An expedient, stereoselective synthesis of highly functionalized cyclic compounds†

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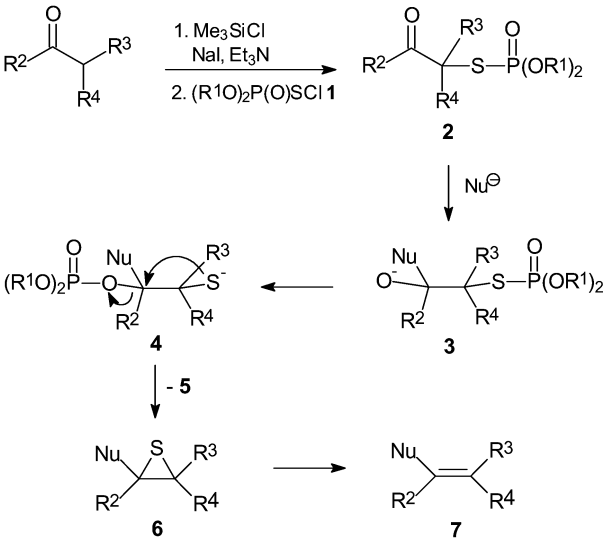
New thiophosphates containing functionalized cyclic ketone derivatives as ligands have been stereoselectively prepared from readily available starting materials. Full axial stereoselectivity of the $NaBH_4$ reduction of the carbonyl group in thiophosphates providing the corresponding thiols or sulfides has been demonstrated. The sulfides have been transformed into new functionalized cyclic Baylis–Hillman type adducts of defined configuration. The prospects for the useful synthetic application of these adducts appear to be very promising.

The carbon–carbon double bond is one of the most important functional groups in organic synthesis. Although numerous methods have been reported for the preparation of unsaturated compounds, stereoselective synthesis needs further development. We have elaborated a novel strategy for the stereoselective conversion of carbonyl compounds into unsaturated ones.[1,2] The key steps in this methodology involve formation of the corresponding thiophosphates **2** and their reactions with nucleophiles (Scheme 1).

Phosphates **2** are readily prepared from appropriate carbonyl compounds, generally in very high yield.[3] The carbonyl compounds are converted into silyl enol ethers and then addition of the thiophosphorylating agent dialkoxyoxophosphoranesulfenyl chloride **1** affords thiophosphates **2**. Addition of a nucleophile to the carbonyl group in **2** involves formation of the corresponding diastereoisomeric oxyanions **3**. These anions undergo rearrangement, involving migration of a phosphoryl group from sulfur to oxygen, affording thiolate anions **4**. Subsequent cyclization of **4** with elimination of phosphate anion **5** provides the episulfides **6**. Spontaneous desulfurization or desulfurization of **6** using P^{III} compounds gives the corresponding olefins **7**. We have demonstrated that our methodology is very useful in the synthesis of a variety of acyclic unsaturated compounds.[4–7]

As part of a continuing programme of research we have undertaken a study of the construction of exocyclic and endocyclic carbon–carbon double bonds. Recently, we have elaborated a "one-pot" procedure for the α-methylenation of lactones, including racemic frullanolide and α-methylenecycloalkanones.[8] In this paper we describe the synthesis of new thiophosphates **8** and **9** containing cyclic ligands and their further synthetically useful transformations, involving also formation of compounds containing an endocyclic unsaturated bond (Scheme 2).

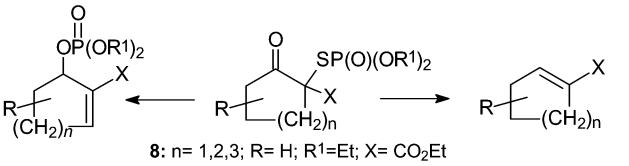


Scheme 1

Results and discussion

Synthesis of thiophosphates 8 and 9

We decided to synthesize thiophosphates bearing cyclic ligands, as well as this ligand containing different substituents,



8: n= 1,2,3; R= H; R^1=Et; X= CO_2Et
9: n= 2; R= H, 3-Me; R^1= Et; X= Me
n= 2; R= 3-Me, 4-Me, 5-^{t}Bu, 5-Ph, 4,4',6-Me; X= CO_2Et

Scheme 2

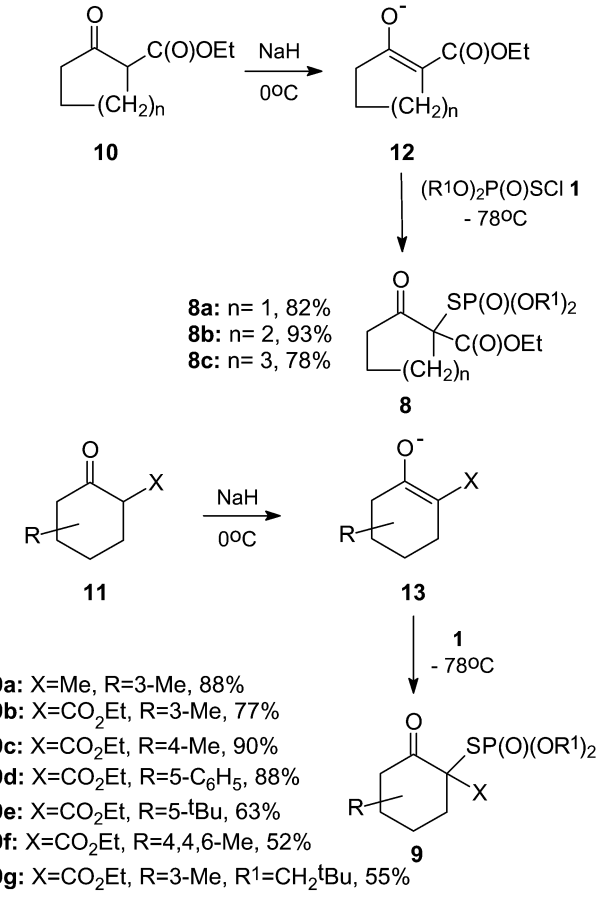
† Electronic supplementary information (ESI) available: crystallographic data tables described in the text. See http://www.rsc.org/suppdata/nj/b2/b207700k/.

in order to test their stereochemistry and synthetic utility. Application of our method, previously used in the synthesis of thiophosphates **2**,[3] afforded thiophosphates **8** and **9** in only moderate yield. Therefore, we used a modified, two-step procedure to prepare **8** and **9**. Treatment of the corresponding carbonyl compounds **10** and **11** with sodium hydride at 0 °C generated enolate anions **12** and **13**. Thiophosphorylation of these anions with dialoxyoxophosphoranesulfenyl chloride (R^1 = Et,^{t}BuCH$_2$) **1** provided thiophosphates **8** and **9** in good to high yield (Scheme 3).

Addition of sulfenyl chloride **1** to enolate anions **13** is stereoselective, leading to a mixture of two diastereoisomers. The resulting diastereoisomers could be easily separated by silica gel column chromatography and each was subjected to further transformations. However, some of them are not very stable under chromatographic conditions. In these cases, we used crude mixtures of diastereoisomers. The stereochemical distinction between isomers is illustrated in Fig. 1.

The question which arose was which isomer predominates, by how much and under what circumstances. We established the ratio of diastereoisomers on the basis of ^{31}P NMR data. We found that the main factors affecting the ratio of stereochemical products are the structure of the cyclohexanone element and to some extent the solvent (see Table 1).

The configuration of the major isomer was determined on the basis of X-ray data and to some extent by ^{13}C NMR (see Table 2). X-Ray analysis of single crystals of **9g** and **9d** confirmed their anticipated molecular structures and revealed a *trans* relationship between the equatorial 3-Me and 5-Ph substituents and the axial thiophosphates group $(RO)_2P(O)S$. Inspection of the torsion angles and asymmetry parameters reveals that the cyclohexane ring (C1,C2,C3,C4,C5,C6) adopts a deformed chair conformation, with the C2 and C5 atoms in the flap positions.



Scheme 3

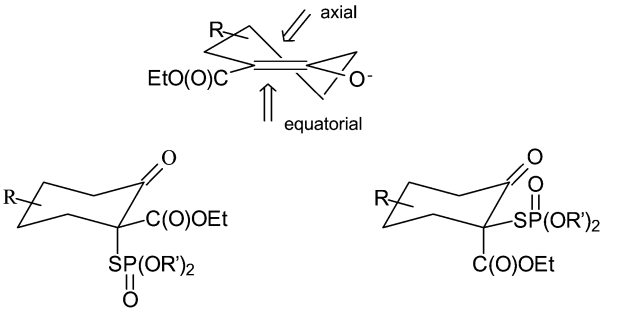


Fig. 1

The molecular structures of **9g** and **9d** are shown in Fig. 2 and 3, respectively. These results prompted us to assume that the thiophosphorylation reagent approaches the enol anion preferentially from the axial side. This is in agreement with data reported in the literature.[10]

Reduction of thiophosphates 8 and 9 with sodium borohydride

The facial stereoselectivity of cyclohexanone derivatives, that is axial or equatorial addition, has intrigued experimental and theoretical chemists for a long time. The development of methods for stereoselective reduction of the carbonyl group continues to be of interest in organic chemistry.[11–13] With this background information we studied the stereochemical course of reduction of the carbonyl group in a number of thiophosphates **8** and **9**.

We first investigated the reduction of thiophosphates **8a–c** having five-, six- and seven-membered rings, respectively. Treatment of **8a** with $NaBH_4$ at −78 °C led to the formation of the thiol **14a** as the unique product. The same reaction performed in the presence of an excess of methyl iodate gave the sulfide **17a** in high yield. However, in the reaction of **8b** and **8c** with the same reagents, episulfides **15b,c** as well as olefins **16b,c** were formed, in addition to the major product, the thiols **14b,c** or sulfides **17b,c** (Scheme 4, Table 3). The small ring shows high selectivity (entries 1 and 4) whereas larger rings produced a mixture of compounds **14, 17** and **15, 16** (entries 2, 3, 5 and 6).

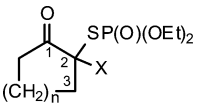
The results of reduction of thiophosphates **9b–e** containing additional substituents on the ring using $NaBH_4$ and $NaBH_4$–MeI are shown in Scheme 5 and Table 4. Reaction of the pure major diastereoisomers **9b,d** with these reagents provided thiols **18b,d** and sulfides **21b** exclusively (entries 1, 4 and 7). From the pure minor diastereoisomer **9d** the unique product was olefin **20d** (entry 5). From the mixture of diastereoisomers of **9c,d,e**, besides thiols **18c,e** or sulfides **21c,d,e**, episulfides **19c,d,e** and olefins **20c,d,e** were formed, respectively (entries 3, 6, 8–10).

We have also found that the reduction reaction of thiophosphates **8a–c** and **9b** in the presence of elemental iodine gave the corresponding disulfides **22a–d** (Scheme 6).

Table 1 Addition of diethoxyoxophosphoranesulfenyl chloride **1** to the enol anions **13**

R	Yield/%	Ratio of diastereoisomers		δ ^{31}P
		In THF	In diglime	
3-Me	77	4:1	5.4:1	21.0; 22.8
4-Me	90	3:1	3:1	21.5; 22.5
5-Ph	88	5:1	6:1	20.8; 22.3
5-*t*-Bu	63	2.5:1	3.5:1	20.9; 22.4
4,4,6-Me	52	1:1.2	1:3	21.4; 22.4

Table 2 Selected ^{13}C NMR data for thiophosphates **8** and **9**



Compound	δ C_1		$^3J_{(C1P)}$[a] /Hz		δ C_3		$^3J_{(C3P)}$[a] /Hz	
	Major	Minor	Major	Minor	Major	Minor	Major	Minor
8a	208.1		4.8		35.9		–	
8b	201.2		7.9		39		2.8	
8c	202.4		7.1		34.4		2.4	
9a	209.0	208.7	7.4	–	42.4	42.9	–	12.0
9b	204.9	202.5	9.1	8.6	37.1	39.7	5.1	–
9c	200.3	200.3	–	–	37.8	34.6	4.3	3.3
9d	201.8	200.4	9.2	6.5	42.9	46.9	4.6	–
9e	202.8	201.2	8.8	5.8	37.7	40.5	5.1	3.4
9f	200.8	202.3	–	–	38.4	37.0	4.9	9.7

[a] see ref. 9.

The ratio and the structure of all compounds obtained were assigned on the basis of ^1H, ^{13}C and ^{31}P NMR data.

The discussed transformations of thiophosphates **8** and **9** can be rationalized on the basis of the following mechanistic schemes (Schemes 7 and 8), which are in agreement with the mechanism proposed by us for the reaction of nucleophilic reagents with thiophosphates **2** containing all acyclic substituents (see Scheme 1).

The approach of a nucleophile of small bulk from the axial side gives, for example, from the major diastereoisomer of thiophosphate **9b** the oxyanion **23** of configuration shown in Scheme 7. The next step involves migration of the phosphoryl group from sulfur to oxygen affording thiolate anion **24**. There is no possibility of cyclization *via* nucleophilic attack of anion **24** on the carbon atom with elimination of the phosphate group and formation of episulfide, since thiolate anion and phosphate group cannot adopt the anti position. Therefore, the final product is the thiol **18b** (after protonation of thiolate anion under reaction conditions) or the sulfide **21b** (after methylation).

The oxyanion **25** obtained from the axial reduction of the minor diastereoisomer of **9b** undergoes also rearrangement involving migration of the phosphoryl group from sulfur to oxygen giving thiolate anion **26**. In spite of the diequatorial positions of the phosphate substituent and thiolate anion, this intermediate **26** is able to undergo cyclization *via* equilibrium between two conformers **26** and **26a** with formation of the episulfide **19b**. The latter undergoes spontaneous desulfurization to afford the cyclohexene derivative **20b**. In the intermediate compound **26a** the phosphate group and thiolate anion are in anti positions (Scheme 8).

In the case of the minor isomer of thiophosphate **9e** containing a 5-^{t}Bu substituent, we observed the formation of olefin. It seems to be reasonable to assume that a cyclization reaction is also possible if this thiolate anion changes its chair conformation into a twist one. In both diastereoisomers of **9**, when the thiophosphate function adopts the axial as well as equatorial dispositions, only the products resulting from the axial approach of the reducing agent are observed. Therefore, stereoelectronic effects must be considered in addition to steric effects to explain the observed products. Equatorial approach of the reduction reagent to the carbonyl group in both the major and minor diastereoisomers of thiophosphates **9** can be excluded. Such an approach should provide different compounds. In the case of the major diastereoisomers of **9,** the products must be functionalized cyclic olefins, whereas in the case of minor diastereoisomers of **9,** these are thiols of different configuration with respect to the thiols **18** obtained by us from the major diastereoisomers of **9** (see NMR data in Table 5 and the X-ray structure of **28d** in Fig. 4). The ^1H NMR data, collected in Table 5, for **18** (in particularly the characteristic values of axial $^3J_{H1H2}$ and equatorial $^3J_{H1H2}$ coupling constants in the

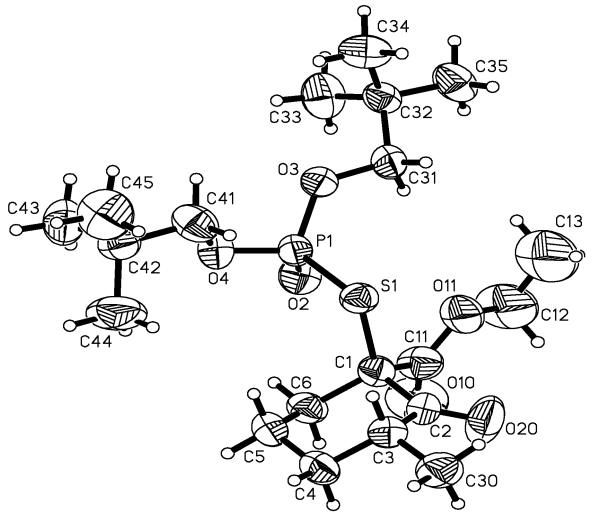


Fig. 2 Thermal ellipsoidal view with the atom numbering scheme of compound **9g**. Ellipsoids are shown with 50% probability.

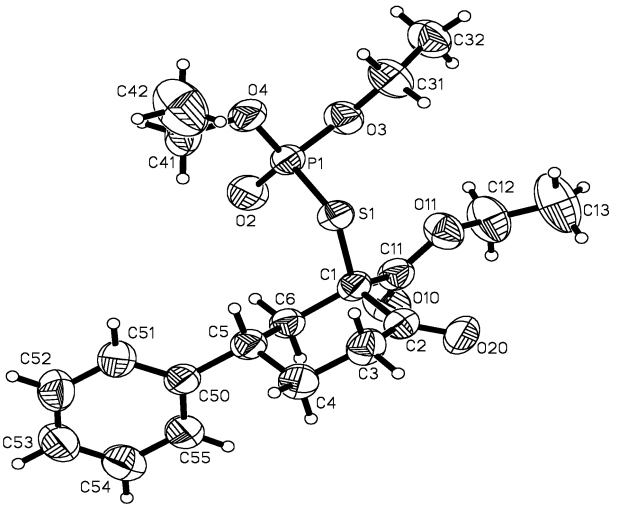
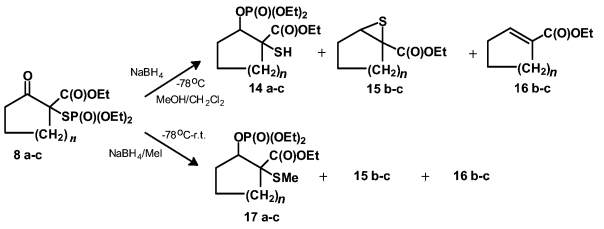
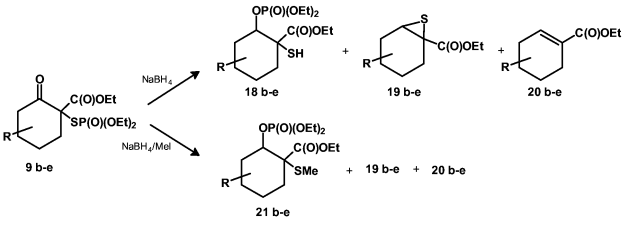


Fig. 3 Thermal ellipsoidal view with the atom numbering scheme of compound **9d**. Ellipsoids are shown with 50% probability.



Scheme 4



Scheme 5

range 9–12 Hz and 4.5–5.0 Hz, respectively) strongly supported the configuration of thiols **18.**

Synthesis of novel cyclic Baylis–Hillman type adducts

Baylis–Hillman adducts are very useful in organic synthesis. They undergo a variety of transformations involving regio- and stereochemical control. The usefulness of these adducts has been demonstrated by a number of reactions and applications.[14–16] However, more can be done to advance these fascinating reactions. Several methods have been devised for the preparation of acyclic Baylis–Hillman adducts.[16] Surprisingly, only two syntheses of such cyclic adducts has been reported.[17] Therefore, it was interesting to determine the utility of intermediate sulfides **17** and **21** as convenient precursors of sterically defined novel cyclic Baylis–Hillman type adducts. Indeed, we found that treatment of the sulfides **17** and **21** with 1.1 equiv. of *m*-CBPA in CH_2Cl_2 at $-78\,^{\circ}C$ provided sulfoxides **27** and **28** in very good yield. The latter after purification is easily and efficiently converted (*via cis* elimination) under thermal conditions into the corresponding adducts. We obtained the best results when transformation of the starting bicarbonyl compounds **10** and **11** into sulfoxides **27** and **28** was performed using crude intermediate thiophosphates **8** and **9** and sulfides **17** and **21** (Schemes 9 and 10).

Suitable crystals of the sulfoxide **28d** were obtained for an X-ray structure determination to establish the relative stereochemistry (Fig. 4). The X-ray analysis revealed a *trans* relation between the phosphate and carboester groups. Therefore, this shows good agreement with the stereochemistry of the product **21d** obtained *via* reduction of the carbonyl group in the major diastereoisomer of thiophosphate **9d**. These results additionally supported axial selectivity in the addition of reductive agent to the carbonyl group in thiophosphates **9**. The cyclohexane ring (C1,C2,C3,C4,C5,C6) of **28d** adopts a deformed chair conformation with the C1 and C4 atoms in the flap positions.

Conclusions

In conclusion, we have obtained new types of thiophosphates **8** and **9** *via* stereoselective addition of an electrophilic thiophosphorylating reagent to the enol anions generated from the corresponding cyclohexanone derivatives. They constitute interesting models for investigation of the reduction reaction of the carbonyl group in **8** and **9**. We have demonstrated that the reduction reaction, using $NaBH_4$, of thiophosphates **9** exhibits full axial selectivity, providing thiols **18** or sulfides **21** and episulfides **19** and olefins **20**. Compounds **17** and **21** are useful precursors of new cyclic Baylis–Hillman type adducts **29** and **30**. Our synthetic approach to these adducts involves reduction of the carbonyl group in readily available thiophosphates **8** and **9** by $NaBH_4$ in the presence of MeI, subsequent oxidation of intermediate sulfides **17, 21** to sulfoxides **27, 28** and *cis* elimination of the latter to afford the desired adducts of defined stereochemistry. The multifunctionality of our new cyclic adducts obtained makes them attractive for numerous further important transformations. The regio- and stereoselectivity of their reactions with various nucleophiles are currently under investigation.

Table 3 Reactions of thiophosphates **8** with $NaBH_4$[a] and with $NaBH_4$ in the presence of an excess of MeI[b]

Entry	Thiophosphate **8**	Products (% yield)		
1	**8a**	**14a** (85)	–	–
2	**8b**	**14b** (89)	–	**16b** (11)
3	**8c**	**14c** (49)	**15c** (6.5)	**16c** (31.5)
4	**8a**	**17a** (72)	–	–
5	**8b**	**17b** (79)	**15b** (8.0)	**16b** (12)
6	**8c**	**17c** (70)	**15c** (24)	–

[a] Reaction conditions: $NaBH_4$ (2 equiv), solvent MeOH–CH_2Cl_2 (1:1), temp. $-78\,^{\circ}C$, time 3 h. [b] $NaBH_4$ (2 equiv) MeI (5 equiv), solvent MeOH–CH_2Cl_2 (1:1), temp. $-78^{\circ} \rightarrow$ r.t., time 3 h ($-78\,^{\circ}C$) and 3–5 h ($-78^{\circ} \rightarrow$ r.t.).

Table 4 Reactions of thiophosphates **9** with $NaBH_4$[a b] and with $NaBH_4$ in the presence of an excess of MeI[c]

Entry	Thiophosphate **9**	Products (% yield)		
1	**9b**[d]	**18b** (90)	–	–
2	**9b**[e]	–	**19b** (60)[b]	**20b** (30)[a]
3	**9c**[f]	**18c** (60)	–	**20c** (20)
4	**9d**[d]	**18d** (85)	–	–
5	**9d**[e]	–	–	**20d** (60)
6	**9e**[g]	**18e** (71)	–	**20e** (25)
7	**9b**[d]	**21b** (99)	–	–
8	**9c**[f]	**21c** (62)	**19c** (15)	**20c** (10)
9	**9d**[f]	**21d** (60)	**19d** (15)	**20d** (15)
10	**9e**[g]	**21e** (60)	**19e** (25)	–

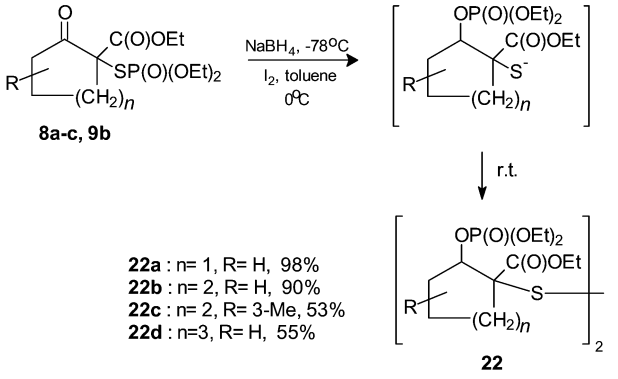
[a] Reaction conditions: $NaBH_4$ (2 equiv), solvent MeOH–CH_2Cl_2 (1:1), temp. $-78\,^{\circ}C$, time 3 h. [b] $NaBH_4$ (2 equiv) solvent MeOH–CH_2Cl_2 (1:1), temp. $0\,^{\circ}C$, time 1 h. [c] $NaBH_4$ (2 equiv) MeI (5 equiv), solvent MeOH–CH_2Cl_2 (1:1), temp. $-78^{\circ} \rightarrow$ r.t., time 3 h ($-78\,^{\circ}C$) and 3–5 h ($-78^{\circ} \rightarrow$ r.t.). [d] Major diastereomer. [e] Minor diastereomer [f] .Major + minor (3:1) diastereomers. [g] Major + minor (2.5:1) diastereomers.

Experimental

General

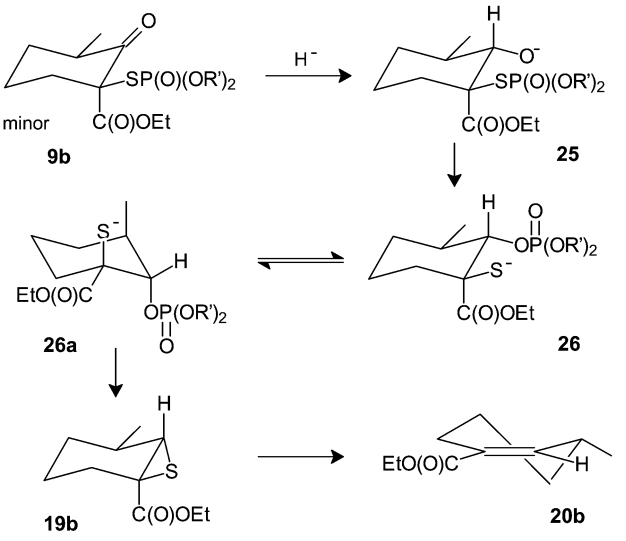
^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer at 200.13, 50.32 and 81.02 MHz, respectively (using deuterochloroform as solvent), unless otherwise noted. IR spectra were measured on an Ati Mattson Infinity FT IR60. MS spectra (EI, CI and HR) were recorded on a Finnigan MAT 95 spectrometer. Microanalyses were obtained on a Carlo Erba CHNS-OEA 1108 elemental analyzer.

Chromatographic purification was performed on silica gel columns (Merck, Kieselgel 60 and 70–230 mesh) with indicated eluents. PLC was carried out on silica gel plates (Merck F_{254}). Chemicals and solvents were obtained from commercial sources and used as received or dried according to standard



Scheme 6

methods. β-Ketoesters[18] and dialkoxyoxophosphoranesulfenyl chlorides **1**[19] were prepared as described.

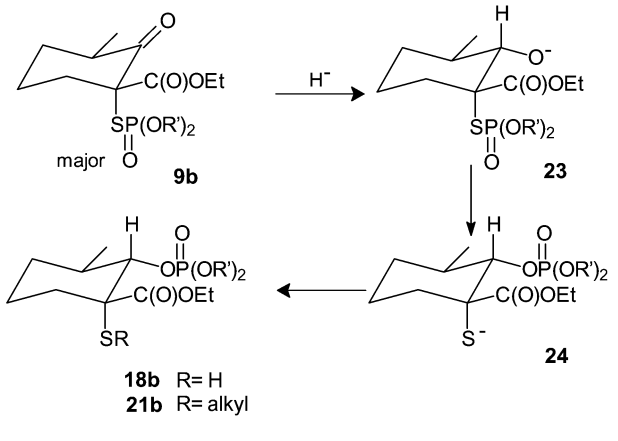


Scheme 8

Crystallography

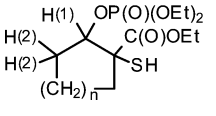
Compound **9g** crystallises in the orthorhombic system, in space group $P2_12_12_1$ with the unit cell consisting of four molecules. Compound **9d** and **28d** each crystallise in the monoclinic system, in space groups $C2/c$ and $P2_1/n$, respectively. The unit cell consists of eight molecules for compound **9d** and of four molecules for compound **28d**. In all three compounds the six-membered ring C1,C2,C3,C4,C5,C6 adopts a slightly deformed chair conformation with the flap position atoms being C1 and C4 for compound **28d** and C2, C5 for the other two compounds. The overall view of the molecules with the atom numbering scheme can be seen respectively in Figs. 2, 3 and 4. In Tables S1, S2 and S3 (Electronic supplementary information, ESI) comparison of selected bond lengths, bond angles and torsional angles are present. In the analysed crystal structures several weak C–H···O contacts occurs (Table S4, ESI).

The crystal and molecular structures of all three compounds were determined using data collected at room temperature on a CAD4 diffractometer with graphite monochromated CuKα radiation. Crystal data and experimental details are shown in Table 6. The lattice constants were refined by least-squares fits of 25 reflections in the θ range 15.44°–30.48° for compound **9g**, 21.86°–27.67° for compound **9d** and 20.38°–27.55° for compound **28d**. The decline in intensities of three control reflections (2,3,−4; 2,4,0; 2,−3,−6 for **9g**, −3,1,11; −3,0,9; −4,5,−4 for **9d** and −4,2,7; −1,2,−7; 3,5,3 for **28d**) was 15.6% during 184.6 h of exposure time for compound **9g**, 3.5% during 111.7 h for compound **9d**; and 27.9% during 128.7 h for compound **28d**; intensity corrections were applied (DECAY program).[20] An empirical absorption correction was applied by the use of the ψ-scan method (EAC program).[20,21] A total of 4459 (**9g**), 4109 (**9d**) and 4577 (**28d**) observed reflections with $I \geqslant 0\sigma(I)$ were used to solve the structure by direct methods and to refine it by full matrix least-squares methods using F^2.[22,23] Hydrogen atoms were placed geometrically at idealised positions, and set as riding with fixed thermal parameters equal to 1.33 times the equivalent isotropic thermal parameter of the parent atom. Anisotropic thermal parameters were refined for all nonhydrogen atoms. For compound **9g** the final calculation converged to $R = 0.0503$ for 262 refined parameters and 3385 observed reflections with $I \geqslant 2\sigma(I)$ while performing a racemic twinning refinement [the Flack absolute structure parameter $\chi = 0.48(3)$[24,25]]. For compound **9d** the final refinement converged to $R = 0.0484$ for 249 refined parameters and 3553 observed reflections with $I \geqslant 2\sigma(I)$ with inclusion of the extinction parameter in the refinement [the obtained value of the extinction parameter was 0.00099(9)]. For compound **28d** the final refinement converged to $R = 0.0570$ for 267 refined parameters and 4089 observed reflections with $I \geqslant 2\sigma(I)$ with inclusion of the extinction parameter in the refinement [the obtained value of the extinction parameter was 0.00017(3)]. The conformation of the six-membered ring was determined on the basis of the



Scheme 7

Table 5 Selected $\{^{31}P\}^1H$ NMR and ^1H NMR data for thiols **14, 18** and disulfides **22a,b**



Tiols **14, 18** and disulfides **22**	δ H1	$^3J_{H1(ax)H2(ax)}$/ Hz	$^3J_{H1(ax)H2(eq)}$/ Hz	$^3J_{H1P}$/ Hz
14a	4.97	6.5	6.5	6.5
14b	4.84	7.5	3.0	14.6
14c	4.94	8.1	2.5	8.1
18b	4.51	9.9	–	8.9
18c	4.79	11.3	4.5	6.4
18d	4.92	12.1	4.9	7.7
18e	4.76	11.5	5.0	6.3
18g	4.50	9.3	–	9.3
22a	5.03	9.9	4.6	5.4
22b	4.94	15.2	3.5	7.0

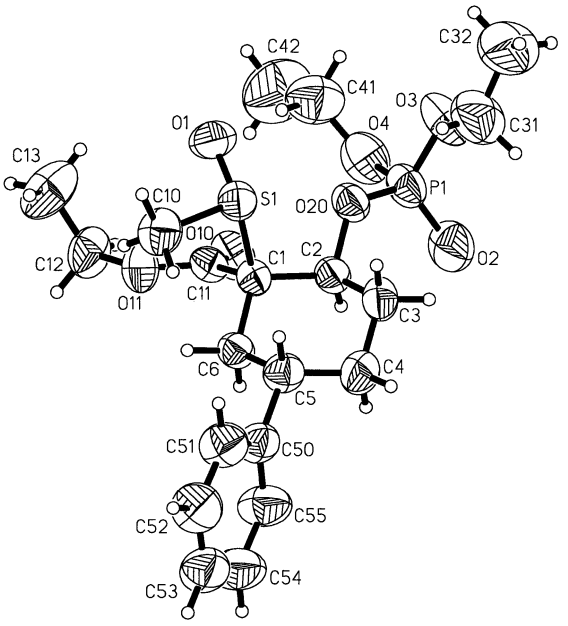


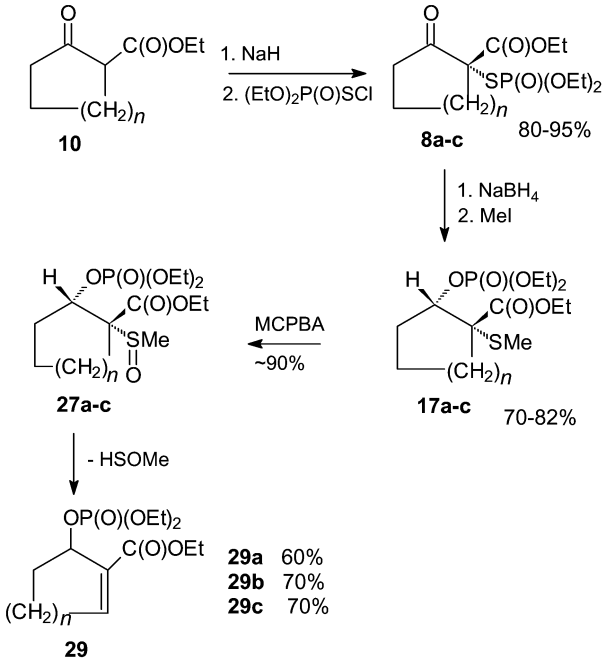
Fig. 4 Thermal ellipsoidal view with the atom numbering scheme of compound **28d**. Ellipsoids are shown with 50% probability.

torsion angles, calculation of the asymmetry parameters,[26,27] and also by dihedral angles between selected least-squares planes[28] (see Tables S5 and S6 in the ESI). Data corrections was carried out with the Enraf-Nonius SDP crystallographic computing package,[20] structure solution with SHELXS[21] and structure refinement with SHELXL.[22]

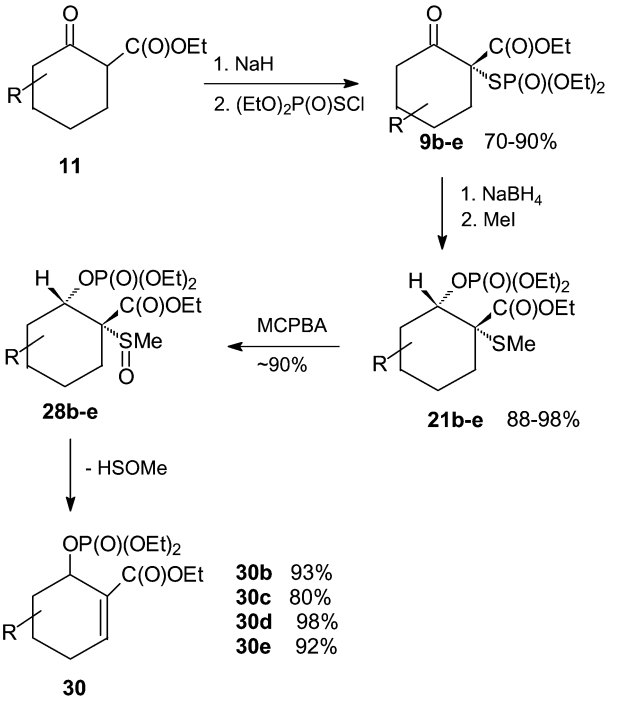
CCDC numbers 195722–24. See http://www.rsc.org/suppdata/nj/b2/b207700k/ for crystallographic files in CIF or other electronic format.

Syntheses

Thiophosphates 8 and 9. General procedure. To a stirred suspension of dry sodium hydride (0.12 g, 5 mmol) in dry tetrahydrofurane (10 mL) was added by syringe at 0 °C under argon atmosphere a solution of the appropriate β-ketoester (3.3 mmol) in tetrahydrofurane (1 mL). Immediately after addition (30 min) the reaction mixture was cooled to −78 °C and was added dropwise a solution of freshly prepared dialkoxyoxophosphoranesulfenyl chloride **1** (0.61 g, 3 mmol) in tetrahydrofuran (2 mL). Stirring was continued for 20 min (TLC analysis) and water–pentane–ether (1:1:1, 20 mL) was added to the reaction mixture. The organic layer was separated and the water layer was extracted with pentane–ether (1:1, 3 × 5 mL). The organic extracts were washed with $NaHCO_3$ (8 mL), water (5 mL) and dried over $MgSO_4$. Evaporation followed by column chromatography (petroleum ether–ethyl acetate 3:1), afforded pure thiophosphates **8** and **9** as colourless oils.



Scheme 9



Scheme 10

Table 6 Crystal data and experimental details

	Compound **9g**	Compound **9d**	Compound **28d**
Molecular formula	$C_{20}H_{37}O_6PS$	$C_{19}H_{27}O_6PS$	$C_{20}H_{31}O_7PS$
Formula weight	436.53	414.44	446.48
Crystallographic system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P2_1/n$
a/Å	6.075(2)	17.797(12)	13.705(3)
b/Å	19.042(5)	10.521(4)	11.378(2)
c/Å	20.889(8)	23.330(12)	15.252(3)
β /°	90.00	106.53(5)	103.02(3)
U/Å^3	2416.4(14)	4188.0(38)	2317.2(8)
Z	4	8	4
μ/cm^{-1}	2.069	2.369	2.209
λ/Å	1.54184	1.54184	1.54184
T/K	293(2)	293(2)	293(2)
Unique reflect.	4976	4315	4757
Reflect. [$I > 0\sigma(I)$]	4459	4109	4577
Obs. reflect. [$I > 2\sigma(I)$]	3385	3553	4089
R_{int}	0.0837	0.0731	0.0384
R_{obs}	0.0503	0.0484	0.0570
wR_{obs}[a]	0.1136	0.1358	0.1641

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

Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-2-oxocycloptanecarboxylate (8a). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.32 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.9 Hz, 6H, $POCH_2CH_3$), 1.98–2.20 (m, 2H, CH_2), 2.28–2.87 (m, 4H, CH_2), 4.06–4.26 (m, 4H, $POCH_2CH_3$), 4.19 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $COCH_2CH_3$). ^{31}P NMR ($CDCl_3$): δ 22.0. ^{13}C NMR ($CDCl_3$): δ 13.4 (s, $COCH_2CH_3$), 15.4 (d, $^3J_{CP}$ = 7.1 Hz, $POCH_2CH_3$), 19.2, 35.9, 36.8 (s, CH_2), 62.3 (s, $COCH_2CH_3$), 63.6 (d, $^2J_{CP}$ = 6.2 Hz, $POCH_2$), 167.4 (d, $^3J_{CP}$ = 8.3 Hz, $COCH_2CH_3$), 208.1 (d, $^3J_{CP}$ = 4.8 Hz, C=O). IR (film): ν/cm^{-1} 1255 s (P=O), 1732 s (C=O), 1760 s (EtC=O). MS (CI-isobutane): m/z (%) 325 (100) $[M+H]^+$. Anal. calcd for $C_{12}H_{21}O_6PS$ (324.37): C, 44.44; H, 6.53; P, 9.55; S, 9.88; found: C, 44.64; H, 6.71; P, 9.24; S, 9.55%. Yield: 82%. R_f (ethyl acetate–petroleum ether 1:2) = 0.30.

Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-2-oxocyclohexanecarboxylate (8b). ^{1}H NMR ($CDCl_3$): δ 1.30 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $COCH_2CH_3$), 1.33 (t, $^3J_{HH}$ = 6.3 Hz, 6H, $POCH_2CH_3$), 1.70–2.08 (m, 4H, CH_2), 2.15 (ddd, $^3J_{HH}$ = $^3J_{HH}$ = 12.7 Hz, $^3J_{HH}$ = 4.3 Hz, 1H, CH_2), 2.48 (ddd, $^3J_{HH}$ = $^3J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, CH_2), 2.65 (m, 1H, CH_2), 3.03 (m, 1H, CH_2), 4.05–4.40 (m, 6H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 22.2. ^{13}C NMR ($CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 7.1 Hz, $POCH_2CH_3$), 22.9, 26.8 (s, CH_2), 39.0 (d, $^3J_{CP}$ = 2.8 Hz, CH_2), 40.4 (s, CH_2), 62.6 (s, $COCH_2CH_3$), 64.1 (d, $^2J_{CP}$ = 6.1 Hz, $POCH_2CH_3$), 67.6 (s, CS), 167.8 (s, $COCH_2CH_3$), 201.2 (d, $^3J_{CP}$ = 7.9 Hz, C=O). IR (film): ν/cm^{-1} 1240 s (P=O), 1721 s (C=O), 1725 s (EtC=O). MS (CI-isobutane): m/z (%) 339 (100) $[M+H]^+$, 293 (25). Anal. calcd for $C_{13}H_{23}O_6PS$ (338.39): C, 46.15; H, 6.85; P, 9.15; S, 9.48; found: C, 46.00; H, 6.82; P, 9.39; S, 9.33%. Yield: 93%. R_f (ethyl acetate–petroleum ether 1:2) = 0.22.

Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-2-oxocycloheptanecarboxylate (8c). ^{1}H NMR ($CDCl_3$): δ 1.30 (t, $^3J_{HH}$ = 6.9 Hz, 3H, $COCH_2CH_3$), 1.34 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 6H, $POCH_2CH_3$), 1.50–1.91 (m, 6H, CH_2), 2.46–2.80 (m, 4H, CH_2), 4.05–4.35 (m, 6H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 22.5. ^{13}C NMR ($CDCl_3$): δ 12.8 (s, $COCH_2CH_3$), 14.9 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 23.6, 25.0, 28.5 (s, CH_2), 34.4 (d, $^3J_{CP}$ = 2.4 Hz, CH_2CS), 61.4 (s, $COCH_2CH_3$), 62.7, 63.0 (d, $^2J_{CP}$ = 6.4 Hz, $POCH_2CH_3$), 69.6 (s, CS), 167.4 (s, $COCH_2CH_3$), 202.4 (d, $^3J_{CP}$ = 7.1 Hz, C=O). IR (film): ν/cm^{-1} 1247 s (P=O), 1712 s (C=O), 1738 s (EtC=O). MS (EI, 70 eV): m/z (%) 352 (32) $[M]^+$, 171 (100) $[H+HSP(O)(OEt)_2]^+$, 155 (37), 109 (47), 81 (49). Anal. calcd for $C_{14}H_{25}O_6PS$ (352.43): C, 47.73; H, 7.15; P, 8.79; S, 9.10; found: C, 47.98; H, 7.39; P, 9.06; S, 8.40%. Yield: 78%. R_f (ethyl acetate–petroleum ether 1:5) = 0.34.

S-*(1,3-Dimethyl-2-oxocyclohexyl)*-O,O-*diethyl thiophosphate (9a).* The ratio of diastereoisomers is 2.8:1. Major isomer of **9a**: ^{1}H NMR ($CDCl_3$): δ 0.99 (d, $^3J_{HH}$ = 6.5 Hz, 3H, $CHCH_3$), 1.26 (t, $^3J_{HH}$ = 7.0 Hz, $COCH_2CH_3$), 1.73 (s, 3H, CCH_3), 1.90–2.05 (m, 2H, CH_2), 2.24 (dd, $^3J_{HH}$ = $^3J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = $^3J_{HH}$ = 5.5 Hz, 2H, CH_2), 2.54 (dd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 6.3 Hz, 2H, CH_2), 2.59 (ddq, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 6.3 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, $CHCH_3$), 3.94–4.18 (m, 4H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 25.1. ^{13}C NMR ($CDCl_3$): δ 14.9 (s, $CHCH_3$), 15.5, 15.7 (s, OCH_2CH_3), 21.9 (s, CH_2), 25.3 (s, CCH_3), 35.1 (s, CH_2), 41.1 (s, CH), 42.4 (s, CH_2), 57.8 (d, $^2J_{CP}$ = 5.0 Hz, CS), 63.21, 63.22 (d, $^2J_{CP}$ = 7.2 Hz, $POCH_2CH_3$), 209.0 (d, $^3J_{CP}$ = 7.4 Hz, C=O). IR (film): ν/cm^{-1} 1254 s (P=O), 1712 s (C=O). MS (CI-isobutane): m/z (%) 295 (100) $[M+H]^+$. HRMS (CI) calcd for $C_{12}O_4H_{23}PS+H$ $[M+H]^+$ 295.1136; found: 295.1135. Yield: 59%. R_f (ethyl acetate–petroleum ether 1:2) = 0.46. Minor isomer of **9a**: ^{1}H NMR ($CDCl_3$): δ 0.97 (d, $^3J_{HH}$ = 6.5 Hz, 3H, $CHCH_3$), 1.29 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 2.5 Hz, 6H, OCH_2CH_3), 1.56 (s, 3H, CCH_3), 1.62–1.79 (m, 2H, CH_2), 1.99–2.06 (m, 2H, CH_2), 2.09–2.29 (m, 2H, CH_2), 2.24 (dd, $^3J_{HH}$ = $^3J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = $^3J_{HH}$ = 5.5 Hz, 2H, CH_2), 2.54 (dd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 6.3 Hz, 2H, CH_2), 3.34 (ddq, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 6.3 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, $CHCH_3$), 3.97–4.19 (m, 4H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 23.7. ^{13}C NMR ($CDCl_3$): δ 14.5 (s, $CHCH_3$), 15.5, 15.7 (s, OCH_2CH_3), 21.3 (s, CH_2), 25.2 (d, $^3J_{CP}$ = 10.0 Hz, CCH_3), 36.7 (s, CH_2), 39.7 (s, CH), 42.9 (d, $^3J_{CP}$ = 12.0 Hz, CH_2), 59.8 (s, CS), 63.51, 63.52 (d, $^2J_{CP}$ = 7.0 Hz, $POCH_2CH_3$), 208.7 (s, C=O). IR (film): ν/cm^{-1} 1254 s (P=O), 1712 s (C=O). MS (CI-isobutane): m/z (%) 295 (100) $[M+H]^+$. HRMS (CI) calcd for $C_{12}O_4H_{23}PS+H$ $[M+H]^+$ 295.1136; found: 295.1135. Yield: 29%. R_f (ethyl acetate–petroleum ether 1:2) = 0.44.

Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-3-methyl-2-oxocyclohexanecarboxylate (9b). The ratio of diastereoisomers is 4:1. Major isomer of **9b**: ^{1}H NMR ($CDCl_3$): δ 1.00 (d, $^3J_{HH}$ = 6.5 Hz, 3H, $CHCH_3$), 1.32 (t, $^3J_{HH}$ = 7.0 Hz, $POCH_2CH_3$), 1.33 (t, $^3J_{HH}$ = 6.0 Hz, $COCH_2CH_3$), 1.36–1.88 (m, 2H, CH_2), 2.05–2.27 (m, 2H, CH_2), 2.53–2.66 (m, 2H, CH_2), 3.09 (m, CH), 4.10–4.35 (m, 6H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 21.0. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.9 (s, CH_3), 14.7 (s, $COCH_2CH_3$), 15.8 (d, $^3J_{CP}$ = 7.1 Hz, $POCH_2CH_3$), 20.8, 36.5 (s, CH_2), 37.1 (d, $^3J_{CP}$ = 5.1 Hz, CH_2), 41.8 (s, CH), 62.3 (s, $COCH_2CH_3$), 64.0, 64.2 (d, $^2J_{CP}$ = 7.1 Hz, $POCH_2CH_3$), 67.2 (d, $^2J_{CP}$ = 5.0 Hz, CS), 168.8 (s, $COCH_2CH_3$), 204.9 (d, $^3J_{CP}$ = 9.1 Hz, C=O). IR (film): ν/cm^{-1} 1254 s (P=O), 1716 s (C=O), 1739 s (EtC=O). MS (EI, 70 eV): m/z (%) 352 (8) $[M]^+$, 182 (100) $[M-HSP(O)(OEt)_2]^+$, 171 (45), 138 (85), 109 (36), 81 (81), 55 (86), 43 (47), 39 (37). Anal. calcd for $C_{14}H_{25}O_6PS$ (352.42): C, 47.71; H, 7.16; P, 8.79; S, 9.10; found: C, 47.21; H, 7.21; P, 8.66; S, 8.75%. Yield: 62%. R_f (ethyl acetate–petroleum ether 1:2) = 0.26. Minor isomer of **9b**:^{1}H NMR ($CDCl_3$): δ 1.09 (d, $^3J_{HH}$ = 6.4 Hz, 3H, $CHCH_3$), 1.15–1.42 (m, 9H, OCH_2CH_3), 1.66–2.10 (m, 5H, CH_2), 2.55 (m, 1H, CH_2), 3.45 (m, 1H, CH), 4.10–4.35 (m, 6H, OCH_2). ^{31}P NMR ($CDCl_3$): δ 22.8. ^{13}C NMR ($CDCl_3$): δ 13.7 (s, CH_3), 14.9 (s, $COCH_2CH_3$), 15.8 (d, $^3J_{CP}$ = 7.4 Hz, $POCH_2CH_3$), 23.2, 35.9, 39.7, (s, CH_2), 44.4 (s, CH), 62.9 (s, $COCH_2CH_3$), 64.0 (d, $^2J_{CP}$ = 6.4 Hz, $POCH_2CH_3$), 67.5 (s, CS), 168.3 (s, $COCH_2CH_3$), 202.5 (d, $^3J_{CP}$ = 8.7 Hz, C=O). IR (film): ν/cm^{-1} 1256 s (P=O), 1714 s (C=O), 1739 s (EtC=O). MS (EI, 70 eV): m/z (%) 352 (10) $[M]^+$, 182 (100) $[M-HSP(O)(OEt)_2)]^+$, 269 (39), 171 (72), 155 (24), 136 (33), 109 (31), 81 (42), 55 (39), 41 (28). Anal. calcd for $C_{14}H_{25}O_6PS$ (352.42): C, 47.71; H, 7.16; P, 8.79; S, 9.10; found: C, 47.49; H, 7.01; P, 8.53; S, 8.84%. Yield: 15%. R_f (ethyl acetate–petroleum ether 1:2) = 0.23.

Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-4-methyl-2-oxocyclohexanecarboxylate (9c). The ratio of diastereoisomers is 3:1. Mixture of two isomers of **9c**: ^{1}H NMR ($CDCl_3$): δ 0.94 (d, $^3J_{HH}$ = 6.4 Hz, 3H, $CHCH_3$, major), 0.97 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHCH_3$, minor), 1.20 (t,$^3J_{HH}$ = 7.1 Hz, 6H, $COCH_2CH_3$), 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 12H, $POCH_2CH_3$), 1.52–2.30 (m, 10H, CH_2), 2.53 (m, 3H, CH_2), 3.12 (m, 1H, CH_2), 3.85–4.40 (m, 12H, OCH_2). ^{31}P NMR ($CDCl_3$): δ 21.5 (major), 22.5 (minor). ^{13}C NMR (DEPT, $CDCl_3$): δ 13.6 (s, $COCH_2CH_3$), 15.7 (d, $^3J_{CP}$ = 7.2 Hz, $POCH_2CH_3$), 20.2 (s, CCH_3, minor), 21.7 (s, CCH_3, major), 28.9 (s, CH_2, major), 29.4 (s, CH_2, minor), 31.4 (s, CH_2), 33.5 (s, $CHCH_3$, minor), 34.3 (s, $CHCH_3$, major), 34.6 (d, $^3J_{CP}$ = 3.3 Hz, CH_2, minor), 37.8 (d, $^3J_{CP}$ = 4.3 Hz, CH_2, major), 46.3, 48.3 (s, CH_2), 62.2 (s, $COCH_2$, major), 62.3 (s, $COCH_2$, minor), 64.0 (d, $^2J_{CP}$ = 6.8 Hz, $POCH_2$), 66.6 (s, CS), 164.5 (s, $COCH_2$), 200.3 (s, C=O). IR (film): ν/cm^{-1} 1256 s (P=O), 1713 s (C=O), 1736 s (EtC=O). MS (CI-isobutane): m/z (%) 353 (100) $[M+H]^+$. Anal. calcd for $C_{14}H_{25}O_6PS$ (352.42): C, 47.71; H, 7.16; P, 8.79; S, 9.10; found: C, 47.38; H, 7.26; P, 8.70; S, 8.78%. Yield = 90%. R_f (ethyl acetate–petroleum ether 1:2) = 0.25.

Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-5-phenyl-2-oxocyclohexanecarboxylate (9d). The ratio of diastereoisomers is 5:1.

Major isomer of **9d**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20–1.45 (m, 9H, OCH_2HC_3), 2.04 (m, 1H, CH_2), 2.08–2.56 (m, 2H, CH_2), 2.67–2.81 (m, 2H, CH_2), 3.16 (ddd, $^2J_{HH} = {}^3J_{HH} =$ 13.9 Hz, $^3J_{HH} = 6.2$ Hz, 1H, CH_2), 3.66 (dddd, $^3J_{HH} = {}^3J_{HH} = 3.8$ Hz, $^3J_{HH} = {}^3J_{HH} = 12.0$ Hz, 1H, PhC*H*), 4.05–4.40 (m, 6H, OCH_2), 7.15–7.42 (m, 5H, CH_{arom}). ^{31}P NMR ($CDCl_3$): δ 20.8. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.8, (d, $^3J_{CP} = 7.1$ Hz, $POCH_2CH_3$), 34.2, 38.1 (s, CH_2), 38.2 (s, CH), 42.9 (d, $^3J_{CP} = 4.6$ Hz, CH_2CS), 62.4 (s, $COCH_2$), 64.1, 64.3 (d, $^2J_{CP} = 8.0$ Hz, $POCH_2$), 66.7 (d, $^2J_{CP} = 3.6$ Hz, CS), 126.7, 128.5, 143.0 (s, CH_{arom}), 168.2 (s, $COCH_2CH_3$), 201.8 (d, $^3J_{CP} = 9.2$ Hz, C=O). IR (KBr): ν/cm^{-1} 1265 s (P=O), 1718 s (C=O), 1734 s (EtC=O). MS (CI-isobutane): m/z (%) 415 (100) $[M+H]^+$. Anal. calcd for $C_{19}H_{27}O_6PS$ (414.50): C, 55.06; H, 6.57; P, 7.47; S, 7.74; found: C, 54.90; H, 6.60; P, 7.48; S, 7.36%. Yield: 72%. R_f (ethyl acetate–petroleum ether 1:2) = 0.24. Minor isomer of **9d**: ^{1}H NMR ($CDCl_3$): δ 1.3–1.44 (m, 9H, OCH_2CH_3), 2.05–2.17 (m, 2H, CH_2), 2.38 (dd, $^2J_{HH} = {}^3J_{HH} = 13.7$ Hz, 1H, CH_2CS), 2.65–3.30 (m, 4H, CH_2), 4.10–4.36 (m, 4H, $POCH_2$), 4.33 (q, $^3J_{HH} = 7.1$ Hz, 2H, $COCH_2CH_3$), 7.12–7.40 (m, 5H, CH_{arom}). ^{31}P NMR ($CDCl_3$): δ 22.3. ^{13}C NMR ($CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.8, 15.9 (d, $^3J_{CP} = 7.8$ Hz, $POCH_2CH_3$), 33.2, 40.0 (s, CH_2), 40.9 (s, CH), 46.9 (s, CH_2CS), 62.8 (s, CH_2) 64.2, 64.3 (d, $^2J_{CP} = 7.7$ Hz, $POCH_2$), 67.1 (d, $^2J_{CP} = 2.3$ Hz, CS), 126.6, 128.6, 142.9 (s, CH_{arom}), 167.6 (d, $^3J_{CP} = 5.4$ Hz, $COCH_2CH_3$), 200.4 (d, $^3J_{CP} = 6.5$ Hz, C=O). IR (KBr): ν/cm^{-1} 1265 s (P=O), 1718 s (C=O), 1734 s (EtC=O). MS (CI-isobutane): m/z (%) 415 (100) $[M+H]^+$. Anal. calcd for $C_{19}H_{27}O_6PS$ (414.50): C, 55.06; H, 6.57; P, 7.47; S, 7.74; found: C, 55.21; H, 6.59; P, 7.32; S, 7.39%. Yield: 16%. R_f (ethyl acetate–petroleum ether 1:2) = 0.27.

*Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-5-*tert*-butyl-2-oxocyclohexanecarboxylate (9e).* The ratio of diastereoisomers is 2.5:1. Major isomer of **9e**: ^{1}H NMR ($CDCl_3$): δ 0.93 (s, 9H, $C(CH_3)_3$), 1.26–1.36 (m, 9H, OCH_2CH_3), 1.55 (m, 1H, CH), 2.00–2.20 (m, 2H, CH_2), 2.32–2.71 (m, 3H, CH_2), 2.90 (m, 1H, CH_2), 4.10–4.30 (m, 6H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 20.9. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.8 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2CH_3$), 27.4 (s, CCH_3), 28.0 (s, CH_2), 32.2 [s, $C(CH_3)_3$], 37.7 (d, $^3J_{CP} = 5.1$ Hz, CH_2), 37.9 (s, CH_2), 41.7 [s, $CHC(CH_3)_3$], 62.3 (s, $COCH_2CH_3$), 64.1, 64.3 (d, $^2J_{CP} = 7.4$ Hz, $POCH_2$), 66.8 (d, $^2J_{CP} = 3.4$ Hz, CS), 168.7 (s, $COCH_2CH_3$), 202.8 (d, $^3J_{CP} = 8.8$ Hz, C=O). IR (film): ν/cm^{-1} 1249 s (P=O), 1721 s (C=O), 1736 s (EtC=O). MS (CI-isobutane): m/z (%) 395 (100) $[M+H]^+$, 349 (18). HRMS (CI) $[M+H]^+$ found: 395.1649; $C_{17}H_{32}O_6PS$ requires 395.1657. Yield: 47%. R_f (ethyl acetate–petroleum ether 1:1) = 0.48. Minor isomer of **9e**: ^{1}H NMR ($CDCl_3$): δ 0.95 (s, 9H, $C(CH_3)_3$), 1.20–1.35 (m, 9H, OCH_2CH_3), 1.42–2.16 (m, 3H, CH_2), 2.21–3.12 (m, 3H, CH_2), 2.21–3.12 (m, 3H, CH, CH_2), 3.82 (m, 1H, CH_2), 4.11–4.32 (m, 6H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 22.4. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.8 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2CH_3$), 27.1 (s, CH_2), 27.3 [s, $C(CH_3)_3$], 32.4 [s, $C(CH_3)_3$], 39.9 (s, CH_2), 40.5 (d, $^3J_{CP} = 3.4$ Hz, CH_2), 44.7 (s, CH), 62.4 (s, $COCH_2CH_3$), 64.1, 64.3 (d, $^2J_{CP} = 7.4$ Hz, $POCH_2CH_3$), 67.2 (d, $^2J_{CP} = 3.5$ Hz, CS), 167.8 (s, $^3J_{CP} =$ 5.0 Hz, $COCH_2CH_3$), 201.2 (d, $^3J_{CP} = 5.8$ Hz, C=O). IR (film): ν/cm^{-1} 1251 s (P=O), 1720 s (C=O), 1739 s (EtC=O). MS (CI-isobutane): m/z (%) 395 (100) $[M+H]^+$. HRMS (CI) calcd for $C_{17}H_{31}O_6PS + H$ $[M+H]^+$ 395.1657; found: 395.1649. Yield: 16%. R_f = (ethyl acetate–petroleum ether 1:1) = 0.39.

Ethyl 1-[(diethoxyphosphoryl)sulfanyl]-4,4,6-trimethyl-2-oxocyclohexanecarboxylate (9f). The ratio of diastereoisomers is 1.2:1. Major isomer of **9f**: ^{1}H NMR ($CDCl_3$): δ 1.02 [s, 6H, $C(CH_3)_2$] 1.24 (d, $^3J_{HH} = 6.8$ Hz, 3H, $CHCH_3$), 1.28 (t, $^3J_{HH} = 7.1$ Hz, 3H, $COCH_2CH_3$), 1.28–1.40 (m, 6H, $POCH_2CH_3$), 1.48 (dd, $^2J_{HH} = 13.1$ Hz, $^3J_{HH} = 3.0$ Hz, 1H, CCH_2CH), 1.80 (dd, $^2J_{HH} = {}^3J_{HH} = 13.1$ Hz, 1H, CCH_2CH), 2.41 [dd, $^2J_{HH} = 14.5$ Hz, 1H, $CH_2C(O)$], 2.64 (m, 1H, $CHCH_3$), 2.86 [d, $^2J_{HH} = 14.5$ Hz, 1H, $CH_2C(O)$], 4.20 (q, $^3J_{HH} = 7.1$ Hz, 2H, $COCH_2CH_3$), 4.10–4.36 (m, 4H, $POCH_2CH_3$). ^{31}P NMR ($CDCl_3$): δ 22.4. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.9 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP} = 3.4$ Hz, $POCH_2CH_3$), 18.2 (s, $CHCH_3$), 26.6, 31.9 [s, $C(CH_3)_2$], 23.4 [s, $C(CH_3)_2$], 38.4 (d, $^3J_{CP} = 4.9$ Hz, $CHCH_3$), 44.1 (s, CCH_2CH), 52.8 [s, $CH_2C(O)$], 62.5 (s, $COCH_2$), 63.8, 64.0 (d, $^2J_{CP} = 5.7$ Hz, $POCH_2$), 75.0 (s, CS), 166.4 (d, $^3J_{CP} =$ 5.3 Hz, $COCH_2CH_3$), 200.8 (s, C=O). IR (film): ν/cm^{-1} 1251 s (P=O), 1715 s (C=O), 1738 s (EtC=O). MS (CI-isobutane): m/z (%) 381 (100) $[M+H]^+$. Anal. calcd for $C_{16}H_{29}O_6PS$ (380.49): C, 50.50; H, 7.70; P, 8.14; S, 8.43; found: C, 50.36; H, 7.61; P, 8.05; S, 8.22%. Yield: 28%. R_f (ethyl acetate–petroleum ether 1:5) = 0.65. Minor isomer of **9f**: ^{1}H NMR ($CDCl_3$): δ 0.92 [s, 3H, $C(CH_3)_2$], 0.98 (d, $^3J_{HH} = 6.7$ Hz, 3H, $CHCH_3$), 1.04 [s, 3H, $C(CH_3)_2$], 1.24–1.36 (m, 10H, OCH_2CH_3, CCH_2CH), 1.87 (dd, $^2J_{HH} = {}^3J_{HH} = 13.3$ Hz, 1H CCH_2CH), 2.03 [dd, $^2J_{HH} = 13.3$ Hz, 1H, $CH_2C(O)$], 2.93 (m, 1H, $CHCH_3$), 3.14 [d, $^2J_{HH} = 13.3$ Hz, 1H, $CH_2C(O)$], 4.05–4.26 (m, 6H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 21.4. ^{13}C NMR (DEPT, $CDCl_3$): δ 14.0 (s, $COCH_2CH_3$), 15.8, 15.9 (d, $^3J_{CP} = 6.5$ Hz, $POCH_2CH_3$), 17.0 (s, $CHCH_3$), 25.9, 31.7 (s, $C(CH_3)_2$), 35.2 (s, $C(CH_3)_2$), 37.0 (d, $^3J_{CP} = 9.7$ Hz, $CHCH_3$), 42.4 (s, CCH_2CH), 49.7 [s, $CH_2C(O)$], 62.3 (s, $COCH_2CH_3$), 64.0, 64.8 (d, $^2J_{CP} = 7.5$ Hz, $POCH_2$), 71.5 (s, CS), 168.5 (s, $COCH_2CH_3$), 202.3 (s, C=O). IR (film): ν/cm^{-1} 1250 s (P=O), 1717 s (C=O), 1732 s (EtC=O). MS (CI-isobutane): m/z (%) 381 (100) $[M+H]^+$. Anal. calcd for $C_{16}H_{29}O_6PS$ (380.49): C, 50.50; H, 7.70; P, 8.14; S, 8.43; found: C, 50.38; H, 7.65; P, 7.95; S, 8.20%. Yield: 24%. R_f (ethyl acetate–petroleum ether 1:2) = 0.43.

Ethyl 1-[(dineopentoxyphosphoryl)sulfanyl]-3-methyl-2-oxocyclohexanecarboxylate (9g). The ratio of diastereoisomers is 3.8:1. Major isomer of **9g**: ^{1}H NMR ($CDCl_3$): δ 0.91 (s, 9H, CCH_3), 0.92 (s, 9H, CCH_3), 0.98 (d, $^3J_{HH} = 6.3$ Hz, 3H, $CHCH_3$), 1.28 (t, $^3J_{HH} = 6.3$ Hz, OCH_2CH_3), 1.40 (m, 1H, CH_2), 1.77 (m, 1H, CH_2), 2.08 (m, 1H, CH_2), 2.22 (m, 1H, CH_2), 2.45–2.63 (m, 2H, CH_2), 3.09 (ddq, $^3J_{HH} = 18.5$ Hz, $^3J_{HP} = 6.3$ Hz, $^3J_{HH} = 1.2$ Hz, $CHCH_3$), 3.65–3.87 9 (m, 4H, OCH_2C), 4.15–4.37 (m, 2H, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 21.0. ^{13}C NMR ($CDCl_3$): δ 13.9 (s, $CHCH_3$), 14.7 (s, OCH_2CH_3), 20.8 (s, CH_2), 25.9 (s, CCH_3), 31.9 (d, $^3J_{CP} = 7.2$ Hz, CCH_3), 36.4 (s, CH_2), 37.1 (d, $^3J_{CP} = 3.3$ Hz, CH_2), 41.9 (s, CH), 62.2 (s, $COCH_2CH_3$), 67.3 (d, $^2J_{CP} = 3.5$ Hz, CS), 76.9, 77.0 (d, $^2J_{CP} = 7.1$ Hz, $POCH_2$), 168.7 (s, $COCH_2$), 204.8 (d, $^3J_{CP} = 10.3$ Hz, C=O). IR (film): ν/cm^{-1} 1266 s (P=O), 1732 s (C=O). MS (CI-isobutane): m/z (%) 437 (100) $[M+H]^+$. Anal. calcd for $C_{20}H_{37}O_6PS$ (436.61): C, 55.01; H, 8.56; P, 7.09; S, 7.35; found: C, 54.70; H, 8.48; P, 6.78; S, 7.02%. Yield: 43%. R_f (ethyl acetate–petroleum ether 1:2) = 0.35.

Reaction of thiophosphates 8 and 9 with sodium borohydride. General procedure. To a stirred suspension of sodium borohydride (0.076 g, 2 mmol) in dry methanol–dichloromethane (40 mL in the ratio 1:1) was added dropwise at −78 °C under argon atmosphere to a solution of the appropriate thiophosphate (1 mmol) in dichloromethane (5 mL). The reaction was monitored by TLC and stirring was continued at −78 °C until no starting thiophosphate **8** or **9** was detectable (3 h). The reaction was stopped by addition of 1 mL of dry acetone and after an additional 30 min ice water was added. The reaction mixture was extracted with dichloromethane (2 × 10 mL), washed with NH_4Cl (5 mL) and dried over $MgSO_4$. Solvent was removed under reduced pressure and the residue was analyzed by ^{31}P and ^{1}H NMR spectroscopy (see Tables 3 and 4). The crude reaction mixture was subjected to silica gel column

chromatography with a gradient of petroleum ether–ethyl acetate (20:1 to 5:1) to provide the pure thiols (colourless oils) **14** and **18**, episulfides (colourless oils) **15** and **19** and olefins (colourless liquids) **16** and **20**.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-sulfanylcyclopentanecarboxylate (14a). Single diastereoisomer.^{1}H NMR ($CDCl_3$): δ 1.25 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $COCH_2CH_3$), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 6H, $POCH_2CH_3$), 1.38–2.21 (m, 5H, CH_2), 2.37 (m, 1H, CH_2), 2.43 (s, 1H, SH), 4.05–4.24 (m, 4H, $POCH_2$), 4.18 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $COCH_2$), 4.97 (ddd, $^3J_{HP}$ = $^3J_{HH}$ = $^3J_{HH}$ = 6.5 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.8. ^{13}C NMR ($CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 6.3 Hz, $POCH_2CH_3$), 19.4, 30.1, 35.3 (s, CH_2), 57.6 (d, $^3J_{CP}$ = 8.6 Hz, CS), 61.7 (s, $COCH_2$), 63.7, 63.8 (d, $^2J_{CP}$ = 6.2 Hz, $POCH_2$), 81.4 (d, $^2J_{CP}$ = 4.8 Hz, CHOP), 172.3 (s, C=O). IR (film): ν/cm^{-1} 1266 s (P=O), 1730 s (C=O). MS (EI, 70 eV): m/z (%) 326 (3) $[M]^+$, 155 (100), 127 (35), 99 (44). Anal. calcd for $C_{12}H_{23}O_6PS$ (326.39): C, 44.16; H, 7.10; P, 9.49; S, 9.82; found: C, 43.93; H, 7.10; P, 9.14; S, 9.38%. Yield: 85%. R_f (ethyl acetate) = 0.42.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-sulfanylcyclohexanecarboxylate (14b). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.33 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 1 Hz, 6H, $POCH_2CH_3$), 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.55–1.78 (m, 4H, CH_2), 1.80–2.00 (m, 2H, CH_2), 2.00–2.16 (m, 2H, CH_2), 2.42 (s, 1H, SH), 4.12 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $COCH_2$), 4.18 (m, 4H, $POCH_2$), 4.84 (ddd, $^3J_{HP}$ = 14.6 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 3.0 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.8. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 16.0 (d, $^3J_{CP}$ = 6.7 Hz, $POCH_2CH_3$), 20.9, 21.9, 29.0, 33.9 (s, CH_2), 55.6 (d, $^3J_{CP}$ = 8.6 Hz, CS), 61.8 (s, $COCH_2$), 63.6, 63.8 (d, $^2J_{CP}$ = 6.0 Hz, $POCH_2$), 77.8 (d, $^2J_{CP}$ = 4.5 Hz, CHOP), 172.1 (s, C=O). IR (film): ν/cm^{-1} 1264 s (P=O), 1729 s (C=O). MS (CI-isobutane): m/z (%) 341 (100) $[M+H]^+$, 155 (7) $[H+HOP(O)(OEt)_2]^+$. Anal. calcd for $C_{13}H_{25}O_6PS$ (340.42): C, 45.87; H, 7.40; P, 9.10; S, 9.42; found: C, 45.30; H, 6.67; P, 8.78; S, 8.92%. Yield:89%. R_f (ethyl acetate) = 0.42.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-sulfanylcycloheptanecarboxylate (14c). Single diastereoisomer.^{1}H NMR ($CDCl_3$): δ 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.30 (dt,$^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 6H, $POCH_2CH_3$), 1.35–2.32 (m, 10H, CH_2), 2.50 (s, 1H, SH), 4.05–4.28 (m, 6H, OCH_2), 4.94 (ddd, $^3J_{HP}$ = $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.9. ^{13}C NMR ($CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 6.9 Hz, $POCH_2CH_3$), 22.2, 23.0, 26.7, 31.3, 35.0 (s, CH_2), 58.9 (d, $^3J_{CP}$ = 8.7 Hz, CS), 61.8 (s, $COCH_2$), 63.5, 63.7 (d, $^2J_{CP}$ = 6.9 Hz, $POCH_2$), 81.7 (d, $^2J_{CP}$ = 5.0 Hz, CHOP), 172.6 (s, C=O) ppm. IR (film): ν/cm^{-1} 1264 s (P=O), 1729 s (C=O). MS (CI-isobutane): m/z (%) 355 (100) $[M+H]^+$, 155 (10) $[H+HOP(O)(OEt)_2]^+$. Anal. calcd for $C_{14}H_{27}O_6PS$ (354.45): C, 47.46; H, 7.68; P, 8.74; S, 9.05; found: C, 47.62; H, 7.81; P, 8.43; S, 8.93%. Yield: 49%. R_f (ethyl acetate–petroleum ether 1:5) = 0.12.

Ethyl 2-[(diethoxyphosphoryl)oxy]-3-methyl-1-sulfanylcyclohexanecarboxylate (18b). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.00 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHCH_3$), 1.23 (m, 9H, OCH_2CH_3), 1.42–2.35 (m, 7H, CH and CH_2), 2.43 (s, 1H, SH), 4.00–4.30 (m, 4H, $POCH_2$), 4.14 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $COCH_2$), 4.51 (dd, $^3J_{HP}$ = 8.9 Hz, $^3J_{HH}$ = 9.9 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.1. ^{13}C NMR ($CDCl_3$): δ 13.5 (s, $COCH_2CH_3$), 15.6 (d, $^3J_{CP}$ = 6.6 Hz, $POCH_2CH_3$), 18.0 (s, $CHCH_3$), 20.5, 31.8, 33.7 (s, CH_2), 36.5 (s, $CHCH_3$), 59.2 (s, CS), 62.0 (s, $COCH_2$), 63.2, 63.4 (d, $^2J_{CP}$ = 6.7 Hz, $POCH_2$), 84.2 (d, $^2J_{CP}$ = 5.0 Hz, CHOP), 172.0 (s, C=O). IR (film): ν/cm^{-1} 1268 s (P=O), 1731 s (C=O). MS (CI-isobutane): m/z (%) 355 (100) $[M+H]^+$, 155 (12) $[H+HOP(O)(OEt)_2]^+$. Anal. calcd for $C_{14}H_{27}O_6PS$ (354.45): C, 47.45; H, 7.68; P, 8.74; S, 9.05; found: C, 46.90; H, 7.51; P, 8.41; S, 8.48%. Yield: 90%. R_f (ethyl acetate) = 0.50.

Ethyl 2-[(diethoxyphosphoryl)oxy]-4-methyl-1-sulfanylcyclohexanecarboxylate (18c). Single diastereoisomer.^{1}H NMR ($CDCl_3$): δ 0.93 (d, $^3J_{HH}$ = 5.9 Hz, 3H, $CHCH_3$), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.29 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 6H, $POCH_2CH_3$), 1.44–1.60 (m, 4H, CH_2), 1.74–2.15 (m, 3H, CH_2), 2.34 (s, 1H, SH), 4.00–4.12 (m, 4H, $POCH_2$), 4.12–4.20 (m, 2H, $COCH_2$), 4.79 (ddd, $^3J_{HH}$ = 11.3 Hz, $^3J_{HP}$ = 6.4 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.2. ^{13}C NMR ($CDCl_3$): δ 13.9 (s, $COCH_2CH_3$), 16.0 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 21.5 (s, $CHCH_3$), 28.9 (s, CH_2), 30.9 (s, $CHCH_3$), 35.5, 36.9 (s, CH_2), 57.8 (d, $^3J_{CP}$ = 8.2 Hz, CS), 62.2 (s, $COCH_2$), 63.7, 63.8 (d, $^2J_{CP}$ = 6.8 Hz, $POCH_2$), 78.7 (d, $^2J_{CP}$ = 5.4 Hz, CHOP), 172.7 (s, C=O). IR (film): ν/cm^{-1} 1264 s (P=O), 1732 s (C=O). MS (CI-isobutane): m/z (%) 355 (100) $[M+H]^+$, 155 (8) $[H+HOP(O)(OEt)_2]^+$. Anal. calcd for $C_{14}H_{27}O_6PS$ (354.45): C, 47.45; H, 7.68; P, 8.74; S, 9.05; found: C, 46.90; H, 7.65; P, 8.52; S, 8.66%. Yield: 83%. R_f (ethyl acetate) = 0.48.

Ethyl 2-[(diethoxyphosphoryl)oxy]-5-phenyl-1-sulfanylcyclohexanecarboxylate (18d). Single diastereoisomer.^{1}H NMR ($CDCl_3$): δ 1.20–1.33 (m, 9H, OCH_2CH_3), 1.66 (m, 1H, CH_2), 1.87 (m, 1H, CH), 2.08–2.25 (m, 4H, CH_2), 2.56 (s, 1H, SH), 3.05 (m, 1H, CH_2), 4.05–4.27 (m, 6H, OCH_2), 4.92 (ddd, $^3J_{HH}$ = 12.1 Hz, $^3J_{HP}$ = 7.7 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.9. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.8 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 28.8, 31.0 (s, CH_2), 37.9 (s, CH), 42.9 (s, CH_2), 58.2 (d, $^3J_{CP}$ = 8.6 Hz, CS), 62.2 (s, $COCH_2$), 63.5, 63.6 (d, $^2J_{CP}$ = 5.2 Hz, $POCH_2$), 78.2 (d, $^2J_{CP}$ = 4.6 Hz, CHOP), 126.6, 128.4, 143.8 (s, CH_{arom}) 171.9 (s, C=O). IR (film): ν/cm^{-1} 1250 s (P=O), 1729(C=O). MS (EI, 70 eV): m/z 416 (3) $[M]^+$, 155 (100), 127 (60), 104 (99), 91 (56). Anal. calcd for $C_{19}H_{29}O_6PS$ (416.52): C, 54.78; H, 7.03; P, 7.43; S, 7.70; found: C, 54.58; H, 6.81; P, 7.29; S, 7.32%. Yield: 85%. R_f (ethyl acetate–petroleum ether 1:1) = 0.10.

*Ethyl 2-[(diethoxyphosphoryl)oxy]-5-*tert*-butyl-1-sulfanylcyclohexanecarboxylate (18e).* Single diastereoisomer.^{1}H NMR ($CDCl_3$): δ 0.85 (s, 9H, CCH_3), 1.10–1.32 (m, 9H, OCH_2CH_3), 1.42–2.30 (m, 7H, CH_2), 2.44 (s, 1H, SH), 4.00–4.20 (m, 6H, OCH_2), 4.76 (ddd, $^3J_{HH}$ = 11.5 Hz, $^3J_{HP}$ = 6.3 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.1. ^{13}C NMR ($CDCl_3$): δ 13.9 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 6.3 Hz, $POCH_2CH_3$), 24.8 (s, CH_2), 27.2 [s, $C(CH_3)_3$], 28.7 (s, CH_2), 31.9 [s, $C(CH_3)_3$], 37.1 (s, CH_2), 41.5 [s, $CHC(CH_3)_3$], 58.5 (d, $^3J_{CP}$ = 8.4 Hz, CS), 62.2 (s, $COCH_2$), 63.5, 63.6 (d, $^2J_{CP}$ = 4.6 Hz, $POCH_2$), 78.9 (d, $^2J_{CP}$ = 4.4 Hz, CHOP), 172.6 (s, C=O). IR (film): ν/cm^{-1} 1252 s (P=O), 1731 s (C=O). MS (CI-isobutane): m/z (%) 397 (100) $[M+H]^+$, 155 (20) $[H+HOP(O)(OEt)_2]^+$. Anal. calcd for $C_{17}H_{33}O_6PS$ (396.54): C, 51.49; H, 8.41; P, 7.81; S, 8.07; found: C, 51.03; H, 8.30; P, 7.14; S, 7.63%. Yield: 71%. R_f (ethyl acetate) = 0.30.

Ethyl 7-thiabicyclo[4.1.0]heptane-1-carboxylate (15b). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.29–2.20 (m, 8H, CH_2), 3.75 (dd, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 2.4 Hz, 1H, CHS), 4.15 (q, $^3J_{HH}$ = 7.1 7.1 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$): δ 14.3 (s, OCH_2CH_3), 21.4, 23.7, 25.7, 31.6 (s, CH_2), 41.3 [s, *C*C(O)OEt], 60.1 (s, OCH_2), 63.5 (s, CHS), 171.5 (s, C=O). IR (film): ν/cm^{-1} 1745 s (C=O). MS (CI-isobutane): m/z (%) 187 (30) $[M+H]^+$, 145 (100), 83 (43). Anal. calcd for $C_9H_{14}O_2S$ (186.27): C, 58.03, H, 7.58, S, 17.21; found: C, 57.80, H, 7.57, S, 16.98%. Yield: 10%. R_f (ethyl acetate–petroleum ether 1:2) = 0.67.

Ethyl 8-thiabicyclo[5.1.0]octane-1-carboxylate (15c). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.29–1.95 (m, 8H, CH_2), 2.54 (m, 1H, CH_2), 2.90 (m, 1H, CH_2), 3.63 (dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, CHS), 4.17 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$): δ 13.8 (s, OCH_2CH_3), 26.3, 26.5, 30.9, 32.2,

32.5 (s, CH_2), 43.9 (s, CHS), 47.6 [s, *C*C(O)OEt], 61.5 (s, OCH_2), 171.8 (s, C=O). IR (film): ν/cm^{-1} 1727 s (C=O). MS (CI-isobutane): m/z (%) 187 (100) $[M+H]^+$. Anal. calcd for $C_{10}H_{16}O_2S$ (200.30): C, 59.96, H, 8.05, S, 16.01; found: C, 59.62, H, 8.09, S, 15.63%. Yield: 24%. R_f (ethyl acetate–petroleum ether 1:5) = 0.60.

Ethyl5-methyl-7-thiabicyclo[4.1.0]heptane-1-carboxylate (19b). Single diastereoisomer. ^1H NMR ($CDCl_3$): δ 1.12 (d, $^3J_{HH}$ = 6.5 Hz, 3H, $CHCH_3$), 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.47–1.70 (m, 4H, CH_2), 2.14–2.19 (m, 3H, CH_2), 2.59 (dtq, $^3J_{HH}$ = 4.0, 5.0, 6.9 Hz, 1H, $CHCH_3$), 3.82 (d, $^3J_{HH}$ = 3.8 Hz, 1H, CHS), 4.17 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2). IR (film): ν/cm^{-1} 1734 s (C=O), 795 s. MS (EI, 70 eV): m/z (%) 200 (19) $[M]^+$, 167 (15), $[M^+-SH]$, 93 (100). HRMS found 200.0874; $C_{10}H_{16}O_2S$ requires 200.0871. Yield: 60%. R_f (ethyl acetate–petroleum ether 1:2) = 0.7.

Ethyl4-methyl-7-thiabicyclo[4.1.0]heptane-1-carboxylate (19c). Single diastereoisomer. ^1H NMR ($CDCl_3$): δ 0.88 (d, $^3J_{HH}$ = 6.3 Hz, 3H, $CHCH_3$), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.72 (dd, $^3J_{HH}$ = 3.5, 8.5 Hz, 2H, CH_2), 2.30 (ddq, $^3J_{HH}$ = 3.0, 6.6, 11.2 Hz, 1H, $CHCH_3$), 2.32 (td, $^3J_{HH}$ = 2.0, 8.2 Hz, 2H, CH_2), 2.68 (dd, $^3J_{HH}$ = 3.3, 6.8 Hz, 1H, CH_2), 2.76 (dd, $^3J_{HH}$ = 3.2, 6.7 Hz, 1H, CH_2), 3.88 (dd, $^3J_{HH}$ = 1.8, 3.4 Hz, 1H, CHS), 4.15 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2). IR (film): ν/cm^{-1} 1721 s (C=O). MS (EI, 70 eV): m/z (%) 200 (3) $[M]^+$, 168 (15), $[M^+-S]$, 95 (100) $[M^+-S-COOC_2H_5]$. Yield: 15%. R_f (ethyl acetate–petroleum ether 1:2) = 0.68.

Ethyl3-phenyl-7-thiabicyclo[4.1.0]heptane-1-carboxylate (19d). Single diastereoisomer. ^1H NMR ($CDCl_3$): δ 1.31 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.45–2.95 (m, 7H, CH, CH_2), 3.97 (dd, $^3J_{HH}$ = 3.7 Hz, $^3J_{HH}$ = 1.5 Hz, 1H, CHS), 4.20 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2), 7.15–7.58 (m, 5H, CH_{arom}). ^{13}C NMR ($CDCl_3$): δ 14.3 (s, OCH_2CH_3), 28.2, 30.3, 32.1 (s, CH_2), 60.3 (s, $COCH_2$), 63.6 [s, *C*C(O)OEt], 72.8 (s, CHS), 170.2 (s, C=O). IR (film): ν/cm^{-1} 1740 s (C=O). MS (CI-isobutane): m/z (%) 263 (16) $[M+H]^+$, 247 (75), 231 (100). Anal. calcd for $C_{15}H_{18}O_2S$ (262.37): C, 68.67, H, 6.92, S, 12.22; found: C, 6835, H, 6.90, S, 11.83%. Yield: 15%.R_f (ethyl acetate–petroleum ether 1:2) = 0.68.

*Ethyl 3-*tert*-butyl-7-thiabicyclo[4.1.0]heptane-1-carboxylate (19e).* Single diastereoisomer. ^1H NMR ($CDCl_3$): δ 0.83 [s, 9H, $C(CH_3)_3$], 1.24 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 0.95–2.42 (m, 6H, CH, CH_2), 3.86 (dd, $^3J_{HH}$ = 3.7 Hz, $^3J_{HH}$ = 1.6 Hz, 1H, CHS), 4.15 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$): δ 14.3 (s, OCH_2CH_3), 21.5, 23.7 (s, CH_2), 27.2 [s, $C(CH_3)_3$], 30.6 (s, CH_2), 47.7 [s, $CHC(CH_3)_3$], 60.1 (s, OCH_2), 63.5 [s, *C*C(O)OEt], 73.4 (s, CHS), 169.0 (s, C=O). IR (film): ν/cm^{-1} 1741 s (C=O). MS (CI-isobutane): m/z (%) 243 (5) $[M+H]^+$, 227 (100), 211 (55) $[C_{13}H_{22}O_2]$. Anal. calcd for $C_{13}H_{22}O_2S$ (242.38): C, 64.42, H, 9.15, S, 13.23; found: C, 64.02, H, 8,87, S, 12.71%. Yield: 25%. R_f (ethyl acetate–petroleum ether 1:1) = 0.75.

Cyclohex-1-enecarboxylic acid ethyl ester (16b)[29]. ^1H NMR ($CDCl_3$): δ 1.36 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.54–1.69 (m, 4H, CH_2), 1.97–2.08 (m, 2H, CH_2), 2.11–2.32 (m, 2H, CH_2), 4.26 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2), 6.92 (dd, $^3J_{HH}$ = 3.6 Hz, $^3J_{HH}$ = 1.9 Hz, 1H, CH=C). Yield: 11%. R_f (ethyl acetate–petroleum ether 1:1) = 0.7.

Cyclohept-1-enecarboxylic acid ethyl ester (16c)[30]. ^1H NMR ($CDCl_3$): δ 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.47–2.02 (m, 8H, CH_2), 2.25, 2.29 (AB, $^2J_{HH}$ = 6.6 Hz, 2H, CH_2), 4.15 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2), 7.15 (t, $^3J_{HH}$ = 6.7 Hz, 1H, CH=C). Yield: 31%. R_f (ethyl acetate–petroleum ether 1:1) = 0.63.

3-Methylcyclohex-1-enecarboxylic acid ethyl ester (20b)[31]. ^1H NMR ($CDCl_3$): δ 1.04 (d, $^3J_{HH}$ = 7.0 Hz, 3H, $CHCH_3$), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.73–1.82 (m, 3H, CH_2), 2.21–2.29 (m, 4H, CH_2), 2.53 (dtq, $^3J_{HH}$ = 1.8, 5.9, 6.9 Hz, 1H, $CHCH_3$), 4.16 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2), 6.8 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH=C). MS (EI, 70 eV): m/z (%) 168 (19.9) $[M]^+$, 139 (10). $[M^+-C_2H_5]$, 123 (26), 122 (22), 95 (100), 94 (40).%. Yield: 25%. R_f (ethyl acetate–petroleum ether 1:1) = 0.75.

4-Methylcyclohex-1-enecarboxylic acid ethyl ester (20c)[32]. ^1H NMR ($CDCl_3$): δ 0.97 (d, $^3J_{HH}$ = 6.4 Hz, 3H, $CHCH_3$), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.56 (dd, $^3J_{HH}$ = 3.3, 6.5 Hz, 1H, CH_2), 1.59–1.68 (m, 2H, CH_2), 2.05 (dd, $^3J_{HH}$ = 1.8, 6.4 Hz, 1H, CH_2), 2.31 (ddq, $^3J_{HH}$ = 2.2, 6.5, 8.4 Hz, 1H, $CHCH_3$), 2.41–2.48 (m, 1H, CH_2), 2.60 (dd, $^3J_{HH}$ = 2.4, 6.0 Hz, 1H, CH_2), 4.17 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2), 6.9 (dd, $^3J_{HH}$ = 1.3, 3.6. Hz, 1H, C=CH). Yield: 20%. R_f (ethyl acetate–petroleum ether 1:1) = 0.7.

5-Phenylcyclohex-1-enecarboxylic acid ethyl ester (20d). ^1H NMR ($CDCl_3$): δ 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.77 (dd, $^3J_{HH}$ = 8.8, 12.2 Hz, 1H, CH_2), 1.93–2.05 (m, 1H, CH_2), 2.32–2.43 (m, 2H, CH_2), 2.71 (dd, $^3J_{HH}$ = 3.0, 8.9 Hz, 1H, CHC_6H_5), 2.77 (10 lines, 2H, CH_2), 4.20 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2), 7.06 (dd, $^3J_{HH}$ = 2.0, 4.0. Hz, 1H, C=CH), 7.15–7.58 (m, 5H, CH_{arom}). MS (EI, 70 eV): m/z (%) 230 (68) $[M]^+$, 185 (13), $[M^+-OC_2H_5]$, 156 (17), 104 (100), 77 (11) $[C_6H_5]$. HRMS found 230.1309; $C_{15}H_{18}O_2S$ requires 230.1307. Yield: 60%. R_f (ethyl acetate–petroleum ether 1:1) = 0.71

*5-*tert*-Butylcyclohex-1-enecarboxylic acid ethyl ester (20e)*[33]. ^1H NMR ($CDCl_3$): δ 0.91 [s, 9H, $C(CH_3)_3$], 1.07 (dd, $^3J_{HH}$ = 5.7, 10.8 Hz, 1H, CH_2), 1.13–1.23 (m, 1H, CH_2) 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.79–1.95 (m, 3H, CH_2), 2.18–2.29 and 2.37–2.39 [m, 3H, CH_2 and $CHC(CH_3)_3CH_2$], 4.19 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2), 6.97 (dd, $^3J_{HH}$ = 1.4, 2.8 Hz, 1H, C=C*H*). MS (EI, 70 eV): m/z (%) 210 (22) $[M]^+$, 165 (14), 154 (60) $[M^+-C_4H_8]$, 153 (30) $[M^+-C_4H_9]$, 57 (100) $[C_4H_9]$. Yield: 25%. R_f (ethyl acetate–petroleum ether 1:1) = 0.78.

Reaction of thiophosphates 8 and 9 with sodium borohydride in the presence of methyl iodide. General procedure. To a suspension of sodium borohydride (0.076 g, 2 mmol) in dry methanol–dichloromethane (40 mL in the ratio 1:1) was added a solution of the appropriate thiophosphate **8** or **9** (1 mmol) in dichloromethane as described above, followed by addition of methyl iodide (0.71 g, 5 mmol). Stirring was continued at −78 °C for 3 h and the reaction mixture was allowed to warm slowly to room temperature. The reaction was monitored by TLC and stopped after 5–7 h by addition of dry acetone (1 mL) and ice water. The reaction mixture was diluted with dichloromethane (20 mL), washed with NH_4Cl (5 mL) and water (5 mL), then dried ($MgSO_4$). Solvent was removed under vacuum and the residue was analyzed by ^{31}P and ^1H NMR spectroscopy (see Tables 3 and 4). Crude sulfides **17** and **21** were purified by column chromatography with a gradient of petroleum ether–ethyl acetate (20:1 to 5:1), and were obtained as colourless oils.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-(methylsulfanyl)cyclopentanecarboxylate (17a). Single diastereoisomer. ^1H NMR ($CDCl_3$): δ 1.25 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $COCH_2CH_3$), 1.34 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.1 Hz, 6H, $POCH_2CH_3$), 1.48–2.25 (m, 7H, CH_2), 2.14 (s, 3H, SCH_3), 2.41 (m, 1H, CH_2), 4.00–4.30 (m, 6H, OCH_2), 5.13 (m, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.6. ^{13}C NMR ($CDCl_3$): δ 13.0 (s, $COCH_2CH_3$), 13.7 (s, SCH_3), 15.7 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 19.7, 30.7, 32.1 (s, CH_2), 60.7 (d, $^3J_{CP}$ = 8.4 Hz, CS), 61.1 (s, $COCH_2$), 63.3, 63.5 (d, $^2J_{CP}$ = 6.9 Hz, $POCH_2$), 80.5 (d, $^2J_{CP}$ = 4.9 Hz, CHOP), 170.8 (s, C=O). IR (film): ν/cm^{-1} 1263 s (P=O), 1722 s (C=O). MS (CI-isobutane): m/z (%) 341 (100) $[M]^+$, 187 (10). Anal. calcd for $C_{13}H_{25}O_6PS$ (340.42): C, 45.88; H, 7.40; P, 9.10; S, 9.42; found: C, 45.86; H, 7.42; P, 9.01; S, 9.21%. Yield: 82%. R_f (ethyl acetate) = 0.45.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-(methylsulfanyl)cyclohexanecarboxylate (17b). Single diastereoisomer. ^1H NMR

($CDCl_3$): δ 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.33 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 1.0 Hz, 6H, $POCH_2CH_3$), 0.88–1.80 (m, 6H, CH_2), 2.08 (s, 3H, SCH_3), 2.10–2.16 (m, 2H, CH_2), 4.05–4.23 (m, 4H, $POCH_2$), 4.21 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $COCH_2$), 4.93 (ddd, $^3J_{HH}$ = $^3J_{HP}$ = 5.2 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.7. ^{13}C NMR ($CDCl_3$): δ 11.5 (s, SCH_3), 14.0 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 18.9, 22.7, 28.6, 29.0 (s, CH_2), 55.3 (d, $^3J_{CP}$ = 8.5 Hz, CS), 61.0 (s, $COCH_2$), 63.5, 63.7 (d, $^2J_{CP}$ = 6.0 Hz, $POCH_2$), 73.7 (d, $^2J_{CP}$ = 4.0 Hz, CHOP), 170.1 (s, C=O). IR (film): ν/cm^{-1} 1259 s (P=O), 1714 s (C=O). MS (CI-isobutane): m/z (%) 355 (100) $[M+H]^+$, 201 (12). Anal. calcd for $C_{14}H_{27}O_6PS$ (354.45): C, 47.45; H, 7.68; P, 8.74; S, 9.05; found: C, 47.45; H, 7.68; P, 8.50; S, 8.48%. Yield: 79%. R_f (ethyl acetate–petroleum ether 1:2) = 0.49.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-(methylsulfanyl)cycloheptanecarboxylate (17c). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.30 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 6H, $POCH_2CH_3$), 1.36–2.08 (m, 9H, CH_2), 2.13 (s, 3H, SCH_3), 2.18–2.25 (m, 3H, CH_2), 4.05–4–37 (m, 6H, OCH_2), 5.03 (m, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.4. ^{13}C NMR ($CDCl_3$): δ 12.6 (s, SCH_3), 13.6 (s, $COCH_2CH_3$), 15.6 (d, $^3J_{CP}$ = 6.9 Hz, $POCH_2CH_3$), 21.0, 22.1, 26.1, 29.9, 30.9 (s, CH_2), 57.5 (d, $^3J_{CP}$ = 8.5 Hz, CS), 60.6 (s, $COCH_2$), 63.4, 63.1 (d, $^2J_{CP}$ = 6.1 Hz, $POCH_2$), 76.5 (d, $^2J_{CP}$ = 5.0 Hz, CHOP), 169.9 (s, C=O). IR (film): ν/cm^{-1} 1272 s (P=O), 1713 s (C=O). MS (CI-isobutane): m/z (%) 369 (100) $[M+H]^+$, 215 (50), 155 (5) $[H+HOP(O)(OEt)_2]^+$. Anal. calcd for $C_{15}H_{29}O_6PS$ (368.48): C, 48.89; H, 7.95; P, 8.40; S, 8.43; found: C, 47.50; H, 7.80; P, 8.61; S, 8.90%. Yield: 70%. R_f (ethyl acetate–petroleum ether 1:2) = 0.12.

Ethyl 2-[(diethoxyphosphoryl)oxy]-3-methyl-1-(methylsulfanyl)cyclohexanecarboxylate (21b). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.01 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CHCH_3$), 1.25–1.35 (m, 9H, OCH_2CH_3), 1.48–1.90 (m, 6H, CH_2), 2.13 (s, 3H, SCH_3), 2.30 (m, 1H, CH_2), 4.03–4.20 (m, 6H, OCH_2), 4.75 (dd, $^3J_{HP}$ = $^3J_{HH}$ = 8.5 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.0. ^{13}C NMR ($CDCl_3$): δ 12.3 (s, SCH_3), 13.9 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 7.0 Hz, $POCH_2CH_3$), 17.8 (s, $CHCH_3$), 20.8, 31.1, 32.0 (s, CH_2), 34.0 (s, $CHCH_3$), 57.9 (s, CS), 61.4 (s, $COCH_2$), 63.3, 63.6 (d, $^2J_{CP}$ = 6.0 Hz, $POCH_2$), 84.0 (d, $^2J_{CP}$ = 5.8 Hz, CHOP), 171.5 (s, C=O). IR (film): ν/cm^{-1} 1250 s (P=O), 1732 s (C=O). MS (CI-isobutane): m/z (%) 369 (100) $[M+H]^+$, 215 (10). Anal. calcd for $C_{15}H_{29}O_6PS$ (368.48): C, 48.90; H, 7.93; P, 8.41; S, 8.70; found: C, 48.88; H, 8.07; P, 8.21; S, 7.98%. Yield: 86%. R_f (ethyl acetate) = 0.54.

Ethyl 2-[(diethoxyphosphoryl)oxy]-4-methyl-1-(methylsulfanyl)cyclohexanecarboxylate (21c). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 0.95 (d, $^3J_{HH}$ = 6.3 Hz, 3H, $CHCH_3$), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.30 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 6H, $POCH_2CH_3$), 1.35–1.48 (m, 4H, CH_2), 1.74–2.15 (m, 4H, CH_2), 2.14 (s, 3H, SCH_3), 4.05–4.28 (m, 6H, OCH_2), 4.97 (ddd, $^3J_{HH}$ = 4.2 Hz, $^3J_{HP}$ = 6.7 Hz, $^3J_{HH}$ = 11.2 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.2. ^{13}C NMR (DEPT, $CDCl_3$): δ 12.4 (s, SCH_3), 13.8 (s, $COCH_2CH_3$), 15.7 (d, $^3J_{CP}$ = 6.9 Hz, $POCH_2CH_3$), 21.2 (s, $CHCH_3$), 28.4 (s, CH_2), 30.5 (s, $CHCH_3$), 31.9, 36.6 (s, CH_2), 57.4 (d, $^3J_{CP}$ = 8.3 Hz, CS), 61.2 (s, $COCH_2$), 63.1, 63.3 (d, $^2J_{CP}$ = 6.9 Hz, $POCH_2$), 79.5 (d, $^2J_{CP}$ = 5.3 Hz, CHOP), 171.9 (s, C=O). IR (film): ν/cm^{-1} 1260 s (P=O), 1733 s (C=O). MS (CI-isobutane): m/z (%) 369 (100) $[M+H]^+$, 215 (8). Anal. calcd for $C_{15}H_{29}O_6PS$ (368.48): C, 48.90; H, 7.93; P, 8.41; S, 8.70; found: C, 47.88; H, 7.88; P, 8.28; S, 8.36%. Yield: 62%. R_f (ethyl acetate) = 0.52.

Ethyl 2-[(diethoxyphosphoryl)oxy]-5-phenyl-1-(methylsulfanyl)cyclohexanecarboxylate (21d). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, 3H, $COCH_2CH_3$), 1.15–1.40 (m, 4H, $POCH_2CH_3$) 1.45–2.10 (m, 4H, CH_2), 2.20 (s, 3H, SCH_3), 2.25–2.35 (m, 2H, CH_2), 2.94 (dddd, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 12.4 Hz, 1H, CHPh), 4.05–4.30 (m, 6H, OCH_2), 5.13 (m, 1H, CHOP), 7.10–7.45 (m, 5H, CH_{arom}). ^{31}P NMR ($CDCl_3$): δ −2.1. ^{13}C NMR (DEPT, $CDCl_3$): δ 12.6 (s, SCH_3), 13.8 (s, $COCH_2CH_3$), 15.8 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 28.7, 30.9 (s, CH_2), 37.4 (s, CH), 40.0 (s, CH_2), 58.1 (d, $^3J_{CP}$ = 8.6 Hz, CS), 62.3 (s, $COCH_2$), 63.1, 63.2 (d, $^2J_{CP}$ = 6.8 Hz, $POCH_2$), 79.5 (d, $^2J_{CP}$ = 5.1 Hz, CHOP), 126.3, 126.4, 128.2, 143.9 (s, CH_{arom}), 171.2 (s, C=O). IR (film): ν/cm^{-1} 1272 s (P=O), 1719 s (C=O). MS (CI-isobutane): m/z (%) 431 (100) $[M+H]^+$. Anal. calcd for $C_{20}H_{31}O_6PS$ (430.55): C, 55.79; H, 7.27; P, 7.19; S, 7.45; found: C, 55.40; H, 7.19; P, 6.88; S, 7.02%. Yield: 60%. R_f (ethyl acetate–petroleum ether 1:2) = 0.12.

*Ethyl 2-[(diethoxyphosphoryl)oxy]-5-*tert*-butyl-1-(methylsulfanyl)cyclohexanecarboxylate (21e).* Single diastereoisomer.^{1}H NMR ($CDCl_3$): δ 0.85 (s, 9H, CCH_3), 1.20–1.45 (m, 9H, OCH_2CH_3), 1.40–1.70 (m, 4H, CH_2), 1.83 (m, 1H, CH_2), 2.08–2.20 (m, 2H, CH, CH_2), 2.17 (s, 3H, SCH_3), 4.00–4.50 (m, 6H, OCH_2), 4.92 (m, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.2. ^{13}C NMR (DEPT, $CDCl_3$): δ 12.6 (s, SCH_3), 13.9 (s, $COCH_2CH_3$), 15.8 (d, $^3J_{CP}$ = 6.9 Hz, $POCH_2CH_3$), 24.8 (s, CH_2), 27.2 [s, $C(CH_3)_3$], 28.7 (s, CH_2), 31.9 [s, $C(CH_3)_3$], 34.2 (s, CH_2), 40.7 (s, $CHCCH_3$), 58.3 (d, $^3J_{CP}$ = 8.4 Hz, CS), 61.4 (s, $COCH_2$), 63.2, 63.4 (d, $^2J_{CP}$ = 5.0 Hz, $POCH_2$), 80.2 (d, $^2J_{CP}$ = 5.1 Hz, CHOP), 172.6 (s, C=O). IR (film): ν/cm^{-1} 1247 s (P=O), 1730 s (C=O). MS (CI-isobutane): m/z (%) 411 (100) $[M+H]^+$, 257 (16), 155 (30). HRMS (CI) calcd for $C_{18}H_{35}O_6PS+H$ $[M+H]^+$ 411.1970; found: 411.1925. Yield: 60%. R_f (ethyl acetate–petroleum ether 1:1) = 0.28

Reaction of thiophosphates 8 and 9 with sodium borohydride in the presence of elemental iodine. General procedure. To a suspension of sodium borohydride (0.038 g, 1 mmol) in dry DME (20 mL) was added a solution of the appropriate thiophosphate (0.5 mmol) in DME (5 mL) as described above. The reaction was monitored by TLC and after 1.5 h a solution of iodine (0.12 g, 0.5 mmol) in dry toluene (16 mL) was added at −78 °C. Stirring was continued at −78 °C for 1 h and at room temperature for 5 h. The reaction mixture was diluted with toluene (10 mL), washed with sodium thiosulfate (5 mL), NaOH (5 mL) and water (2 × 5 mL) and then dried with $MgSO_4$. Evaporation of solvent afforded the crude disulfides **22** (yellow oils). No analytically pure **22** were obtained owing to its instability during chromatography.

Bis{[1-carboethoxy-2-(diethoxyphosphoryl)oxy]cyclopentan-1-yl} disulfide (22a). ^{1}H NMR ($CDCl_3$): δ 1.25, 1.26 (t, $^3J_{HH}$ = 7.0 and 7.2 Hz, 6H, $COCH_2CH_3$), 1.29, 1.30, 1.32 (t, $^3J_{HH}$ = 7.0 Hz, 12H, $POCH_2CH_3$), 1.64–2.46 (m, 12H, CH_2), 4.04–4.23 (m, 12H, OCH_2), 5.03 (ddd, $^3J_{HP}$ = 9.9 Hz, $^3J_{HP}$ = 5.4 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.0. ^{13}C NMR ($CDCl_3$): δ 13.7 (s, $COCH_2CH_3$), 15.7, 15.9 (s, $POCH_2CH_3$), 19.6, 30.7, 31.0,31.8 (s, CH_2), 61.5 (s, $COCH_2$), 61.7 (s, $COCH_2$), 63.6, 63.7 (d, $^2J_{CP}$ = 7.3 Hz, $POCH_2$), 66.2, 66.3 (d, $^3J_{CP}$ = 8.7 Hz, CS), 82.5, 82.8 (d, $^2J_{CP}$ = 4.8 Hz, CHOP), 170.3, 170.1 (s, C=O). IR (film): ν/cm^{-1} 1240 s (P=O), 1726 s (C=O). MS (CI-isobutane): m/z (%) 651 (100) $[M+H]^+$, 325 (4) $[M/2]^+$. HRMS (EI) calcd for $C_{24}H_{44}O_{12}P_2S_2$ $[M]^+$ 650.1749; found: 650.1745. Yield: 98%. R_f (ethyl acetate) = 0.26.

Bis{[1-carboethoxy-2-(diethoxyphosphoryl)oxy]cyclohexane-1-yl} disulfide (22b). ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 6H, $COCH_2CH_3$), 1.33, 1.35 (t, $^3J_{HH}$ = 7.0 Hz, 12H, $POCH_2CH_3$), 1.47–1.82 (m, 12H, CH_2), 2.18 (brd, $^3J_{HH}$ = 8.0 Hz, 4H, CH_2), 4.10–4.30 (m, 12H, OCH_2), 4.94 (ddd, $^3J_{HH}$ = 15.2 Hz, $^3J_{HP}$ = 7.0 Hz, $^3J_{HH}$ = 3.5 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.0, −2.11. ^{13}C NMR ($CDCl_3$): δ 13.9 (s, $COCH_2CH_3$), 15.8, 15.9 (s, $POCH_2CH_3$), 22.4, 24.1, 31.7, 33.4, 33.7 (s, CH_2), 62.6, 63.5 (d, $^2J_{CP}$ = 4.3 Hz, $POCH_2$),

63.2 (s, $CO\mathit{C}H_2$), 65.7, 65.8 (d, $^3J_{CP} = 7.0$ Hz, CS), 81.2 (d, $^2J_{CP} = 4.2$ Hz, CHOP), 82.6 (s, CHOP), 172.2, 172.4 (s, C=O). IR (film): ν/cm^{-1} 1236 s, 1260 s (P=O), 1720 s, 1731 s (C=O). MS (CI-isobutane): m/z (%) 679 $[M+H]^+$ (100), 341 $[M/2+2H]^+$ (40), 155 $[H+HOP(O)(OEt)_2]^+$ (88). HRMS (CI) calcd. for $C_{26}H_{48}O_{12}P_2S_2+H$ $[M+H]^+$ 679.2141; found: 679.2144. Yield: 90%. R_f (ethyl acetate–hexane 1.5:1) = 0.12.

Bis{[1-carboethoxy-2-(diethoxyphosphoryl)oxy-3-methyl]cyclohexan-1-yl} disulfide (22c). ^{1}H NMR ($CDCl_3$): δ 1.97 (d, $^3J_{HH} = 7.0$ Hz, 3H, $CHC\mathit{H}_3$), 1.03 (d, $^3J_{HH} = 6.5$ Hz, 3H, $CHC\mathit{H}_3$), 1.27 (t, $^3J_{HH} = 4.9$ Hz, 6H, $OCH_2C\mathit{H}_3$), 1.31 (t, $^3J_{HH} = 4.4$ Hz, 6H, $POCH_2C\mathit{H}_3$), 1.34 (t, $^3J_{HH} = 4.6$ Hz, $POCH_2C\mathit{H}_3$), 1.44–1.61 (m, 4H, CH_2), 1.64–1.91 (m, 4H, CH_2), 2.01–2.26 (m, 4H, CH_2), 2.28–2.36 (m, 2H, CH_2), 4.02–4.27 (m, 12H, OCH_2), 4.51 (dd, $^3J_{HP} = {}^3J_{HH} = 9.7$ Hz, 1H, CHOP), 4.67 (dd, $^3J_{HP} = {}^3J_{HH} = 8.1$ Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.0. ^{13}C NMR ($CDCl_3$): δ 13.3 (s, $COCH_2\mathit{C}H_3$), 15.5, 15.7 (s, $POCH_2\mathit{C}H_3$), 19.2, 19.6 (s, $CH\mathit{C}H_3$), 22.4, 27.3, 30.9 (s, CH_2), 37.1 (s, $\mathit{C}HCH_3$), 61.8 (s, $CO\mathit{C}H_2$), 63.2, 63.4 (d, $^2J_{CP} = 7.5$ Hz, $POCH_2$), 64.1, 64.3 (d, $^3J_{CP} = 8.7$ Hz, CS), 83.2 (d, $^2J_{CP} = 4.4$ Hz, CHOP), 84.0 (s, CHOP), 171.3, 171.4 (s, C=O). IR (film): ν/cm^{-1} 1234 s, 1262 s (P=O), 1730 s, 1725 s (C=O). MS (EI, 70 eV): m/z (%) 706 (14) $[M]^+$, 354 (16) $[M/2+H]^+$, 321 (53), 155 (100) $[H+HOP(O)(OEt)_2]^+$. HRMS (EI) calcd for $C_{28}H_{52}O_{12}P_2S_2$ $[M]^+$ 706.2376; found: 706.2374. Yield: 53%. R_f (hexane–ethyl acetate 1:1.5) = 0.19.

Bis{[1-carboethoxy-2-(diethoxyphosphoryl)oxy]cycloheptan-1-yl} disulfide (22d). ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 6H, $COCH_2C\mathit{H}_3$), 1.32, 1.33 (t, $^3J_{HH} = 7.0$ Hz, 12H, $POCH_2C\mathit{H}_3$), 1.40–2.05 (m, 16H, CH_2), 2.13–2.31 (m, 4H, CH_2), 4.11–4.33 (m, 12H, OCH_2), 5.01 (brs, 2H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.1. ^{13}C NMR ($CDCl_3$): δ 14.1 (s, $COCH_2\mathit{C}H_3$), 16.32 (s, $POCH_2\mathit{C}H_3$), 21.5, 24.5, 26.5, 29.7, 31.8 (s, CH_2), 61.5 (s, $CO\mathit{C}H_2$), 64.5, 65.0 (br s, $POCH_2$), 67.1, 67.5 (s, CS), 79.4, 80.5 (br s, CHOP), 171.0 (s, C=O). IR (film): ν/cm^{-1} 1260 s (P=O), 1720 s, 1731 s (C=O). MS (CI-isobutane): m/z (%) 707 (28) $[M+H]^+$, 355 (50) $[M/2+2H]^+$, 169 (83), 155 (100) $[H+HOP(O)(OEt)_2]^+$. HRMS (CI) calcd for $C_{28}H_{52}O_{12}P_2S_2+H$ $[M+H]^+$ 707.2459; found: 707.2454. Yield: 55%. R_f (ethyl acetate–hexane 1.5:1) = 0.12.

Oxidation of sulfides 17 and 21 to sulfoxides 27 and 28. General procedure. A solution of 85% *m*-chloroperbenzoic acid (0.086 g. 0.5 mmol) in dichloromethane (30 mL) was added dropwise to the appropriate sulfide (0.5 mmol) in dichloromethane (20 mL) at −78 °C. Stirring was continued at −78 °C for 2 h and the reaction mixture was diluted with Et_2O (ml), washed with sodium thiosulfate (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 chromatographed on silica gel with ethyl acetate–methanol (50:1) as a eluent to provide pure sulfoxides (colourless oils) as a mixture of two diastereoisomers that were not separable by chromatography.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-(methylsulfinyl)cyclopentanecarboxylate (27a). The ratio of diastereoisomers is 1:1. Mixture of two isomers of **27a**: ^{1}H NMR ($CDCl_3$): δ 1.15–1.45 (m, 18H, $COCH_2C\mathit{H}_3$), 1.57–2.18 (m, 10H, CH_2), 2.20–2.36 (m, 2H, CH_2), 2.48 (s, 3H, SCH_3), 2.50 (s., 3H, SCH_3), 4.00–4.40 (m, 12H, OCH_2), 5.13 (ddd, $^3J_{HH} = {}^3J_{HP} = 6.6$ Hz, $^3J_{HH} = 12.9$ Hz, 1H, CHOP), 5.47 (m, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.0, −2.4. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.5, 13.7 (s, $COCH_2\mathit{C}H_3$), 15.5 (d, $^3J_{CP} = 6.3$ Hz, $POCH_2\mathit{C}H_3$), 20.5, 24.7, 27.0, 31.9, 32.6 (s, CH_2), 34.6 (s, SCH_3), 62.0 (d, $^2J_{CP} = 6.2$ Hz, $POCH_2$), 63.6 (s, $CO\mathit{C}H_2$), 74.0 (d, $^3J_{CP} = 8.4$ Hz, CS), 80.5 (d, $^2J_{CP} = 4.9$ Hz, CHOP), 170.8 (s, C=O). IR (film): ν/cm^{-1} 1264 s (P=O), 1729 s (C=O). MS (CI-isobutane): m/z (%) 357 (100) $[M+H]^+$. Anal. calcd for $C_{13}H_{25}O_7PS$ (356.42): C, 43.80; H, 7.08; P, 8.69; S, 9.00; found: C, 43.43; H, 8.21; P, 8.39; S, 8.79%. Yield: 87%. R_f (ethyl acetate) = 0.12.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-(methylsulfinyl)cyclohexanecarboxylate (27b). The ratio of diastereoisomers is 1.6:1. Major isomer of **27b**: ^{1}H NMR ($CDCl_3$): δ 1.33 (t, $^3J_{HH} = 7.0$ Hz, 3H, $COCH_2C\mathit{H}_3$), 1.37 (dt, $^3J_{HH} = 7.0$ Hz, $^4J_{HP} = 1.0$ Hz, 6H, $POCH_2C\mathit{H}_3$), 1.45–1.60 (m, 3H, CH_2), 1.93–2.20 (m, 4H, CH_2), 2.55 (m, 1H, CH_2), 2.08 (s, 3H, SCH_3), 4.00–4.25 (m, 4H, $POCH_2$), 4.20–4.46 (m, 2H, $COCH_2$), 5.05 (m, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −1.7. ^{13}C NMR (DEPT, $CDCl_3$): δ 14.0 (s, $COCH_2\mathit{C}H_3$), 15.7 (d, $^3J_{CP} = 6.7$ Hz, $POCH_2\mathit{C}H_3$), 18.2, 22.2, 24.2, 29.2 (s, CH_2), 33.7 (s, SCH_3), 61.6 (s, $CO\mathit{C}H_2$), 63.6, 63.7 (d, $^2J_{CP} = 5.4$ Hz, $POCH_2$), 69.8 (d, $^3J_{CP} = 8.5$ Hz, CS), 73.6 (d, $^2J_{CP} = 3.6$ Hz, CHOP), 165.7 (s, C=O). IR (film): ν/cm^{-1} 1264 s (P=O), 1729 s (C=O). MS (CI-isobutane): m/z (%) 371 (100) $[M+H]^+$, 155 (12). HRMS (CI) calcd for $C_{14}H_{27}O_7PS+H$ $[M+H]^+$ 371.1293; found: 371.1305. Yield: 46%. R_f (ethyl acetate) = 0.14. Minor isomer of **27b**: ^{1}H NMR ($CDCl_3$): δ 1.33 (t, $^3J_{HH} = 7.0$ Hz, 3H, $COCH_2C\mathit{H}_3$), 1.35 (dt, $^3J_{HH} = 7.0$ Hz, $^4J_{HP} = 1.0$ Hz, 6H, $POCH_2C\mathit{H}_3$), 1.48–2.45 (m, 8H, CH_2), 2.47 (s, 3H, SCH_3), 4.05–4.45 (m, 6H, OCH_2), 5.32 (m, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.4. ^{13}C NMR (DEPT, $CDCl_3$): δ 14.2 (s, $COCH_2\mathit{C}H_3$), 16.0 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2\mathit{C}H_3$), 17.8, 22.3, 22.7, 28.8 (s, CH_2), 33.5 (s, SCH_3), 61.9 (s, $CO\mathit{C}H_2$), 63.8, 64.0 (d, $^2J_{CP} = 5.8$ Hz, $POCH_2$), 70.7 (d, $^3J_{CP} = 10.2$ Hz, CS), 72.3 (d, $^2J_{CP} = 3.6$ Hz, CHOP), 165.8 (s, C=O). IR (film): ν/cm^{-1} 1262 s (P=O), 1732 s (C=O). MS (CI-isobutane): m/z (%) 371 (100) $[M+H]^+$, 155 (17). HRMS (CI) calcd for $C_{14}H_{27}O_7PS+H$ $[M+H]^+$ 371.1293; found: 371.1306. Yield: 29%. R_f (ethyl acetate) = 0.17.

Ethyl 2-[(diethoxyphosphoryl)oxy]-1-(methylsulfinyl)cycloheptanecarboxylate (27c). The ratio of diastereoisomers is 2.5:1. Mixture of two isomers of **27c**: ^{1}H NMR ($CDCl_3$): δ 1.29 (t, $^3J_{HH} = 7.1$ Hz, 6H, $COCH_2C\mathit{H}_3$), 1.31 (m, 12H, $POCH_2C\mathit{H}_3$), 1.30–1.80 (m, 12H, CH_2), 1.90–2.41 (s, 8H, CH_2), 2.43 (s, 3H, SCH_3, minor), 2.59 (s, 3H, SCH_3, major), 4.00–4.28 (m, 12H, OCH_2), 5.07 (ddd, $^3J_{HP} = {}^3J_{HH} = 7.0$ Hz, $^3J_{HH} < 1$ Hz, 1H, CHOP, major), 5.38 (ddd, $^3J_{HP} = {}^3J_{HH} = 5.9$ Hz, $^3J_{HH} < 1$ Hz, 1H, CHOP, minor). ^{31}P NMR ($CDCl_3$): δ −1.4 (major), −2.4 (minor). ^{13}C NMR ($CDCl_3$): δ 14.2 (d, $^3J_{CP} = 7.5$ Hz, $POCH_2\mathit{C}H_3$), 16.0 (s, $COCH_2\mathit{C}H_3$), 21.0, 25.4, 27.5 (s, CH_2), 30.8 (s, CH_2, minor), 31.5 (s, CH_2, major), 31.7 (s, SCH_3, major), 32.4 (s, SCH_3, minor), 35.2 (s, CH_2, major), 62.4 (s, CS, major), 62.7 (s, CS, minor), 63.7, 64.2 (d, $^2J_{CP} = 5.8$ Hz, $POCH_2$), 81.5 (d, $^2J_{CP} = 5.8$ Hz, CHOP, major), 82.6 (d, $^2J_{CP} = 4.8$ Hz, CHOP, minor), 166.9 (s, C=O, minor), 168.7 (s, C=O, major). IR (film): ν/cm^{-1} 1037 s (S=O), 1247 s (P=O), 1710 s (C=O). MS (CI-isobutane): m/z (%) 385 (48) $[M+H]^+$, 321 (100), 155 (94) $[H+HOP(O)(OEt)_2]^+$; (EI, 70 eV): m/z (%) 384 (8) $[M]^+$, 167 (19), 155 (100). Anal. calcd for $C_{15}H_{29}O_7PS$ (384.47): C, 46.86; H, 7.62; P, 8.05; S, 8.34; found: C, 46.93; H, 7.91; P, 7.81; S, 8.02%. Yield: 61%. R_f (ethyl acetate) = 0.16.

Ethyl 2-[(diethoxyphosphoryl)oxy]-3-methyl-1-(methylsulfinyl)cyclohexanecarboxylate (28b). The ratio of diastereoisomers is 1:1. Fast isomer of **28b**: ^{1}H NMR ($CDCl_3$): δ 0.97 (d, $^3J_{HH} = 7.2$ Hz, 3H, $CHC\mathit{H}_3$), 1.33 (t, $^3J_{HH} = 7.2$ Hz, 9H, $OCH_2C\mathit{H}_3$), 1.45–2.20 (m, 5H, CH_2), 2.23 (m, 1H, CH_2), 2.38 (m, 1H, CH), 2.72 (s, 3H, SCH_3), 4.08–4.40 (m, 6H, OCH_2), 4.93 (dd, $^3J_{HP} = 5.7$ Hz, $^3J_{HH} = 7.6$ Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.0. ^{13}C NMR (DEPT, $CDCl_3$): δ 14.1 (s, $COCH_2\mathit{C}H_3$), 16.0 (d, $^3J_{CP} = 6.7$ Hz, $POCH_2\mathit{C}H_3$), 16.9 (s, $CH\mathit{C}H_3$), 18.4, 26.2, 27.4 (s, CH_2), 34.3 (s, SCH_3), 35.2 (s, $\mathit{C}HCH_3$), 61.9 (s, $CO\mathit{C}H_2$), 63.8, 64.0 (d, $^2J_{CP} = 6.8$ Hz, $POCH_2$), 68.7 (d, $^3J_{CP} = 7.1$ Hz, CS), 80.9 (d, $^2J_{CP} = 5.1$ Hz, CHOP), 167.1 (s, C=O). IR (film): ν/cm^{-1} 1256 s (P=O), 1728 s (C=O). MS (CI-isobutane): m/z (%) 385 (100) $[M+H]^+$, 321 (24). Anal. calcd for $C_{15}H_{29}O_7PS$

(384.42): C, 46.87; H, 7.60; P, 8.06; S, 8.34; found: C, 46.35; H, 7.64; P, 7.43; S, 8.49%. Yield: 44%. R_f (ethyl acetate) = 0.19. Slow isomer of **28b**: ^{1}H NMR ($CDCl_3$): δ 0.93 (d, $^3J_{HH}$ = 7.8 Hz, 3H, $CHCH_3$), 1.22–1.35 (m, 9H, OCH_2CH_3), 1.40–2.10 (m, 6H, CH_2), 2.38 (m, 1H, CH_2), 2.38 (s, 3H, SCH_3), 2.62 (m, 1H, $CHCH_3$), 4.05–4.40 (m, 6H, OCH_2), 5.15 (dd, $^3J_{HP}$ = 3.4 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, CHOP). ^{31}P NMR ($CDCl_3$): δ −2.4. ^{13}C NMR (DEPT, $CDCl_3$): δ 14.1 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 6.9 Hz, $POCH_2CH_3$), 16.1 (s, $CHCH_3$), 17.1, 23.0, 27.4 (s, CH_2), 33.5 (s, $CHCH_3$), 61.8 (s, $COCH_2$), 63.7, 64.0 (d, $^2J_{CP}$ = 6.5 Hz, $POCH_2$), 68.3 (d, $^2J_{CP}$ = 9.3 Hz, CS), 77.8 (d, $^2J_{CP}$ = 4.4 Hz, CHOP), 166.3 (s, C=O). IR (film): ν/cm^{-1} 1024 s (S=O), 1254 s (P=O), 1718 s (C=O). MS (CI-isobutane): m/z (%) 385 (100) $[M+H]^+$ 321 (7). Anal. calcd for $C_{15}H_{29}O_6PS$ (384.42): C, 46.87; H, 7.60; P, 8.06; S, 8.34; found: C, 46.47; H, 7.60; P, 8.20; S, 7.81%. Yield: 41%. R_f (ethyl acetate) = 0.14.

Ethyl 2-[(diethoxyphosphoryl)oxy]-4-methyl-1-(methylsulfinyl)cyclohexanecarboxylate (28c). The ratio of diastereoisomers is 2.1:1. Mixture of two isomers of **28c**: ^{1}H NMR ($CDCl_3$): δ 0.99 (d, $^3J_{HH}$ = 6.0 Hz, 3H, $CHCH_3$, major), 1.07 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHCH_3$, minor), 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$, minor), 1.33 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 1.1 Hz, 6H, $POCH_2CH_3$, minor), 1.34 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 1.1 Hz, 6H, $POCH_2CH_3$, major), 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$, major), 1.43–2.25 (m, 14H, CH, CH_2), 2.68 (s, 3H, SCH_3, minor), 2.74 (s, 3H, SCH_3, minor), 4.00–4.46 (m, 12H, OCH_2), 5.05 (m, 1H, CHOP, major), 5.26 (ddd, $^3J_{HH}$ = $^3J_{HP}$ = 4.1 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, CHOP, minor). ^{31}P NMR ($CDCl_3$): δ −1.9 (major), −2.4 (minor). ^{13}C NMR ($CDCl_3$): δ 14.1 (s, $COCH_2CH_3$), 16.0 (d, $^3J_{CP}$ = 7.2 Hz, $POCH_2CH_3$), 20.7 (s, $CHCH_3$, minor), 21.2 (s, $CHCH_3$, major), 25.3 (s, CH_2), 27.4 (s, $CHCH_3$, minor), 28.4 (s, CH_2, major), 28.6 (s, CH_2,minor), 29.1 (s, $CHCH_3$, major), 29.6 (s, SCH_3, major), 34.3 (s, CH_2,minor), 37.4 (s, SCH_3, minor), 61.6 (s, $COCH_2$, major), 61.9 (s, $COCH_2$, minor), 63.7, 64.0 (d, $^2J_{CP}$ = 6.0 Hz, $POCH_2$), 70.0 (d, $^2J_{CP}$ = 9.0 Hz, CS), 75.5 (d, $^2J_{CP}$ = 4.8 Hz, CHOP, minor), 77.0 (d, $^2J_{CP}$ = 5.0 Hz, CHOP, major),167.0 (s, C=O). IR (film): ν/cm^{-1} 1016 s (S=O),1246 s (P=O), 1725 s (C=O). MS (CI-isobutane): m/z (%) 385 (100) $[M+H]^+$. Anal. calcd for $C_{15}H_{29}O_7PS$ (384.42): C, 46.87; H, 7.60; P, 8.06; S, 8.34; found: C, 46.50; H, 7.10; P, 7.77; S, 7.65%. Yield: 76%. R_f (ethyl acetate) = 0.15.

Ethyl 2-[(diethoxyphosphoryl)oxy]-5-phenyl-1-(methylsulfinyl)cyclohexanecarboxylate (28d). The ratio of diastereoisomers is 2:1. Major isomer of **28d**: ^{1}H NMR ($CDCl_3$): δ 1.12 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 3H, $POCH_2CH_3$), 1.18 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $COCH_2CH_3$), 1.29 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 1.0 Hz, 3H, $POCH_2CH_3$), 1.50–2.62 (m, 8H, CH_2, SCH_3), 3.00 (dddd, $^3J_{HH}$ = $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = $^3J_{HH}$ = 3.2 Hz, 1H, $CHPh$), 3.18 (m, 1H, CH_2), 3.82–4.12 (m, 6H, $COCH_2$), 4.09–4.32 (m, 4H, $POCH_2$), 5.04 (ddd, $^3J_{HH}$ = 12.9 Hz, $^3J_{HP}$ = 7.8 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, CHOP), 7.10–7.45 (m, 5H, CH_{arom}). ^{31}P NMR ($CDCl_3$): δ −2.3. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 28.6, 29.6 (s, CH_2), 34.9 (s, SCH_3), 37.5 (s, $CHPh$), 37.9 (s, CH_2), 61.9 (s, $COCH_2$), 63.6, 63.8 (d, $^2J_{CP}$ = 6.0 Hz, $POCH_2$), 68.0 (d, $^3J_{CP}$ = 8.7 Hz, CS), 76.8 (d, $^2J_{CP}$ = 4.8 Hz, CHOP), 126.4, 126.6, 128.5, 143.1 (s, CH_{arom}) 167.5 (s, C=O). IR (KBr): ν/cm^{-1} 1269 s (P=O), 1736 s (C=O). MS (CI-isobutane): m/z (%) 446 (100) $[M+H]^+$. Anal. calcd for $C_{20}H_{31}O_7PS$ (446.55): C, 53.80; H, 7.00; P, 6.94; S, 7.18; found: C, 54.15; H, 7.24; P, 7.11; S, 7.10%. Yield: 48%. R_f (ethyl acetate) = 0.20. Minor isomer of **28d**: ^{1}H NMR ($CDCl_3$): δ 1.18 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 1.32 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 3H, $POCH_2CH_3$), 1.55–2.41 (m, 8H, CH_2, SCH_3), 2.62 (m, 1H, CH_2), 2.90 (dddd, $^3J_{HH}$ = $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = $^3J_{HH}$ = 12.3 Hz, 1H, CHPh), 3.98 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $COCH_2$), 4.00–4.32 (m, 4H, $POCH_2$), 4.90 (ddd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HP}$ = $^3J_{HH}$ = 7.3 Hz, 1H, CHOP), 7.10–7.42 (m, 5H, CH_{arom}). ^{31}P NMR ($CDCl_3$): δ −2.1. ^{13}C NMR ($CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP}$ = 6.8 Hz, $POCH_2CH_3$), 28.6, 29.5, (s, CH_2), 34.9 (s, SCH_3), 37.5 (s, CH), 37.9 (s, CH_2), 61.9 (s, $COCH_2$), 63.6, 63.9 (d, $^2J_{CP}$ = 6.0 Hz, $POCH_2$), 69.0 (d, $^3J_{CP}$ = 8.7 Hz, CS), 76.8 (d, $^2J_{CP}$ = 4.8 Hz, CHOP), 126.4, 126.6, 128.5, 143.1 (s, CH_{arom}) 167.5 (s, C=O). IR (KBr): ν/cm^{-1} 1271 s (P=O), 1735 s (C=O). MS (CI-isobutane): m/z (%) 447 (100) $[M+H]^+$. Anal. calcd for $C_{20}H_{31}O_7PS$ (446.55): C, 53.80; H, 7.00; P, 6.94; S, 7.18; found: C, 54.21; H, 7.12; P, 7.13; S, 7.25%. Yield: 25%. R_f (ethyl acetate) = 0.25.

*Ethyl 2-[(diethoxyphosphoryl)oxy]-5-*tert*-butyl-1-(methylsulfinyl)cyclohexanecarboxylate (28e).* The ratio of diastereoisomers is 1.8:1. Mixture of two isomers of **28e**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85 (s, 9H, CCH_3, major), 0.88 (s, 9H, CCH_3, minor), 1.20–1.45 (m, 18H, OCH_2CH_3), 1.42 (m, 1H, CH_2), 1.52–1.70 (m, 2H, CH_2), 1.75–1.93 (m, 2H, CH_2), 2.05–2.47 (m, 8H, CH, CH_2), 2.65 (m, 1H, CH, minor), 2.71 (s, 3H, SCH_3, minor), 2.83 (s, 3H, SCH_3, major), 4.00–4.47 (m, 12H, OCH_2), 5.01 (m, 1H, CHOP, minor), 5.16 (m, 1H, CHOP, major). ^{31}P NMR ($CDCl_3$): δ −1.4 (minor), −2.2 (major). ^{13}C NMR ($CDCl_3$): δ 14.0 (s, $COCH_2CH_3$, major), 14.2 (s, $COCH_2CH_3$, minor), 15.9 (d, $^3J_{CP}$ = 4.0 Hz, $POCH_2CH_3$), 23.8 (s, CH_2), 26.8 [s, $C(CH_3)_3$], 29.5 (s, CH_2), 31.1 (s, SCH_3), 32.4 [s, $C(CH_3)_3$], 34.2 (s, CH_2), 41.6 (s, $CHCCH_3$), 61.6 (s, $COCH_2$, minor), 61.9 (s, $COCH_2$, major), 63.5, 63.9 (d, $^2J_{CP}$ = 6.4 Hz, $POCH_2$), 68.5 (d, $^3J_{CP}$ = 8.0 Hz, CS, minor), 70.1 (d, $^3J_{CP}$ = 8.4 Hz, CS, major), 77.4 (d, $^2J_{CP}$ = 5.0 Hz, CHOP), 167.9 (s, C=O). IR (film): ν/cm^{-1} 1263 s (P=O), 1739 s (C=O). MS (CI-isobutane): m/z (%) 427 (100) $[M+H]^+$. Anal. calcd for $C_{18}H_{35}O_7PS$ (426.57): C, 50.68; H, 8.29; P, 7.26; S, 7.52; found: C, 49.98; H, 7.92; P, 6.60; S, 7.10%. Yield: 62%. R_f (ethyl acetate) = 0.19.

Preparation of 2-alkenyl phosphates 29 and 30. General procedure. A solution of the appropriate sulfoxide (0.4 mmol) in dry toluene (5 mL) or, in the case of **27a**, in dry benzene (5 mL), was stirred at 100 °C or, in the case of **27a**, at 70 °C, for 3–6 h (depending on the sulfoxide). The progress of the reaction was followed by TLC chromatography. When the reaction was complete, solvent and volatile products were removed *in vacuo* and the residue was purified by silica gel chromatography (petroleum ether–ethyl acetate 10:3) to provide pure phosphates **29** and **30**

Preparation of 2-alkenyl phosphates 29 and 30 directly from β-keto esters 10 and 11. Thiophosphates **8** and **9** were prepared by the reaction of the appropriate enolate anion of β-keto-esters **10** and **11** (generated with NaH in THF solution at 0 °C) with freshly prepared diethoxyoxophosphoranesulfenyl chloride **1**, performed at −78 °C, as described above. Work-up followed by evaporation of solvents under reduced pressure afforded crude thiophosphate **8** or a crude mixture of diastereoisomers of thiophosphate **9**, which was added dropwise to a suspension of sodium borohydride at −78 °C, followed by addition of excess (5 equiv) methyl iodide. Stirring was continued at −78 °C and the reaction was stopped after 5–7 h by addition of EtOAc and ice water. After standard work-up (see above) the crude reaction mixture containing sulfide **17** or **21** among other products [episulfide **15** (**19**) and olefin **16** (**20**)] was oxidized with 85% MCPBA in CH_2Cl_2 solution at −78 °C. After stirring at −78 °C for 2 h, Et_2O was added and the mixture was washed with $Na_2S_2O_3$, $NaHCO_3$, water and dried ($MgSO_4$). Evaporation of solvent followed by flash chromatography [silica gel, EtOAc–MeOH (50:1) as eluent] afforded pure sulfoxide **27** (**28**). Compound **27** (**28**) was

dissolved in dry toluene (**27a** in dry benzene) and heated with stirring, at 100 °C (**27a** at 70 °C) for a few hours. When the reaction was complete (monitoring of the reaction progress by TLC), solvent and volatile products were removed *in vacuo* and the residue was chromatographed on silica gel with *n*-hexane–ethyl acetate (10:3) to afford a pure phosphates **29** and **30** as colourless oils.

Ethyl 5-[(diethoxyphosphoryl)oxy]cyclopent-1-ene-1-carboxylate (29a). ^{1}H NMR ($CDCl_3$): δ 1.05–1.43 (m, 9H, OCH_2CH_3), 2.16–2.85 (m, 4H, CH_2), 4.05–4.42 (m, 6H, OCH_2), 5.64 (m, 1H, CHOP), 7.13 (dd, $^3J_{HH} = {}^3J_{HH} = 2.5$ Hz, 1H, CH_2CH=C). ^{31}P NMR ($CDCl_3$): δ −1.7. ^{13}C NMR ($CDCl_3$): δ 13.9 (s, $COCH_2CH_3$), 15.9 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2CH_3$), 23.0 (s, CH_2), 39.2 (s, CH_2), 61.9 (s, $COCH_2$), 63.1, 63.2 (d, $^2J_{CP} = 6.5$ Hz, $POCH_2$), 70.3 (d, $^2J_{CP} = 5.0$ Hz, CHOP), 130.2 (s, CH=*C*COOEt), 147.5 (s, *C*H=CCOOEt), 166.7 (s, C=O). IR (KBr): ν/cm^{-1} 1258 s (P=O), 1718 s (C=O). MS (CI- isobutane): *m*/*z* (%) 293 (8) $[M+H]^+$, 155 (100) $[H+HOP(O)(OEt)_2]^+$, 139 (30). Anal. calcd for $C_{12}H_{21}O_6P$ (292.30): C, 49.30; H, 7.26; P, 10.59; found: C, 49.18; H, 7.06; P, 10.48%. Yield: 72%. R_f (ethyl acetate–petroleum ether 1:1) = 0.43.

Ethyl 6-[(diethoxyphosphoryl)oxy]cyclohex-1-ene-1-carboxylate (29b). ^{1}H NMR ($CDCl_3$): δ 1.15–1.43 (m, 9H, OCH_2CH_3), 1.45–1.90 (m, 4H, CH_2), 2.18–2.40 (m, 2H, CH_2), 3.95–4.32 (m, 6H, OCH_2), 5.33 (ddd, $^3J_{HP} = 6.2$ Hz, $^3J_{HH} = {}^3J_{HH} = 3.3$ Hz, 1H, CHOP), 7.20 (dd, $^3J_{HH} = 4.9$ Hz, $^3J_{HH} = 2.8$ Hz, 1H, CH_2CH=C). ^{31}P NMR ($CDCl_3$): δ −2.0. ^{13}C NMR (DEPT, $CDCl_3$): δ 14.0 (s, $COCH_2CH_3$), 15.4 (s, CH_2), 15.9 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2CH_3$), 25.6 (s, CH_2), 28.9 (s, CH_2), 60.4 (s, $COCH_2CH_3$), 63.2, 63.4 (d, $^2J_{CP} = 7.2$ Hz, $POCH_2CH_3$), 68.8 (d, $^2J_{CP} = 5.3$ Hz, CHOP), 129.1 (d, $^3J_{CP} = 8.9$ Hz, CH=*C*COOEt), 145.1 (s, *C*H=CCOOEt), 165.5 (s, C=O). IR (KBr): ν/cm^{-1} 1260 s (P=O), 1720 s (C=O). MS (CI- isobutane): *m*/*z* (%) 307 (100) $[M+H]^+$, 155 (57). HRMS (CI) calcd for $C_{13}H_{23}O_6P+H$ $[M+H]^+$ 307.1311; found: 307.1317. Yield: 70%. R_f (ethyl acetate–petroleum ether 1:1) = 0.47.

Ethyl 7-[(diethoxyphosphoryl)oxy]cyclohept-1-ene-1-carboxylate (29c). ^{1}H NMR ($CDCl_3$): δ 1.10–1.34 (m, 9H, OCH_2CH_3), 1.32–2.61 (m, 8H, CH_2), 3.92–4.23 (m, 6H, OCH_2), 5.63 (ddd, $^3J_{HH} = {}^3J_{HP} = 6.4$ Hz, $^3J_{HH} = 1.2$ Hz, 1H, CHOP), 7.36 (ddd, $^3J_{HH} = 5.2$ Hz, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, CH_2CH=C). ^{31}P NMR ($CDCl_3$): δ −1.5. ^{13}C NMR ($CDCl_3$): δ 14.1 (s, $COCH_2CH_3$), 16.0 (d, $^3J_{CP} = 6.8$ Hz, $POCH_2CH_3$), 24.0 (s, CH_2), 25.9 (s, CH_2), 27.7 (s, CH_2), 31.3 (d, $^3J_{CP} = 4.2$ Hz, CH_2), 60.8 (s, $COCH_2$), 63.4, 63.6 (d, $^2J_{CP} = 6.5$ Hz, $POCH_2$), 73.3 (d, $^2J_{CP} = 6.4$ Hz, CHOP), 134.1 (s, CH=*C*COOEt), 149.2 (s, *C*H=CCOOEt), 166.5 (s, C=O) ppm. IR (KBr): ν/cm^{-1} 1256 s (P=O), 1718 s (C=O). MS (EI, 70 eV): *m*/*z* (%) 320 (5) $[M]^+$, 155 (100) $[H+HOP(O)(OEt)_2]^+$, 127 (37), 99 (40). Anal. calcd for $C_{14}H_{25}O_6P$ (320.39): C, 52.47; H, 7.88; P, 9.69; found: C, 52.25; H, 7.10; P, 9.41%. Yield: 76%. R_f (ethyl acetate–petroleum ether 1:1) = 0.50.

Ethyl 6-[(diethoxyphosphoryl)oxy]-5-mathylcyclohex-1-ene-1-carboxylate (30b). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 0.89 (d, $^3J_{HH} = 7.2$ Hz, 3H, $CHCH_3$), 1.30 (t, $^3J_{HH} = 7.2$ Hz, 9H, OCH_2CH_3), 1.45 (m, 1H, CH_2), 1.95 (m, 1H, CH_2), 2.15–2.33 (m, 2H, CH_2), 3.95–4.36 (m, 6H, OCH_2), 5.01 (dd, $^3J_{HP} = 6.8$ Hz, $^3J_{HP} = 2.4$ Hz, 1H, CHOP), 7.20 (dd, $^3J_{HH} = {}^3J_{HH} = 3.8$ Hz, 1H, CH_2CH=C). ^{31}P NMR ($CDCl_3$): δ −2.0. ^{13}C NMR (DEPT, $CDCl_3$): δ 13.9 (s, $COCH_2CH_3$), 14.4 (s, CH_3), 15.7 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2CH_3$), 20.9 (s, CH_2), 21.4 (s, *C*H$_2$), 31.5 (s, *C*HCH$_3$), 60.3 (s, $COCH_2$), 63.0, 63.2 (d, $^2J_{CP} = 6.9$ Hz, $POCH_2$), 73.3 (d, $^2J_{CP} = 5.4$ Hz, CHOP), 127.2 (d, $^3J_{CP} = 8.0$ Hz, CH=*C*COOEt), 144.4 (s, *C*H=CCOOEt), 165.7 (s, C=O). IR (KBr): ν/cm^{-1} 1257 s (P=O), 1716 s (C=O). MS (CI-isobutane): *m*/*z* (%) 321 (100) $[M+H]^+$, 155 (90). HRMS (CI) calcd for $C_{14}H_{25}O_6P+H$ $[M+H]^+$ 321.1467; found: 321.1475. Yield: 84%. R_f (ethyl acetate) = 0.54.

Ethyl 6-[(diethoxyphosphoryl)oxy]-4-methylcyclohex-1-ene-1-carboxylate (30c). Single diastereoisomer. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (d, $^3J_{HH} = 6.3$ Hz, 3H, $CHCH_3$) 1.15–1.45 (m, 9H, OCH_2CH_3), 1.52–2.00 (m, 3H, CH, CH_2), 2.13–2.35 (m, 2H, CH_2), 4.00–4.42 (m, 6H, OCH_2), 5.35 (m, 1H, CHOP), 6.96 (m, 1H, CH_2CH=C). ^{31}P NMR ($CDCl_3$): δ −1.4. ^{13}C NMR ($CDCl_3$): δ 13.8 (s, $COCH_2CH_3$), 15.6 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2CH_3$), 20.3 (s, $CHCH_3$), 27.7, 31.4, 36.0 (s, CH_2), 62.3 (s, $COCH_2$), 63.5, 63.6 (d, $^2J_{CP} = 6.8$ Hz, $POCH_2$), 75.0 (d, $^2J_{CP} = 5.3$ Hz, CHOP), 129.3 (d, $^3J_{CP} = 8.0$ Hz, CH=*C*COOEt), 146.4 (s, *C*H=CCOOEt), 166.2 (s, C=O). IR (KBr): ν/cm^{-1} 1252 s (P=O), 1724 s (C=O). MS (CI- isobutane): *m*/*z* (%) 321 (100) $[M+H]^+$. Anal. calcd for $C_{14}H_{25}O_6P$ (320.36): C, 52.48; H, 7.88; P, 9.67; found: C, 52.30; H, 7.67; P, 9.66%. Yield: 70%. R_f (ethyl acetate) = 0.54.

Ethyl 6-[(diethoxyphosphoryl)oxy]-3-phenylcyclohex-1-ene-1-carboxylate (30d). Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.32 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.8$ Hz, 6H, $POCH_2CH_3$), 1.34 (t, $^3J_{HH} = 7.1$ Hz, 3H, $COCH_2CH_3$), 1.65–1.98 (m, 2H, CH_2), 2.05–2.30 (m, 2H, CH_2), 3.72 (m, 1H, CH), 3.95–4.40 (m, 6H, OCH_2CH_3), 5.42 (ddd, $^3J_{HH} = 6.6$ Hz, $^3J_{HP} = {}^3J_{HH} = 3.8$ Hz, 1H, CHOP), 7.10 (d, $^3J_{HH} = 7.3$ Hz, 1H, $CHCH$=C). ^{31}P NMR ($CDCl_3$): δ −1.8. ^{13}C NMR (DEPT, $CDCl_3$): δ 14.1 (s, $COCH_2CH_3$), 16.0 (d, $^3J_{CP} = 6.9$ Hz, $POCH_2CH_3$), 25.1 (s, CH_2), 25.7 (s, CH_2), 40.4 (s, *C*HPh), 60.7 (s, $COCH_2$), 63.3, 63.5 (d, $^2J_{CP} = 6.8$ Hz, $POCH_2$), 69.2 (d, $^2J_{CP} = 5.1$ Hz, CHOP), 126.7, 127.8, 128.5 (s, CH_{arom}), 130.7 (d, $^3J_{CP} = 8.8$ Hz, CH=*C*COOEt), 141.9 (s, *i*-CH_{arom}) 145.3 (s, *C*H=CCOOEt), 165.5 (s, C=O). IR (KBr): ν/cm^{-1} 1264 s (P=O), 1717 s (C=O). MS (EI, 70eV): *m*/*z* (%) 382 (3) $[M^+]$, 228 (85), 183 (10), 155 (100), 99 (16). Anal. calcd for $C_{19}H_{27}O_6P$ (382.43): C, 59.67; H, 7.13; P, 8.10; found: C, 59.43; H, 6.72; P, 8.23. Yield: 79%. R_f (ethyl acetate) = 0.41.

*Ethyl 6-[(diethoxyphosphoryl)oxy]-3-*tert*-butylcyclohex-1-ene-1-carboxylate (30e).* Single diastereoisomer. ^{1}H NMR ($CDCl_3$): δ 0.91 [s, 9H, $C(CH_3)_3$], 1.15–1.40 (m, 9H, OCH_2CH_3), 1.62–2.38 (m, 5H, CH_2), 3.81–4.38 (m, 6H, OCH_2), 5.30 (m, 1H, CHOP), 7.09 (d, $^3J_{HH} = 2.5$ Hz, 1H, $CHCH$=C). ^{31}P NMR ($CDCl_3$): δ −0.8. ^{13}C NMR (DEPT, 500 MHz, $CDCl_3$): δ 14.2 (s, $COCH_2CH_3$), 16.0 (d, $^3J_{CP} = 7.1$ Hz, $POCH_2CH_3$), 20.3 (s, CH_2), 27.6 [s, $C(CH_3)_3$], 29.5 (s, CH_2), 33.7 [s, $C(CH_3)_3$], 45.7 [s, $CHC(CH_3)_3$], 60.6 (s, $COCH_2$), 63.4, 63.6 (d, $^2J_{CP} = 5.9$ Hz, $POCH_2$), 71.4 (s, CHOP), 131.5 (d, $^3J_{CP} = 9.8$ Hz, CH=*C*COOEt), 145.3 (s, *C*H=CCOOEt), 166.1 (s, C=O). IR (KBr): ν/cm^{-1} 1267 s (P=O), 1724 s (C=O). MS (CI-isobutane): *m*/*z* (%) 363 (100) $[M+H]^+$, 309 (13), 209 (20), 155 (58). HRMS (CI) calcd for $C_{17}H_{31}O_6P+H$ $[M+H]^+$ 363.1936; found: 363.1933. Yield: 68%. R_f (ethyl acetate–petroleum ether 1:1) = 0.56.

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