.35 (1H, m), 3.77 (3H, s, $COOCH_3$), 3.78 (3H, s, $COOCH_3$), 4.06–4.33 (4H, m, 2×OCH_2), 4.58–4.65 (1H, m, CHS); *m/z* (15 eV) 448 (M^+, 33%), 387 (100, M^+-SEt), 155 (13, $(H+HOP(O)(OEt)_2)^+$). Found: C, 51.0; H, 6.5; P, 6.9. Calcd for $C_{19}H_{29}O_8PS$: C, 50.9; H, 6.5; P, 6.9%.

4.3.6.2. 6-Acetylsulfanyl-7-(diethoxyphosphoryloxy)-2,3,3a,6-tetrahydro-1*H*-indene-4,5-dicarboxylic acid dimethyl ester 11c. Yield: 66%—orange dense oil. R_f 0.59; δ_P (80.96 MHz, $CDCl_3$) −4.80; δ_C (50.32 MHz, $CDCl_3$) 15.53 (d, J_{PC} 6.5, 2×$POCH_2CH_3$), 22.14, 24.68, 29.56, 29.94, 43.54, 44.36, 51.75 (s, OCH_3), 51.84 (s, OCH_3), 64.00 (d, J_{PC} 6.3, $POCH_2$), 64.13 (d, J_{PC} 6.0, $POCH_2$), 129.71 (d, J_{PC} 5.8, =COP), 129.91, 131.53 (d, J_{PC} 8.5), 136.84, 164.88 (s, OC=O), 167.13 (s, OC=O), 191.94 (s, SC=O); δ_H (200.13 MHz, $CDCl_3$) 1.34 (6H, dt, J_{PH} 1.1, J_{HH} 7.1, 2×$POCH_2CH_3$), 1.46–1.64 (1H, m), 1.71–1.93 (2H, m), 2.07–2.21 (1H, m), 2.31 (3H, s, $SC(O)CH_3$), 2.34–2.65 (2H, m), 3.23–3.39 (1H, m), 3.72 (3H, s, $COOCH_3$), 3.79 (3H, s, $COOCH_3$), 4.08–4.27 (4H, m, 2×$POCH_2$), 5.26–5.36 (1H, m, CHS); *m/z* (15 eV) 462 (M^+, 0.1%), 386 (8, M^+-SAc), 354 (100, $M^+(-HSAc, -MeOH)$), 326 (4, $M^+(-HSAc, -HCOOMe)$), 296 (3, $M^+(-SAc, -MeOH, -COOMe)$), 268 (15, $M^+(-SAc, HCOOMe, -COOMe)$), 155 (3, $(H+HOP(O)(OEt)_2)^+$). Found: C, 49.5; H, 5.8; P, 6.7. Calcd for $C_{19}H_{27}O_9PS$: C, 49.4; H, 5.9; P, 6.7%.

4.3.7. Reactions with fumaronitrile. Preparation of adducts **12** and **13** was performed according to procedure C at 80 °C for 10 h to give the mixture of diastereoisomeric adducts **12** and **13** (1.4:1) (71%) and according to procedure **B** in THF at 60 °C for 8 h to provide the mixture of adducts **12** and **13** (3:1) (68%). The individual isomers were obtained after separation using column chromatography benzene–ethyl acetate (1:1).

4.3.7.1. (5r,6c,7t,7ac)-Phosphoric acid diethyl ester 6,7-dicyano-5-ethylsulfanyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 12. Yield: 51% (B) or 42% (C)—pale yellow oil. R_f 0.41; δ_P (80.96 MHz, $CDCl_3$) −5.22; δ_C (50.32 MHz, $CDCl_3$) 14.08 (s, SCH_2CH_3), 15.50 (d, J_{PC} 4.2, 2×OCH_2CH_3), 22.22, 26.04, 28.38, 30.79, 31.47, 37.46, 43.48, 43.96, 64.09 (d, J_{PC} 5.9, 2×OCH_2), 116.30 (s, CN), 117.54 (s, CN), 129.65 (d, J_{PC} 6.4, =COP), 134.87 (d, J_{PC} 7.6); δ_H (200.13 MHz, $CDCl_3$) 1.33 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.39 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.58–1.74 (1H, m), 1.82–1.97 (1H, m), 2.29 (2H, ddd, J_{HH} 6.1, 7.1, and 12.6), 2.40–2.49 (2H, m), 2.55–2.69 (1H, m), 2.89 (1H, dd, J_{HH} 11.1 and 11.3, CHCN), 2.95 (2H, q, J_{HH} 7.4, SCH_2), 3.51 (1H, dd, J_{HH} 4.0 and 11.3, CHCN), 4.07 (1H, ddd, J_{PH} 1.8, J_{HH} 1.9 and 4.0, CHS), 4.12–4.27 (4H, m, 2×OCH_2); *m/z* (70 eV) (Finnigan MAT 95) 384 (M^+, 4%), 356 (4, M^+-H_2CN), 355 (19, M^+-Et), 324 (100, $M^+(-SEt, +H)$), 295 (8, $M^+(-HSEt, -HCN)$), 202 (9, $M^+(-OP(O)(OEt)_2, -Et)$), 168 (6, $M^+(-HOP(O)(OEt)_2, -HSEt)$), 155 (53, $(H+HOP(O)(OEt)_2)^+$), 142 (20, $M^+(-HOP(O)(OEt)_2, -SEt, -HCN)$), 116 (9, $M^+(-(HCN)_2, -OP(O)(OEt)_2, -SEt)$), 115 (13, $M^+(-(HCN)_2, -HOP(O)(OEt)_2, -SEt)$); *m/z* (15 eV) 384 ($M^+$, 6%), 355 (18, M^+-Et), 324 (12, $M^+(-SEt, +H)$), 296 (4, $M^+(-HCN, -SEt)$), 295 (3, $M^+(-HCN, -HSEt)$), 267 (3, $M^+(-H_2CN, -HCN, -HSEt)$), 168 (12, $M^+(-HSEt, -HOP(O)(OEt)_2)$), 155 (47, $(H+HOP(O)(OEt)_2)^+$), 141 (10, $M^+(-HOP(O)(OEt)_2, -HCN, -HSEt)$), 139 (23, $M^+(-H_2OP(O)(OEt)_2, -HSEt, -H_2CN)$), 115 (15, $M^+(-SEt, -(HCN)_2, -HOP(O)(OEt)_2)$). Found: C, 53.0; H, 6.5; N, 7.3; P, 8.0. Calcd for $C_{17}H_{25}N_2O_4PS$: C, 53.1; H, 6.6; N, 7.3; P, 8.1%.

4.3.7.2. (5r,6t,7c,7ac)-Phosphoric acid diethyl ester 6,7-dicyano-5-ethylsulfanyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 13. Yield: 17% (B) or 29% (C)—pale yellow oil. R_f 0.78; δ_P (80.96 MHz, $CDCl_3$) −5.07; δ_C (50.32 MHz, $CDCl_3$) 14.72 (s, SCH_2CH_3), 16.12 (d, J_{PC} 6.8, 2×OCH_2CH_3), 23.25, 27.26, 28.12, 28.69, 30.55, 37.01, 39.53, 44.44, 64.76 (d, J_{PC} 6.4, 2×OCH_2), 115.98 (s, CN), 117.44 (s, CN), 130.18 (d, J_{PC} 6.4, =COP), 135.10 (d, J_{PC} 8.7); δ_H (300.13 MHz, $CDCl_3$) 1.35 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.38 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.68–1.79 (1H, m), 1.89–2.03 (2H, m), 2.06–2.13 (1H, m), 2.48–2.70 (2H, m), 2.78 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 12.5, SCH_2), 2.84 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 12.5, SCH_2), 2.94–3.06 (1H, m, =C–CH), 3.41 (1H, dd, J_{HH} 2.9 and 5.3, CHCN), 3.79 (1H, dd, J_{HH} 1.2 and 2.9, CHCN), 4.07–4.10 (1H, m, CHS), 4.14–4.29 (4H, m, 2×OCH_2); *m/z* (70 eV) (Finnigan MAT 95) 384 (M^+, 24%), 357 (6, M^+-HCN), 356 (16, M^+-H_2CN), 355 (100, M^+-Et), 324 (58, $M^+(-SEt, +H)$), 299 (18, $M^+(-Et, -(H_2CN)_2)$), 296 (10, $M^+(-SEt, -HCN)$), 272 (6, $M^+(-(CN)_2, -SEt, +H)$), 202 (11, $M^+(-Et, -OP(O)(OEt)_2)$), 169 (7, $M^+(-SEt, -HOP(O)(OEt)_2)$), 155 (32, $(H+HOP(O)(OEt)_2)^+$), 142 (13, $M^+(-SEt, -HCN, -HOP(O)(OEt)_2)$), 116 (10, $M^+(-SEt, -(HCN)_2, -OP(O)(OEt)_2)$), 115 (15, $M^+(-HSEt, -(HCN)_2, -OP(O)(OEt)_2)$). Found: C, 53.0; H, 6.5; P, 7.9. Calcd for $C_{17}H_{25}N_2O_4PS$: C, 53.1; H, 6.6; P, 8.1%.

4.3.8. Reaction with PTAD. To a solution of 1 equiv of 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (PTAD) in CH_2Cl_2 (5 mL), diene **1b** (3 mmol) in CH_2Cl_2 (5 mL) was added at ambient temperature and stirred for 5 min. Then the solvent was removed in vacuo (0.1 mmHg) and the residue was purified by column chromatography to give cycloadduct with quantitative yield.

4.3.8.1. Phosphoric acid diethyl ester 5-ethylsulfanyl-1,3-dioxo-2-phenyl-2,3,7,8,9,9a-hexahydro-1*H*,5*H*-cyclopenta[*c*][1,2,4]triazolo[1,2-*a*]pyridazin-6-yl ester 14. Yield: 85%—pale yellow dense oil. R_f 0.71; δ_P (80.96 MHz, $CDCl_3$) −4.74; δ_C (50.32 MHz, $CDCl_3$) 14.45 (s, SCH_2CH_3), 15.56 (d, J_{PC} 4.8, 2×OCH_2CH_3), 21.32, 23.71, 25.74, 31.30, 59.08, 59.21, 64.31 (d, J_{PC} 5.8, 2×OCH_2), 124.76 (s, *o*-C_6H_5), 127.62 (s, *p*-C_6H_5), 128.50 (s, *m*-C_6H_5), 129.12 (d, J_{PC} 6.7, =COP), 130.52 (s, *ipso*-C_6H_5), 132.84 (d, J_{PC} 8.0), 150.30 (s, C=O), 153.62 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.27 (3H, t, J_{HH} 7.5, SCH_2CH_3), 1.38 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.40 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.65–1.94 (2H, m), 1.95–2.14 (1H, m), 2.49–2.78 (4H, m), 2.86 (1H, $d_{AB}q$, J_{HH}(AB) 12.2, J_{HH} 7.5, SCH_2), 2.97 (1H, $d_{AB}q$, J_{HH}(AB) 12.2, J_{HH} 7.5, SCH_2), 4.21 (2H, q, J_{PH} 7.1, J_{HH} 7.1, OCH_2), 4.28 (2H, q, J_{HH} 7.1, OCH_2), 5.86–5.91 (1H,

m, CHS), 7.36–7.55 (5H, m, C_6H_5); *m/z* (15 eV) 481 (M^+, 0.1%), 420 (100, M^+-SEt), 266 (3, $M^+(-HOP(O)(OEt)_2, -SEt)$), 155 (4, $(H+HOP(O)(OEt)_2)^+$). Found: C, 52.3; H, 5.8; N, 8.7; P, 6.4. Calcd for $C_{21}H_{28}N_3O_6PS$: C, 52.4; H, 5.9; N, 8.7; P, 6.4%.

4.3.9. Reaction with cyclohex-2-enone. The synthesis of **15** was performed according to procedure B in THF in the presence of large excess (10 equiv) of cyclohex-2-enone. The reaction mixture was heated in sealed ampoule at 100 °C for 8 h.

4.3.9.1. Phosphoric acid diethyl ester 5-ethylsulfanyl-6-oxo-2,3,5,5a,6,7,8,9,9a,9b-decahydro-1*H*-cyclopenta[*a*]-naphthalen-4-yl ester 15. Yield: 38%—pale yellow dense oil. R_f 0.29; δ_P (80.96 MHz, $CDCl_3$) −4.49; δ_C (50.32 MHz, $CDCl_3$) 14.17 (s, SCH_2CH_3), 15.97 (d, J_{PC} 6.7, 2×OCH_2CH_3), 18.85, 21.96, 23.57, 27.03, 29.00, 29.76, 34.76, 39.53, 42.80, 44.12, 53.79, 64.05 (d, J_{PC} 4.5, 2×OCH_2), 129.87 (d, J_{PC} 5.7, =COP), 136.35 (d, J_{PC} 8.5), 211.53 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.17 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.42–2.64 (13H, m), 2.64 (1H, q, J_{HH} 7.4, SCH_2), 2.65 (1H, q, J_{HH} 7.4, SCH_2), 2.95 (1H, ddd, J_{HH} 8.0, 8.2, and 17.3, $CH_2C(O)$), 3.09 (1H, dd, J_{HH} 4.9 and 7.0, CH–C(O)), 3.70 (1H, ddd, J_{HH} 2.2, 4.5, and 7.0, CHS), 4.10–4.29 (4H, m, 2×OCH_2); *m/z* (15 eV) 404 ($M^+(+H_2)$, 6%), 373 (3, M^+-Et), 342 (21, $M^+(-SEt, +H)$), 341 (19, M^+-SEt), 340 (15, M^+-HSEt), 246 (22, $M^+-H_2OP(O)(OEt)_2$), 187 (36, $M^+(-SEt, -HOP(O)(OEt)_2)$), 155 (94, $(H+HOP(O)(OEt)_2)^+$). Found: C, 56.8; H, 7.7; P, 7.7. Calcd for $C_{19}H_{31}O_5PS$: C, 56.7; H, 7.8; P, 7.7%.

4.3.10. Reactions with MVK. Reaction of diene **1** with methyl vinyl ketone (MVK) was performed according to procedures D and B. In the latter procedure 2 equiv of MVK was used.

4.3.10.1. Phosphoric acid diethyl ester 6-acetyl-5-methylsulfanyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 16a. Yield: 52% (D)—pale yellow dense oil. R_f 0.44; δ_P (80.96 MHz, $CDCl_3$) −4.43; δ_C (50.32 MHz, $CDCl_3$) 15.45, 15.78 (d, J_{PC} 6.1, 2×OCH_2CH_3), 23.22, 25.60, 26.06, 28.22, 33.19, 41.01, 44.73, 54.20, 63.94 (d, J_{PC} 5.9, 2×OCH_2), 133.66 (d, J_{PC} 6.6, =COP), 136.24 (d, J_{PC} 8.7), 206.43 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.36 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.37 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.47–1.68 (2H, m), 1.69–1.86 (2H, m), 1.88–2.08 (2H, m), 2.11 (3H, s, $C(O)CH_3$), 2.12–2.25 (1H, m), 2.23 (3H, s, SCH_3), 2.37–2.55 (2H, m), 3.04 (1H, ddd, J_{HH} 2.6, 5.0, and 11.5, CHC(O)), 4.00–4.04 (1H, m, CHS), 4.11–4.29 (4H, m, 2×OCH_2); *m/z* (15 eV) 362 (M^+, 3%), 315 (5, M^+-SMe), 155 (26, $(H+HOP(O)(OEt)_2)^+$). Found: C, 52.9; H, 7.5; P, 8.5. Calcd for $C_{16}H_{27}O_5PS$: C, 53.0; H, 7.5; P, 8.6%.

4.3.10.2. Phosphoric acid diethyl ester 6-acetyl-5-ethylsulfanyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 16b. Yield: 62% (B) or 56% (D)—pale yellow dense oil. R_f 0.43; δ_P (80.96 MHz, $CDCl_3$) −4.47; δ_C (50.32 MHz, $CDCl_3$) 14.39 (s, SCH_2CH_3), 15.92 (d, J_{PC} 6.4, 2×OCH_2CH_3), 23.32, 25.81, 26.26, 26.89, 28.42, 33.20, 41.24, 44.35, 54.11, 64.04 (d, J_{PC} 6.3, 2×OCH_2), 133.00 (d, J_{PC} 6.8, =COP), 137.35 (d, J_{PC} 8.5), 206.84 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.21 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.38 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.43–1.69 (3H, m), 1.75–1.87 (1H, m), 2.00 (1H, dt, J_{HH} 5.7 and 12.3), 2.16 (1H, ddd, J_{HH} 1.7, 4.6, and 13.1), 2.24 (3H, s, $COCH_3$), 2.26–2.38 (1H, m), 2.41–2.50 (2H, m), 2.62 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 11.8, SCH_2), 2.69 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 11.8, SCH_2), 3.02 (1H, ddd, J_{HH} 2.5, 4.3, and 12.7, CHC(O)), 4.01–4.07 (1H, m, CHS), 4.11–4.29 (4H, m, 2×OCH_2); *m/z* (15 eV) 376 (M^+, 12%), 316 (61, $M^+(-SEt, +H)$), 315 (8, M^+-SEt), 273 (100, $M^+(-Ac, -SEt, +H)$), 272 (17, $M^+(-Ac, -SEt)$), 155 (63, $(H+HOP(O)(OEt)_2)^+$), 119 (56, $M^+(-SEt, -Ac, -OP(O)(OEt)_2)$). Found: C, 54.2; H, 7.7; P, 8.1. Calcd for $C_{17}H_{29}O_5PS$: C, 54.2; H, 7.8; P, 8.2%.

4.3.10.3. Thioacetic acid *S*-[6-acetyl-4-(diethoxyphosphoryloxy)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-yl] ester 16c. Yield: 81% (B) or 84% (D)—pale yellow dense oil. R_f 0.45; δ_P (80.96 MHz, $CDCl_3$) −4.30; δ_C (50.32 MHz, $CDCl_3$) 15.87 (d, J_{PC} 6.7, 2×OCH_2CH_3), 23.23, 26.55, 26.76, 28.42, 30.15, 33.02, 41.10, 43.58, 52.87, 63.95 (d, J_{PC} 6.8, OCH_2), 64.09 (d, J_{PC} 7.5, OCH_2), 134.76 (d, J_{PC} 6.0, =COP), 135.40 (d, J_{PC} 8.1), 193.82 (s, C=O), 206.68 (s, SC=O); δ_H (200.13 MHz, $CDCl_3$) 1.34 (6H, dt, J_{PH} 1.1, J_{HH} 7.0, 2×OCH_2CH_3), 1.51–1.91 (4H, m), 1.91–2.08 (1H, m), 2.08–2.55 (4H, m), 2.16 (3H, s, $SC(O)CH_3$), 2.30 (3H, s, $C(O)CH_3$), 3.21 (1H, ddd, J_{HH} 2.1, 4.2, and 12.3, CHC(O)), 4.06–4.23 (4H, m, 2×OCH_2), 4.92–4.96 (1H, m, CHS); *m/z* (15 eV) 390 (M^+, 7%), 347 (31, M^+-Ac), 315 (41, M^+-SAc), 273 (65, $M^+(-HSAc, -Ac)$), 236 (4, $M^+-HOP(O)(OEt)_2$), 194 (11, $M^+(-Ac, -OP(O)(OEt)_2)$), 161 (10, $M^+(-HOP(O)(OEt)_2, -SAc)$), 155 (100, $(H+HOP(O)(OEt)_2)^+$), 119 (20, $M^+(-Ac, -SAc, -OP(O)(OEt)_2)$). Found: C, 52.4; H, 7.2; P, 7.9. Calcd for $C_{17}H_{27}O_6PS$: C, 52.3; H, 7.0; P, 7.9%.

4.3.10.4. 2,2-Dimethyl thiopropionic acid *S*-[6-acetyl-4-(diethoxyphosphoryloxy)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-yl] ester 16d. Yield: 77% (D)—yellow dense oil. R_f 0.49; δ_P (80.96 MHz, $CDCl_3$) −4.59; δ_C (50.32 MHz, $CDCl_3$) 15.91 (d, J_{PC} 6.8, 2×OCH_2CH_3), 23.28, 26.58, 26.83, 27.02 (s, $C(CH_3)_3$), 28.38, 33.06, 41.15, 42.78, 46.46 (s, $C(CH_3)_3$), 53.06, 64.02 (d, J_{PC} 7.5, OCH_2), 64.16 (d, J_{PC} 7.5, OCH_2), 134.60 (d, J_{PC} 6.0, =COP), 135.69 (d, J_{PC} 8.7), 204.83 (s, C=O), 206.71 (s, SC=O); δ_H (200.13 MHz, $CDCl_3$) 1.19 (9H, s, $C(CH_3)_3$), 1.33 (3H, dt J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.34 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.42–1.89 (4H, m), 1.91–2.06 (1H, m), 2.12 (3H, s, $C(O)CH_3$), 2.13–2.57 (4H, m), 3.20 (1H, ddd, J_{HH} 2.3, 4.3, and 12.4, CHC(O)), 4.05–4.20 (4H, m, 2×OCH_2), 4.91–4.95 (1H, m, CHS); *m/z* (15 eV) 432 (M^+, 5%), 347 (54, M^+-Piv), 315 (30, M^+-SPiv), 305 (70, $M^+(-Ac, -Piv, +H)$), 273 (76, $M^+(-SPiv, -Ac, +H)$), 194 (5, $M^+(-Piv, -OP(O)(OEt)_2)$), 161 (7, $M^+(-SPiv, -HOP(O)(OEt)_2)$), 155 (100, $(H+HOP(O)(OEt)_2)^+$). Found: C, 55.6; H, 7.7; P, 7.1. Calcd for $C_{20}H_{33}O_6PS$: C, 55.5; H, 7.7; P, 7.2%.

4.3.11. Reactions with acrylonitrile. Preparation of cycloadducts **17** was performed according to procedures C and B in THF at 80 °C for 8 h.

4.3.11.1. Phosphoric acid diethyl ester 6-cyano-5-methylsulfanyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 17a. Yield: 46% (C)—pale orange dense oil. R_f 0.45; δ_P (80.96 MHz, $CDCl_3$) −4.68; δ_C (50.32 MHz, $CDCl_3$) 15.79 (d, J_{PC} 6.2, 2×OCH_2CH_3), 17.49, 22.98, 25.99, 27.71, 32.71, 33.97, 40.72, 46.30, 64.08 (d, J_{PC} 6.3, 2×OCH_2), 119.60 (s, CN), 132.76 (d, J_{PC} 6.5, =COP), 135.00 (d, J_{PC} 8.1); δ_H (200.13 MHz, $CDCl_3$) 1.34 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.38 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.45–1.90 (4H, m), 1.93–2.07 (1H, m), 2.14–2.27 (2H, m), 2.33–2.48 (2H, m), 2.37 (3H, s, SCH_3), 3.25 (1H, ddd, J_{HH} 2.5, 4.2, and 12.6, CHCN), 3.80–3.84 (1H, m, CHS), 4.15 (2H, q, J_{PH} 7.1, J_{HH} 7.1, OCH_2), 4.23 (2H, q, J_{PH} 7.1, J_{HH} 7.1, OCH_2); *m/z* (15 eV) 345 (M^+, 36%), 330 (6, M^+-Me), 318 (2, M^+-HCN), 298 (100, M^+-SMe), 271 (16, $M^+(-HCN, -SMe)$), 191 (25, $M^+(-HOP(O)(OEt)_2)$), 163 (5, $M^+(-HCN, -H_2OP(O)(OEt)_2)$), 155 (55, $(H+HOP(O)(OEt)_2)^+$), 144 (12, $M^+(-SMe, -HOP(O)(OEt)_2)$), 117 (17, $M^+(-SMe, -HCN, -HOP(O)(OEt)_2)$). Found: C, 52.3; H, 7.0; N, 4.0; P, 9.0. Calcd for $C_{15}H_{24}NO_4PS$: C, 52.2; H, 7.0; N, 4.1; P, 9.0%.

4.3.11.2. Phosphoric acid diethyl ester 6-cyano-5-ethylsulfanyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 17b. Yield: 51% (B) or 47% (C)—pale orange dense oil. R_f 0.34; δ_P (80.96 MHz, $CDCl_3$) −4.48; δ_C 14.49 (s, SCH_2CH_3), 15.85 (d, J_{PC} 6.2, 2×OCH_2CH_3), 23.01, 26.14, 27.82, 28.39, 32.71, 34.07, 40.79, 44.60, 64.12 (d, J_{PC} 6.1, 2×OCH_2), 119.72 (s, CN), 132.66 (d, J_{PC} 6.4, =COP), 135.33 (d, J_{PC} 8.1); δ_H 1.32 (3H, t, J_{HH} 7.5, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.1, J_{HH} 7.0, OCH_2CH_3), 1.38 (3H, dt, J_{PH} 1.1, J_{HH} 7.0, OCH_2CH_3), 1.50–1.86 (5H, m), 1.93–2.05 (1H, m), 2.16–2.29 (1H, m), 2.29–2.43 (2H, m), 2.89 (2H, q, J_{HH} 7.5, SCH_2), 3.25 (1H, ddd, J_{HH} 2.4, 4.2, and 12.6, CHCN), 3.86–3.91 (1H, m, CHS), 4.09–4.30 (4H, m, 2×OCH_2); *m/z* (15 eV) 359 (M^+, 10%), 330 (7, M^+-Et), 299 (100, $M^+(-SEt, +H)$), 298 (21, M^+-SEt), 272 (6, $M^+(-SEt, -HCN)$), 155 (51, $(H+HOP(O)(OEt)_2)^+$); *m/z* (CI) (Finnigan MAT 95) 360 (M^+ (+H), 100%), 298 (34, M^+-SEt), 271 (4, $M^+(-SEt, -HCN)$), 155 (3, $(H+HOP(O)(OEt)_2)^+$); HRMS (CI) calcd for $C_{16}H_{26}NO_4PS+H$ (M^++H): 360.139845. Found: 360.138500.

4.3.11.3. Thioacetic acid *S*-[6-cyano-4-(diethoxyphosphoryloxy)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-yl] ester 17c. Yield: 59% (B) or 51% (C)—deep orange dense oil. R_f 0.23; δ_P (80.96 MHz, $CDCl_3$) −4.49; δ_C (50.32 MHz, $CDCl_3$) 15.88 (d, J_{PC} 6.3, 2×OCH_2CH_3), 23.11, 26.59, 29.11, 30.80, 32.79, 33.61, 40.86, 42.56, 64.20 (d, J_{PC} 6.4, OCH_2), 64.32 (d, J_{PC} 6.4, OCH_2), 118.80 (s, CN), 133.19 (d, J_{PC} 8.8), 134.85 (d, J_{PC} 5.6, =COP), 192.73 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.33 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.34 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.46–2.07 (5H, m), 2.14–2.55 (4H, m), 2.41 (3H, s, $C(O)CH_3$), 3.34 (1H, ddd, J_{HH} 2.5, 4.4, and 12.7, CHCN), 4.10 (1H, dq, J_{PH} 0.8, J_{HH} 7.1, OCH_2), 4.13 (1H, dq, J_{PH} 0.5, J_{HH} 7.1, OCH_2), 4.14 (1H, dq, J_{PH} 0.6, J_{HH} 7.1, OCH_2), 4.16 (1H, dq, J_{PH} 0.6, J_{HH} 7.1, OCH_2), 4.75–4.79 (1H, m, CHS); *m/z* (15 eV) 373 (M^+, 2%), 330 (39, M^+-Ac), 298 (100, M^+-SAc), 271 (10, $M^+(-SAc, -HCN)$), 219 (8, $M^+-HOP(O)(OEt)_2$), 176 (7, $M^+(-Ac, -HOP(O)(OEt)_2)$), 155 (97, $(H+HOP(O)(OEt)_2)^+$), 144 (5, $M^+(-SAc, -HOP(O)(OEt)_2)$). Found: C, 51.6; H, 6.5; N, 3.7; P, 8.3. Calcd for $C_{16}H_{24}NO_5PS$: C, 51.5; H, 6.5; N, 3.8; P, 8.3%.

4.3.11.4. 2,2-Dimethyl thiopropionic acid *S*-[6-cyano-4-(diethoxyphosphoryloxy)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-yl] ester 17d. Yield: 55% (C)—deep orange dense oil. R_f 0.27; δ_P (80.96 MHz, $CDCl_3$) −4.68; δ_C (50.32 MHz, $CDCl_3$) 15.86 (d, J_{PC} 6.6, 2×OCH_2CH_3), 23.12, 26.55, 27.07 (s, $C(CH_3)_3$), 29.13, 32.79, 33.69, 40.86, 41.58, 46.58 (s, $C(CH_3)_3$), 64.18 (d, J_{PC} 7.2, OCH_2), 67.63 (d, J_{PC} 7.2, OCH_2), 118.83 (s, CN), 133.52 (d, J_{PC} 8.7), 134.68 (d, J_{PC} 5.5, =COP), 203.41 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.27 (9H, s, $C(O)C(CH_3)_3$), 1.32 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.34 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.41–1.92 (4H, m), 1.93–2.08 (1H, m), 2.23–2.54 (4H, m), 3.33 (1H, ddd, J_{HH} 2.5, 4.4, and 12.7, CHCN), 4.00–4.23 (4H, m, 2×OCH_2), 4.72–4.75 (1H, m, CHS); *m/z* (15 eV) 415 (M^+, 5%), 330 (100, M^+-Piv), 298 (80, M^+-SPiv), 271 (8, $M^+(-SPiv, -HCN)$), 261 (9, $M^+(-HOP(O)(OEt)_2)$), 155 (95, $(H+HOP(O)(OEt)_2)^+$). Found: C, 55.1; H, 7.2; N, 3.4; P, 7.5. Calcd for $C_{19}H_{30}NO_5PS$: C, 54.9; H, 7.3; N, 3.4; P, 7.5%.

4.3.12. Reactions with ethyl acrylate. Synthesis of **18b** was performed according to procedure B in THF at 100 °C for 5 h and according to procedure C at 80 °C for 5 h using 10 equiv of ethyl acrylate. The **18c** was obtained according to procedure C at 80 °C for 8 h using 10 equiv of dienophile.

4.3.12.1. 7-(Diethoxyphosphoryloxy)-6-ethylsulfanyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5-carboxylic acid ethyl ester 18b. Yield: 55% (B) or 24% (C)—orange oil. R_f 0.72; δ_P (80.96 MHz, $CDCl_3$) −4.63; δ_C (50.32 MHz, $CDCl_3$) 13.93 (s, $COOCH_2CH_3$), 14.53 (s, SCH_2CH_3), 15.89 (d, J_{PC} 6.4, 2×$POCH_2CH_3$), 23.29, 25.91, 26.21, 27.36, 33.09, 41.20, 45.34, 47.25, 60.30 (s, $COOCH_2$), 64.00 (d, J_{PC} 6.4, 2×$POCH_2$), 132.72 (d, J_{PC} 6.4, =COP), 137.33 (d, J_{PC} 7.8), 171.54 (s, C=O); δ_H (300.13 MHz, $CDCl_3$) 1.22 (3H, t, J_{HH} 7.5, SCH_2CH_3), 1.28 (3H, t, J_{HH} 7.1, $COOCH_2CH_3$), 1.36 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, $POCH_2CH_3$), 1.37 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, $POCH_2CH_3$), 1.51–1.66 (2H, m), 1.66–1.74 (1H, m), 1.74–1.87 (1H, m), 1.99 (1H, ddd, J_{HH} 6.4, 6.6, and 11.7), 2.20 (1H, ddd, J_{HH} 1.8, 5.5, and 12.6), 2.26–2.39 (1H, m), 2.39–2.50 (2H, m), 2.63 (1H, $d_{AB}q$, J_{HH} 7.5, J_{HH}(AB) 12.0, SCH_2), 2.73 (1H, $d_{AB}q$, J_{HH} 7.5, J_{HH}(AB) 12.0, SCH_2), 3.08 (1H, ddd, J_{HH} 2.6, 4.7, and 12.9, CHC(O)), 3.94–3.97 (1H, m, CHS), 4.06–4.27 (6H, m, 2×$POCH_2$, $COOCH_2$); *m/z* (15 eV) 406 (M^+, 1%), 378 (1, M^+-Et), 346 (13, $M^+(-SEt, +H)$), 271 (39, $M^+(-HSEt, -COOEt)$), 242 (11, $M^+(-COOEt, -SEt, -Et)$), 215 (26, $M^+(-COOEt, -Et_2, -SEt, +H_2)$), 191 (15, $M^+(-HOP(O)(OEt)_2, -SEt)$), 155 (87, $(H+HOP(O)(OEt)_2)^+$), 117 (100, $M^+(-HSEt, -HOP(O)(OEt)_2, -COOEt)$); *m/z* (CI) (Finnigan MAT 95) 407 (M^+(+H), 100%), 345 (40, M^+-SEt), 361 (1, M^+-OEt), 271 (3, $M^+(-HSEt, -COOEt)$), 155 (1, $(H+HOP(O)(OEt)_2)^+$). HRMS (CI) calcd for $C_{18}H_{31}O_6PS+H$ (M^+ +H): 407.165725. Found: 407.163400.

4.3.13. 6-Acetylsulfanyl-7-(diethoxyphosphoryloxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene-5-carboxylic acid ethyl ester 18c. Yield: 38% (C)—pale orange dense oil. R_f

0.70; δ_P (80.96 MHz, $CDCl_3$) −4.69; δ_C (50.32 MHz, $CDCl_3$) 13.65 (s, $COOCH_2CH_3$), 15.76 (d, J_{PC} 6.5, 2×$POCH_2CH_3$), 23.15, 26.48, 27.22, 29.98, 32.89, 41.07, 43.74, 45.82, 60.37, 63.84 (d, J_{PC} 6.2, $POCH_2$), 63.96 (d, J_{PC} 6.4, $POCH_2$), 134.22 (d, J_{PC} 5.6, =COP), 135.41 (d, J_{PC} 8.6), 171.05 (s, OC=O), 192.40 (s, SC=O); δ_H (200.13 MHz, $CDCl_3$) 1.19 (3H, t, J_{HH} 7.2, $COOCH_2CH_3$), 1.34 (6H, dt, J_{PH} 1.1, J_{HH} 7.1, 2×$POCH_2CH_3$), 1.49–1.90 (4H, m), 1.90–2.07 (1H, m), 2.19–2.54 (4H, m), 2.28 (3H, s, $SC(O)CH_3$), 3.16 (1H, ddd, J_{HH} 2.4, 4.5, and 12.9, CHC(O)), 4.05 (1H, q, J_{HH} 7.2, $C9(O)OCH_2$), 4.06 (1H, q, J_{HH} 7.2, $C(O)OCH_2$), 4.07–4.23 (4H, m, 2×$POCH_2$), 4.83–4.90 (1H, m, CHS); *m/z* (15 eV) 420 (M^+, 6%), 377 (39, M^+-Ac), 345 (61, M^+-SAc), 333 (7, M^+(−HCOOEt, −Me)), 303 (6, M^+(−HCOOEt, −Ac)), 271 (91, M^+(−HCOOEt, −SAc)), 266 (5, M^+(−$HOP(O)(OEt)_2$)), 223 (11, M^+(−Ac, −$HOP(O)(OEt)_2$)), 191 (24, M^+(−SAc, −$HOP(O)(OEt)_2$)), 155 (100, $(H+HOP(O)(OEt)_2)^+$), 151 (23, M^+(−Ac, −COOEt, −$OP(O)(OEt)_2$)), 117 (26, M^+(−Ac, −HCOOEt, −$HOP(O)(OEt)_2$)). Found: C, 51.3; H, 6.9; P, 7.4. Calcd for $C_{18}H_{29}O_7PS$: C, 51.4; H, 7.0; P, 7.4%.

4.3.14. Reactions with acrolein and methacrolein. Synthesis of **19b** was performed according to procedure B for 6 h in the presence of 5 equiv of dienophile. Reactions of dienes **1b** and **1c** with acrolein were carried out according to procedure A at 100 °C for 8 h and procedure C for 8 h (both in the presence of 5 equiv of dienophile) to provide **20**.

4.3.14.1. Phosphoric acid diethyl ester 5-ethylsulfanyl-6-formyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 19b. Yield: 71% (B)—pale yellow oil. R_f 0.27; δ_P (80.96 MHz, $CDCl_3$) −4.63; δ_C (50.32 MHz, $CDCl_3$) 14.35 (s, SCH_2CH_3), 15.66 (d, J_{PC} 5.7, 2×OCH_2CH_3), 23.05, 24.17, 26.03, 27.25, 32.88, 40.79, 43.11, 52.72, 63.84 (d, J_{PC} 5.9, 2×OCH_2), 133.16 (d, J_{PC} 5.8, =COP), 136.77 (d, J_{PC} 8.0), 199.83 (s, CHO); δ_H (200.13 MHz, $CDCl_3$) 1.25 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.38 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.50–1.91 (3H, m), 1.91–2.09 (1H, m), 2.21–2.52 (5H, m), 2.71 (1H, q, J_{HH} 7.4, SCH_2), 2.72 (1H, q, J_{HH} 7.4, SCH_2), 2.97 (1H, ddd, J_{HH} 2.6, 4.8, and 12.7, CHC(O)), 4.07–4.13 (1H, m, CHS), 4.17 (2H, q, J_{HH} 7.1, OCH_2), 4.24 (2H, q, J_{HH} 7.1, OCH_2), 9.74 (1H, s, CHO); *m/z* (15 eV) 362 (M^+, 6%), 333 (2, M^+-CHO or M^+-Et), 302 (46, M^+(−SEt, +H)), 301 (17, M^+-SEt), 300 (18, M^+-HSEt), 274 (19, M^+(−CHO, −Et, +H_2)), 273 (19, M^+(−SEt, −CHO, +H)), 272 (18, M^+(−SEt, −CHO)), 271 (21, M^+(−HSEt, −CHO)), 155 (100, $(H+HOP(O)(OEt)_2)^+$), 146 (19, M^+(−HSEt, −$HOP(O)(OEt)_2$)), 119 (59, M^+(−SEt, −CHO, −$OP(O)(OEt)_2$)), 117 (97, M^+(−HSEt, −CHO, −$HOP(O)(OEt)_2$)). Found: C, 52.9; H, 7.5; P, 8.5. Calcd for $C_{16}H_{27}O_5PS$: C, 53.0; H, 7.5; P, 8.6%.

4.3.14.2. Phosphoric acid diethyl ester 6-formyl-2,3,7,7a-tetrahydro-1*H*-inden-4-yl ester 20. Yield: 66% (A, from **1b**) or 46% (A, from **1c**)—orange dense oil. R_f 0.42; δ_P (80.96 MHz, $CDCl_3$) −4.76; δ_C (50.32 MHz, $CDCl_3$) 15.45 (d, J_{PC} 6.4, 2×OCH_2CH_3), 23.87, 24.03, 26.97, 33.31, 41.23, 63.87 (d, J_{PC} 6.2, 2×OCH_2), 136.34 (d, J_{PC} 8.4), 137.87 (s, =*C*–CHO), 140.82 (s, =CH), 141.54 (d, J_{PC} 6.9, =COP), 190.44 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.37 (6H, dt, J_{PH} 0.9, J_{HH} 7.1, 2×OCH_2CH_3), 1.51–2.21 (6H, m), 2.27–3.03 (3H, m), 4.17 (2H, q, J_{HH} 7.1, OCH_2), 4.21 (2H, q, J_{HH} 7.1, OCH_2), 6.81 (1H, d, J_{PH} 2.8, =CH), 9.52 (1H, s, CHO); *m/z* (15 eV) 300 (M^+, 100%), 271 (11, M^+-CHO), 155 (17, $(H+HOP(O)(OEt)_2)^+$), 147 (21, $M^+-HOP(O)(OEt)_2$), 117 (5, M^+(−CHO, −$HOP(O)(OEt)_2$)). Found: C, 55.9; H, 7.0; P, 10.2. Calcd for $C_{14}H_{21}O_5P$: C. 56.0; H, 7.1; P, 10.3%.

Synthesis of **22** was performed according to procedure B for 6 days in the presence of 5 equiv of methacrolein.

4.3.14.3. Phosphoric acid diethyl ester 5-ethylsulfanyl-6-formyl-6-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 22. Yield: 55%—pale yellow oil. R_f 0.56; δ_P (80.96 MHz, $CDCl_3$) −4.63; δ_C (50.32 MHz, $CDCl_3$) 14.37 (s, SCH_2CH_3), 15.84 (d, J_{PC} 5.7, 2×OCH_2CH_3), 19.19, 23.15, 25.92, 27.41, 29.31, 32.97, 37.78, 48.48, 51.48 (s, >C<), 63.93 (d, J_{PC} 6.2, 2×OCH_2), 131.66 (d, J_{PC} 5.8, =COP), 135.84 (d, J_{PC} 7.7), 201.13 (s, CHO); δ_H (200.13 MHz, $CDCl_3$) (NOSY) 1.18 (3H, s, $C(CHO)CH_3$), 1.23 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.37 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.54–2.09 (5H, m), 2.30–2.50 (4H, m), 2.64 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 12.0, SCH_2), 2.69 (1H, $d_{AB}q$, J_{HH} 7.4, J_{HH}(AB) 12.0, SCH_2), 3.50–3.53 (1H, m, CHS), 4.16 (2H, dq, J_{PH} 4.5, J_{HH} 7.1, OCH_2), 4.21 (2H, dq, J_{PH} 4.5, J_{HH} 7.1, OCH_2), 9.58 (1H, s, CHO); *m/z* (15 eV) 376 (M^+, 5%), 347 (1, M^+-CHO), 316 (27, M^+(−SEt, +H)), 315 (14, M^+-SEt), 288 (21, M^+(−SEt, −CHO, +H_2)), 287 (34, M^+(−SEt, −CHO, +H)), 286 (26, M^+(−SEt, −CHO)), 285 (20, M^+(−HSEt, −CHO)), 221 (1, $M^+-HOP(O)(OEt)_2$), 193 (3, M^+(−Et, −OP(O)(OEt)$_2$) or M^+(−$OP(O)(OEt)_2$, −CHO)), 161 (10, M^+(−HSEt, −$OP(O)(OEt)_2$)), 155 (99, $(H+HOP(O)(OEt)_2)^+$), 134 (24, M^+(−CHO, −SEt, −$OP(O)(OEt)_2$)), 133 (100, M^+(−CHO, −SEt, −$HOP(O)(OEt)_2$)), 132 (40, M^+(−CHO, −HSEt, −$HOP(O)(OEt)_2$)), 131 (29, M^+(−HCHO, −HSEt, −$HOP(O)(OEt)_2$)), 105 (26, M^+(−Me, −CHO, −HSEt, −$HOP(O)(OEt)_2$)), 104 (21, M^+(−Me, −HCHO, −HSEt, −$HOP(O)(OEt)_2$)); *m/z* (CI) (Finnigan MAT 95) 377 (M^+(+H), 100%), 316 (17, M^+(−SEt, +H)), 315 (99, M^+-SEt), 287 (19, M^+(−SEt, −CHO, +H)), 155 (4, $(H+HOP(O)(OEt)_2)^+$). HRMS (CI) calcd for $C_{17}H_{29}O_5PS$+H (M^++H): 377.155161. Found: 377.153400.

4.3.15. Reduction of cycloadducts 19b and 22 to the corresponding hydroxy systems 23 and 24. To a stirred suspension of $NaBH_4$ (22.4 mg, 0.6 mmol) in EtOH (5 mL) was added dropwise at −20 °C a solution of **19b** or **22** (0.6 mmol) in EtOH (5 mL). Stirring was continued at the same temperature for additional 1 h. After addition of acetone (1 mL) at room temperature the reaction mixture was extracted with $CHCl_3$ (50 mL), washed with water (2×10 mL), and dried ($MgSO_4$). Solvents were removed under reduced pressure and the residue was purified by column chromatography (ethyl acetate–MeOH) to give product **23** or **24**.

4.3.15.1. Phosphoric acid 5-ethylsulfanyl-6-hydroxymethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 23. Yield: 70%—clear dense oil. R_f 0.28; δ_P (80.96 MHz, $CDCl_3$) −4.79; δ_C (50.32 MHz, $CDCl_3$) 14.98 (s, SCH_2CH_3), 16.07 (d, J_{PC} 6.6, 2×$POCH_2CH_3$), 23.46, 26.27, 27.18, 27.39, 33.30, 42.28, 43.38, 47.26,

64.17 (d, J_{PC} 6.1, 2×$POCH_2$), 64.52 (s, CH_2OH), 132.85 (d, J_{PC} 6.2, =COP), 138.49 (d, J_{PC} 8.4); δ_H (200.13 MHz, $CDCl_3$) 1.27 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, $POCH_2CH_3$), 1.36 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, $POCH_2CH_3$), 1.45–1.72 (1H, m), 1.72–1.84 (1H, m), 1.77 (1H, ddd, J_{HH} 6.0, 6.2, and 12.9), 1.84–2.15 (2H, m), 1.95 (1H, ddd, J_{HH} 6.1, 6.5, and 11.7), 2.15–2.50 (4H, m), 2.73 (1H, q, J_{HH} 7.4, SCH_2), 2.74 (1H, q, J_{HH} 7.4, SCH_2), 3.71–3.83 (1H, m, CHS), 3.78 (1H, dd_{AB}, J_{HH} 5.1, J_{HH}(AB) 11.1, CH_2OH), 3.85 (1H, dd_{AB}, J_{HH} 7.5, J_{HH}(AB) 11.1, CH_2OH), 4.17 (2H, dq, J_{PH} 5.0, J_{HH} 7.1, $POCH_2$), 4.20 (2H, dq, J_{PH} 5.0, J_{HH} 7.1, $POCH_2$); *m/z* (15 eV) 364 (M^+, 3%), 347 (0.1, M^+-OH), 334 (1, $M^+-C_2H_6$), 304 (18, M^+(−SEt, +H)), 284 (5, $M^+(-H_2O, -HSEt)$), 273 (75, M^+(−SEt, $-CH_2OH$, +H)), 272 (24, M^+(−SEt, $-CH_2OH$)), 210 (2, $M^+-HOP(O)(OEt)_2$), 155 (100, $(H+HOP(O)(OEt)_2)^+$), 119 (70, M^+(−SEt, $-CH_2OH$, $-OP(O)(OEt)_2$)), 117 (32, M^+(−HSEt, $-CH_2OH$, $-HOP(O)(OEt)_2$)). Found: C, 52.9; H, 8.1. Calcd for $C_{16}H_{29}O_5PS$: C, 52.7; H, 8.0%.

4.3.15.2. Phosphoric acid 5-ethylsulfanyl-6-hydroxymethyl-6-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 24. Yield: 83%—clear dense oil. R_f 0.38; δ_P (80.96 MHz, $CDCl_3$) −4.68; δ_C (50.32 MHz, $CDCl_3$) 14.70 (s, SCH_2CH_3), 16.01 (d, J_{PC} 6.6, 2×$POCH_2CH_3$), 21.55, 23.32, 26.00, 26.98, 32.14, 33.17, 38.50, 41.69 (s, CCH_2OH), 52.19, 63.99 (d, J_{PC} 5.6, 2×$POCH_2$), 70.51 (s, CH_2OH), 131.51 (d, J_{PC} 6.6, =COP), 137.42 (d, J_{PC} 8.6); δ_H (200.13 MHz, $CDCl_3$) 1.06 (3H, s, CCH_3), 1.27 (3H, t, J_{HH} 7.5, SCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.4, J_{HH} 7.1, $POCH_2CH_3$), 1.36 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, $POCH_2CH_3$), 1.50–2.03 (5H, m), 2.27–2.54 (5H, m), 2.72 (1H, q, J_{HH} 7.5, SCH_2), 2.73 (1H, q, J_{HH} 7.5, SCH_2), 3.29–3.32 (1H, m, CHS), 3.52 (1H, d_{AB}, J_{HH}(AB) 11.5, CH_2OH), 3.67 (1H, d_{AB}, J_{HH}(AB) 11.5, CH_2OH), 4.09–4.26 (4H, m, 2×$POCH_2$); *m/z* (CI) (Finnigan MAT 95) 379 (M^++H, 27%), 361 (4, M^+-OH), 317 (17, M^+-SEt), 287 (100, M^+(−SEt, $-CH_2O$)), 155 (4, $(H+HOP(O)(OEt)_2)^+$). HRMS (CI) calcd for $C_{17}H_{31}O_5PS$+H (M^++H): 379.170811. Found: 379.169200.

4.3.16. Hydrolysis of adduct 8b to adduct 25. To a stirred solution of **8b** (0.170 g, 0.460 mmol) in EtOH (2 mL) 1 N NaOH (1 mL) was added at ambient temperature. The reaction mixture was extracted with $CHCl_3$ (20 mL), washed with water (2×10 mL), and dried ($MgSO_4$). The crude product was purified by column chromatography on silanized silica gel with $CHCl_3$–EtOH (10:1 v/v) as the eluant to give **25** (0.170 g, 94%).

4.3.16.1. 7-(Diethoxyphosphoryloxy)-6-ethylsulfanyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-4,5-dicarboxlic acid 25. Yield: 94%—white crystal; mp≈30 °C; R_f 0.48 (TLC, silanized silica gel, $CHCl_3$–EtOH (10:1, v/v)); δ_P (80.96 MHz, $CDCl_3$) −4.96; δ_C (50.32 MHz, $CDCl_3$) 14.21 (s, SCH_2CH_3), 15.96 (d, J_{PC} 6.3, 2×OCH_2CH_3), 23.81, 27.25, 29.27, 29.96, 39.53, 43.14, 44.45, 50.10, 64.55 (d, J_{PC} 5.7, 2×OCH_2), 130.09 (d, J_{PC} 6.4, =COP), 136.49 (d, J_{PC} 8.5), 174.26 (s, C=O), 175.14 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.69 (3H, t, J_{HH} 7.4, SCH_2CH_3), 1.29–1.50 (6H, m, 2×OCH_2CH_3), 1.55–1.78 (2H, m), 1.82–1.91 (2H, m), 2.35–2.65 (3H, m), 2.74 (2H, dt, J_{HH} 7.4 and 7.6), 3.19 (1H, dd, J_{HH} 3.8 and 5.6, CHC(O)), 3.54 (1H, dd, J_{HH} 3.8 and 5.9, CHC(O)), 3.95–4.05 (1H, m, CHS), 4.12–4.34 (4H, m, 2×OCH_2), 7.26 (2H, br s, 2×COOH); *m/z* (15 eV) (120 °C) 422 (M^+, 3%), 405 (2, M^+-OH), 390 (13, $M^+-2\times H_2O$), 362 (12, M^+(−SEt, +H)), 344 (100, $M^+-2\times COOH$), 271 (49, $M^+(-2\times COOH, -SEt)$). Found: C, 48.4; H, 6.5; P, 7.3. Calcd for $C_{17}H_{27}O_8PS$: C, 48.3; H, 6.4; P, 7.3%.

4.3.17. Esterification of 25. A solution of **25** (0.170 g, 0.403 mmol) in Et_2O (10 mL) was treated with CH_2N_2 in Et_2O (10 mL) at 20 °C and stirred for 1 h. After evaporation of solvent in vacuo the residue was purified by column chromatography to give diester **26** (0.148 g) (82%).

4.3.17.1. Dimethyl 7-(diethoxyphosphoryloxy)-6-ethylsulfanyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-4,5-dicarboxylate 26. Yield: 82%—pale yellow oil. R_f 0.67; δ_P (80.96 MHz, $CDCl_3$) −4.55; δ_C (50.32 MHz, $CDCl_3$) 14.15 (s, SCH_2CH_3), 16.05 (d, J_{PC} 6.5, 2×OCH_2CH_3), 23.59, 27.06, 29.92, 30.18, 39.86, 43.09, 44.45, 49.28, 51.15, 51.76, 64.16 (d, J_{PC} 5.7, 2×OCH_2), 128.71 (d, J_{PC} 6.4, =COP), 137.46 (d, J_{PC} 8.4), 171.05 (s, C=O), 171.57 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.18 (3H, t, J_{HH} 7.5, SCH_2CH_3), 1.34 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.44–1.96 (4H, m), 2.25–2.70 (3H, m), 2.72 (1H, d_{AB}q, J_{HH} 7.6, J_{HH}(AB) 12.2, SCH_2), 2.78 (1H, d_{AB}q, J_{HH} 7.6, J_{HH}(AB) 12.2, SCH_2), 3.16 (1H, dd, J_{HH} 4.2 and 6.8, CHC(O)), 3.44 (1H, dd, J_{HH} 4.0 and 7.0, CHC(O)), 3.66 (3H, s, $C(O)OCH_3$), 3.74 (3H, s, $C(O)OCH_3$), 3.95 (1H, ddd, J_{PH} 2.4, J_{HH} 4.2 and 7.0, CHS), 4.05–4.27 (4H, m, 2×OCH_2); *m/z* (15 eV) 450 (M^+, 13%), 389 (24, M^+-SEt), 155 (17, $(H+HOP(O)OEt)_2)^+$). Found: C, 50.6; H, 6.9; P, 6.8. Calcd for $C_{19}H_{31}O_8PS$: C, 50.7; H, 6.9; P, 6.9%.

4.3.18. Oxidation of sulfides 17b and 5a to sulfones 28 (*n*=2) and 43. *General procedure:* a solution of 85% *m*CPBA (1.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to the sulfides **17b** and **5a** (0.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C. Stirring was continued at 0 °C for 3 h and then at room temperature for 1 h. The reaction mixture was washed with Na_2SO_3 (2×5 mL), $KHCO_3$ (2×5 mL), and water (2×5 mL). The organic layer was dried over $MgSO_4$ and solvent was removed in vacuo. The residue was purified by column chromatography to provide pure sulfones **28** (*n*=2) and **43**.

4.3.18.1. Phosphoric acid 6-cyano-5-ethanesulfonyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 28 (*n*=2). Yield: 42%—yellow deep dense oil. R_f 0.43; δ_P (80.96 MHz, $CDCl_3$) −4.33; δ_C (50.32 MHz, $CDCl_3$) 6.20 (s, $SO_2CH_2CH_3$), 16.04 (d, J_{PC} 5.8, 2×OCH_2CH_3), 23.05, 26.46, 27.53, 29.14, 32.32, 41.42, 50.50, 59.51, 64.75 (d, J_{PC} 4.1, 2×OCH_2), 118.49 (s, CN), 128.99 (d, J_{PC} 4.2), 139.42 (d, J_{PC} 6.7, =COP); δ_H (200.13 MHz, $CDCl_3$) 1.35 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.37 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.47 (3H, t, J_{HH} 7.4, $SO_2CH_2CH_3$), 1.55–2.11 (3H, m), 2.19–2.34 (2H, m), 2.34–2.66 (4H, m), 3.26 (1H, ddd, J_{HH} 2.0, 3.8, and 6.7, CHCN), 3.27 (2H, q, J_{HH} 7.4, SO_2CH_2), 4.15 (2H, dq, J_{PH} 7.3, J_{HH} 7.1, OCH_2), 4.22 (2H, q, J_{PH} 7.1, J_{HH} 7.1, OCH_2), 4.46–4.51 (1H, m, $CHSO_2$); *m/z* (CI) (Finnigan MAT 95) 392 (M^++H, 33%),

299 (100, M^+-SOEt), 155 (7, $(H+HOP(O)(OEt)_2)^+$). Found: C, 49.3; H, 6.6. Calcd for $C_{16}H_{26}NO_6PS$: C, 49.1; H, 6.7%.

4.3.18.2. Phosphoric acid diethyl ester 4-methylsulfonyl-1,3-dioxo-2-phenyl-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-5-yl ester 43. Yield: 55%—orange dense oil. R_f 0.62; δ_P (80.96 MHz, $CDCl_3$) −6.21; δ_C (50.32 MHz, $CDCl_3$) 15.69 (d, J_{PC} 6.4, OCH_2CH_3), 15.80 (d, J_{HH} 6.4, OCH_2CH_3), 26.35, 27.96, 28.73, 41.65, 42.14, 44.11, 45.84, 64.44 (d, J_{PC} 5.6, OCH_2), 64.77 (d, J_{PC} 6.2, $CHSO_2$), 64.96 (d, J_{PC} 5.6, OCH_2), 126.21 (s, *o*-C_6H_5), 128.56 (s, *p*-C_6H_5), 128.90 (s, *m*-C_6H_5), 129.85 (d, J_{PC} 3.3, =COP), 130.90 (d, J_{PC} 8.6), 131.21 (s, *ipso*-C_6H_5), 174.65 (s, C=O), 175.02 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.32 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.35 (3H, dt, J_{PH} 1.2, J_{HH} 7.0, OCH_2CH_3), 1.55–1.85 (2H, m), 1.94–2.24 (2H, m), 2.36–2.68 (2H, m), 2.70–2.87 (1H, m), 3.42 (1H, dd, J_{HH} 8.7 and 9.4, CHC(O)), 3.53 (3H, d, J_{HH} 0.7, SO_2CH_3), 3.95–3.98 (1H, m, $CHSO_2$), 4.02–4.17 (3H, m, OCH_2, CHC(O)), 4.21 (1H, q, J_{HH} 7.0, OCH_2), 4.28 (1H, q, J_{HH} 7.0, OCH_2), 7.17–7.34 (2H, m, *o*-C_6H_5), 7.36–7.51 (3H, m, *p*-C_6H_5, *m*-C_6H_5); *m/z* (15 eV) 497 (M^+, 0.1%), 418 (8, M^+-SO_2Me), 417 (16, M^+-HSO_2Me), 279 (5, $M^+(-HSO_2Me, -H(CO)_2NPh)$), 263 (5, $M^+(-HOP(O)(OEt)_2, -HSO_2Me)$), 155 (21, $(H+HOP(O)(OEt)_2)^+$), 117 (23, $M^+(-HOP(O)(OEt)_2, -SO_2Me, -(CO)_2NPh)$), 116 (9, $M^+(-HOP(O)(OEt)_2, -HSO_2Me, -(CO)_2NPh)$), 115 (23, $M^+(-HOP(O)(OEt)_2, -HSO_2Me, -H(CO)_2NPh)$). Found: C, 53.3; H, 5.6; N, 2.9; P, 6.3. Calcd for $C_{22}H_{28}NO_8PS$: C, 53.1; H, 5.7; N, 2.8; P, 6.2%.

4.3.19. Synthesis of sulfoxides 28 (*n*=1), 29, and 30. *General procedure:* a solution of 85% *m*CPBA (1.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to the sulfides **12**, **13** or **17b** (0.5 mmol) in CH_2Cl_2 (50 mL) at −20 °C. Stirring was continued at the same temperature for 3 h and then at 0 °C for 1 h. The reaction mixture was washed with Na_2SO_3 (2×5 mL), $KHCO_3$ (2×5 mL), and water (2×5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography to provide pure sulfoxides **28** (*n*=1), **29**, and **30**.

4.3.19.1. Phosphoric acid 6-cyano-5-ethanesulfinyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 28 (*n*=1). Yield: 96%—orange dense oil. Ratio of diastereoisomers: 1.6:1. Major isomer: R_f 0.23; δ_P (80.96 MHz, $CDCl_3$) −3.98; δ_C (50.32 MHz, $CDCl_3$) 6.80 (s, $S(O)CH_2CH_3$), 14.87 (d, J_{PC} 5.0, $2\times OCH_2CH_3$), 21.86, 25.01, 26.26, 29.76, 31.47, 39.68, 44.91, 56.55, 63.30 (d, J_{PC} 5.6, $2\times OCH_2$), 117.85 (s, CN), 127.31 (d, J_{PC} 8.2), 138.45 (d, J_{PC} 6.0, =COP); δ_H (200.13 MHz, $CDCl_3$) 1.35 (3H, dt, J_{PH} 1.6, J_{HH} 6.7, OCH_2CH_3), 1.39 (3H, dt, J_{PH} 1.6, J_{HH} 6.7, OCH_2CH_3), 1.39 (3H, t, J_{HH} 7.6, $S(O)CH_2CH_3$), 1.52–2.80 (9H, m), 2.95 (1H, $d_{AB}q$, J_{HH} 7.6, J_{HH}(AB) 13.1, $S(O)CH_2$), 3.19 (1H, $d_{AB}q$, J_{HH} 7.6, J_{HH}(AB) 13.1, $S(O)CH_2$), 3.37 (1H, ddd, J_{HH} 3.3, 4.4, and 12.9, CHCN), 3.85–3.97 (1H, m, CHS(O)), 4.05–4.25 (4H, m, $2\times OCH_2$). Minor isomer: R_f 0.23; δ_P (80.96 MHz, $CDCl_3$) −4.36; δ_C (50.32 MHz, $CDCl_3$) 6.49 (s, $S(O)CH_2CH_3$), 14.87 (d, J_{PC} 5.0, $2\times OCH_2CH_3$), 22.03, 25.42, 26.26, 27.60, 31.47, 39.68, 44.28, 55.41, 63.30 (d, J_{PC} 5.6, $2\times OCH_2$), 117.85 (s, CN), 130.97 (d, J_{PC} 8.2), 134.87 (d, J_{PC} 6.7, =COP); δ_H (200.13 MHz, $CDCl_3$) 1.35 (dt, J_{PH} 1.6, J_{HH} 6.7, 3H, OCH_2CH_3), 1.39 (dt, J_{PH} 1.6, J_{HH} 6.7, 3H, OCH_2CH_3), 1.39 (t, J_{HH} 7.6, 3H, $S(O)CH_2CH_3$), 1.52–2.80 (m, 9H), 2.95 ($d_{AB}q$, J_{HH} 7.6, J_{HH}(AB) 13.1, 1H, $S(O)CH_2$), 3.19 ($d_{AB}q$, J_{HH} 7.6, J_{HH}(AB) 13.1, 1H, $S(O)CH_2$), 3.37 (ddd, J_{HH} 3.3, 4.4, and 12.9, 1H, CHCN), 3.85–3.97 (m, 1H, CHS(O)), 4.05–4.25 (m, 4H, $2\times OCH_2$); *m/z* (70 eV) 376 (M^++H, 1%), 298 (73, $M^+-S(O)Et$), 297 (26, $M^+-HS(O)Et$), 271 (21, $M^+(-S(O)Et, -HCN)$), 155 (34, $(H+HOP(O)(OEt)_2)^+$), 143 (37, $M^+(-HS(O)Et, -HOP(O)(OEt)_2)$), 117 (52, $M^+(-HCN, -S(O)Et, -HOP(O)(OEt)_2)$); *m/z* (15 eV) 376 ($M^+$+H, 1%), 298 (100, $M^+-S(O)Et$), 271 (24, $M^+(-S(O)Et, -HCN)$), 155 (30, $(H+HOP(O)(OEt)_2)^+$), 144 (17, $M^+(-S(O)Et, -HOP(O)(OEt)_2)$), 117 (17, $M^+(-HCN, -S(O)Et, -HOP(O)(OEt)_2)$). Found: C, 51.1; H, 7.0. Calcd for $C_{16}H_{26}NO_5PS$: C, 51.2; H, 7.0%.

4.3.19.2. (5r,6t,7c,7ac)-Phosphoric acid diethyl ester 6,7-dicyano-5-ethylsulfinyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 29. Yield: 64%—yellow deep dense oil. Ratio of diastereoisomers: 2.2:1. Major isomer: R_f 0.18; δ_P (80.96 MHz, $CDCl_3$) −4.25; δ_C (50.32 MHz, $CDCl_3$) 7.66 (s, $S(O)CH_2CH_3$), 15.63 (d, J_{PC} 3.3, $2\times OCH_2CH_3$), 22.18, 26.11, 29.75, 31.38, 34.27, 43.62, 45.49, 56.29, 64.54 (d, J_{PC} 5.6, $2\times OCH_2$), 115.50 (s, CN), 117.30 (s, CN), 127.54 (d, J_{PC} 8.1), 141.13 (d, J_{PC} 5.9, =COP); δ_H (200.13 MHz, $CDCl_3$) 1.36 (6H, dt, J_{PH} 1.1, J_{HH} 7.0, $2\times OCH_2CH_3$), 1.40 (3H, t, J_{HH} 7.5, $S(O)CH_2CH_3$), 1.56–1.82 (1H, m), 1.82–2.04 (1H, m), 2.21–2.29 (1H, m), 2.45–2.82 (4H, m), 3.00 (1H, $d_{AB}q$, J_{HH} 7.5, J_{HH}(AB) 13.1, $S(O)CH_2$), 3.21 (1H, $d_{AB}q$, J_{HH} 7.5, J_{HH}(AB) 13.1, $S(O)CH_2$), 3.42 (1H, dd_{AB}, J_{HH} 2.3, J_{HH}(AB) 12.0, CHCN), 3.67 (1H, dd_{AB}, J_{HH} 4.3, J_{HH}(AB) 12.0, CHCN), 3.96–4.05 (1H, m, CHS(O)), 4.09–4.27 (4H, m, $2\times OCH_2$). Minor isomer: R_f 0.18; δ_P (80.96 MHz, $CDCl_3$) −4.85; δ_C (50.32 MHz, $CDCl_3$) 7.45 (s, $S(O)CH_2CH_3$), 15.63 (d, J_{PC} 3.3, $2\times OCH_2CH_3$), 22.41, 26.60, 30.15, 30.82, 31.57, 43.63, 45.27, 53.82, 64.54 (d, J_{PC} 5.6, $2\times OCH_2$), 115.63 (s, CN), 117.47 (s, CN), 131.95 (d, J_{PC} 8.1), 133.15 (d, J_{PC} 6.9, =COP); δ_H (200.13 MHz, $CDCl_3$) 1.36 (6H, dt, J_{PH} 1.1, J_{HH} 7.0, $2\times OCH_2CH_3$), 1.40 (3H, t, J_{HH} 7.5, $S(O)CH_2CH_3$), 1.56–1.82 (1H, m), 1.82–2.04 (1H, m), 2.21–2.29 (1H, m), 2.45–2.82 (4H, m), 3.05 (2H, q, J_{HH} 7.5, $S(O)CH_2$), 3.50 (1H, dd_{AB}, J_{HH} 2.7, J_{HH}(AB) 11.0, CHCN), 3.55 (1H, dd_{AB}, J_{HH} 1.2, J_{HH}(AB) 11.0, CHCN), 3.96–4.05 (1H, m, CHS(O)), 4.09–4.27 (4H, m, $2\times OCH_2$); *m/z* (15 eV) 400 (M^+, 1%), 323 (15, $M^+-S(O)Et$), 155 (42, $(H+HOP(O)(OEt)_2)^+$). Found: C, 51.1; H, 6.3. Calcd for $C_{17}H_{25}N_2O_5PS$: C, 51.0; H, 6.3%.

4.3.19.3. (5r,6c,7t,7ac)-Phosphoric acid diethyl ester 6,7-dicyano-5-ethylsulfinyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 30. Yield: 68%—yellow deep dense oil. R_f 0.22; δ_P (80.96 MHz, $CDCl_3$) −4.31; δ_C (50.32 MHz, $CDCl_3$) 7.61 (s, $S(O)CH_2CH_3$), 16.13 (d, J_{PC} 4.2, $2\times OCH_2CH_3$), 21.18, 26.75, 30.48, 31.22, 35.39, 45.11, 45.92, 59.46, 64.50 (d, J_{PC} 5.1, $2\times OCH_2$), 114.37 (s, CN), 119.52 (s, CN), 130.78 (d, J_{PC} 8.0), 142.70 (d, J_{PC} 5.5, =COP); δ_H (200.13 MHz, $CDCl_3$) 1.33 (6H, dt, J_{PH} 1.1, J_{HH} 7.1, $2\times OCH_2CH_3$), 1.38 (3H, t, J_{HH} 7.5, $S(O)CH_2CH_3$), 1.51–1.81 (1H, m), 1.82–2.05 (1H, m), 2.20–2.40 (1H, m), 2.44–2.81 (4H, m), 3.03 (1H, $d_{AB}q$, J_{HH} 7.5, J_{HH}(AB) 13.7, $S(O)CH_2$), 3.22 (1H, $d_{AB}q$, J_{HH} 7.5, J_{HH}(AB) 13.7,

S(O)CH_2), 3.37 (1H, dd_{AB}, J_{HH} 2.5, J_{HH}(AB) 10.3, CHCN), 3.60 (1H, dd_{AB}, J_{HH} 4.1, J_{HH}(AB) 10.3, CHCN), 3.91–4.02 (1H, m, CHS(O)), 4.10–4.27 (4H, m, 2×OCH_2); *m/z* (15 eV) 400 (M^+, 1%), 323 (22, M^+-S(O)Et), 155 (50, (H+HOP(O)$(OEt)_2)^+$). Found: C, 51.0; H, 6.4. Calcd for $C_{17}H_{25}N_2O_5PS$: C, 51.0; H, 6.3%.

4.3.20. Elimination reactions promoted by bases and silica gel. To a solution of **17a** or **17b** (1 mmol) in MeOH (10 mL) an aqueous solution of NaOH (1 N, 0.5 mL) was added dropwise. The reaction mixture was stirred for 1 h at ambient temperature. After addition of $CHCl_3$ (50 mL) the organic layer was washed with water (3×10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography to give pure diene **27** (82% from **17a** or 77% from **17b**).

To a stirring solution of **28** (*n*=1, 2) (1 mmol) in CH_2Cl_2 (5 mL), Et_2NH (1 mL) was added at room temperature and the reaction mixture was stirred for additional 1 h. The solvent was removed in vacuo and the residue was purified by column chromatography to give the diene **27** (78% from sulfoxide and 68% from sulfone).

Elimination reaction on silica gel: a solution of **17a–d** (2 mmol) in benzene–ethyl acetate (1:1 v/v) was deposited on silica gel (200 g) at room temperature for 12 h. The product was eluted using ethyl acetate to give **27** (48% from **17a**, 45% from **17b**, 53% from **17c**, and 49% from **17d**).

4.3.20.1. Phosphoric acid diethyl ester 6-cyano-2,3,7,7a-tetrahydro-1*H*-inden-4-yl ester 27. Orange dense oil. R_f 0.74; δ_P (80.96 MHz, $CDCl_3$) −6.12; δ_C (50.32 MHz, $CDCl_3$) 15.36 (d, J_{PC} 6.2, 2×OCH_2CH_3), 25.84, 27.64, 30.73, 31.28, 32.93, 44.17, 64.41 (d, J_{PC} 5.8, 2×OCH_2CH_3), 117.52 (s, CN), 121.69 (s, >C<), 131.25 (s, =CH), 132.33 (d, J_{PC} 6.3), 145.82 (d, J_{PC} 5.2, =COP); δ_H (200.13 MHz, $CDCl_3$) 1.35 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.50–1.67 (2H, m), 1.87–2.28 (4H, m), 2.45–2.95 (4H, m), 2.51 (1H, dd, J_{HH} 8.0 and 16.2, CH_2–C(CN)=), 4.15 (2H, dq, J_{PH} 0.7, J_{HH} 7.1, OCH_2), 4.19 (2H, dq, J_{PH} 0.7, J_{HH} 7.1, OCH_2), 6.69 (1H, d, J_{PH} 3.1, =CH); *m/z* (15 eV) 297 (M^+, 14%), 295 (64, M^+-H_2), 254 (24, M^+-Ac), 155 (36, (H+HOP(O)$(OEt)_2)^+$), 143 (54, $M^+(-$HOP(O)$(OEt)_2)$), 100 (100, $M^+(-$HOP(O)$(OEt)_2$, −Ac)). Found: C, 56.5; H, 6.7; N, 4.8; P, 10.5. Calcd for $C_{14}H_{20}NO_4P$: C, 56.6; H, 6.8; N, 4.7; P, 10.4%.

To a solution of **29** or **30** (1 mmol) in CH_2Cl_2 (10 mL), Et_2NH or Et_3N (1 mL) was added dropwise. The reaction mixture was stirred for 1 h at room temperature. After evaporation of solvents the residue was purified by column chromatography to give **31** or **32**.

4.3.20.2. (7r,7at)-Phosphoric acid diethyl ester 6,7-dicyano-2,3,7,7a-tetrahydro-1*H*-inden-4-yl ester 31. Yield: 58%—orange dense oil. R_f 0.33; δ_P (80.96 MHz, $CDCl_3$) −4.85; δ_C (50.32 MHz, $CDCl_3$) (DEPT) 16.08 (d, J_{PC} 6.2, 2×OCH_2CH_3), 24.13 (s, CH_2), 28.06 (s, CH_2), 30.25 (s, CH_2), 30.74 (s, CH), 42.44 (s, *C*HCN), 65.00 (d, J_{PC} 6.2, 2×OCH_2), 102.60 (s, =*C*–CN), 115.01 (s, CN), 116.51 (s, CN), 137.06 (d, J_{PC} 6.0, =COP), 138.54 (d, J_{PC} 6.5), 140.64 (s, =CH); δ_H (200.13 MHz, $CDCl_3$) 1.35 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.2, J_{HH} 7.1, OCH_2CH_3), 1.54–1.61 (1H, m), 1.82 (1H, dq, J_{HH} 11.9 and 6.5), 2.03–2.25 (2H, m), 2.44–2.61 (1H, m), 2.77 (1H, ddd, J_{HH} 1.4, 7.9, and 19.9, =C–CH), 2.93–3.07 (1H, m), 3.59 (1H, d, J_{HH} 7.9, CHCN), 4.17 (2H, q, J_{HH} 7.1, OCH_2), 4.20 (2H, q, J_{HH} 7.1, OCH_2), 6.99 (1H, s, =CH); *m/z* (15 eV) 322 (M^+, 13%), 295 (20, M^+-HCN), 268 (17, $M^+(-$HCN$)_2$), 155 (32, (H+HOP(O)$(OEt)_2)^+$). Found: C, 56.0; H, 5.8. Calcd for $C_{15}H_{19}N_2O_4P$: C, 55.9; H, 5.9%.

4.3.20.3. (7r,7ac)-Phosphoric acid diethyl ester 6,7-dicyano-2,3,7,7a-tetrahydro-1*H*-inden-4-yl ester 32. Yield: 52%—orange dense oil. R_f 0.48; δ_P (80.96 MHz, $CDCl_3$) −4.90; δ_C (50.32 MHz, $CDCl_3$) 16.05 (d, J_{PC} 6.4, 2×OCH_2CH_3), 24.09, 28.03, 30.22, 30.70, 42.41, 65.04 (d, J_{PC} 6.3, 2×OCH_2), 115.02 (s, CN), 116.48 (s, CN), 129.95, 133.03, 138.51 (d, J_{PC} 6.9, =COP), 140.59 (s, =CH); δ_H (200.13 MHz, $CDCl_3$) 1.36 (3H, dt, J_{PH} 0.9, J_{HH} 7.1, OCH_2CH_3), 1.37 (3H, dt, J_{PH} 0.9, J_{HH} 7.1, OCH_2CH_3), 1.51–1.95 (2H, m), 2.03–2.30 (2H, m), 2.43–2.67 (1H, m), 2.67–2.91 (1H, m), 2.91–3.12 (1H, m), 3.59 (1H, d, J_{HH} 7.8, CHCN), 4.18 (2H, q, J_{HH} 7.1, OCH_2), 4.22 (2H, q, J_{HH} 7.1, OCH_2), 7.00 (1H, s, =CH); *m/z* (15 eV) (100 °C) 322 (M^+, 11%), 294 (4, M^+-H_2CN), 267 (10, $M^+(-H_2$CN, −HCN)), 167 (3, M^+-HOP(O)$(OEt)_2$), 155 (3, (H+HOP(O)$(OEt)_2)^+$), 141 (100, $M^+(-$HOP(O)$(OEt)_2$, −HCN)), 115 (10, $M^+(-$OP(O)$(OEt)_2$, −(HCN)$_2$)). Found: C, 55.9; H, 5.9. Calcd for $C_{15}H_{19}N_2O_4P$: C, 55.9; H, 5.9%.

Elimination reaction on silica gel: a solution of **16a–d** (2 mmol) in benzene–ethyl acetate (1:1, v/v) was deposited on silica gel (200 g) at room temperature for 12 h. The product was eluted using ethyl acetate to give **33** (59% from **16a**, 55% from **16b**, 68% from **16c**, and 75% from **16d**). Deposition of the solution of **16a–d** on silica gel at room temperature over 24 h provided aromatic phosphate **34** (48%).

Thermal eliminations: a solution of **16b** and **19b** (1 mmol) in benzene (10 mL) under air was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography with benzene–ethyl acetate as the eluant to give **33** (54% after 4 h) or **34** (45% after additional refluxing of **16b** for 18 h) or **35** (43% from **19b**).

4.3.20.4. Phosphoric acid diethyl ester 6-acetyl-2,3,7,7a-tetrahydro-1*H*-inden-4-yl ester 33. Pale yellow dense oil. R_f 0.57; δ_P (80.96 MHz, $CDCl_3$) −5.32; δ_C (50.32 MHz, $CDCl_3$) 16.95 (d, J_{PC} 6.7, 2×OCH_2CH_3), 23.75, 25.73, 27.39, 29.73, 34.04, 35.94, 65.07 (d, J_{PC} 5.8, 2×OCH_2), 124.62 (s, =CH), 132.38 (d, J_{PC} 6.1), 143.79, 148.16 (d, J_{PC} 5.6, =COP), 199.24 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.35 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.36 (3H, dt, J_{PH} 1.1, J_{HH} 7.1, OCH_2CH_3), 1.47–2.24 (4H, m), 2.25–2.77 (3H, m), 2.33 (3H, s, C(O)CH_3), 2.98 (1H, d, J_{HH} 8.1, CH_2CC(O)), 3.00 (1H, d, J_{HH} 8.0, CH_2CC(O)), 4.17 (2H, q, J_{HH} 7.1, OCH_2), 4.21 (2H, q, J_{HH} 7.1, OCH_2), 6.91 (1H, d, J_{PH} 2.9, =CH); *m/z* (15 eV) 314 (M^+, 5%), 313 (16, M^+-H), 312 (100, M^+-H_2), 297 (4, $M^+(-H_2$, −Me)), 269 (5, $M^+(-H_2$, −Ac)), 158 (20, $M^+(-H_2$, −HOP(O)$(OEt)_2$)), 155 (10,

(H+HOP(O)(OEt)$_2$)), 143 (12, M$^+$(−H$_2$, −Me, −HOP(O)(OEt)$_2$)). Found: C, 57.2; H, 7.3; P, 9.8. Calcd for $C_{15}H_{23}O_5P$: C, 57.3; H, 7.4; P, 9.9%.

4.3.20.5. Phosphoric acid diethyl ester 6-acetyl-indan-4-yl ester 34. Yield: 48% (oxidation on SiO_2) or 45% (oxidation in refluxing benzene)—pale yellow oil. R_f 0.60; δ_P (80.96 MHz, $CDCl_3$) −5.40; δ_C (50.32 MHz, $CDCl_3$) 15.98 (d, J_{PC} 6.4, 2×OCH$_2$*C*H$_3$), 24.82, 26.62, 29.87, 32.92 (s, C(O)CH$_3$), 64.58 (d, J_{PC} 5.7, 2×OCH$_2$), 117.87 (s, =CH), 121.00 (s, =CH), 137.36, 140.87 (d, J_{PC} 5.2, =COP), 146.93 (d, J_{PC} 6.8), 147.57, 197.06 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.37 (6H, dt, J_{PH} 1.0, J_{HH} 7.1, 2×OCH$_2$C*H*$_3$), 2.13 (2H, quint, J_{HH} 7.4, CH$_2$), 2.56 (3H, s, C(O)CH$_3$), 3.00 (4H, t, J_{HH} 7.4, 2×CH$_2$–C=), 4.21 (2H, q, J_{HH} 7.1, OCH$_2$), 4.25 (2H, q, J_{HH} 7.1, OCH$_2$), 7.63 (1H, s, =CH), 7.64 (1H, s, =CH); *m/z* (15 eV) 312 (M$^+$, 68%), 269 (37, M$^+$−Ac), 155 (13, (H+HOP(O)(OEt)$_2$)$^+$). Found: C, 57.8; H, 6.9; P, 9.9. Calcd for $C_{15}H_{21}O_5P$: C, 57.7; H, 6.8; P, 9.9%.

4.3.21. Elimination reactions promoted by fluoride anion. Elimination reactions of **19b**, **11b**, and **11c** were carried out according to literature procedure but for 12 h only to give **35** and **37**.[18] The compound **37** was obtained also by the oxidation of **11b** using *m*CPBA according to procedure described for the synthesis of sulfoxides with 58% of yield.

4.3.21.1. Phosphoric acid diethyl ester 6-formyl-indan-4-yl ester 35. Yield: 44% or 43% (thermal elimination)—pale yellow dense oil. R_f 0.57; δ_P (80.96 MHz, $CDCl_3$) −5.45; δ_C (50.32 MHz, $CDCl_3$) 16.01 (d, J_{PC} 6.5, 2×OCH$_2$*C*H$_3$), 24.84, 30.05, 32.82, 64.70 (d, J_{PC} 6.4, 2×OCH$_2$), 119.23 (s, =CH), 122.01 (s, =CH), 137.05, 141.55, 142.53 (d, J_{PC} 5.2, =COP), 148.18, 191.16 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.37 (6H, dt, J_{PH} 1.0, J_{HH} 7.1, 2×OCH$_2$C*H*$_3$), 2.15 (2H, quint, J_{HH} 7.3), 3.02 (4H, q, J_{HH} 7.3, 2×CH$_2$–C=), 4.10–4.32 (4H, m, 2×OCH$_2$), 7.57 (2H, s, 2×=CH), 9.92 (1H, s, CHO); *m/z* (15 eV) 298 (M$^+$, 100%), 270 (36, M$^+$(−Et, +H) or M$^+$(−CHO, +H)), 269 (8, M$^+$−Et or M$^+$−CHO), 242 (34, M$^+$(−Et, +H$_2$, −CHO)), 213 (19, M$^+$(−Et$_2$, −CHO, +H$_2$)), 155 (14, (H+HOP(O)(OEt)$_2$)$^+$), 144 (29, M$^+$−HOP(O)(OEt)$_2$), 115 (11, M$^+$(−HOP(O)(OEt)$_2$, −CHO)). Found: C, 56.5; H, 6.4; P, 10.3. Calcd for $C_{14}H_{19}O_5P$: C, 56.4; H, 6.4; P, 10.4%.

4.3.21.2. 7-(Diethoxyphosphoryloxy)-indan-4,5-dicarboxylic acid dimethyl ester 37. Yield: 57% (from **11b**) or 53% (from **11c**)—pale yellow dense oil. R_f 0.77; δ_P (80.96 MHz, $CDCl_3$) −5.69; δ_C (50.32 MHz, $CDCl_3$) 15.84 (d, J_{PC} 6.6, 2×OCH$_2$*C*H$_3$), 24.36 (s, CH$_2$), 29.77 (s, CH$_2$), 31.88 (s, CH$_2$), 52.23 (s, OCH$_3$), 52.29 (s, OCH$_3$), 64.65 (d, J_{PC} 5.7, 2×OCH$_2$), 119.26 (s, =CH), 127.42, 128.95, 140.31 (d, J_{PC} 6.6, =COP), 146.10, 147.18 (d, J_{PC} 7.1), 165.85 (s, C=O), 168.40 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.37 (6H, dt, J_{PH} 1.1, J_{HH} 7.1, 2×OCH$_2$C*H*$_3$), 2.14 (2H, quint, J_{HH} 7.5), 3.00 (2H, t, J_{HH} 7.5, CH$_2$–C=), 3.02 (2H, t, J_{HH} 7.5, CH$_2$–C=), 3.87 (3H, s, C(O)OCH$_3$), 3.90 (3H, s, C(O)OCH$_3$), 4.15–4.30 (4H, m, 2×OCH$_2$), 7.26 (1H, s, =CH); *m/z* (15 eV) 386 (M$^+$, 19%), 355 (45, M$^+$−MeO), 354 (100, M$^+$−MeOH), 326 (3, M$^+$−COOMe), 268 (8, M$^+$−2×COOMe). Found: C, 52.8; H, 6.1; P, 8.1. Calcd for $C_{17}H_{23}O_8P$: C, 52.9; H, 6.0; P, 8.0%.

4.3.21.3. Dephosphorylation reactions promoted by fluoride anion. Dephosphorylation reactions of **19b**, **35**, **11b**, and **37** were carried out according to literature procedure in 1 mmol scale.[18]

4.3.21.4. 6-Formyl-4-hydroxy-indane 36. Yield: 64% (from **19b**) or 61% (from **35**)—pale yellow oil. R_f 0.94; δ_C (50.32 MHz, $CDCl_3$) 24.95, 29.42, 32.82, 113.20, 119.56, 136.68, 138.30, 147.54, 152.86, 193.06 (s, C=O). δ_H (200.13 MHz, $CDCl_3$) 2.16 (2H, quint, J_{HH} 7.4, CH$_2$), 2.93 (2H, t, J_{HH} 7.4, CH$_2$–C=), 2.99 (2H, t, J_{HH} 7.4, CH$_2$–C=), 5.30–6.10 (1H, br s, OH), 7.19 (1H, s, =CH), 7.33 (1H, s, =CH), 9.87 (1H, s, CHO); *m/z* (15 eV) 162 (M$^+$, 100%), 133 (57, M$^+$−CHO). Found: C, 74.2; H, 6.3. Calcd for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2%.

4.3.21.5. 7-Hydroxy-indan-4,5-dicarboxylic acid dimethyl ester 38. Yield: 73% (from **11b**) or 92% (from **37**)—white crystal. R_f=0.93; mp 92–95 °C (from benzene); δ_C (50.32 MHz, $CDCl_3$) 24.50 (s, CH$_2$), 29.01 (s, CH$_2$), 32.44 (s, CH$_2$), 52.33 (s, OCH$_3$), 52.50 (s, OCH$_3$), 114.52 (s, =CH), 121.33, 130.10, 134.70, 146.55, 153.75, 168.08 (s, C=O), 169.47 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 2.12 (2H, quint, J_{HH} 7.4, CH$_2$), 2.87 (2H, t, J_{HH} 7.4, CH$_2$–C=), 3.01 (2H, t, J_{HH} 7.4, CH$_2$–C=), 3.86 (3H, s, OCH$_3$), 3.87 (3H, s, OCH$_3$), 7.10 (1H, s, =CH); *m/z* (15 eV) 250 (M$^+$, 84%), 219 (100, M$^+$−OMe), 218 (99, M$^+$−MeOH), 191 (2, M$^+$−COOMe), 132 (12, M$^+$−2×COOMe). Found: C, 62.3; H, 5.6. Calcd for $C_{13}H_{14}O_5$: C, 62.4; H, 5.6%.

4.3.22. Dephosphorylation reactions promoted by base. To a solution of **39** or **41** (1 mmol) in MeOH (10 mL) aqueous solution of NaOH (1 N, 0.5 mL) was added. The reaction mixture was stirred and heated at reflux for 1 h. After addition of $CHCl_3$ (50 mL) the organic layer was washed with water (3×10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography to give diene **40** or **42**.

4.3.22.1. 7-(Diethoxyphosphoryloxy)-indan-5-carboxylic acid ethyl ester 40. Yield: 55%—pale yellow oil. R_f 0.63; δ_P (80.96 MHz, $CDCl_3$) −5.58; δ_C (50.32 MHz, $CDCl_3$) 14.08 (s, COOCH$_2$*C*H$_3$), 15.87 (d, J_{PC} 6.5, 2×POCH$_2$*C*H$_3$), 24.74, 29.79, 32.82, 60.81 (s, C(O)O*C*H$_2$), 64.58 (d, J_{PC} 5.8, 2×POCH$_2$), 118.87 (s, =CH), 122.22 (s, =CH), 129.87, 131.62, 140.63 (d, J_{PC} 5.0, =COP), 147.30, 166.40 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.36 (3H, t, J_{HH} 7.2, COOCH$_2$C*H*$_3$), 1.37 (6H, dt, J_{PH} 0.8, J_{PH} 7.0, 2×POCH$_2$C*H*$_3$), 2.12 (2H, quint, J_{HH} 7.4), 2.97 (2H, t, J_{HH} 7.4, CH$_2$–C=), 3.01 (2H, t, J_{HH} 7.4, CH$_2$–C=), 4.21 (2H, q, J_{HH} 7.0, POCH$_2$), 4.25 (2H, q, J_{HH} 7.0, POCH$_2$), 4.34 (2H, q, J_{HH} 7.2, COOCH$_2$), 7.72 (1H, s, =CH), 7.73 (1H, s, =CH); *m/z* (15 eV) 342 (M$^+$, 8%), 313 (2, M$^+$−Et), 296 (87, M$^+$−EtOH), 268 (100, M$^+$−HCOOEt), 239 (96, M$^+$(−Et, −HCOOEt)), 188 (2, M$^+$−HOP(O)(OEt)$_2$), 155 (10, (H+HOP(O)(OEt)$_2$)$^+$), 115 (64, M$^+$(−HCOOEt, −HOP(O)(OEt)$_2$)). Found: C, 56.2; H, 6.8; P, 8.9. Calcd for $C_{16}H_{23}O_6P$: C, 56.1; H, 6.8; P, 9.1%.

4.3.22.2. Phosphoric acid diethyl ester 1,3-dioxo-2-phenyl-1,2,3,6,7,8-hexahydro-2-aza-as-indacen-5-yl ester 42. Yield: 42%—pale orange dense oil. R_f 0.79; δ_P

(80.96 MHz, $CDCl_3$) −5.88; δ_C (50.32 MHz, $CDCl_3$) 15.98 (d, J_{PC} 6.3, 2×OCH_2CH_3), 25.04, 29.70, 31.15, 64.93 (d, J_{PC} 5.7, 2×OCH_2), 113.68 (s, =CH), 126.36 (s, *o*-C_6H_5), 127.76 (s, *p*-C_6H_5), 128.47, 128.85 (s, *m*-C_6H_5), 131.68, 132.45 (s, *ipso*-C_6H_5), 143.74 (d, J_{PC} 5.0), 146.17, 151.02, 175.01 (s, C=O), 177.05 (s, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.38 (6H, dt, J_{PH} 1.0, J_{HH} 7.1, 2×OCH_2CH_3), 2.24 (2H, quint, J_{HH} 7.6, CH_2), 3.05 (2H, t, J_{HH} 7.6, CH_2–C=), 3.29 (2H, t, J_{HH} 7.6, CH_2–C=), 4.11–4.34 (4H, m, 2×OCH_2), 7.26–7.58 (5H, m, C_6H_5), 7.64 (1H, s, =CH); *m/z* (15 eV) 416 (M^++H, 100%), 387 (28, M^+(−Et, +H)), 358 (26, M^+(−Et_2, +H)), 261 (10, M^+−HOP(O)$(OEt)_2$), 155 (12, (H+HOP(O)$(OEt)_2)^+$). Found: C, 60.8; H, 5.3. Calcd for $C_{21}H_{22}NO_6P$: C, 60.7; H, 5.3%.

4.3.23. Epimerization of 43 to 44. The mixture of **43** (0.380 g, 0.764 mmol) in EtOH (6 mL), H_2O (1 mL), and Et_3N (0.2 mL) was heated at 50 °C for 1 h. The solvents were removed in vacuo (0.1 mmHg). The residue was purified by column chromatography to provide epimer **44** (0.239 g, 52%).

4.3.23.1. Phosphoric acid diethyl ester 4-methylsulfonyl-1,3-dioxo-2-phenyl-1,2,3,3a,4,6,7,8,8a,8b-decahydro-2-aza-as-indacen-5-yl ester 44. Yield: 55%—orange dense oil. R_f 0.63; δ_P (80.96 MHz, $CDCl_3$) −4.68; δ_C (50.32 MHz, $CDCl_3$) 15.85 (d, J_{PC} 6.0, CH_3, 2×OCH_2CH_3), 24.79 (s, CH_2), 28.79 (s, CH_2), 29.96 (s, CH_2), 40.19 (s, CH_3, SO_2CH_3), 40.20 (s, CH), 40.55 (s, CH), 41.36 (s, CH), 63.64 (s, CH, $CHSO_2$), 64.65 (d, J_{PC} 6.4, CH_2, OCH_2), 64.77 (d, J_{PC} 6.4, CH_2, OCH_2), 126.41 (s, CH, *o*-C_6H_5), 128.59 (s, CH, *p*-C_6H_5), 128.91 (s, CH, *p*-C_6H_5), 129.52 (d, J_{PC} 8.7, >C<), 131.57 (s, >C<, *ipso*-C_6H_5), 139.21 (d, J_{PC} 6.7, >C<, =COP), 174.58 (s, >C<, C=O), 175.24 (s, >C<, C=O); δ_H (200.13 MHz, $CDCl_3$) 1.30 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.32 (3H, dt, J_{PH} 1.0, J_{HH} 7.1, OCH_2CH_3), 1.53–1.78 (1H, m), 1.80–2.04 (2H, m), 2.05–2.31 (1H, m), 2.47–2.63 (2H, m), 3.09 (3H, s, SO_2CH_3), 3.27–3.49 (1H, m), 3.61 (1H, dd, J_{HH} 9.0 and 9.2, CHC(O)), 4.05–4.23 (5H, m, 2×OCH_2, CHC(O)), 4.70 (1H, s, $CHSO_2$), 7.26–7.50 (5H, m, C_6H_5); *m/z* (15 eV) 497 (M^+, 1%), 418 (8, M^+−SO_2Me), 417 (10, M^+−HSO_2Me), 279 (2, M^+(−HSO_2Me, −H$(CO)_2$NPh)), 263 (9, M^+ (−HOP(O)$(OEt)_2$, −HSO_2Me)), 155 (15, (H+HOP(O)$(OEt)_2)^+$), 117 (19, M^+(−HOP(O)$(OEt)_2$, −SO_2Me, −$(CO)_2$NPh)), 116 (13, M^+(−HOP(O)$(OEt)_2$, −HSO_2Me, −$(CO)_2$NPh)), 115 (16, M^+(−HOP(O)$(OEt)_2$, −HSO_2Me, −H$(CO)_2$NPh)). Found: C, 52.9; H, 5.6; N, 2.8. Calcd for $C_{22}H_{28}NO_8PS$: C, 53.1; H, 5.7; N, 2.8%.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.11.049.

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