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Stereospecific [2,3] sigmatropic rearrangement of allylic sulfoxides and selenoxides. Synthesis of novel polycyclic allylic alcohols and α-hydroxy ketones

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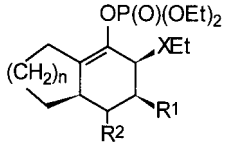
Abstract—A stereospecific [2,3] sigmatropic rearrangement of functionalized bi- or tricyclic allylic sulfoxides and selenoxides as a route to new allylic alcohols and their transformation into the corresponding α-hydroxy ketones having a defined stereochemistry is described. It has been demonstrated that cycloadducts, derived from [4+2] cycloaddition of (Z)-1-alkylthio-2-diethoxyphosphoryloxy-1,3-dienes to a various dienophiles, are versatile synthons carrying much structural and stereochemical information.

1. Introduction

The [2,3] sigmatropic rearrangement of allylic sulfoxides and allylic selenoxides leads to allylic alcohols.[1–3] This rearrangement in particular applied to cycloalkenyl sulfoxides and selenoxides is highly stereoselective.[3–5] A possible side reaction is 1,2-elimination to give the conjugated dienes. Competition between rearrangement and elimination is generally in favour of rearrangement, but in some special cases the diene is the major or even exclusive product.[6–8]

α-Hydroxy carbonyl compounds are key structural subunits of natural products and valuable synthetic intermediates.[9–10] As a consequence of their importance many methods have been devised for their preparation.[11–12] Surprisingly, many fewer syntheses of bicyclic or polycyclic α-hydroxy ketones have been reported.[13–17] In addition they often give a mixture of isomers in moderate yield. This situation provided the motivation to develop a novel approach to such systems.

We have previously described regio- and *endo*-stereospecific synthesis of new allylic sulfides **1** and selenides **2**.[18]



n = 1,2 **1**: X = S
2: X = Se

In this paper we describe a stereospecific entry to novel functionalized bi- and tricyclic allylic alcohols and the corresponding α-hydroxy ketones. The former were synthesized from **1** or **2** via oxidation and stereospecific [2,3] sigmatropic rearrangement.

2. Results and discussion

The allylic sulfides **1** and selenides **2** were readily obtained by regio- and *endo*-stereospecific [4+2] cycloaddition reactions of dienes **3** to a variety of dienophiles **4** in toluene solution under reflux or with Lewis acid catalysis in good yield[18] (Scheme 1). The dienes **3**[19] are easily available from the corresponding thiophosphates[20] or selenophosphates[21] containing an α,β-unsaturated carbonyl moiety as shown in Scheme 1. Treatment of both mentioned phosphates with sodium hydride results in the formation of their enolate anions which undergo rearrangement involving migration of a phosphoryl group from sulfur to oxygen affording thiolate anions. The latter react very readily with ethyl iodide producing the desired dienes **3** in high yield.[19]

Keywords: rearrangements; cyclic ketones; cyclitols; phosphoric acid and derivatives.

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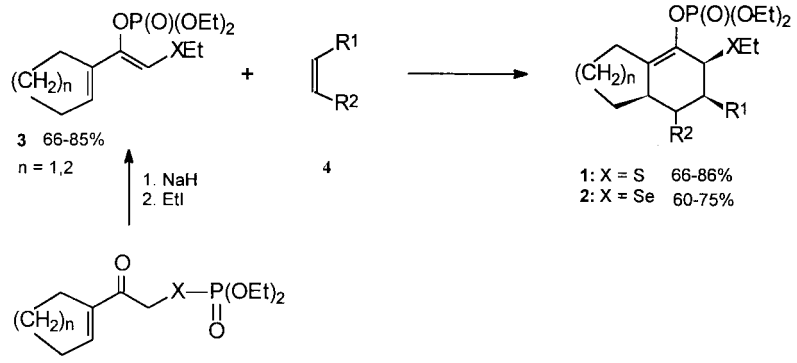


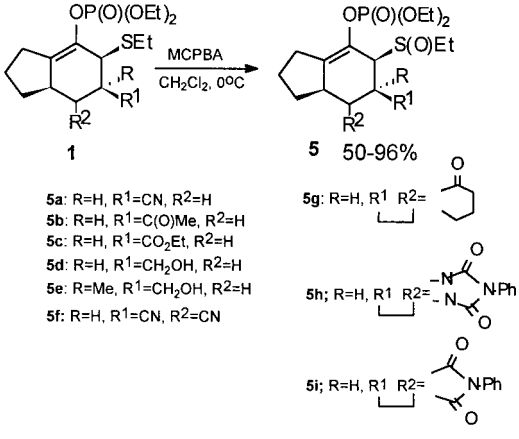
Scheme 1.

Oxidation of the cycloadducts **1** with one equivalent of *m*-chloroperbenzoic acid (MCPBA) at 0°C in dichloromethane affords the sulfoxides **5** in good to high yield (50–96%) (Scheme 2). According to ^{1}H NMR data sulfoxides **5a,c,d,f** were formed as mixtures of two diastereoisomers in 1.6:1; 1:1; 1.5:1 and 2.2:1 ratios respectively. It was not possible to separate diastereoisomers using chromatography. However, formation of a single diastereoisomer was observed in the cases of sulfoxides **5b,e,g,h**.

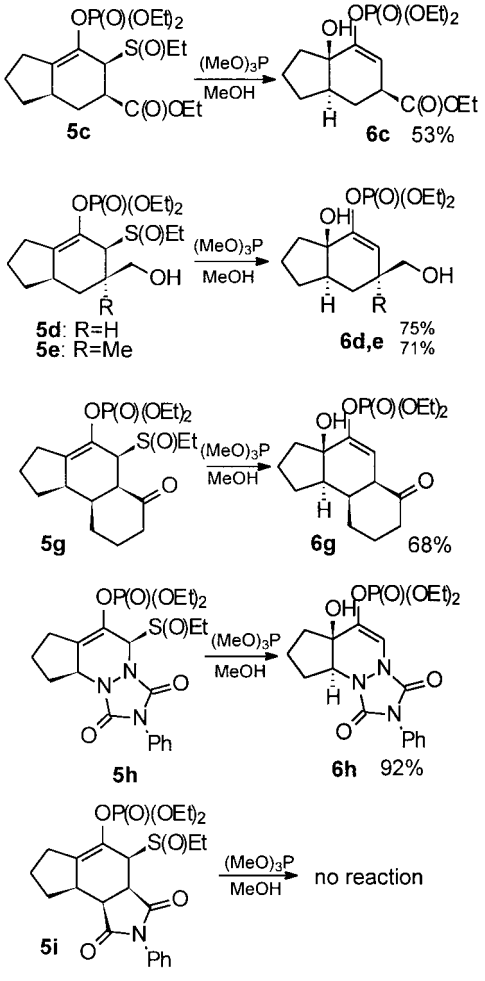
The [2,3] sigmatropic rearrangement of sulfoxides **5c,d, e,g,h,i** performed in the presence of excess trimethyl phosphite in methanol at room temperature led stereospecifically to the corresponding new functionalized bi- or tricyclic allylic alcohols **6** in good yield (53–92%) (Scheme 3).

Sulfoxides **5a,b,** undergo competitive elimination under the same reaction conditions leading to the conjugated dienes **7a,b** (Scheme 4). The main factor governing elimination is the high acidity of the proton in the position β- to an excellent sulfoxide leaving group. Therefore, even in the presence of such a weak base as trimethyl phosphite, elimination takes place. In the case of sulfoxide **5f** in addition to the allylic alcohol the rearrangement product **6f**, its dehydration product conjugated diene **8f** and aromatic compound **9** are formed. The ratio was 5.2:1:1, respectively as shown by ^{1}H and ^{31}P NMR and the products could be separated by chromatography (Scheme 4). A dramatic solvent effect favoring selective [2,3] sigmatropic rearrangement or 1,2-elimination of allylic sulfoxides has been reported.[4,22] We have also found that rearrangement of the sulfoxides **5a** and **5b** in benzene instead of methanol produced much more of the allylic alcohols **6a** and **6b** via a [2,3] sigmatropic rearrangement (the ratio was 5:1 instead of about 2:1 in methanol).

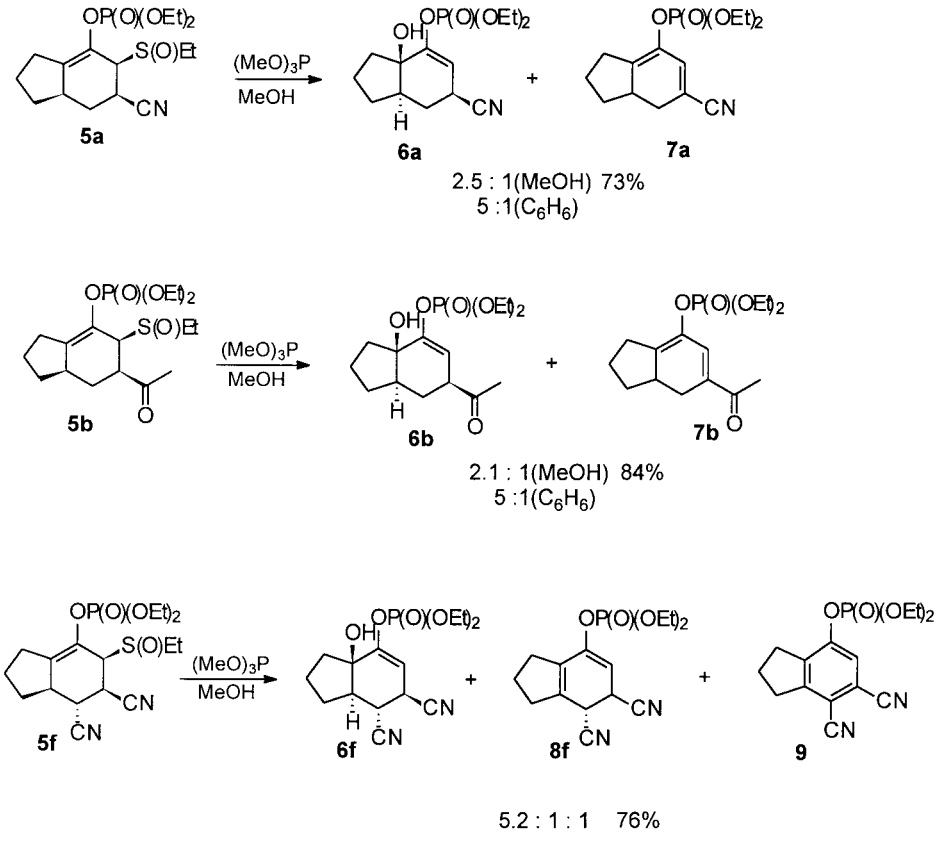
It was of interest to compare the [2,3] sigmatropic rearrangement of sulfoxides **5a,b,i** with the analogous selenoxides derived from cycloadducts **2a,b,i**. Treatment of the latter with the excess H_2O_2 in the presence of pyridine at



Scheme 2.



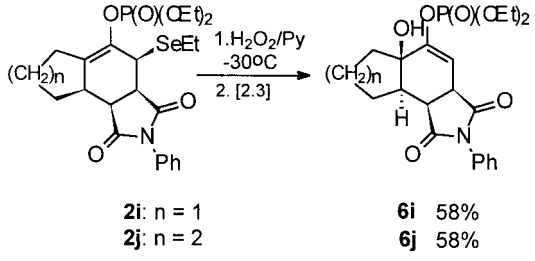
Scheme 3.



Scheme 4.

−30°C and concomitant [2,3] sigmatropic rearrangement of the allylic selenoxides afforded nearly the same ratio of the allylic alcohols **6a, 6b** and conjugated dienes **7a, 7b** as in the case of sulfoxide mentioned above. It is noteworthy that, in contrast to the sulfoxide **5i**, selenoxides obtained via oxidation of cycloadducts **2i** and **2j** easily undergo [2,3] rearrangement giving the tricyclic allylic alcohols **6i** and **6j** stereospecifically (Scheme 5).

When the adduct of **2i** was allowed to react with excess

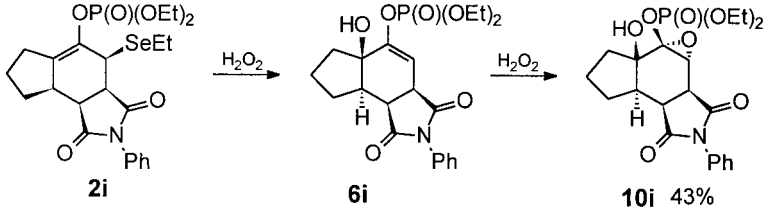


Scheme 5.

H_2O_2 for a long time (20 h at −10°C) in the absence of pyridine, the epoxide **10i** was obtained in 43% yield. Presumably epoxidation of **6i** occurs with H_2O_2 in the presence of selenenic acid generated in situ.[5,22] The epoxidation process is highly stereoselective leading to the epoxy alcohol **10i** (Scheme 6).

X-Ray analysis of a single crystal of **10i** confirmed its anticipated molecular structure and revealed *trans*-fusion of the bicyclic skeleton and *trans* configuration of the epoxide ring relative to the hydroxy group and to *N*-phenylmaleimide (Fig. 1). Epoxide **10i** is very stable and does not undergo rearrangement to the corresponding carbonyl compound. This contrasts with the behaviour of enol phosphate epoxides previously reported.[23]

In all cases presented here, [2,3] sigmatropic rearrangement of sulfoxides **5** and selenoxides is stereospecific giving *trans* isomers. The stereoconfiguration of **6a–i** was determined on the basis of ^{13}C and ^{1}H NMR and X-ray data. *trans*-Fusion of the bicyclic skeleton of allylic alcohols is strongly supported by X-ray analysis of the alcohols **6h** and **6i**.



Scheme 6.

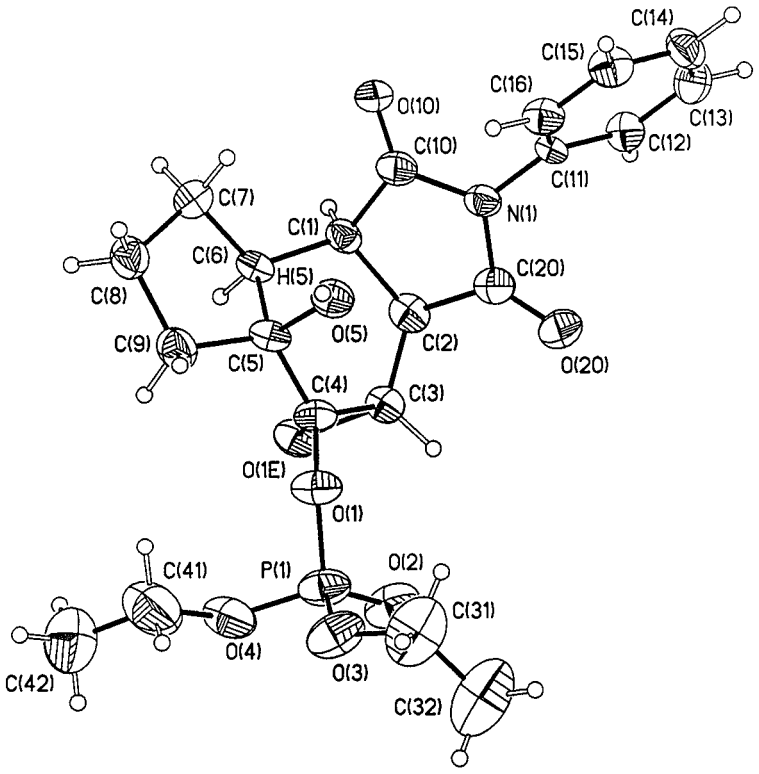


Figure 1. The molecular structure of **10i**. The hydroxy group OH(5) is hydrogen bonded to the P═O group of a neighboring molecule related by a unit cell translation. [O(5)…O(2A) 2.707 and H(5)…O(2A) 1.579 Å].

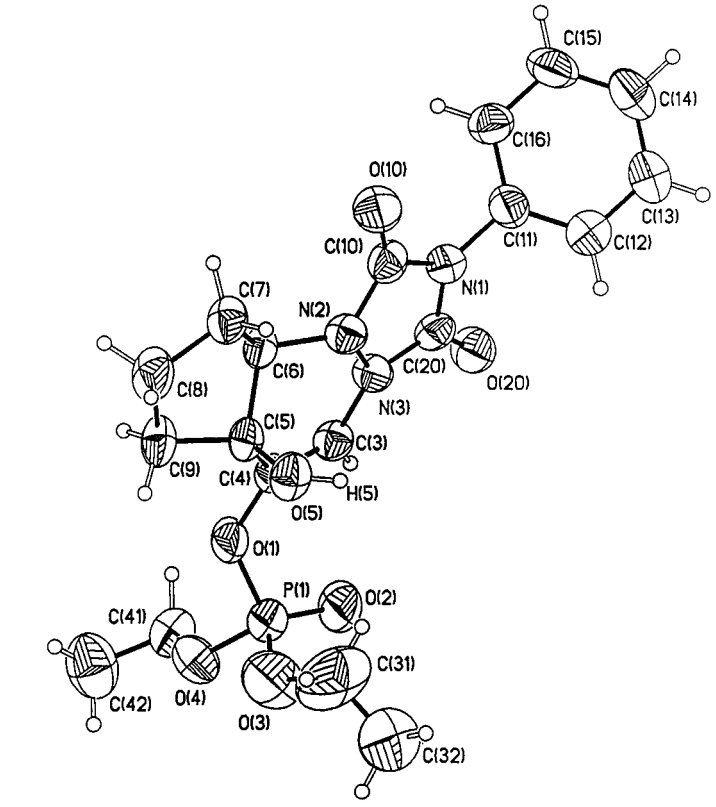


Figure 2. The molecular structure of **6h** in the crystal of **6h**. $0.5(C_6H_{14})$. The hydroxy group OH(5) is hydrogen bonded to the P═O group of a neighboring molecule related by the 2_1-screw axis. [O(5)…O(2A) 2.761 and H(5)…O(2A) 1.736 Å].

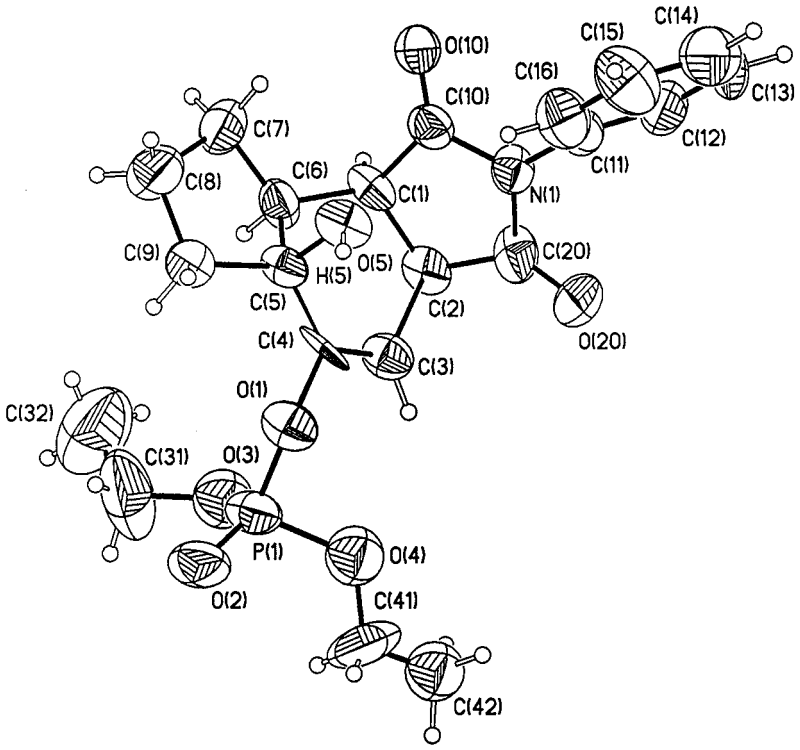
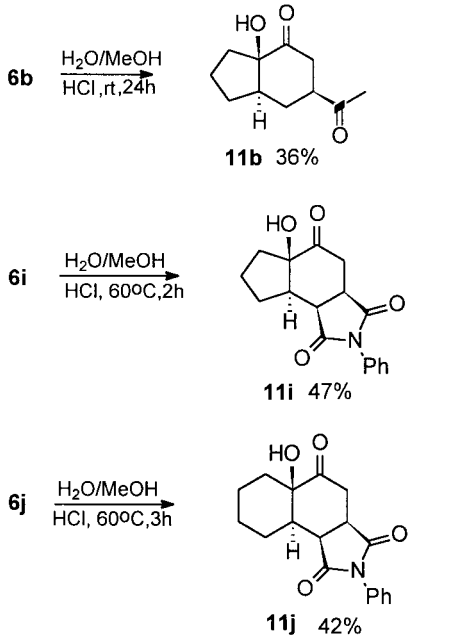


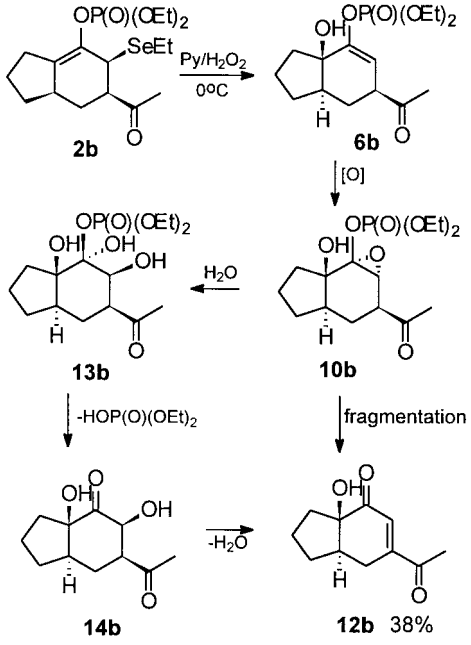
Figure 3. The molecular structure of **6i** (major component). The hydroxy group OH(5) is hydrogen bonded to the P═O group of a neighboring molecule related by an *a*-glide. [O(5)…O(2A) 2.730 and H(5)…O(2A) 1.925 Å].

The molecular structures of **6h** and **6i** are shown in Figs. 2 and 3 respectively, and confirm the *trans* relationship between the hydrogen atom H (6) and the hydroxy group OH (5). Consistent with their double bond character, the unbridged C(3)–C(4) bond lenghts of 1.314(8) and 1.31(2) Å in **6h** and **6i** are significantly shorter than the corresponding epoxide bridged length of 1.444(7) Å in **10i**.

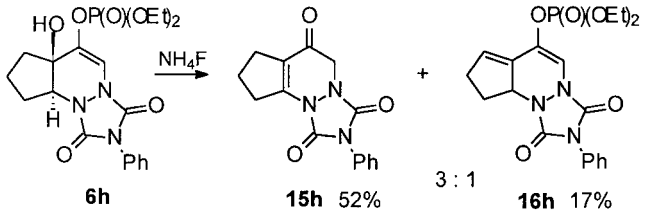
In order to determine the usefulness of allylic alcohols **6** as precursors of the sterically defined novel functionalized bi- or tricyclic α-hydroxy ketones, further investigation of their dephosphorylation was undertaken. Although a number of different chemical transformations of enol phosphates have been reported,[24] there is a lack of efficient methods for dephosphorylation. Therefore the synthetic utility of enol



Scheme 7.



Scheme 8.



Scheme 9.

phosphate systems has been severely limited. The results of our attempts are shown in Schemes 7 and 8.

Acid catalysed hydrolysis of **6** (10% HCl) gave the α-hydroxy ketones **11** in good to moderate yield (Scheme 7).

We also found a new route for the conversion of allylic alcohols **6** to α-hydroxy ketone **12** via an unusual specific elimination (Scheme 8). Oxidation of the selenide **2b** using excess H_2O_2 in the presence of pyridine at 0°C afforded stereospecifically epoxy enol phosphate **10b** via alcohol **6b**. **10b** decomposes under the reaction conditions to ketone **12b**. Transformation of selenide **2b** into **12b** proceeds with 38% overall yield.

There are two possible ways in which formation of **12b** could be accounted for. First, **12b** could be formed by fragmentation. Second, epoxide **10b** in the presence of traces of water undergoes hydrolysis catalyzed by base giving the intermediate triol **13b**. Following elimination of diethyl phosphoric acid from **13b** affords dihydroxy ketone **14b**. Elimination of water from the latter gives the final product **12b**.

It is well known that fluoride anion is a strong base but also an excellent nucleophile towards the phosphoryl phosphorus atom. Therefore, we investigated the reaction of allylic alcohol **6h** (which contains an enol phosphate moiety) with ammonium fluoride. As shown in Scheme 9 this reaction produces a mixture of compounds **15h** and **16h** in a 3:1 ratio. The compounds were separated using gel column chromatography.

Elimination of water and dephosphorylation (via nucleophilic attack of fluoride anion at P^{IV} with the formation of diethyl phosphorofluoridate and the corresponding enol anion) gives tricyclic alkenone **15h**, whereas elimination of water with participation of another hydrogen atom leads to the formation of the new conjugated diene **16h**.

In summary, we have demonstrated a) that cycloadducts **1** and **2** are functionalized versatile synthons having fixed stereochemistry; b) that their [2,3] sigmatropic rearrangement via allylic sulfoxides and selenoxides provides a direct stereospecific entry to new functionalized bi- or tricyclic allylic alcohol systems; c) the ability of the latter to be transformed into the corresponding α-hydroxy ketones.

3. Experimental

All commercial reagents were purchased from Aldrich Chemical Co. or Fluka Chemica or Jansen-Chimica or Merck. Solvent and reagents were purified and dried by conventional methods. Chromatographic purifications were performed on silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with indicated eluents. O,O-dialkyl-S-β-oxoalkenyl thiophosphates,[20] O,O-dialkyl-Se-β-oxoalkenyl seleno-phosphates,[21] (Z)-1,2-dihetero-substituted-1,3-dienes **3**,[19] allyl sulfides **1**,[18] allyl selenides **2**[18] were prepared according to the published procedures. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H, 200.13; ^{13}C, 50.32 and ^{31}P, 81.02 MHz) unless otherwise noted. IR spectra were measured on a Ati Mattson Infinity FTIR 60. MS spectra were recorded on Finnigan MAT 95 spectrometer and LKB 2091 spectrometer. Microanalyses were obtained on a Carlo Erba CHNS-OEA 1108 Elemental Analyzer.

3.1. Oxidation of sulfides 1 to sulfoxides 5

3.1.1. General procedure: A solution of 85% *m*-chloroperbenzoic acid (0.5 mmol) in dichloromethane (50 mL) was added dropwise to the sulfide **1** (0.5 mmol) in dichloromethane (40 mL) at 0°C. Stirring was continued at 0°C for 2 h and then at room temperature for 1 h. The reaction mixture was washed with sodium thiosulphate (2×5 mL), potassium hydrogen carbonate (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 silica gel column chromatography with benzene-ethyl acetate (1:1) as the eluent or, the case of **5d,e** with ethyl acetate-methanol (50:1) as the eluent, to provide pure sulfoxides **5**.

3.1.2. Phosphoric acid 6-cyano-5-ethanesulfinyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 5a: deep orange oil (dense); yield 96%, ratio of diastereoisomers 1.6:1; *Major isomer* of 5a R_f=0.23 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 2240 (CN), 1672 (C=C), 1256 (P=O), 1036 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.35 (dt, $^4J_{PH}$=1.6 Hz, $^3J_{HH}$=6.7 Hz, 3H, OCH_2CH_3), 1.39 (dt, $^4J_{PH}$=1.6 Hz, $^3J_{HH}$=6.7 Hz, 3H, OCH_2CH_3), 1.39 (t, $^3J_{HH}$=7.6 Hz, 3H, $S(O)CH_2CH_3$), 1.52–2.80 (m, 9H), 2.95 (d_{AB}q, $^2J_{HH}$(AB)= 13.1 Hz, $^3J_{HH}$=7.6 Hz, 1H, $S(O)CH_2$), 3.19 (d_{AB}q, $^2J_{HH}$(AB)=13.1 Hz, $^3J_{HH}$=7.6 Hz, 1H, $S(O)CH_2$), 3.37 (ddd, $^3J_{HH}$=3.3, 4.4, 12.9 Hz, 1H, CHCN), 3.85–3.97 (m, 1H, CHS(O)), 4.05–4.25 (m, 4H, 2×OCH_2); ^{13}C NMR ($CDCl_3$) δ 6.80 (s, $S(O)CH_2CH_3$), 14.87 (s, 2×OCH_2CH_3), 21.86 (s), 25.01 (s), 26.26 (s), 29.76 (s), 31.47 (s), 39.68 (s), 44.91 (s), 56.55 (s), 63.30 (d, $^2J_{PC}$=5.6 Hz, 2×OCH_2), 117.85 (s, CN), 127.31 (d, $^3J_{PC}$=8.2 Hz), 138.45 (d, $^2J_{PC}$=6.0 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ –3.98; MS (70 eV) *m/z* 376 (M^+(+H), 0.25), 298 (M^+ (–S(O)Et) 73.02), 297 (M^+ (–HS(O)Et), 25.77), 271 (M^+ (–HCN, –S(O)Et), 21.32), 155 ((H+HOP(O)(OEt)$_2$), 33.59), 143 (M^+ (–HS(O)Et, –HOP(O)(OEt)$_2$), 37.26), 117 (M^+ (–HCN, –S(O)Et, –HOP(O)(OEt)$_2$, 52.40); Anal. Calcd for $C_{16}H_{26}NO_5PS$ (375.42): C, 51.19; H, 6.98; N, 3.73; P, 8.25; Found: C, 51.05; H, 7.03; N, 3.74; P, 8.20; *Minor isomer* of 5a, R_f=0.23 (C_6H_6/EtOAc 1:1); ^{1}H NMR ($CDCl_3$) δ 1.35 (dt; $^4J_{PH}$=1.6 Hz, $^3J_{HH}$=6.7 Hz, 3H, OCH_2CH_3), 1.39 (dt, $^4J_{PH}$=1.6 Hz, $^3J_{HH}$=6.7 Hz, 3H, OCH_2CH_3), 1.39 (t, $^3J_{HH}$=7.6 Hz, 3H, $S(O)CH_2CH_3$), 1.52–2.80 (m, 9H), 2.95 (d_{AB}q; $^2J_{HH}$(AB)=13.1 Hz,

$^3J_{HH}$=7.6 Hz, 1H, S(O)CH_2), 3.19 (d_{AB}q, $^2J_{HH}$(AB)= 13.1 Hz, $^3J_{HH}$=7.6 Hz, 1H, S(O)CH_2), 3.37 (ddd, $^3J_{HH}$=3.3, 4.4, 12.9 Hz, 1H, CHCN), 3.85–3.97 (m, 1H, CHS(O)), 4.05–4.25 (m, 4H, 2×OCH_2); ^{13}C NMR ($CDCl_3$) δ 6.49 (s, S(O)CH_2CH_3), 14.87 (s, 2×OCH_2CH_3), 22.03 (s), 25.42 (s), 26.26 (s), 27.60 (s), 31.47 (s), 39.68 (s), 44.28 (s), 55.41 (s), 63.30 (d, $^2J_{PC}$= 5.6 Hz, 2×OCH_2), 117.85 (s, CN), 130.97 (d, $^3J_{PC}$=8.2 Hz), 134.87 (d, $^2J_{PC}$=6.7 Hz,=COP), ^{31}P NMR ($CDCl_3$) δ −4.36; MS (70 eV) *m/z* 376 (M^+ (+H), 0.25), 298 (M^+ (−S(O)Et), 73.02), 297 (M^+ (−HS(O)Et), 25.77), 271 (M^+ (−HCN, −S(O)Et), 21.32), 155 ((H+ $HOP(O)(OEt)_2$), 33.59), 143 (M^+ (−HS(O)Et, $-HOP(O)(OEt)_2$), 37.26), 117 (M^+ (−HCN, −S(O)Et, $-HOP(O)(OEt)_2$), 52.40); MS (15 eV) *m/z* 376 (M^+ (+H), 0.30), 375 (M^+, 0), 298 (M^+ (−S(O)Et), 100.00), 271 (M^+ (−S(O)Et, −HCN), 23.94), 144 (M^+ (−S(O)Et, $-HOP(O)(OEt)_2$), 17.79), 117 (M^+ (−HCN, −S(O)Et, $-HOP(O)(OEt)_2$), 16.55).

3.1.3. Phosphoric acid 6-acetyl-5-ethanesulfinyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 5b: pale yellow oil; yield 50%; single diastereoisomer; R_f=0.41 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 1700–1695 (C=O, C=C), 1240 (P=O), 1024 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.32 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.36 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.40 (t, $^3J_{HH}$=7.5 Hz, 3H, S(O)CH_2CH_3), 1.47–2.19 (m, 7H), 2.21 (s, 3H, C(O)CH_3), 2.22–2.70 (m, 2H), 3.20 (d_{AB}q, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=13.9 Hz, 1H, S(O)CH_2), 3.28 (d_{AB}q, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=13.9 Hz, 1H, S(O)CH_2), 3.75–3.79 (m, 1H, CHC(O)), 4.01–4.32 (m, 5H, 2×OCH_2, CHC(O)), 4.40–4.44 (m, 1H, CHS(O)); ^{13}C NMR ($CDCl_3$) δ 5.98 (s, S(O)CH_2CH_3), 15.89 (d, $^3J_{PC}$=5.0 Hz, 2×OCH_2CH_3), 23.09 (s), 26.40 (s), 26.48 (s), 26.71 (s), 32.89 (s), 38.87 (s), 47.09 (s), 49.70 (s), 59.20 (s), 64.76 (d, $^2J_{PC}$=5.8 Hz, 2×OCH_2), 130.27 (d, $^2J_{PC}$=9.3 Hz, =COP), 138.37 (d, $^3J_{PC}$=6.6 Hz), 205.28 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −4.24; MS (15 eV) *m/z* 392 (M^+, 0.20), 315 (M^+ (−S(O)Et), 73.30), 314 (M^+ (−HS(O)Et), 10.84), 312 (M^+ ($-H_2$, −HS(O)Et), 71.32), 273 (M^+ (−S(O)Et, −Ac, +H), 69.58), 272 (M^+ (−S(O)Et, −Ac), 5.84), 271 (M^+ (−HS(O)Et, −Ac), 27.57), 155 ((H+$HOP(O)(OEt)_2$), 100.00); Anal. Calcd for $C_{17}H_{29}O_6PS$ (392.45): C, 52.03; H, 7.45; O, 24.46; P, 7.89; Found: C, 52.04; H, 7.43; O, 24.37; P, 7,93.

3.1.4. 7-(Diethoxy-phosphoryloxy)-6-ethanesulfinyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5-carboxylic acid ethyl ester 5c: orange, dense oil; yield 64%; ratio of diastereoisomers: ≈ 1:1; Fast isomer of 5c: R_f=0.1 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 1728 (C=O), 1680 (C=C), 1226 (P=O), 1030 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, $^3J_{HH}$=7.2 Hz, 3H, C(O)OCH_2CH_3), 1.34 (t, $^3J_{HH}$=7.5 Hz, 3H; S(O)CH_2CH_3), 1.35 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.0 Hz, 3H, $POCH_2CH_3$), 1.36 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.0 Hz, 3H, $POCH_2CH_3$), 1.54–1.72 (m, 2H), 1.73–2.09 (m, 3H), 2.37–2.78 (m, 4H), 2.93 (d_{AB}q, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)= 12.9 Hz, 1H, S(O)CH_2), 3.15 (d_{AB}q, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=12.9 Hz, 1H, S(O)CH_2), 3.10–3.20 (m, 1H, CHC(O)O), 4.09–4.27 (m, 6H, 2×$POCH_2$, C(O)OCH_2), 4.31–4.40 (m, 1H, CHS(O)); ^{13}C NMR ($CDCl_3$) δ 8.10 (s, S(O)CH_2CH_3), 13.88 (s, C(O)OCH_2CH_3), 15.92 (d, $^3J_{PC}$=6.3 Hz, 2×$POCH_2CH_3$), 23.21 (s), 25.33 (s), 25.92 (s), 32.66 (s), 41.86 (s), 44.83 (s), 46.24 (s), 59.92 (s), 60.81 (s, C(O)OCH_2), 64.29 (d, $^2J_{PC}$=5.9 Hz, 2×$POCH_2$), 129.89 (d, $^3J_{PC}$=9.0 Hz), 139.91 (d, $^2J_{PC}$=5.8 Hz,=COP), 171.00 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −4.14; MS (15 eV) *m/z* 422 (M^+, 0.05), 345 (M^+ (−S(O)Et), 23.92), 298 (M^+ (−EtOH, −HS(O)Et), 51.62), 270 (M^+ (−HS(O)Et, −C(O)OEt), 84.03), 155 ((H+$HOP(O)(OEt)_2$), 50.87), 117 (M^+ (−C(O)OEt, −HS(O)Et, $-HOP(O)(OEt)_2$), 100.00); Anal. Calcd for $C_{18}H_{31}O_7PS$ (422.48): C, 51.17; H, 7.40; O, 26.51; P, 7.33; Found: C, 51.06; H, 7.36; O, 26.58, P, 7.31. *Slow isomer* of 5c: R_f=0.09 (C_6H_6/EtOAc 1:1); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, $^3J_{HH}$=7.2 Hz, 3H, C(O)OCH_2CH_3), 1.34 (t, $^3J_{HH}$=7.5 Hz, 3H, S(O)CH_2CH_3), 1.35 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.0 Hz, 3H, $POCH_2CH_3$), 1.36 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.0 Hz, 3H, $POCH_2CH_3$), 1.54–1.72 (m, 2H), 1.73–2.09 (m, 3H), 2.37–2.78 (m, 4H), 2.93 (d_{AB}q, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=12.9 Hz, 1H, S(O)CH_2), 3.15 (d_{AB}q, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=12.9 Hz, 1H, S(O)CH_2), 3.10–3.20 (m, 1H, CHC(O)O), 4.09–4.27 (m, 6H, 2×$POCH_2$, C(O)OCH_2), 4.31–4.40 (m, 1H, CHS(O)); ^{13}C NMR ($CDCl_3$) δ 7.06 (s, S(O)CH_2CH_3), 13.88 (s, C(O)OCH_2CH_3), 15.92 (d, $^3J_{PC}$=6.3 Hz, 2×$POCH_2CH_3$), 23.21 (s), 26.20 (s), 26.23 (s), 32.85 (s), 42.92 (s), 44.83 (s), 46.24 (s), 60.53 (s), 61.13 (s, C(O)OCH_2), 64.29 (d; $^2J_{PC}$=5.9 Hz, 2×$POCH_2$), 131.12 (d, $^3J_{PC}$=8.0 Hz), 136.36 (d, $^2J_{PC}$=5.5,Hz,=COP), 171.91 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −4.31; MS (15 eV) *m/z* 422 (M^+, 0.05), 345 (M^+ (−S(O)Et), 23.92), 298 (M^+ (−EtOH, −HS(O)Et), 51.62), 270 (M^+ (−HS(O)Et, −C(O)OEt), 84.03), 155 ((H+$HOP(O)(OEt)_2$), 50.87), 117 (M^+ (−COOEt, −HS(O)Et, $-HOP(O)(OEt)_2$), 100.00).

3.1.5. Phosphoric acid 5-ethanesulfinyl-6-hydroxymethyl-2,3,5,6,7,7a-hexahydro-1-H-inden-4-yl ester diethyl ester 5d: pale yellow oil; yield 86%; ratio of diastereoisomers: 1.5:1; *Major isomer* of 5d: R_f=0.17 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 3350 (br, OH), 1672 (C=O), 1240 (P=O), 1027 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.35 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, $POCH_2CH_3$), 1.36 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, $POCH_2CH_3$), 1.40 (t, $^3J_{HH}$=7.5 Hz, 3H, S(O)CH_2CH_3), 1.47–1.91 (m, 4H), 1.91–2.07 (m, 1H), 2.30–2.70 (m, 5H), 2.93 (q, $^3J_{HH}$=7.5 Hz, 1H, S(O)CH_2), 2.96 (q, $^3J_{HH}$=7.5 Hz, 1H, S(O)CH_2), 3.78 (dd_{AB}, $^3J_{HH}$= 5.3 Hz, $^2J_{HH}$(AB)=12.5 Hz, 1H, CH_2OH), 3.87 (dd_{AB}, $^3J_{HH}$=6.2 Hz, $^2J_{HH}$(AB)=12.5 Hz, 1H, CH_2OH), 3.96–4.03 (m, 1H, CHS(O)), 4.16 (dq, $^3J_{PH}$=0.5 Hz, $^3J_{HH}$=7.1 Hz, 2H, $POCH_2$), 4.19 (dq, $^3J_{PH}$=0.5 Hz, $^3J_{HH}$=7.1 Hz, 2H, $POCH_2$); ^{13}C NMR ($CDCl_3$) δ 7.11 (s, S(O)CH_2CH_3), 16.00 (d, $^3J_{PC}$=5.9 Hz, 2×$POCH_2CH_3$), 23.00 (s), 26.30 (s), 26.89 (s), 32.71 (s), 42.11 (s), 42.52 (s), 43.00 (s), 43.80 (s), 63.17 (s, CH_2OH), 64.23 (d, $^2J_{PC}$=6.6 Hz, 2×$POCH_2$), 130.66 (d, $^3J_{PC}$=8.5 Hz), 140.15 (d, $^2J_{PC}$=6.1 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ −4.23; MS (15 eV) *m/z* 381 (M^+ (+H), 0.18), 363 (M^+ (−OH), 0.10), 303 (M^+ (−S(O)Et), 8.22), 285 (M^+ ($-H_2O$, −S(O)Et), 5.46), 284 (M^+ ($-H_2O$, −HS(O)Et), 5.52), 273 (M^+ (−S(O)Et, $-CH_2OH$, +H), 100.00), 272 (M^+ (−S(O)Et, $-CH_2OH$), 17.71), 271 (M^+ (−HS(O)Et, $-CH_2OH$), 10.73), 243 (M^+ (−HS(O)Et, $-CH_2$=$CHCH_2OH$), 4.93), 227 (M^+ ($-OP(O)(OEt)_2$), 1.15), 155 ((H+$HOP(O)(OEt)_2$), 60.44), 149 (M^+ ($-HOP(O)(OEt)_2$, −S(O)Et), 10.48), 119 (M^+ ($-CH_2OH$, −S(O)Et, $-HOP(O)(OEt)_2$), 51.81), 117 (M^+ ($-CH_2OH_2$, −HS(O)Et, $-HOP(O)(OEt)_2$), 33.10), 91 (M^+ (−S(O)Et, $-OP(O)(OEt)_2$, $-CH_2$=$CHCH_2OH$), 44.43); Anal. Calcd for $C_{16}H_{29}O_6PS$ (380.44): C, 50.51; H, 7.68; O, 25.23; P, 8.14; Found: C,

50.43; H, 7.63; O, 25.27; P, 8.18. *Minor isomer* of 5d: R_f=0.17 (C_6H_6/EtOAc 1:1); ^{1}H NMR ($CDCl_3$) δ 1.35 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, $POCH_2CH_3$), 1.36 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, $POCH_2CH_3$), 1.39 (t, $^3J_{HH}$=7.5 Hz, 3H, $S(O)CH_2CH_3$), 1.47–1.91 (m, 4H), 1.91–2.07 (m, 1H), 2.30–2.70 (m, 5H), 2.85 (dq, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$=13.0 Hz, 1H, $S(O)CH_2$), 3.17 (dq, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$=13.0 Hz, 1H, $S(O)CH_2$), 3.85 (d, $^3J_{HH}$=9.5 Hz, 2H, CH_2OH), 3.91–3.96 (m, 1H, CHS(O)), 4.16 (dq, $^3J_{PH}$= 0.5 Hz, $^3J_{HH}$=7.1 Hz, 2H, $POCH_2$), 4.19 (dq, $^3J_{PH}$=0.5 Hz, $^3J_{HH}$=7.1 Hz, 2H, $POCH_2$); ^{13}C NMR ($CDCl_3$) δ 8.36 (s, $S(O)CH_2CH_3$), 16.05 (d, $^3J_{PC}$=5.9 Hz, $2\times POCH_2CH_3$), 23.19 (s), 26.05 (s), 26.57 (s), 32.85 (s), 42.15 (s), 42.52 (s), 43.01 (s), 45.28 (s), 63.00 (s, CH_2OH), 64.29 (d, $^2J_{PC}$=6.6 Hz, $2\times POCH_2$), 130.83 (d, $^3J_{PC}$=8.6 Hz), 140.17 (d, $^2J_{PC}$= 6.1 Hz, =COP); ^{31}P NMR ($CDCl_3$) δ −4.38; MS (15 eV) *m/z* 381 (M^+ (+H), 0.18), 363 (M^+ (–OH), 0.10), 303 (M^+ (–S(O)Et), 8.22), 285 (M^+ (–H_2O, –S(O)Et), 5.46), 284 (M^+ (–H_2O, –HS(O)Et), 5.52), 273 (M^+ (–S(O)Et, –CH_2OH, +H), 100.00), 272 (M^+ (–S(O)Et, –CH_2OH), 17.71), 271 (M^+ (–HS(O)Et, –CH_2OH), 10.73), 243 (M^+ (–HS(O)Et, –CH_2=$CHCH_2OH$), 4.93), 227 (M^+ (–$OP(O)(OEt)_2$), 1.15), 155 ((H+$HOP(O)(OEt)_2$), 60.44), 149 (M^+ (–$HOP(O)(OEt)_2$, –S(O)Et), 10.48), 119 (M^+ (–CH_2OH, –S(O)Et, –$HOP(O)(OEt)_2$), 51.81), 117 (M^+ (–CH_2OH_2, –HS(O)Et, –$HOP(O)(OEt)_2$), 33.10), 91 (M^+ (–S(O)Et, –$OP(O)(OEt)_2$, –CH_2=$CHCH_2OH$), 44.43).

3.1.6. Phosphoric acid 5-ethanesulfinyl-6-hydroxymethyl-6-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 5e: pale yellow oil; yield 82%, single diastereoisomer; R_f=0.23 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 3313 (br, OH), 1678 (C=C), 1243 (P=O), 1027 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 3H, CCH_3), 1.33 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, $POCH_2CH_3$), 1.35 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, $POCH_2CH_3$), 1.36 (t, $^3J_{HH}$=7.5 Hz, 3H, $S(O)CH_2CH_3$), 1.55–2.12 (m, 5H), 2.33–2.60 (m, 4H), 3.00 (d_{AB}q, $^2J_{HH}$(AB)=13.2 Hz, $^3J_{HH}$=7.5 Hz, 1H, $S(O)CH_2$), 3.13 (d_{AB}, $^2J_{HH}$(AB)=18.0 Hz, 1H, CH_2OH), 3.14 (d_{AB}q, $^2J_{HH}$(AB)=13.2 Hz, $^3J_{HH}$=7.5 Hz, 1H, $S(O)CH_2$), 3.21 (d_{AB}, $^2J_{HH}$(AB)=18.0 Hz, 1H, CH_2OH), 3.48–3.55 (m, 1H, CHS(O)), 4.10–4.24 (m, 5H, $2\times POCH_2$, CH_2OH); ^{13}C NMR ($CDCl_3$) δ 7.42 (s, $S(O)CH_2CH_3$), 16.32 (d, $^3J_{PC}$=6.1 Hz, $2\times POCH_2CH_3$), 23.19 (s), 24.82 (s), 25.84 (s), 32.61 (s), 32.90 (s), 36.15 (s), 41.27 (s, CCH_2OH), 45.34 (s), 64.31 (d, $^2J_{PC}$=5.5 Hz, $2\times POCH_2$), 65.72 (s), 68.41 (s, CH_2OH), 128.95 (d, $^3J_{PC}$=8.3 Hz), 139.55 (d, $^2J_{PC}$=6.0 Hz, =COP); ^{31}P NMR ($CDCl_3$) δ −5.37; MS (CI-isobutane) *m/z* 395 (M^+ (+H), 83.62), 317 (M^+ (–SOEt), 100.00), 299 (M^+ (–SOEt, –H_2O), 34.85); HRMS(CI) Calcd for $C_{17}H_{31}O_6PS$+H (M^++H) 395.1657; Found: 395.1641.

3.1.7. Phosphoric acid diethyl ester 6,7-dicyano-5-ethanesulfinyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl ester 5f: deep dense oil; yield 64%; ratio of diastereoisomers: 2.2:1. *Major isomer* of 5f: R_f=0.18 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 2236 (CN), 1680 (C=C), 1252 (P=O), 1030 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.36 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.0 Hz, 6H, $2\times OCH_2CH_3$), 1.40 (t, $^3J_{HH}$=7.5 Hz, 3H, $S(O)CH_2CH_3$), 1.56–1.82 (m, 1H), 1.82–2.04 (m, 1H), 2.21–2.39 (m, 1H), 2.45–2.82 (m, 4H), 3.00 (d_{AB}q, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=13.1 Hz, 1H, $S(O)CH_2$), 3.21 (d_{AB}q, $^3J_{HH}$= 7.5 Hz, $^2J_{HH}$(AB)=13.1 Hz, 1H, $S(O)CH_2$), 3.42 (dd_{AB}, $^3J_{HH}$=2.3 Hz, $^2J_{HH}$(AB)=12.0 Hz, 1H, CHCN), 3.67 (dd_{AB}, $^3J_{HH}$=4.3 Hz, $^2J_{HH}$(AB)=12.0 Hz, 1H, CHCN), 3.96–4.05 (m, 1H, CHS(O)), 4.09–4.27 (m, 4H, $2\times OCH_2$); ^{13}C NMR ($CDCl_3$) δ 7.66 (s, $S(O)CH_2CH_3$), 15.63 (d, $^3J_{PC}$=3.3 Hz, $2\times OCH_2CH_3$), 22.18 (s), 26.11 (s), 29.75 (s), 31.38 (s), 34.27 (s), 43.62 (s), 45.49 (s), 56.29 (s), 64.54 (d, $^2J_{PC}$=5.6 Hz, $2\times OCH_2$), 115.50 (s, CN), 117.30 (s, CN), 127.54 (d, $^3J_{PC}$=8.1 Hz), 141.13 (d, $^2J_{PC}$= 5.9 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ −4.25; MS (15 eV) *m/z* 400 (M^+, 0.09), 323 (M^+ (–S(O)Et), 15.47), 155 ((H+ $HOP(O)(OEt)_2$), 42.03); Anal. Calcd for $C_{17}H_{25}N_2O_5PS$ (400.43): C, 50.99; H, 6.29; N, 7.00; O, 19.98; P, 7.74; Found: C, 51.12; H, 6.27; N, 6.95; O, 20.01; P, 7.03. *Minor isomer* of 5f: R_f=0.18 (C_6H_6/EtOAc 1:1); ^{1}H NMR ($CDCl_3$) δ 1.36 (dt, $^4J_{PH}$= 1.1 Hz, $^3J_{HH}$=7.0 Hz, 6H, $2\times OCH_2CH_3$), 1.40 (t, $^3J_{HH}$= 7.5 Hz, 3H, $S(O)CH_2CH_3$), 1.56–1.82 (m, 1H), 1.82–2.04 (m, 1H), 2.21–2.39 (m, 1H), 2.45–2.82 (m, 4H), 3.05 (q, $^3J_{HH}$=7.5 Hz, 1H, $S(O)CH_2$), 3.15 (q, $^3J_{HH}$=7.5 Hz, 1H, $S(O)CH_2$), 3.50 (dd_{AB}, $^3J_{HH}$=2.7 Hz, $^2J_{HH}$(AB)=11.0 Hz, 1H, CHCN), 3.55 (dd_{AB}, $^3J_{HH}$=1.2 Hz, $^2J_{HH}$(AB)=11.0 Hz, 1H, CHCN), 3.96–4.05 (m, 1H, CHS(O)), 4.09–4.27 (m, 4H, $2\times OCH_2$); ^{13}C NMR ($CDCl_3$) δ 7.45 (s, $S(O)CH_2CH_3$), 15.63 (d, $^3J_{PC}$=3.3Hz, $2\times OCH_2CH_3$), 22.41 (s), 26.60 (s), 30.15 (s), 30.82 (s), 31.57 (s), 43.63 (s), 45.27 (s), 53.82 (s), 64.54 (d, $^2J_{PC}$=5.6 Hz, $2\times OCH_2$), 115.63 (s, CN), 117.47 (s, CN), 131.95 (d, $^3J_{PC}$=8.1 Hz), 133.15 (d, $^2J_{PC}$=6.9 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ −4.85; MS (15 eV) *m/z* 400 (M^+, 0.09), 323 (M^+ (–S(O)Et), 15.47), 155 ((H+$HOP(O)(OEt)_2$), 42.03).

3.1.8. Phosphoric acid 5-ethanesulfinyl-6-oxo-2,3,5,5a, 6,7,8,9,9a,9b-decahydro-1-H-cyclopenta [*a*] naphthalen-4-yl ester diethyl ester 5g: pale yellow dense oil; yield 72%, single diastereoisomer, R_f=0.19 (EtOAc); IR (film) cm^{-1} 1675 (d, C=O, C=C), 1258 (P=O), 1020 (S(O)Et); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28 (t, $^3J_{HH}$=7.8 Hz, 3H, $S(O)CH_2CH_3$), 1.33 (t, $^3J_{HH}$=6.9 Hz, 3H, OCH_2CH_3), 1.34 (t, $^3J_{HH}$=6.9 Hz, 3H, OCH_2CH_3), 1.48 (dtt, *J*=6.8, 11.8, 12.0 Hz, 1H), 1.53–1.64 (m, 1H), 1.65–1.72 (m, 1H), 1.76–1.91 (m, 4H), 1.99–2.07 (m, 1H), 2.40–2.50 (m, 2H), 2.53–2.72 (m, 3H), 2.59 (dd, $^3J_{HH}$=7.4, 7.8 Hz, 1H), 2.86 (dq, $^3J_{HH}$=7.6 Hz, $^2J_{HH}$=13.1 Hz, 1H, $S(O)CH_2$), 3.17 (dd, $^3J_{HH}$=7.4, 6.0 Hz, 1H, CHC(O)), 3.21 (dq, $^3J_{HH}$=7.6 Hz, $^2J_{HH}$=13.1 Hz, 1H, $S(O)CH_2$), 4.01 (ddd, $^4J_{PH}$=1.8 Hz, $^4J_{HH}$=1.9 Hz, $^3J_{HH}$=6.0 Hz, 1H, CHS(O)), 4.16 (q, $^3J_{HH}$= 6.9 Hz, 2H, OCH_2), 4.21 (q, $^3J_{HH}$=6.9 Hz, 2H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 8.28 (s, $S(O)CH_2CH_3$), 16.08 (d, $^3J_{PC}$=6.7 Hz, $2\times OCH_2CH_3$), 18.33 (s), 19.94 (s), 23.39 (s), 26.65 (s), 28.92 (s), 32.71 (s), 39.05 (s), 44.32 (s), 46.94 (s), 52.24 (s), 59.26 (s), 64.41 (d, $^2J_{PC}$=6.8 Hz, $2\times OCH_2$), 129.62 (d, $^3J_{PC}$=8.6 Hz), 137.85 (d, $^2J_{PC}$=6.8 Hz,=COP), 212.84 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −3.91; MS (15 eV) *m/z* 418 (M^+, 0), 340 (M^+ (–HS(O)Et), 81.32), 312 (M^+ (–HS(O)Et, –CO), 20.05); 186 (M^+ (–$HOP(O)(OEt)_2$, –HS(O)Et), 100.00), 158 (M^+ (–HS(O)Et, –HOP(O) $(OEt)_2$, –CO), 64.12), 155 ((H+$HOP(O)(OEt)_2$), 76.41); Anal. Calcd for $C_{19}H_{31}O_6PS$ (418.49): C, 54.53; H, 7.47; O, 22.94; P, 7.40; Found: C, 54.58; H, 7.51; O, 22.99; P, 7.47.

3.1.9. Phosphoric acid 5-ethanesulfinyl-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 diethyl ester 5h: pale yellow dense oil; yield 92%; single diastereoisomer;

R_f=0.37 (C_6H_6/EtOAc 1:1), mp 55–57°C (recrystallization from: benzene – hexane); IR (film) cm^{-1} 1750 (C=O), 1690 (C=C), 1265 (d, P=O), 1041 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.38 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.39 (t, $^3J_{HH}$=7.5 Hz, 3H, $S(O)CH_2CH_3$), 1.40 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.75–2.10 (m, 4H), 2.46–2.80 (m, 3H), 3.09 ($d_{AB}q$, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=13.3 Hz, 1H, $S(O)CH_2$), 3.25 ($d_{AB}q$, $^3J_{HH}$= 7.5 Hz, $^2J_{HH}$(AB)=13.3 Hz, 1H, $S(O)CH_2$), 4.05–4.32 (m, 4H, 2×OCH_2), 5.76–5.81 (m, 1H, CHS(O)), 7.32–7.55 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 7.22 (s, $S(O)CH_2CH_3$), 15.87 (d, $^3J_{PC}$=3.9 Hz, 2×OCH_2CH_3), 21.68 (s), 24.38 (s), 31.71 (s), 47.04 (s), 59.44 (s), 65.01 (d, $^2J_{PC}$=6.3 Hz, 2×OCH_2), 69.03 (s), 125.59 (s, *o*-C_6H_5), 128.04 (s, *p*-C_6H_5), 128.78 (s, *m*-C_6H_5), 130.33 (d, $^2J_{PC}$=6.8 Hz, =COP), 130.82 (s, *i*-C_6H_5), 131.63 (d, $^3J_{PC}$=8.2 Hz), 151.40 (s, C=O), 153.28 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −4.31; MS (15 eV) *m/z* 419 (M^+ (–HS(O)Et), 31.51), 155 ((H+HOP(O)$(OEt)_2$), 10.37), 78 ((HS(O)Et), 47.16), 77 ((S(O)Et) or (C_6H_5), 23.20), 61 ((SEt) 100.00); Anal. Calcd for $C_{21}H_{28}N_3O_7PS$ (497.51): C, 50.70; H, 5.67; N, 8.45; O, 22.51; P, 6.23; Found: C, 50.83; H, 5.70; N, 8.41; O, 22.59; P, 6.24.

3.1.10. Phosphoric acid 4-ethanesulfinyl-1,3-dioxo-2-phenyl-1,2,3,3a,4,6,7,8,8a,8b-deca-hydro-2-aza-*as*-indacen-5-yl ester diethyl ester 5i: pale yellow dense oil; yield 86%, single diastereoisomer, R_f=0.33 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 1718 (C=O), 1600 (C=C), 1250 (P=O), 1030 (S(O)Et); ^{1}H NMR ($CDCl_3$) δ 1.33 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.35 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.38 (t, $^3J_{HH}$=7.5 Hz, 3H, $SOCH_2CH_3$), 1.60–1.91 (m, 2H), 2.08–2.34 (m, 2H), 2.44–2.71 (m, 2H), 2.70–2.93 (m, 1H), 3.36 (dd, $^3J_{HH}$= 7.0, 9.2 Hz, 1H, CHC(O)), 3.03 ($d_{AB}q$, $^3J_{HH}$=7.5 Hz, $^2J_{HH}$(AB)=13.0 Hz, 1H, $SOCH_2$), 3.54 ($d_{AB}q$, $^3J_{HH}$= 7.5 Hz, $^2J_{HH}$(AB)=13.0 Hz, 1H, $SOCH_2$), 3.60 (dd, $^3J_{HH}$= 7.0, 8.5 Hz, 1H, CHC(O)), 3.65–3.77 (m, 1H, $CHSO_2$), 4.06–4.26 (m, 4H, 2×OCH_2), 7.18–7.25 (m, 2H, *o*-C_6H_5), 7.39–7.51 (m, 3H, *p*-C_6H_5, *m*-C_6H_5); ^{13}C NMR ($CDCl_3$) δ 8.39 (s, $SOCH_2CH_3$), 15.03 (d, $^3J_{PC}$=6.3 Hz, OCH_2CH_3), 15.98 (d, $^3J_{PC}$=6.3 Hz, OCH_2CH_3), 25.81 (s), 27.23 (s), 40.92 (s), 41.19 (s), 46.60 (s), 50.03 (s), 60.41 (d, $^3J_{PC}$= 6.5 Hz, CHSO), 64.84 (d, $^2J_{PC}$=6.1 Hz, OCH_2), 65.05 (d, $^2J_{PC}$=6.1 Hz, OCH_2), 126.75 (s, *o*-C_6H_5), 127.87 (s, *p*-C_6H_5), 130.37 (s, *m*-C_6H_5), 131.39 (d, $^3J_{PC}$=5.9 Hz), 133.16 (s, *i*-C_6H_5), 133.44 (d, $^2J_{PC}$=5.3 Hz,=COP), 175.28 (s, C=O), 175.72 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −4.93; MS (CI-isobutane) *m/z* 496 (M^+ (+H), 47.82), 418 (M^+ (–SOEt), 100.00), 155 ((H+HOP(O)$(OEt)_2$), 21,47); HRMS(CI) Calcd for $C_{23}H_{30}NO_7PS$ + H (M^+ +H) 496.1559; Found: 496.1547.

3.2. Sigmatropic rearrangement of 5a–i. Preparation of allylic alcohols 6a–i

3.2.1. General procedure. To a solution of sulfoxide **5** (5 mmol) in dry methanol (10 mL), or benzene under dry argon was added trimethyl phosphite (100 mmol). The reaction mixture was stirred at 20°C for 5 to 20 days (depending on sulfoxide). Progress of the reaction was followed by TLC chromatography. When the reaction was complete, solvent and the excess of phosphite were removed in vacuo (0.1 mmHg). The concentrate was purified by silica gel column chromatography with benzene-ethyl acetate (1:1) but in the case of allylic alcohols **6d,e** with ethyl acetate-methanol (10:1) as the eluent.

3.2.2. Phosphoric acid 6-cyano-3a-hydroxy 2,3,3a,6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 6a and **Phosphoric acid 6-cyano-2,3,7,7a-tetrahydro-1*H*-inden-4-yl ester diethyl ester 7a**. **6a** and **7a** are prepared as in general procedure. Reaction of **5a** in methanol solution afforded the mixture of **6a** and **7a** in the ratio 2.5:1, in benzene solution the mixture of **6a** and **7a** in the ratio 5:1 respectively. After workup compounds **6a** and **7a** were separated by column chromatography. 6a: pale yellow oil; yield 53%, R_f=0.41 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 3420 (OH), 2241 (CN), 1672 (C=C), 1260 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.34 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.37 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.61–2.05 (m, 4H), 2.21–2.77 (m, 3H), 2.98–3.64 (m, 3H), 4.14 (dq, $^3J_{PH}$=1.2 Hz, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 4.19 (dq, $^3J_{PH}$= 1.2 Hz, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 5.27 (dd, $^3J_{HH}$=2.5 Hz, $^4J_{PH}$=3.0 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 16.46 (d, $^3J_{PC}$=5.7 Hz, 2×OCH_2CH_3), 22.82 (s), 25.04 (s), 31.48 (s), 33. (s), 33.85 (s), 45.73 (s), 64.18 (d $^2J_{PC}$=5.0 Hz, 2×OCH_2), 79.12 (s, C-OH), 101.52 (d, $^3J_{PC}$=6.3 Hz,=CH), 104.59 (CN), 136.26 (d, $^2J_{PC}$= 5.1 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ −3.49; MS (15 eV) *m/z* 315 (M^+, 16.84), 297 (M^+ (–H_2O), 34.92), 155 ((H+HOP(O)$(OEt)_2$), 8.42); HRMS(CI) Calcd for $C_{14}H_{22}NO_5P$ + H (M^+ +H) 316.1314; Found: 316.1325. – 7a: deep yellow dense oil; yield 20%; R_f=0.74 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 2242 (CN), 1672 (C=C), 1261 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.35 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.36 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.50–1.67 (m, 1H), 1.87–2.28 (m, 4H), 2.45–2.95 (m, 4H), 2,51 (dd, $^3J_{HH}$=8.0, 16.2 Hz, 1H, CH_2–C(CN)=), 4.15 (dq, $^3J_{PH}$= 0.7 Hz, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 4.19 (dq, $^3J_{PH}$=0.7 Hz, $^3J_{HH}$= 7.1 Hz, 2H, OCH_2), 6.69 (d, $^4J_{PH}$=3.1 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 15.36 (d, $^3J_{PC}$=6.2 Hz, 2×OCH_2CH_3), 25.84 (s), 27.64 (s), 30.73 (s), 31.28 (s), 32.93 (s), 44.17 (s), 64.41 (d, $^2J_{PC}$=5.8 Hz, 2×OCH_2CH_3), 117.52 (s, CN), 121.69 (s, ⟩C⟨), 131.25 (s,=CH), 132.33 (d, $^3J_{PC}$=6.3 Hz), 145.82 (d, $^2J_{PC}$=5.2 Hz,=COP), ^{31}P NMR ($CDCl_3$) δ −4.78; MS (15 eV) *m/z* 297 (M^+ 13.75), 295 (M^+ (–H_2), 63.94), 254 (M^+ (–Ac), 23.78), 155 ((H+HOP(O)$(OEt)_2$), 35.75), 143 (M^+ (–HOP(O)$(OEt)_2$), 53.71), 100 (M^+ (–HOP(O)$(OEt)_2$, –Ac), 100.00); Anal. Calcd for $C_{14}H_{20}NO_4P$ (297.29): C, 56.56; H, 6.78; N, 4.71; O, 21.53; P, 10.42; Found: C, 56.51; H, 6.71; N, 4.75; O, 21.54; P, 10.46.

3.2.3. Phosphoric acid 6-acetyl-3a-hydroxy-2,3,3a,6,7,7a-hexahydro-1*H*-inden-4yl ester diethyl ester 6b and **Phosphoric acid 6-acetyl-2,3,7,7a-tetrahydro-1*H*-inden-4-yl ester diethyl ester 7b**. **6b** and **7b** are prepared as in general procedure. The reaction of **5b** in methanol solution afforded the mixture of **6b** and **7b** in the ratio 2.1:1, in benzene solution the mixture of **6b** and **7b** in the ratio 5:1 respectively. After workup compounds **6b** and **7b** were separated by column chromatography. **6b**: pale yellow oil; yield 57%; R_f=0,36 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 3452 (OH), 1680 (d, C=O, C=C), 1229 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.33 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.35 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.60–2.07

(m, 4H), 2.19–2.75 (m, 3H), 2.96–3.66 (m, 3H), 3.12 (s, 3H, $C(O)CH_3$), 4.13 (dq, $^3J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 4.20 (dq, $^3J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 5.32 (dd, $^3J_{HH}$= 2.4 Hz, $^4J_{PH}$=2.8 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 16.05 (d, $^3J_{PC}$=6.1 Hz, 2×OCH_2CH_3), 20.12 (s), 24.52 (s), 30.34 (s), 32.73 (s), 35.96 (s), 38.02 (s), 47.08 (s), 64.33 (d, $^2J_{PC}$=6.1 Hz, 2×OCH_2), 81.30 (s, C–OH), 103.53 (d, $^3J_{PC}$=6.0 Hz,=CH), 135.49 (d, $^2J_{PC}$=5.7 Hz,=COP) 194.07 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −3.41; HRMS(CI) Calcd for $C_{15}H_{25}O_6P$ + H (M^+ +H) 333.1467; Found: 333.1474. – 7b: pale yellow oil; yield 27%; R_f=0.57 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 1699, 1657, 1580 (C=O, C=C), 1263 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.35 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.36 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.47–2.24 (m, 4H), 2.25–2.77 (m, 3H), 2.33 (s, 3H, $C(O)CH_3$), 2.98 (d, J=8.1 Hz, 1H, $CH_2CC(O)$), 3.00 (d, $^3J_{HH}$=8.0 Hz, 1H, $CH_2CC(O)$), 4.17 (q, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 4.21 (q, J=7.1 Hz, 2H, OCH_2), 6.91 (d, $^4J_{PH}$=2.9 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 16.95 (d, $^3J_{PC}$=6.7 Hz, 2×OCH_2CH_3), 23.75 (s), 25.73 (s), 27.39 (s), 29.73 (s), 34.04 (s), 35.94 (s), 65.07 (d, $^2J_{PC}$=5.8 Hz, 2×OCH_2), 124.62 (s,=CH), 132.38 (d, $^3J_{PC}$=6.1 Hz), 143.79 (s), 148.16 (d, $^2J_{PC}$= 5.6 Hz,=COP), 199.24 (s, C=O). ^{31}P NMR ($CDCl_3$) δ −4.87; MS (15 eV) *m/z* 314 (M^+, 5.14), 313 (M^+ (–H), 15.58), 312 (M^+ ($-H_2$), 100.00), 297 (M^+ ($-H_2$, –Me), 3.75), 269 (M^+ ($-H_2$, –Ac), 5.43), 158 (M^+ ($-H_2$, –HOP(O)$(OEt)_2$), 20.10), 155 ((H+HOP(O)$(OEt)_2$), 9.78), 143 (M^+ ($-H_2$, –Me, –HOP(O)$(OEt)_2$), 11.78); Anal. Calcd for $C_{15}H_{23}O_5P$ (314.32): C, 57.32; H, 7.38; O, 25.45; P, 9.85; Found: C, 57.21; H, 7.34; O, 25.39; P, 9.89.

3.2.4. 7-(Diethoxyphosphoryloxy)-7a-hydroxy-2, 3, 3a, 4, 5, 7a-hexahydro-1*H*-indene-5-carboxylic acid ethyl ester 6c: pale yellow oil; yield 53%, R_f=0.39 (EtOAc); IR (film) cm^{-1} 3510 (OH), 1710, 1670 (C=O, C=C), 1226 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.33 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.34 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.35 (t, $^3J_{HH}$=7.5 Hz, 3H, $C(O)OCH_2CH_3$), 1.57–2.09 (m, 4H), 2.16–2.73 (m, 3H), 2.95–3.69 (m, 3H), 4.06–4.32 (m, 6H, $C(O)OCH_2$, 2×OCH_2), 5.24 (dd, $^3J_{HH}$=2.7 Hz, $^4J_{PH}$=2.9 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 15.31 (s, $C(O)OCH_2CH_3$), 16.16 (d, $^3J_{PC}$=6.3 Hz, 2×OCH_2CH_3), 22.92 (s), 25.71 (s), 31.33 (s), 37.90 (s), 45.55 (s), 64.08 (d, $^2J_{PC}$=6.2 Hz, 2×OCH_2), 65.73 (s, $C(O)OCH_2$), 79.58 (s, C–OH), 105.52 (d, $^3J_{PC}$=6.6 Hz,=CH), 137.79 (d, $^2J_{PC}$=5.6 Hz,=COP), 195.71 (s, C=O); ^{31}P NMR ($CDCl_3$) δ −4.51; HRMS(CI) Calcd for $C_{16}H_{27}O_7P$ + H (M^+ +H) 363.1572; Found: 363.1586.

3.2.5. Phosphoric acid diethyl ester 3a-hydroxy-6-hydroxymethyl-2,3,3a,6,7,7a-hexahydro-1*H*-inden-4-yl ester 6d: pale yellow oil; yield 75%; R_f=0.12 (EtOAc); IR (film) cm^{-1} 3350 (br, OH), 1630 (C=C), 1243 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.35 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.37 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.35–2.03 (m, 7H), 2.12–2.32 (m, 2H, 2×OH), 2.47–2.95 (m, 3H), 3.85–4.04 (m, 2H, CH_2OH), 4.04–4.36 (m, 4H, 2×OCH_2), 5.36 (dd, $^4J_{PH}$=2.7 Hz, $^3J_{HH}$=3.1 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 15.82 (d, $^3J_{PC}$=6.2 Hz, 2×OCH_2CH_3), 17.28 (s), 25.81 (s), 27.43 (s), 33.47 (s), 42.97 (s), 43.10 (s), 64.03 (d, $^2J_{PC}$=5.2 Hz, 2×OCH_2), 68.28 (s, CH_2OH), 77.21 (C–OH), 111.54 (d, $^4J_{PC}$= 4.2 Hz,=CH), 132.86 (d, $^3J_{PC}$=5.3 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ −3.05; MS (15 eV) *m/z* 320 (M^+, 0.7), 302 (M^+ ($-H_2O$), 1.76), 284 (M^+ (−2×H_2O), 17.87), 272 (M^+ (–OH, $-CH_2OH$), 4.87), 155 ((H+HOP(O)$(OEt)_2$), 49.77), 149 (M^+ ($-H_2O$, –HOP(O)$(OEt)_2$), 17.88), 130 (M^+ (-2×H_2O, –HOP(O)$(OEt)_2$), 23.54); HRMS(CI) Calcd for $C_{14}H_{25}O_6P$ + H (M^+ +H) 321.1467; Found: 321.1452.

3.2.6. Phosphoric acid diethyl ester 3a-hydroxy-6-hydroxymethyl-6-methyl-2, 3, 3a, 6, 7, 7a-hexahydro-1*H*-inden-4-yl ester 6e: pale yellow oil; yield 71%; R_f=0.22 (EtOAc); IR (film) cm^{-1} 3300 (br, OH), 1670 (C=C), 1243 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.34 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.36 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.34–2.04 (m, 6H), 2.10–2.30 (m, 2H, 2×OH), 2.45–2.97 (m, 3H), 3.83–4.05 (m, 2H, CH_2OH), 4.06–4.38 (m, 4H, 2×OCH_2), 5.31 (d, $^4J_{PH}$=2.5 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 16.07 (d, $^3J_{PC}$=6.0 Hz, 2×OCH_2CH_3), 17.32 (s), 24.84 (s), 26.37 (s), 28.18 (s), 32.46 (s), 43.29 (s), 43.91 (s), 64.16 (d, $^2J_{PC}$=5.7 Hz, 2×OCH_2), 68.83 (s, CH_2OH), 79.37 (C–OH), 110.39 (d, $^4J_{PC}$=4.7 Hz,=CH), 133.03 (d, $^3J_{PC}$= 5.0 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ −3.81; MS (15 eV) *m/z* 334 (M^+, 21.58), 316 (M^+ ($-H_2O$), 36.90); HRMS(CI) Calcd for $C_{15}H_{27}O_6P$ + H (M^+ +H) 335.1623; Found: 335.1616.

3.2.7. Phosphoric acid 6,7-dicyano-3a-hydroxy-2,3,3a, 6,7,7a-hexahydro-1*H*-inden-4-yl ester diethyl ester 6f and **Phosphoric acid 6,7-dicyano-2,3,6,7-tetrahydro-1*H*-inden-4-yl ester diethyl ester 8** and **Phosphoric acid 6,7-dicyano-indan-4-yl ester diethyl ester 9**. **6f**, **8** and **9** are prepared as in general procedure. The reaction of **5f** in methanol solution afforded the mixture of **6f**, **8**, **9** in the ratio 5.2:1:1 respectively. After workup compounds **6f**, **8** and **9** were separated by column chromatography. **6f**: deep yellow dense oil, yield 46%; R_f=0.45 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 3450 (OH), 2236 (CN), 1668 (C=C), 1260 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.36 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.38 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.66–2.04 (m, 3H), 2.24–2.75 (m, 3H), 3.00–3.62 (m, 3H), 4.15 (dq, $^3J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 4.20 (dq, $^3J_{PH}$=1.0 Hz, $^3J_{HH}$= 7.1 Hz, 2H, OCH_2), 5.31 (dd, $^3J_{HH}$=2.7 Hz, $^4J_{PH}$=2.9 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$) δ 15.96 (d, $^3J_{PC}$=6.2 Hz, 2×OCH_2CH_3), 21.48 (s), 25.73 (s), 27.92 (s), 30.04 (s), 33.11 (s), 43.08 (s), 64.07 (d, $^2J_{PC}$=5.7 Hz, 2×OCH_2), 112.42 (d, $^3J_{PC}$=5.3 Hz), 113.73 (s,=CH), 120.37 (s, CN), 123.30 (s, CN), 144.92 (d, $^2J_{PC}$= 5.2 Hz,=COP); ^{31}P NMR ($CDCl_3$) δ −3.64; MS (15 eV) *m/z* 340 (M^+, 1.29), 323 (M^+ (–OH), 8.91), 322 (M^+ ($-H_2O$), 5.67), 295 (M^+ ($-H_2O$, –HCN), 5.84), 294 (M^+ ($-H_2O$, $-H_2CN$), 13.54), 266 (M^+ ($-(H_2CN)_2$, $-H_2O$), 13.22), 185 (M^+ (–HOP(O)$(OEt)_2$), 2.13), 168 (M^+ ($-H_2O$, –HOP(O)$(OEt)_2$), 5.18), 155 ((H+HOP(O)$(OEt)_2$), 19.07), 141 (M^+ ($-H_2O$, –HCN, –HOP(O)$(OEt)_2$), 10.75), 115 (M^+ ($-H_2O$, $-(HCN)_2$, –OP(O)$(OEt)_2$), 4.03); HRMS(CI) Calcd for $C_{15}H_{21}N_2O_5P$ + H (M^+ +H) 341.1266; Found: 341.1277. – 8: deep yellow dense oil; yield 20%; R_f=0.39 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 2236 (CN), 1673 (d, C=C), 1253 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.36 (dt, $^4J_{PH}$= 1.0 Hz, $^3J_{HH}$=7.1 Hz, 6H, 2×OCH_2CH_3), 1.87 (quint, $^3J_{HH}$=7.2 Hz, 1H), 1.89 (quint,

$^3J_{HH}$=7.2 Hz, 1H), 2.51–2.63 (m, 2H), 2.69 (dt, $^3J_{HH}$= 7.2 Hz, $^4J_{HH}$=1.8 Hz, 1H, CH–C═), 2.71 (dt, $^3J_{HH}$= 7.2 Hz, $^4J_{HH}$=1.8 Hz, 1H, CH–C═), 2.88–3.00 (m, 2H, 2×CHCN), 3.70–3.81 (m, 1H,═CH), 4.05–4.23 (m, 4H, 2×OCH_2); ^{13}C NMR ($CDCl_3$) δ 15.90 (d, $^3J_{PC}$=6.6 Hz, 2×OCH_2CH_3), 23.66 (s), 27.38 (s), 28.41 (s), 30.10 (s), 32.10 (s), 64.96 (d, $^2J_{PC}$=5.6 Hz, 2×OCH_2), 116.13 (s, CN), 117.56 (s, CN), 125.17 (d, $^2J_{PC}$=6.0 Hz,═COP), 140.46 (s), 142.99 (d, $^3J_{PC}$=8.1 Hz), 143.12 (s), 162.67 (s); ^{31}P NMR ($CDCl_3$) δ −6.19; MS (15 eV) *m/z* 322 (M^+, 0.94), 320 (M^+ (–H_2), 28.63), 296 (M^+ (–HCN), 22.03), 268 (M^+ (–$(HCN)_2$), 18.05), 155 ((H+ HOP(O)$(OEt)_2$), 10.06); Anal. Calcd for $C_{15}H_{19}N_2O_4P$ (322.30): C, 55.90; H, 5.94; N, 8.69; Found: C, 55.77; H, 5.94; N, 8.63.– 9: white crystal, mp. 87–90°C (recrystallization from $CHCl_3$-n-hexane); yield 10%; R_f=0.49 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 2227 (d, CN), 1233 (P═O); ^{1}H NMR ($CDCl_3$) δ 1.39 (dt, $^4J_{PH}$=1.2 Hz, $^3J_{HH}$=7.1 Hz, 6H, 2×OCH_2CH_3), 2.24 (quint, $^3J_{HH}$=7.4 Hz, 2H), 3.09 (t, $^3J_{HH}$=7.4 Hz, 2H, CH_2–C═), 3.19 (t, $^3J_{HH}$= 7.4 Hz, 2H, CH_2–C═), 4.23 (dq, $^3J_{PH}$=0.6 Hz, $^3J_{HH}$= 7.1 Hz, 2H, OCH_2), 4.27 (dq, $^3J_{PH}$=0.6 Hz, $^3J_{HH}$=7.1 Hz, 2H, OCH_2), 7.56 (d, $^4J_{PH}$=0.5 Hz, 1H,═CH); ^{13}C NMR ($CDCl_3$) δ 16.52 (d, $^3J_{PC}$=6.1 Hz, 2×OCH_2CH_3), 28.37 (s), 28.72 (s), 33.83 (s), 44.21 (s), 64.32 (d, $^2J_{PC}$=5.5 Hz, 2×OCH_2), 110.42 (s), 114.68 (s, CN), 119.54 (s, CN), 120.42 (s), 122.04 (s,═CH), 131.85 (d, $^3J_{PC}$=6.3 Hz), 138.82 (d, $^2J_{PC}$= 5.8 Hz,═COP); ^{31}P NMR ($CDCl_3$) δ −4.59; MS (15 eV) *m/z* 320 (M^+, 29.70), 292 (M^+ (–H_2CN), 20.00), 264 (M^+ (– ($H_2CN)_2$), 87.64); 166 (M^+ (–HOP(O)$(OEt)_2$), 24.28), 155 ((H+HOP(O)$(OEt)_2$), 9.20); 139 (M^+ (–HOP(O)$(OEt)_2$, –HCN), 8.58), 111 (M^+ (–HOP(O)$(OEt)_2$, –$(H_2CN)_2$) 2.23); Anal. Calcd for $C_{15}H_{17}N_2O_4P$ (320.28): C, 56.25; H, 5.35; N, 8.75; Found: C, 56.13; H, 5.32; N, 8.69.

3.2.8. Phosphoric acid diethyl ester 3a-hydroxy-6-oxo-2,3,3a,5a,6,7,8, 9,9a,9b-decahydro-1*H*-cyclopenta [*a*] naphthalen-4-yl ester 6g: pale yellow oil; yield 68%; R_f=0.27 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 3320 (OH), 1663 (C═O), 1252 (P═O); ^{1}H NMR ($CDCl_3$) δ 1.33 (dt, $^4J_{PH}$=1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.37 (dt, $^4J_{PH}$= 1.0 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.52–2.11 (m, 10H), 2.13–2.54 (m, 4H), 3.16–3.34 (m, 1H, CHC(O)), 3.41–3.91 (m, 1H, OH), 4.06–4.30 (m, 4H, 2×OCH_2), 5.20 (dd, $^4J_{PH}$=2.7 Hz, $^3J_{HH}$=2.7 Hz, 1H,═CH); ^{13}C NMR ($CDCl_3$) δ 16.05 (d, $^3J_{PC}$=6.2 Hz, 2×OCH_2CH_3), 20.03 (s), 22.48 (s), 25.09 (s), 28.26 (s), 33.72 (s), 35.19 (s), 37.38 (s), 43.04 (s), 55.91 (s), 64.21 (d, $^2J_{PC}$=5.0 Hz, 2×OCH_2), 78.47 (C–OH), 123.53 (d, $^3J_{PC}$=4.8 Hz,═CH), 135.81 (d, $^2J_{PC}$= 5.5 Hz,═COP), 207.06 (C═O); ^{31}P NMR ($CDCl_3$) δ −4.04; MS (15 eV) *m/z* 358 (M^+, 0.14), 338 (M^+ (–H_2, –H_2O), 100.00), 310 (M^+ (–H_2, –H_2O, –CO), 35.47), 155 ((H+HOP(O)$(OEt)_2$), 27.42); Anal. Calcd for $C_{17}H_{27}O_6P$ (358.37): C, 56.98; H, 7.59; Found: C, 57.26; H, 7.66.

3.2.9. Phosphoric acid diethyl ester 6a-hydroxy-1,3-dioxo-2-phenyl-2, 3, 7, 8, 9, 9a-hexahydro-1*H*,6a*H*-cyclopenta [*c*] [1,2,4] triazolo [1,2-*ai*] pyridazin-6-yl ester 6h: orange oil; yield: 92%; overall yield 87% (from 1h), white crystal, mp 125-128°C (recrystallization from $CHCl_3$ –n-hexane); R_f=0.37 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 3880–3100 (v br, OH), 1780, 1726 (C═O, C═C), 1271 (d, P═O); ^{1}H NMR ($CDCl_3$) δ 1.38 (dt, $^4J_{PH}$=1.2 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.41 (dt, $^4J_{PH}$=1.2 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.72–2.35 (m, 6H), 2.38–2.60 (m, 1H), 3.05 (s, 1H, C–OH), 4.06–4.34 (m, 4H, 2×OCH_2), 7.00 (d, $^4J_{PH}$=3.2 Hz, 1H,═CH), 7.27–7.50 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 15.47 (d, $^3J_{PC}$= 5.6 Hz, OCH_2CH_3), 15.56 (d, $^3J_{PC}$=5.6 Hz, OCH_2CH_3), 19.81 (s), 23.46 (s), 29.11 (s), 63.42 (s, C–OH), 64.79 (d, $^2J_{PC}$=6.2 Hz, OCH_2), 64.91 (d, $^2J_{PC}$=6.2 Hz, OCH_2), 75.07 (s), 108.64 (d, $^3J_{PC}$=5.7 Hz,═CH), 125.05 (s, *o*-C_6H_5), 127.68 (s, *p*-C_6H_5), 128.56 (s, *m*-C_6H_5), 130.65 (s, *i*-C_6H_5), 136.60 (d, $^2J_{PC}$=9.1 Hz,═COP), 144.81 (s, C═O), 150.50 (s, C═O); ^{31}P NMR ($CDCl_3$) δ −3.25; MS (15 eV) *m/z* 437 (M^+, 100.00), 419 (M^+ (–H_2O), 19.50), 284 (M^+ (–OP(O)$(OEt)_2$), 1.21), 283 (M^+ (–HOP(O)$(OEt)_2$), 1.87); 155 ((H+HOP(O)$(OEt)_2$), 22.45); Anal. Calcd for $C_{19}H_{24}N_3O_7P$ (437.39): C, 52.18; H, 5.53; N, 9.61; O, 25.61; P, 7.08; Found: C, 52.22; H, 5.49; N, 9,54; O, 25.67; P, 7.02.

3.2.10. [2,3] Sigmatropic rearrangments of selenoxides to allylic alcohols 6a,b,i,j via oxidation of selenides 2a,b,i,j. General Procedure A: To a solution of selenides 2a,b,i,j (1 mmol) in EtOH (1 mL) was added dropwise 30% hydrogen peroxide (1 mL,) at room temperature. After stirring for 2 h the reaction mixture was concentrated in vacuo to afford the mixture of **6a** and **7a** in the ratio 2.4:1 (from **2a**), the mixture of **6b** and **7b** in the ratio 2:1 (from **2b**), and crude **6i** (from **2i**), and crude **6j** (from **2j**). The mixtures were chromatographed on silica gel column using a gradient of C_6H_6/EtOAc as eluent to give pure compounds **6a** and **7a**, **6b** and **7b** and **6i** and **6j**. General Procedure B: To stirred solution of selenides **2i,j** (2 mmol) in THF (30 mL) cooled to –40°C, pyridine (10 mL) was added followed by addition dropwise 30% H_2O_2 (45 mL). Stirring was continued at –30°C for 2 h. Then the reaction mixture was quenched with saturated ammonium chloride (40 mL), extracted with $CHCl_3$ (5×40 mL); combined organic layers washed with 10% of hydrochloric acid (2×20 mL) and dried $MgSO_4$. After evaporation of solvent the residue was chromatographed on silica gel as described above.

3.2.11. Phosphoric acid diethyl ester 5a-hydroxy-1,3-dioxo-2-phenyl-1, 2, 3, 3a, 5a, 6, 7, 8, 8a, 8b-decahydro-2-aza-*as*-indacen-5-yl ester 6i: white crystal, mp 85-87°C (recrystallization from C_6H_6/EtOAc); yield 51% (procedure A); yield 58% (procedure B); R_f=0.32 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 3490 (br, OH), 1715, 1598 (C═O, C═C), 1273 (P═O); ^{1}H NMR ($CDCl_3$, COSY) δ 1.29 (dt, $^4J_{PH}$= 1.2 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.38 (dt, $^4J_{PH}$= 1.2 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.68–2.09 (m, 4H), 2.09–2.30 (m, 2H), 2.53–2.73 (m, 1H, C*H*–C–OH), 3.22 (dd, $^3J_{HH}$=6.8, 8.8 Hz, 1H, CHC(O)), 3.84 (ddd, $^3J_{HH}$=2.4, 5.8, 8.8 Hz, 1H, CHC(O)), 4.12 (q, $^3J_{HH}$= 7.1 Hz, 1H, OCH_2), 4.16 (q, $^3J_{HH}$=7.1 Hz, 1H, OCH_2), 4.19 (dq, $^3J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 1H, OCH_2), 4.22 (dq, $^3J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 1H, OCH_2), 5.67 (dd, $^4J_{PH}$= 3.4 Hz, $^3J_{HH}$=5.8 Hz, 1H,═CH), 7.18–7.27 (m, 2H, *o*-C_6H_5), 7.31–7.48 (m, 3H, *p*-C_6H_5, *m*-C_6H_5); ^{13}C NMR ($CDCl_3$, DEPT) δ 15.52 (d, $^3J_{PC}$=5.7 Hz, OCH_2CH_3), 15.64 (d, $^3J_{PC}$=5.7 Hz, OCH_2CH_3), 20.39 (s, CH_2), 23.98 (s, CH_2), 33.27 (s, CH_2), 36.28 (s, CH), 42.35 (s, CH), 48.87 (s, CH), 64.51 (d, $^2J_{PC}$=5.8 Hz, CH_2, OCH_2), 65.07 (d,

$^2J_{PC}$=5.8 Hz, CH_2, OCH_2), 76.01 (s, ⟩C⟨, C–OH), 109.40 (d, $^3J_{PC}$=7.0 Hz, CH,=CH), 126.17 (s, CH, *o*-C_6H_5), 127.94 (s, CH, *p*-C_6H_5), 128.54 (s, CH, *m*-C_6H_5), 131.80 (s, ⟩C⟨, *i*-C_6H_5), 154.09 (d, $^2J_{PC}$=8.4 Hz,=C<), 175.96 (s, ⟩C⟨, C=O); ^{31}P NMR ($CDCl_3$) δ −2.86; MS (15 eV) *m/z* 435 (M^+,14.64), 417 (M^+ (-H_2O), 10.27), 279 (M^+ (-H_2, -HOP(O)$(OEt)_2$), 100.00), 155 ((H+HOP(O)$(OEt)_2$) 26.46); Anal. Calcd for $C_{21}H_{26}NO_7P$ (435.41): C, 57.93; H, 6.02; N, 3.22; O, 25.72; P, 7.11; Found: C, 57.84; H, 6.02; N, 3.28; O, 25.66; P, 7.05.

3.2.12. Phosphoric acid diethyl ester 5a-hydroxy-1,3-dioxo-2-phenyl-2, 3, 3a, 5a, 6, 7, 8, 9, 9a, 9b-decahydro-1*H* benzo [*e*]-isoindol-5-yl ester 6j: white crystal, mp ≈10°C; yield 45% (procedure A); yield 58% (procedure B); R_f=0.61 (C_6H_6/EtOAc 1:1); IR (film) cm^{-1} 3492 (br, OH), 1718, 1617 (C=O, C=C), 1270 (P=O); ^{1}H NMR ($CDCl_3$,300 MHz, COSY) δ 1.24 (dt, $^4J_{PH}$=1.2 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.37 (dt, $^4J_{PH}$=1.2 Hz, $^3J_{HH}$= 7.1 Hz, 3H, OCH_2CH_3), 1.56-1.93 (m, 6H), 1.98 (ddd, $^3J_{HH}$=3.4, 5.9 Hz, $^2J_{HH}$=13.0 Hz, 1H), 2.38 (d, $^2J_{HH}$= 13.0 Hz, 1H), 2.52 (dq, $^3J_{HH}$=3.4 Hz, $^2J_{HH}$=13.2 Hz, 1H), 3.03 (dd, $^3J_{HH}$=5.9, 8.7 Hz, 1H, CHC(O)), 3.73 (ddd, $^3J_{HH}$=2.9, 5.1, 8.7 Hz, 1H, CHC(O)), 4.08 (dq, $^3J_{PH}$= 3.0 Hz, $^3J_{HH}$=7.1 Hz, 1H, OCH_2), 4.11 (dq, $^3J_{PH}$=2.9 Hz, $^3J_{HH}$=7.1Hz, 1H, OCH_2), 4.19 (dq, $^3J_{PH}$=1.8 Hz, $^3J_{HH}$= 7.1 Hz, 1H, OCH_2), 4.21 (dq, $^3J_{PH}$=2.0 Hz, $^3J_{HH}$=7.1 Hz, 1H, OCH_2), 5.70 (dd, $^4J_{PH}$=3.4 Hz, $^3J_{HH}$=5.1 Hz, 1H,=CH), 7.19-7.25 (m, 2H, *o*-C_6H_5), 7.29-7.47 (m, 3H, *p*-C_6H_5, *m*-C_6H_5); ^{13}C NMR ($CDCl_3$, DEPT) δ 15.77 (d, $^3J_{PC}$=3.8 Hz, 2×OCH_2CH_3), 20.27 (s, CH_2), 24.91 (s, CH_2), 26.00 (s, CH_2), 33.14 (s, CH_2), 39.89 (s, CH), 40.77 (s, CH), 44.22 (s, CH), 64.77 (d, $^2J_{PC}$=6.4 Hz, OCH_2), 65.29 (d, $^2J_{PC}$=6.4 Hz, OCH_2), 69.19 (s, ⟩C⟨, C-OH), 109.62 (d, $^3J_{PC}$=5.8 Hz, CH,=CH), 126.35 (s, CH, *o*-C_6H_5), 128.12 (s, CH, *p*-C_6H_5), 128.70 (s, CH, *m*-C_6H_5), 131.96 (s, ⟩C⟨, *i*-C_6H_5), 153.84 (d, $^2J_{PC}$=8.7 Hz, ⟩C⟨,=COP), 175.10 (d, $^5J_{PC}$=3.0 Hz, ⟩C⟨, C=O), 176.04 (s, C=O); ^{31}P NMR ($CDCl_3$) δ -2.90; MS (15 eV) *m/z* 449 (M^+, 100.00), 431 (M^+ (-H_2O), 23.86), 329 (M^+ (-CONHPh), 5.39), 295 (M^+ (-HOP(O)$(OEt)_2$), 66.78), 155 ((H+HOP(O)$(OEt)_2$), 47.00), 148 (M^+ (-HOP(O)$(OEt)_2$, -$(CO)_2$NPh), 7.25), 130 (M^+ (-H_2O, -HOP(O)$(OEt)_2$, -$(CO)_2$NPh) 10.79); Anal. Calcd for $C_{22}H_{28}NO_7P$ (449.44): C, 58.79; H, 6.28; N, 3.12; O, 24.92; P, 6.89; Found: C, 58.93; H, 6.26; N, 3.11; O, 24.97; P, 6.87.

3.2.13. Phosphoric acid diethyl ester 7a-hydroxy-2,4-dioxo-3-phenyl-decahydro-1-oxa-3-aza-cyclopropa [*e*]-*as*-indacen-7b-yl ester 10i: The selenide **2i** (1.50 g, 2.85 mmol) in 60 mL of ethanol was cooled to 0°C and 30% H_2O_2 was added dropwise. The mixture was stirred at this temperature for 2 hours and for additional 20 hours at −10°C. Chloroform (200 mL) was added and the organic phase was washed with water (2×20 mL) and dried over magnesium sulfate. After evaporation to dryness, the product **10i** was purified by silica gel column chromatography with benzene-ethyl acetate as the eluent and then recrystallized from toluene: yield 0.553 g (43%); white plates, mp 77-79°C; R_f=0.82 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 3500-3000 (v br, OH), 1718 (C=O), 1258 (P=O); ^{1}H NMR ($CDCl_3$) δ 1.25 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.35 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 3H, OCH_2CH_3), 1.65-2.13 (m, 6H), 2.31-2.58 (m, 2H), 3.07 (dd, $^3J_{HH}$=6.8, 9.2 Hz, 1H, CHC(O)), 3.61 (dd, $^3J_{HH}$=2.4, 9.2 Hz, 1H, CHC(O)), 4.02-4.30 (m, 4H, 2×OCH_2), 4.18 (d, $^3J_{HH}$=2.4 Hz, 1H, C*H*(OH), 7.18-7.50 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 15.65 (d, $^3J_{PC}$=5.9 Hz, 2×OCH_2CH_3), 19.94 (s), 24.24 (s), 32.54 (s), 38.22 (s), 40.27 (s), 43.90 (s), 59.46 (s), 64.98 (d, $^2J_{PC}$= 6.2 Hz, OCH_2), 65.41 (d, $^2J_{PC}$=5.7 Hz, OCH_2), 80.80 (s, C-OH), 85.68 (d, $^2J_{PC}$=4.8 Hz, COP), 126.43 (s, *o*-C_6H_5), 128.35 (s, *p*-C_6H_5), 128.84 (s, *m*-C_6H_5), 131.91 (s, *i*-C_6H_5), 173.96 (s, C=O), 175.97 (s, C=O); ^{31}P NMR ($CDCl_3$) δ -2.74; MS (15 eV) *m/z* 451 (M^+, 40.49), 433 (M^+ (-H_2O), 10.78), 406 (M^+ (-OH, -H_2O), 1.76), 297 (M^+ (-HOP(O)$(OEt)_2$), 28.31), 279 (M^+ (-OP(O)$(OEt)_2$, -H_2O), 10.12), 155 ((H+HOP(O)$(OEt)_2$), 100.00).

3.2.14. 6-Acetyl-3a-hydroxy-1,2,3,3a,7,7a-hexahydro-inden-4-one 12b: To a stirred solution of selenide **2b** (0.211g, 0.5 mmol) in THF (10 mL) cooled to −40°C, pyridine (2.5 mL) was added followed by addition 30% H_2O_2 (1.2 mL). Stirring was continued at rt for 3 days. Then the saturated ammonium chloride (10 mL) was added, the mixture was extracted with chloroform (4×5 mL), organic layers washed with 10% of HCl and dried $MgSO_4$. Evaporation of solvent followed by column chromatography on silica gel afforded pure **12b** as a white powder (0.037g, 38%), mp 121-124° (recrystallization from C_6H_6); R_f=0.91 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 3395 (br, OH), 1733, 1646 (C=O, C=C); ^{1}H NMR ($CDCl_3$) δ 1.60-2.10 (m, 5H), 2.15-2.58 (m, 2H), 2.42 (s, 3H, C(O)CH_3), 2.73 (d_{AB}d, $^4J_{HH}$=3.1 Hz, $^2J_{HH}$(AB)=18.3 Hz, 1H, CH_2-C=), 6.59 (dd, $^4J_{HH}$=3.1, 0.6 Hz, 1H,=CH); ^{13}C NMR ($CDCl_3$, 300MHz, DEPT) 19.95 (s, CH_2), 25.68 (s, CH_2), 26.31 (s, CH_3), 26.96 (s, CH_2), 31.36 (s, CH_2), 45.81 (s, CH), 79.93 (s, ⟩C⟨, C-OH), 131.37 (s,=CH), 154.91 (s, ⟩C⟨,=*C*-C(O)), 199.81 (s, ⟩C⟨, C=O), 200.16 (s, ⟩C⟨, C=O); MS (15 eV) *m/z* 194 (M^+, 26.90), 176 (M^+ (-H_2O), 3.15), 151 (M^+ (-Ac), 10.19), 138 (M^+ (-CAc), 38.18), 133 (M^+ (-H_2O, -Ac), 2.67), 124 (M^+ (-CO, -Ac, +H), 23.39), 111 (M^+ (-CO, -CAc), 69.59); Anal. Calcd for $C_{11}H_{14}O_3$ (194.23): C, 68.02; H, 7.27; O, 24.71; Found: C, 68.31; H, 7.18; O, 24.76.

3.3. General procedure for the hydrolysis of allylic alcohols 6b,i,j

A solution of allylic alcohol (0.5 mmol) in ethanol (5 mL) and 10% HCl 5 mL was heated at 60°C for 5 hours in the case of **6i,j** and at 20°C in the case of **6b**. The mixture was washed with sodium hydrogen carbonate. Chloroform (10 mL) was added and the organic layer was separated, washed with water (2×5 mL) and dried ($MgSO_4$). After removal of the solvent the products **11** were purified by silica gel column chromatography using C_6H_6/EtOAc (3:1) as eluent.

3.3.1. 6-Acetyl-3a-hydroxy-octahydro-inden-4-one 11b: white powder; yield 36%; R_f=0.57 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 3449 (br, OH), 1710, 1685 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.60-2.08 (m, 11H), 2.42 (s, 3H, C(O)CH_3), 2.70-2.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.07 (s), 25.77 (s), 27.01 (s), 29.04 (s), 30.39 (s), 31.48 (s) 31.84 (s), 45.89 (s), 80.23 (s), 154.97 (s, C=O), 197.65 (s, C=O); MS (15 eV) *m/z* 196 (M^+, 14.82); Anal. Calcd for $C_{11}H_{16}O_3$

(196.24): C, 67.32; H, 8.22; O, 24.45; Found: C, 67.62; H, 8.43.

3.3.2. 5a-Hydroxy-2-phenyl-octahydro-2-aza-*as*-indacene-1,3,5-trione 11i: white plates; mp 75-77°C (recrystallization: benzene-EtOAc); yield 47%; R_f=0.22 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 3490 (br, OH), 1718, 1698 (C=O); ^1H NMR ($CDCl_3$) δ 1.28-1.90 (m, 3H), 1.90-2.09 (m, 3H), 2.70-3.05 (m, 3H, CHC(O), $CH_2C(O)$), 3.39-3.58 (m, 2H, 2× CHC(O)N), 7.06-7.54 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 23.01 (s), 27.38 (s), 28.58 (s), 33.04 (s), 35.04 (s), 41.43 (s), 49.55 (s), 78.95 (s, C-OH), 126.10 (s, *o*-C_6H_5), 128.47 (s, *p*-C_6H_5), 128.92 (s, *m*-C_6H_5), 131.45 (s, *i*-C_6H_5), 176.64 (s, NC=O), 177.35 (s, NC=O), 210.32 (s, C=O); Anal. Calcd for $C_{17}H_{17}NO_4$ (299.32): C, 68.21; H, 5.72; N, 4.68; Found: C, 67.87; H, 6.07; N, 4.51.

3.3.3. 5a-Hydroxy-2-phenyl-octahydro-benzo [*e*] isoindole-1,3,5-trione 11j: white plates, mp 83-85°C (recrystallization: benzene -EtOAc); yield: 42%; R_f=0.26 (C_6H_6/EtOAc 1:1); IR (KBr) cm^{-1} 3480 (br, OH), 1700, 1680 (C=O); ^1H NMR ($CDCl_3$) δ 1.25-1.91 (m, 6H), 1.91-2.19 (m, 3H), 2.71-3.08 (m, 3H, CHC(O), $CH_2C(O)$), 3.41-3.56 (m, 2H, 2×CHC(O)N), 7.05-7.53 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.28 (s), 26.39 (s), 25.70 (s), 27.39 (s), 34.27 (s), 36.26 (s), 38.96 (s), 40,62 (s), 74.38 (s, C-OH), 125.38 (s, *o*-C_6H_5), 128.59 (s, *p*-C_6H_5), 129.02 (s, *m*-C_6H_5), 132.33 (s, *i*-C_6H_5), 177.39 (s, NC=O), 177.79 (s, NC=O), 209.53 (s, C=O); Anal. Calcd for $C_{18}H_{19}NO_4$ (313.35): C, 68.99; H, 6.11; N, 4.47; Found: C, 68.80; H, 6.06; N, 4.63.

3.3.4. 2-Phenyl-8,9-dihydro-7*H*-cyclopenta[*c*][1,2,4]triazolo[1,2-*a*] pyridazine-1,3,6-trione 15h and **Phosphoric acid 1,3-dioxo-2-phenyl-2,3,9,9a-tetrahydro-1*H*,8*H*-cyclopenta[*c*][1,2,4]triazolo[1,2-*a*] pyridazin-6-yl ester diethyl ester 16h:** To a solution of **6h** (0.22 g,0.5 mmol) in dry MeOH (10 mL) was added ammonium fluoride (5 mmol). The resulting mixture was stirred at room temperature for 20 h. After evaporation of solvent the residue was dissolved in $CHCl_3$ (50 mL), washed with water (2×5 mL), dried ($MgSO_4$) and concentrated to leave a dense oil which was a mixture of **15h** and **16h** by ^1H and ^{31}P NMR spectroscopy. The mixture was separated by chromatography on silica gel using a gradient of C_6H_6/EtOAc to afford **15h** (0.07 g, 52%), R_f=0.67 (C_6H_6/EtOAc 1:1) first and then **16h** (0.036 g, 17%), R_f=0.42 (C_6H_6/EtOAc 1:1). Compound 15h was obtained as dark red crystals, mp 195-197°C, after recrystallization from $CHCl_3$:acetone. Spectral data of *15h*: IR (KBr) cm^{-1} 1700, 1680, 1660 (C=O, C=C); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.12 (quint, $^3J_{HH}$=7.6 Hz, 2H, CH_2), 2.65 (t, $^3J_{HH}$=7.6 Hz, 2H, CH_2-C=), 3.27 (t, $^3J_{HH}$=7.6 Hz, 2H, CH_2-C=), 4.43 (s, 2H, $CH_2C(O)$), 7.35-7.56 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 21.26 (s), 26.48 (s), 32.10 (s), 50.26 (s), 117.29 (s, =C), 125.55 (s, *o*-C_6H_5), 128.77 (s, *p*-C_6H_5), 129.30 (s, *m*-C_6H_5), 130.22 (s, *i*-C_6H_5), 150.60 (s, C=O), 174.25 (s, NC=O), 181.90 (s, NC=O); MS (CI-isobutane) 284 (M^+ (+H), 100.00); HRMS(CI) Calcd for $C_{15}H_{13}N_3O_3$ + H (M^+ +H) 284.1035; Found: 284.1047; 16h: deep orange oil, yield 17%; IR (film) cm^{-1} 1720, 1710, 1690, 1675 (C=O, C=C), 1250 (P=O); ^1H NMR ($CDCl_3$) δ 1.39 (dt, $^4J_{PH}$=1.1 Hz, $^3J_{HH}$=7.1 Hz, 6H, 2×OCH_2CH_3), 2.36 (dq, $^3J_{HH}$=12.5, 9.6 Hz, 1H, $CHCH_2$), 2.58-2.69 (m, 2H), 2.80-2.90 (m, 1H), 4.16-4.32 (m, 4H, 2×OCH_2), 4.64-4.75 (m, 1H, POC=CH), 7.35-7.52 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 8.92 (s), 16.12 (d, $^3J_{PC}$= 6.1 Hz, 2×OCH_2CH_3), 31.57 (s), 31.89 (s), 64.42 (d, $^2J_{PC}$=6.0 Hz, 2×OCH_2), 108.61 (d, $^3J_{PC}$=5.5 Hz,=CHN), 125.50 (d, $^3J_{PC}$=5.0 Hz, CH=C<), 125.60 (s, *o*-C_6H_5), 127.80 (s, =CH-CH_2), 128.43 (s, *p*-C_6H_5), 129.23 (s, *m*-C_6H_5), 132.85 (s, *i*-C_6H_5), 141.30 (d, $^2J_{PC}$= 5.8 Hz,=COP), 178.20 (s, C=O), 180.22 (s, C=O); ^{31}P NMR ($CDCl_3$) δ -4.57; MS (CI-isobutane): *m/z* 420 (M^+ (+H),100.00); 155 ((H+HOP(O)$(OEt)_2$), 8.24); HRMS (CI) Calcd for $C_{19}H_{22}N_3O_6P$ + H (M^+ + H) 420.1324; Found: 420.1325.

3.4. X-Ray single-crystal structure determination

Data for all crystals were collected at a temperature of −50±1°C using a ω-2θ scan technique on a Bruker P4 four-circle diffractometer with graphite monochromated radiation, Cu-K_α (λ=1.54178 Å) for **6i** and **10i**, and Mo-K_α (λ=0.71703 Å) for **6h**. Hydrogen atoms were assigned idealised positions (except those of the OH groups of the **10i** and **6h** which were directly located) and were included in the refinement with displacement parameters of 1.2 U_{eq} of the parent carbon atom (or 1.5 U_{eq} for methyl groups). The P(O)$(OEt)_2$ group in **6i** showed evidence of some rotational disorder, consistent with the relatively poor diffraction by this crystal; two oxygen atoms and three carbon atoms were resolved into separate components in a *ca* 50:50 ratio. The structure of **6h** had residual electron density which was interpreted as due to four carbon atoms of a lattice hexane molecule severely disordered over two sites. Full matrix least squares refinement was on F^2 with anisotropic displacement parameters assigned to all full occupancy non-hydrogen atoms except those of the phenyl ring and ring carbon atoms C(1) to C(6) in **6h** for which there was a shortage of data.[25]

3.4.1. Compound 10i: Colorless block shaped crystal of $C_{21}H_{26}NO_8P$ dimension of 0.40×0.35×0.20 mm. Monoclinic, space group $P2_1/n$ with a=17.832(1), b=6.9807(9), c=17.997(2) Å, β=106.364(5)°, V=2149.5(4) $Å^3$, Z=4, $F(000)$=952, ρ=1.395 g cm^{-3}, R_1=0.0628 [$I>2\sigma(I)$], wR_2=0.1647 (all data), S=0.996.

3.4.2. Compound 6h: 0.5 (C_6H_{14}) Colourless cuboid crystals of $C_{22}H_{31}N_3O_7P$, dimension of 0.48×0.46×0.45 mm. Monoclinic, space group $P2_1/n$ with a=10.706(2), b= 8.999(2), c=23.042(4) Å, β=95.03(2)°, V= 2211.3(8) $Å^3$, Z=4, $F(000)$=1020, ρ=1.443 g cm^{-3}, R_1=0.0669 [$I>2\sigma(I)$], wR_2=0.1982 (all data), S=1.039.

3.4.3. Compound 6i: Colourless cuboid crystals of $C_{21}H_{26}NO_7P$ of approximate dimension of 0.50×0.48× 0.48 mm. Orthorhombic, space group $Pna2_1$ with a=10.1722(5) Å, b=12.7695(7) Å, c=16.9244(1) Å, α=90, β=90, γ=90°, V= 298.4(2) $Å^3$, Z=4, $F(000)$=920, ρ=1.316 g cm^{-3}, R_1= 0.0747 [$I>2\sigma(I)$], wR_2=0.2111 (all data), S=1.151.

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