

Asymmetric oxidation of enol phosphates to α -hydroxy ketones by (salen)manganese(III) complex. Effects of the substitution pattern of enol phosphates on the stereochemistry of oxygen transfer

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Abstract—This paper presents a study of enantioselective catalytic oxidation of a variety of differently substituted, cyclic (*E*) and acyclic (*Z*)-enol phosphates. The asymmetric oxidation of acyclic (*Z*)-enol phosphates containing alkoxy substituents in the phosphate group **2a**, **c**, **e–g**, **i**, and **j** and *Z*-configured enol phosphates containing aryloxy substituents in the phosphate group **2b**, **d**, and **h** afforded optically active α -hydroxy ketones **4a–j** of opposite configuration with good to high enantioselectivity. The influence of electronic and steric effects of the enol phosphate substituents on the stereoselectivity of oxidation was studied.

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1. Introduction

The α -hydroxy carbonyl unit is found in many biologically active natural products such as sugars and antibiotics.¹ Enantiomerically pure α -hydroxy carbonyl compounds are also important synthons for the asymmetric synthesis of natural products.^{1a,2} Consequently, efficient methods for the construction of enantiomerically pure, or at least enriched, α -hydroxy carbonyl derivatives are in demand.³ This class of compounds has been prepared by both nonoxidative⁴ and oxidative methods.^{3a,b,5} Among the latter, the asymmetric oxidation of enolate or enol ethers using chiral *N*-sulfonyloxaziridine^{3a} or a Sharpless dihydroxylation catalyst^{3b} has been applied with success. Epoxidation is among the most useful oxidation reactions, since the epoxides may be transformed by stereoselective ring opening into highly functionalized products.⁶ A recent major advance in catalytic enantioselective epoxidation is oxidation of prochiral unsaturated compounds with readily accessible (salen) Mn(III) complexes. It has been demonstrated that these complexes are highly enantioselective catalysts for the epoxidation of various conjugated substituted olefins,⁷ enol ethers,^{5a,8} and esters.^{5a,8a} These epoxy derivatives were easily converted into optically active α -hydroxy carbonyl compounds.

Enol phosphates constitute a class of important organic compounds exhibiting biological activity.⁹ They are very easy to prepare.¹⁰ However, the utility of enol phosphates in organic synthesis is still limited.¹¹

We have previously described the application of cyclic enol phosphates in the stereoselective synthesis of newly functionalized polycyclic compounds including functionalized enol phosphates with an allyl hydroxy group. We also found that epoxidation of these compounds led to α -hydroxy ketones.¹² We then elaborated methodology, based on epoxy phosphate intermediates,^{12,13} for an alternative general synthesis of acyclic and cyclic α -hydroxy carbonyl compounds.¹⁴

In a recent paper¹⁵ we showed that readily available enol phosphates can be stereoselectively oxidized to α -hydroxy ketones with high enantioselectivity using (salen) Mn(III) Jacobsen's catalyst **1**¹⁶ (Fig. 1). We observed that reactions

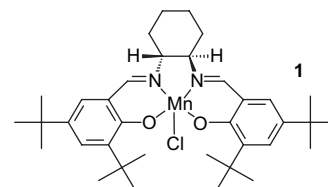


Figure 1. (*R,R*)-(-)-*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine manganese(III) chloride.

Keywords: Enol phosphates; Asymmetric oxidation; α -Hydroxy ketones; Jacobsen's catalyst.

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of asymmetric epoxidation of enol phosphates bearing phenoxy instead of ethoxy substituents at phosphorus led to α -hydroxy ketones of opposite configuration to that of other α -hydroxy carbonyl compounds obtained. We decided to develop these studies, which could provide an insight into factors controlling stereoselection in the epoxidation of enol phosphates.

2. Results and discussion

We first prepared a set of enol phosphates **2** (Table 1), substituted with phenyl in the α -position and alkyl or phenyl in the β -position, which would afford the more persistent α -hydroxy ketones. Besides the phosphates containing ethoxy groups at phosphorus atom, the phosphorus compounds with bulky alkoxy and phenoxy groups at phosphorus were also chosen for oxidation. This allowed us to test the influence of steric and electronic aspects of the substrates on the stereochemistry of their asymmetric epoxidation. All compounds **2a–j** were obtained by the reaction of dialkyl (R=Et, *i*-Pr, and *t*-BuCH₂) and diaryl (R=Ph and *p*-MeO-Ph) phosphorochloridates with enolate anions. The latter were generated from the appropriate ketones by action of LDA.^{10d}

Table 1. Acyclic *Z*-enol phosphates **2**

2	R ¹	Ar	R
a	Me	Ph	Et
b	Me	Ph	Ph
c	Et	Ph	Et
d	Et	Ph	Ph
e^a	Et	Ph	<i>t</i> -BuCH ₂
f	Pr	Ph	Et
g	Pr	Ph	<i>i</i> -Pr
h	Pr	Ph	4-MeOC ₆ H ₄
i^a	Ph	Ph	Et
j	Me	4-MeOC ₆ H ₄	Et

^a Mixture of *E* and *Z* isomers.

Most enol phosphates **2** were formed as single isomers. All compounds had *Z*-configuration, assigned on the basis of ¹H NMR spectral analysis and in particular for compound **2g** on the observation of a positive nuclear Overhauser effect (NOE)—a 3% increase in area for the vinyl proton *cis* to phenyl.¹⁷ *Z*-Configuration of the other enol phosphates was determined by comparison of the chemical shift of vinyl protons and the coupling constant (⁴*J*_{PH}) observed for **2g** and **2a–d**, **f**, and **h–j**¹⁸ and additionally by a NOESY experiment carried out on compound **2d**.

Catalytic oxidation of phosphates **2a–j** was carried out with NaOCl in phosphate buffer (pH~11) as oxygen source, 4-phenylpyridine *N*-oxide (PPNO) as additive and 7% of (salen) Mn(III) complex **1** as catalyst.^{7b,19} The best conversion of enol phosphates to α -hydroxy ketones was achieved in the oxidation performed at 0 °C for 24 h. Opening of the intermediate epoxides **3** was carried out with 25% CF₃COOH at 5 °C (Scheme 1) and pure α -hydroxy ketones **4** were obtained by flash chromatography. All the results of epoxidation of enol phosphates **2** are summarized in Table 2.

(*Z*)-Configured enol phosphates **2a**, **c**, **f**, **g**, and **j** with an alkyl substituent β to the phosphate group afforded *S* enantiomers of the corresponding α -hydroxy ketones **4a**, **c**, **f**, and **j** with high ee (83–96%) (entries 1, 3, 6, 7, and 10).

Catalytic oxidation of enol phosphate **2i** containing a phenyl group in both α - and β -positions gave the benzoin **4i** with 89% ee (entry 9), whereas oxidation of diphenyl substituted silyl enol ether by chiral complex **1** led to the formation of benzoin with only 12% ee.^{5a}

To test the steric influence of the phosphoryloxy group on asymmetric induction and enantioselectivity, enol phosphates with bulkier isopropoxy (R=*i*-Pr, R¹=Pr) **2g** and neopentoxy substituents (R=*t*-BuCH₂, R¹=Et) **2e** were selected. Compound **2g** afforded (*S*)-configured α -hydroxy ketone **4g** with 88% ee, which is only a slightly better value than for **2f** (R=Et, R¹=Pr), ee=83% (entries 6 and 7). For compound **2e** enantioselectivity is very low (13% estimated

Table 2. Enantioselective synthesis of α -hydroxy ketones **4a**, **4c**, **4f**, **4i**, and **4j** by catalyst (*R,R*)-(–) salen Mn(III) **1** with NaOCl

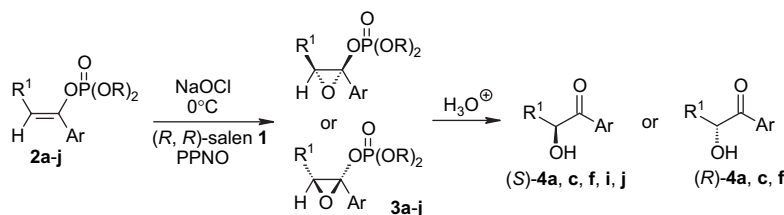
Entry	Substrate	Product	Yield ^a (%)	ee ^b (%)	Config. ^c of 4
1	2a	4a	57	96	<i>S</i> (–)
2	2b	4a	47	68	<i>R</i> (+)
3	2c	4c	50	93	<i>S</i> (–)
4	2d	4c	58	81	<i>R</i> (+)
5	2e	4c	50	13 ^d	<i>S</i> (–)
6	2f	4f	58	83	<i>S</i> (–)
7	2g	4f	70	88	<i>S</i> (–)
8	2h	4f	50	68	<i>R</i> (+)
9	2i	4i	56	89	<i>S</i> (+)
10	2j	4j	60	87	<i>S</i> (–)

^a Yield of pure, isolated compounds **4** (not optimized) based on enol phosphates **2**.

^b Determined by HPLC analysis (Chiracel OD, for details see Section 4) using racemic compounds as references.

^c Configurations were assessed by comparison of sign of the optical rotation with literature data, for **4f** in analogy to the elution order of the enantiomers of **4a** and **4c** (see Section 4).

^d Enantiomeric excess was estimated by comparison of values of optical rotation of *S*(–)- α -hydroxy ketones **4f**.



Scheme 1. Asymmetric oxidation of enol phosphates **2** by (*R,R*)-(–) salen Mn(III) catalyst **1**.

on optical rotation of **4c** compared to reported data), but the starting enol phosphate **2e** is a mixture of *Z* and *E* isomers.

Enol phosphates **2b**, **d**, and **h**, bearing phenoxy groups at phosphorus, afforded *R* enantiomers of α -hydroxy ketones **4a**, **c**, and **f** with enantiomeric excess of 68–81% (Table 2, entries 2, 4, and 8). Comparing the absolute configuration of these products with the *S* configuration of **4a**, **c**, and **f** obtained from enol phosphates **2a**, **c**, **f**, and **g** (entries 1, 3, 6, and 7) reveals that the change of *R* substituent in phosphate group from Alk (**2a**, **c**, **f**, and **g**) to Ar (**2b**, **d**, and **h**) leads to the opposite absolute configuration of α -hydroxy ketones formed, and has influence on the enantioselectivity of the oxidation. Decrease in enantioselectivity was observed for **2b**—68% ee compared to 96% ee for **2a**; 81% ee for **2d** versus 93% ee for **2c** and 68% ee for **2h** compared to 83–88% ee for **2f** and **g** (entries 1–4 and 6–8). Oxidation of the enol phosphate with electronically modified phenoxy groups (R=4-MeOC₆H₄) **2h** afforded the corresponding α -hydroxy ketone **4f** of *R* configuration (entry 8). This stereochemical result confirms that the phenoxy substituents in enol phosphates are responsible for the opposite sense of asymmetric induction in these oxidations.

In order to determine the usefulness of enol phosphates as prochiral substrates for metal-catalyzed oxidation by a chiral oxygen complex, and to test the influence of the substitution pattern of the enol phosphate substrates on the stereochemistry, further studies with cyclic compounds were undertaken. We chose bi- and tricyclic systems containing enol phosphate and aromatic moieties. Similar α -hydroxy ketones simulate functionalities in natural products.²⁰

The corresponding enol phosphates **5a–f** (Fig. 2) were prepared according to the procedure described above. Pure **5a–f** were the subject of asymmetric epoxidation, performed as before and after hydrolysis of the intermediate epoxides **6** the α -hydroxy ketones **7** were obtained and isolated by flash chromatography (Fig. 3). Their enantiomeric purity was determined by chiral HPLC (Table 3).

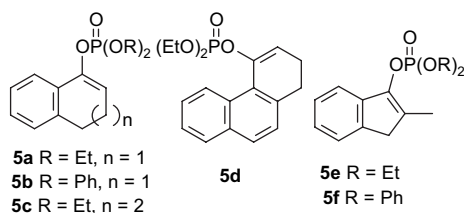


Figure 2. Cyclic *E*-enol phosphates **5**.

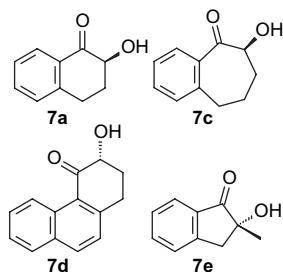


Figure 3. Cyclic α -hydroxy ketones **7**.

Table 3. Enantioselective synthesis of α -hydroxy ketones **7a** and **7c–e** by catalyst (*R,R*)-(–) (salen) Mn(III) **1** with NaOCl

Entry	Substrate	Product	Yield ^a (%)	ee ^b (%)	Config. of 6 ^c
1	5a	7a	37	89	<i>S</i> -(–)
2	5b	7a	35	88	<i>S</i> -(–)
3	5c	7c	54	94	<i>S</i> -(+) ^d
4	5d	7d	22	81	<i>R</i> -(+) ^d
5	5e	7e	57	69	<i>R</i> -(+)
6	5f	7e	49	60	<i>R</i> -(+)

^a Yield of isolated pure compounds **7** (not optimized) based on enol phosphates **5** (see text).

^b Determined by HPLC analysis (Chiracel OD, for details see Section 4) using racemic compounds as references.

^c Configurations were assessed by comparison of the sign of optical rotation with literature data (see Section 4).

^d Absolute configurations were assigned by comparing circular dichroism (CD) spectra of the purified α -hydroxy ketones **7c** and **7d** to the CD spectrum of (*S*)-2-hydroxy tetralone **7a** (see Supplementary information).

The degree of conversion of cyclic enol phosphates **5a**, **b**, and **d** to α -hydroxylated products **7a** and **d** is not as good as for phosphates **5c**, **e**, and **f** (Table 3). Low yields of **7a** and **d** are due in part to the participation of an aromatization pathway leading to the corresponding naphthalene and phenanthrene derivatives.^{7c}

Oxidation of enol phosphates **5a**, **b**, and **c** afforded (*S*)-(–)-2-hydroxy tetralone **7a** and (*S*)-(+)-2-hydroxy benzosuberone **7c** in high enantioselectivity 88–94% (Table 3, entries 1–3). High enantioselectivity 81% was also observed for the oxidation of the enol phosphate **5d** but for **7d** the *R* configuration prevailed (Table 3, entry 4).

Stereoselectivity of the oxidation of tetrasubstituted enol phosphates **5e** and **f** leading to (*R*)-(+)-2-hydroxy-2-methyl-1-indanone **7e** is substantially lower at 69–60% ee (Table 3, entries 5 and 6).

The change of substituents RO in the phosphate group from EtO (**5a** and **e**) to PhO (**5b** and **f**) had no influence on the absolute configuration of products **7** (Table 3 entries 1, 2 and 5, 6).

The results presented in Tables 2 and 3 demonstrate that the degree of enantioselectivity and absolute configuration of α -hydroxy ketones in the catalytic oxidation of enol phosphates **2** and **5** by Jacobsen's chiral oxo complex is controlled by the substitution pattern of these phosphates, and particularly by the steric and electronic factors of the phosphate group in enol compounds. In order to rationalize the stereochemical results we have analyzed the mechanistic models proposed for metal-catalyzed asymmetric oxidation of trisubstituted olefins. Generally two proposals for the mechanism of oxygen-atom transfer from metal oxo complexes have been considered. One invokes substrate attack at both the metal and oxo centers to form an oxametallacycle intermediate.²¹ The other widely accepted mechanism involves direct substrate attack at the oxo ligand with concerted or stepwise C–O bond formation.^{19b,22} Two approaches of the olefin to the metal–oxygen bond have been proposed (Fig. 4): side-on along the direction of the chiral diamine bridge **b** (Jacobsen model)²³ and a skewed side-on attack **c** or **c'** along the metal C=N ligand of the diamine bridge (Katsuki model),^{7c,g,h} which is more adequate for oxofunctionalization of trisubstituted olefins.

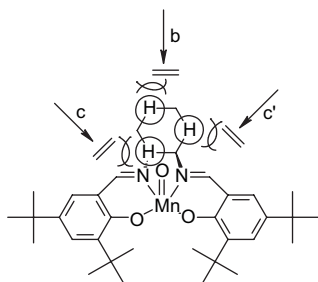
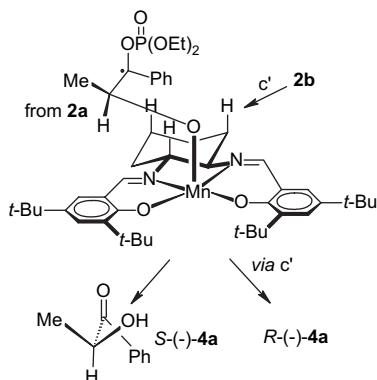


Figure 4. The view of the olefin approaches to the metal–oxygen bond.

Oxidation of (*Z*) acyclic enol phosphates, containing alkoxy substituents at the phosphorus atom **2a**, **c**, **e–g**, **i**, and **j** led to the formation of *S*-configured α -hydroxy ketones. This means that one of the two possible enantiofacial orientations of these enol phosphates is favored. Following the suggestion by Adam^{5a} we considered a skewed side-on approach of the enol phosphate to the oxo ligand of the catalyst, which would avoid steric and electronic interaction between the substrate's substituents and its salen framework. This enantiofacial approach, illustrated in **Scheme 2**, should lead to *S*-configured α -hydroxy ketones, in accord with our experimental data.

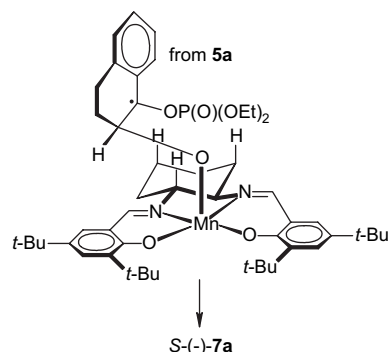


Scheme 2. Mechanistic proposal for the oxidation of enol phosphates **2a** and **2b** by the oxo-metal complex of catalyst **1**.

Enol phosphates with PhO groups at the phosphorus atom **2b**, **d**, and **h** display the opposite facial selectivity in the resulting α -hydroxy ketones. Again we considered the privileged enantiofacial orientation of enol phosphates, which means that the phosphate groups should avoid the arene rings of the salen ligand. The opposite configuration of α -hydroxy ketones **4a**, **c**, and **f** obtained from **2b**, **d**, and **h**, and the lower enantioselectivity in the oxidation of these substrates compared with the enantioselectivity of α -hydroxy ketones **4a**, **c**, and **f** derived from **2a**, **c**, **f**, and **g** can suggest that approach along trajectory **c'** is also possible (**Scheme 2**). A similar proposal explaining the stereoselectivity of catalytic oxidation of some aromatic derivatives has been reported in the literature.^{7f}

The stereochemistry of epoxides obtained from the Mn–salen catalyzed oxidation of 1- or 2-methyl-3,4-dihydronaphthalene has been rationalized by taking the electronic effects of the aromatic moiety into consideration.^{7c} So we proposed the approach of enol phosphate tetralone derivatives **5a** and **b** and enol phosphate benzosuberone derivative **5c** to the

metal–oxo bond, shown in **Scheme 3**. In this approach the electronic interactions between salen benzene ring and arene substituents, including phenoxy groups in compound **5b**, orient these unsaturated substituents away from the salen benzene ring.



Scheme 3. Mechanistic proposal for the oxidation of the phosphate **5a** by the oxo-metal complex of catalyst **1**.

The α -hydroxy ketones of opposite configuration (*R*) **7d–e** were formed from catalytic epoxidation of the enol phosphate derivatives of 2,3-dihydro-phenanthren-4-one **5d** and of 2-methyl indanone **5e** and **f**. Such stereochemical results can be analyzed in terms of electronic as well as steric interactions of bulkier aromatic substituent with the salen framework. The lower enantiomeric excesses of 2-hydroxy-2-methyl indanone **7e** correlate with the poorer stereoselectivity of manganese-assisted oxidation of tetrasubstituted olefins.^{7c} Thus, we have considered the top-on approach (the olefin and salen-ligand planes parallel)^{7c} of enol phosphates **5d–f** to the oxo-metal catalyst.

Likely transition states were proposed for oxygen transfer from oxo Mn–salen complex to olefin to form the possible radical²² or metallaoxetane intermediates.^{21b} Adam et al. considered a metallaoxetane mechanism as more adequate for the oxofunctionalization of silyl enol ethers and ketene acetals to the corresponding α -hydroxy ketones and α -hydroxy acetals.^{5a} It seems reasonable to assume on the basis of presented data for salen Mn-catalyzed epoxidation of enol phosphates, that direct attack of enol phosphate on an (oxo) manganese species generates a radical intermediate, which collapses to the epoxide, which then transposes to an α -hydroxy ketone.

3. Conclusion

We have shown that a variety of readily available (*Z*) and (*E*)-enol phosphates **2** and **5** are good synthons in the stereoselective syntheses of the corresponding α -hydroxy ketones **4** and **7**. Asymmetric epoxidation of these phosphates using Jacobsen's (salen) Mn(III) complex afforded α -hydroxy ketones **4** and **7** in high enantioselectivity up to 96%.

Our results demonstrate that absolute configuration of these target compounds is controlled by steric bulk and electronic aspects of the phosphate group in enol phosphates. By choosing the right substituents in the remote phosphate group of acyclic (*Z*)-enol phosphate **2** ArO or AlkO, both enantiomers of α -hydroxy ketones **4** may be obtained with

the same chiral catalyst. In contrast bulky aromatic groups display an influence on the enantioselectivity as well as on the sense of stereoselectivity of catalytic oxidation of cyclic (*E*)-enol phosphates **5**.

4. Experimental

4.1. 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 deuteriochloroform as solvent) unless otherwise noted. IR spectra were measured on an Ati Mattson Infinity FT IR 60. GC spectra were performed on a Hewlett–Packard 5890. MS spectra (EI, CI, and HRMS) were recorded on a Finnigan MAT 95 spectrometer. Microanalyses were carried out on EA1108 apparatus. Melting points were measured with PHMK Boetius (VEB Analytik Dresden) apparatus. Optical rotation values were measured in 100 mm cell on Perkin Elmer 241 MC under Na lamp radiation. The enantiomeric ratios were determined by HPLC analysis on the commercially available column Chiracel OD under conditions specified.

Chromatographic purification was performed on silica gel columns (Merck, Kieselgel 70–230 mesh) with an indicated eluent. Chemicals and solvents were obtained from commercial sources and distilled or dried according to standard methods. The products were characterized by comparison of their data with those of known samples or by their spectral data.

4.1.1. Phosphoric acid diethyl ester 1-phenyl-propenyl ester 2a.^{10d} **General procedure.** To a solution of freshly prepared LDA (21 mmol) in THF (50 mL) at -78°C was added propiophenone (2.68 g, 20 mmol) in THF solution (10 mL) and the mixture was stirred under an Ar atmosphere for 1 h, then the solution of diethylphosphorochloridate (5.1 g, 30 mmol) in THF (5 mL) was dropped at the same temperature. The mixture was stirred and allowed to warm slowly to room temperature. After 1 h of stirring at ambient temperature the solvent was evaporated, the residue was dissolved in ether, washed with saturated NH_4Cl and water and dried (MgSO_4). Evaporation of solvent afforded the crude reaction mixture, which was analyzed by ^1H and ^{31}P NMR spectroscopy. Pure enol phosphate was obtained from column chromatography with petroleum ether–EtOAc (5:1 v/v) as single isomer, yellow oil (4.9 g, 91%); R_f 0.34 (1:1 petroleum ether–EtOAc); $\nu_{\text{max}}/\text{cm}^{-1}$ 2984, 2911, 2866, 1665, 1445, 1392, 1269, 1165, 1027, 979; δ_{H} (200 MHz, CDCl_3) 7.51–7.45 (2H, m, Ph), 7.35–7.24 (3H, m, Ph), 5.65 (1H, dq, $J=7.0$, 2.2 Hz, C=CH), 4.06 (4H, q, $J=7.3$ Hz, OCH_2CH_3), 1.87 (3H, dd, $J=7.0$, 3.0 Hz, C=CCH₃), 1.22 (6H, t, $J=7.1$ Hz, OCH_2CH_3); δ_{C} (50.3 MHz, CDCl_3) 146.6 (d, $J=9.1$ Hz, POC=CH), 135.5 (*ipso*-Ph), 127.9, 127.8, 125.0 (Ph), 111.9 (d, $J=5.9$ Hz, POC=CH), 64.0 (d, $J=5.9$ Hz, POCH_2CH_3), 15.7 (d, $J=6.8$ Hz, POCH_2CH_3), 11.5 (CH₃); δ_{P} (81.0 MHz, CDCl_3) -5.6 ; MS (CI-isobutane): m/z (%) 271 (80) $[\text{M}+\text{H}]^+$, 155 (100).

4.1.2. Phosphoric acid diphenyl ester 1-phenyl-propenyl ester 2b.²³ Single isomer, yellow oil (85%); R_f 0.51 (1:1

petroleum ether–EtOAc); $\nu_{\text{max}}/\text{cm}^{-1}$ 3061, 1667, 1591, 1490, 1294, 1216, 1189, 1024, 954, 764, 689; δ_{H} (200 MHz, CDCl_3) 7.51–7.45 (2H, m, Ph), 7.33–7.26 (7H, m, Ph, PhO), 7.19–7.11 (6H, m, PhO), 5.74 (1H, dq, $J=7.0$, 2.0 Hz, C=CH), 1.85 (3H, dd, $J=7.0$, 3.1 Hz, C=CCH₃); δ_{C} (50.3 MHz, CDCl_3) 150.3 (d, $J=7.2$ Hz, *ipso*-PhO), 146.8 (d, $J=9.6$ Hz, POC=CH), 134.8 (*ipso*-Ph), 129.5, 128.1, 125.1 (Ph, PhO), 119.8 (d, $J=4.9$ Hz, POPh), 112.6 (d, $J=6.8$ Hz, POC=CH), 11.5 (CH₃); δ_{P} (81.0 MHz, CDCl_3) -16.98 ; MS (CI-isobutane): m/z (%) 367 (36) $[\text{M}+\text{H}]^+$, 251 (100), 95 (10).

4.1.3. Phosphoric acid diethyl ester 1-phenyl-but-1-enyl ester 2c. Single isomer, colorless oil (90%); R_f 0.25 (1:1 petroleum ether–EtOAc); $\nu_{\text{max}}/\text{cm}^{-1}$ 2980, 2934, 2874, 1660, 1494, 1446, 1273, 1165, 1099, 980, 767; δ_{H} (200 MHz, CDCl_3) 7.53–7.49 (2H, m, Ph), 7.35–7.26 (3H, m, Ph), 5.56 (1H, dt, $J=7.3$, 2.0 Hz, C=CH), 4.06 (4H, q, $J=7.2$ Hz, OCH_2CH_3), 2.38 (2H, dq, $J=7.5$, 2.5 Hz, C=CCH₂), 1.23 (6H, t, $J=7.1$ Hz, OCH_2CH_3), 1.08 (3H, t, $J=7.5$ Hz, C=CCH₂CH₃); δ_{C} (50.3 MHz, CDCl_3) 145.2 (d, $J=9$ Hz, POC=CH), 135.5 (*ipso*-Ph), 127.9, 127.8, 125.1 (Ph), 119.4 (d, $J=6.4$ Hz, POC=CH), 64.0 (d, $J=5.9$ Hz, POCH_2CH_3), 19.4 (CH₂), 15.7 (d, $J=6.9$ Hz, POCH_2CH_3), 13.4 (CH₃); δ_{P} (81.0 MHz, CDCl_3) -5.64 ; MS (EI, 15 eV): m/z (%) 284 (38) $[\text{M}]^+$, 155 (100), 130 (42). Anal. calcd for $\text{C}_{14}\text{H}_{21}\text{O}_4\text{P}$ (284.29): C, 59.15; H, 7.44; P, 10.89. Found: C, 58.59; H, 7.71; P, 10.53%.

4.1.4. Phosphoric acid diphenyl ester 1-phenyl-but-1-enyl ester 2d. Single isomer, yellow oil (72%); R_f 0.42 (1:1 petroleum ether–EtOAc); $\nu_{\text{max}}/\text{cm}^{-1}$ 3062, 2968, 1590, 1489, 1299, 1216, 1189, 1042, 1011, 959, 765; δ_{H} (200 MHz, CDCl_3) 7.51–7.46 (2H, m, Ph), 7.40–7.32 (7H, m, Ph, PhO), 7.22–7.10 (6H, m, PhO), 5.64 (1H, dt, $J=7.4$, 1.8 Hz, C=CH), 2.33 (2H, dq, $J=7.5$, 2.5 Hz, C=CCH₂), 1.04 (3H, t, $J=7.5$ Hz, C=CCH₂CH₃); NOESY (^1H – ^1H): cross peak [5.64 (C=CH) and 7.51–7.46 (*o*-Ph)]; δ_{C} (50.3 MHz, CDCl_3) 150.3 (d, $J=7.2$ Hz, *ipso*-PhO), 145.4 (d, $J=9.5$ Hz, POC=CH), 132.7 (*ipso*-Ph), 129.6, 129.5, 129.3, 128.3, 128.1 (Ph, PhO), 125.3 (d, $J=6.3$ Hz, POPh), 119.8 (d, $J=4.7$ Hz, POC=CH), 19.4 (CH₂), 14.2 (CH₃); δ_{P} (81.0 MHz, CDCl_3) -17.0 ; MS (CI-isobutane): m/z (%) 381 (56) $[\text{M}+\text{H}]^+$, 251 (100); calcd for $\text{C}_{22}\text{H}_{21}\text{O}_4\text{P}$ $[\text{M}]^+$: 380.1177; found $[\text{M}]^+$: 380.1179.

4.1.5. Phosphoric acid 2,2-dimethyl-propyl ester 1-phenyl-but-1-enyl ester 2e. Prepared as the mixture *E/Z* (1:1.5), a dark yellow oil (30%); R_f 0.6 (1:1 petroleum ether–EtOAc); $\nu_{\text{max}}/\text{cm}^{-1}$ 2980, 2870, 1671, 1668, 1495, 1440, 1394, 1360, 1275, 1268, 1200, 1165, 1020, 890, 880; δ_{H} (200 MHz, CDCl_3) 7.54–7.46 (2H, m, Ph), 7.45–7.40 (2H, m, Ph), 7.39–7.28 (6H, m, Ph), 5.68 (1H, dt, $J=7.8$, 2.6 Hz, C=CH, '*E*'), 5.57 (1H, dt, $J=7.2$, 2.1 Hz, C=CH, '*Z*'), 3.86–3.59 (8H, m, OCH_2C), 2.40 (2H, dq, $J=7.5$, 2.5 Hz, C=CCH₂, '*Z*'), 2.17 (2H, dq, $J=7.6$, 2.3 Hz, C=CCH₂, '*E*'), 1.08 (3H, t, $J=7.5$ Hz, C=CCH₂CH₃), 1.03 (3H, t, $J=7.5$ Hz, C=CCH₂CH₃), 0.89 (9H, m, CCH₃), 0.86 (9H, m, CCH₃); δ_{C} (50.3 MHz, CDCl_3) 146.9 (d, $J=9.1$ Hz, POC=CH, '*E*'), 145.5 (d, $J=8.9$ Hz, POC=CH, '*Z*'), 134.7 (*ipso*-Ph), 128.1, 127.8, 127.5, 125.5 (Ph), 118.2 (d, $J=6.2$ Hz, POC=CH, '*E*'), 116.9

(d, $J=7.0$ Hz, POC=CH, 'Z'), 78.0, 77.8 (d, $J=7.1$ Hz, POCH₂), 32.1 (d, $J=8.8$ Hz, C(CH₃)₃), 26.8 (C(CH₃)₃), 20.5 (CH₂, 'Z'), 19.8 (CH₂, 'E'), 15.1 (CH₃); δ_P (81.0 MHz, CDCl₃) -5.55 (Z), -5.46 (E); MS (EI, 15 eV): m/z (%) 368 (35) [M]⁺, 239 (100), 117 (25); calcd for C₂₀H₃₃O₄P [M]⁺: 368.2116; found [M]⁺: 368.2109.

4.1.6. Phosphoric acid diethyl ester 1-phenyl-pent-1-enyl ester 2f. Single isomer, yellowish oil (76%); R_f 0.20 (2:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2981, 2934, 2900, 1670, 1471, 1369, 1280, 1028, 1013, 980, 801; δ_H (200 MHz, CDCl₃) 7.53–7.42 (2H, m, Ph), 7.36–7.26 (3H, m, Ph), 5.58 (1H, dt, $J=7.3$, 2.0 Hz, C=CH), 4.07, 4.06 (4H, 2q, $J=7.2$ Hz, OCH₂CH₃), 2.34 (2H, dq, $J=7.4$, 2.5 Hz, C=CCH₂), 1.49 (2H, q, $J=7.5$ Hz, C=CCH₂CH₂), 1.23 (6H, t, $J=7.1$ Hz, OCH₂CH₃), 0.97 (3H, t, $J=7.3$ Hz, C=CCH₂CH₂CH₃); δ_C (50.3 MHz, CDCl₃) 145.7 (d, $J=9$ Hz, POC=CH), 135.5 (*ipso*-Ph), 127.9, 127.5, 125.2 (Ph), 117.4 (d, $J=6.1$ Hz, POC=CH), 63.6 (d, $J=6.0$ Hz, POCH₂CH₃), 28.7, 22.3 (CH₂), 15.7 (d, $J=6.5$ Hz, POCH₂CH₃), 13.7 (CH₃); δ_P (81.0 MHz, CDCl₃) -5.3 ; MS (CI-isobutane): m/z (%) 299 (100) [M+H]⁺, 155 (12); calcd for C₁₅H₂₃O₄P [M]⁺: 298.1334; found [M]⁺: 298.1331.

4.1.7. Phosphoric acid diisopropyl ester 1-phenyl-pent-1-enyl ester 2g. Single isomer, yellowish oil (90%); R_f 0.44 (2:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2980, 2934, 2873, 1649, 1450, 1386, 1267, 1179, 1010; δ_H (200 MHz, CDCl₃) 7.53–7.49 (2H, m, Ph), 7.37–7.26 (3H, m, Ph), 5.57 (1H, dt, $J=7.4$, 2.0 Hz, C=CH), 4.65 (2H, octet, $J=6.3$ Hz, OCHCH₃), 2.37 (2H, dq, $J=7.3$, 2.5 Hz, C=CCH₂), 1.51 (2H, sext, $J=7.4$ Hz, C=CCH₂CH₂CH₃), 1.31 (6H, t, $J=6.1$ Hz, OCHCH₃), 1.19 (6H, t, $J=6.1$ Hz, OCHCH₃), 0.99 (3H, t, $J=7.3$ Hz, C=CCH₂CH₂CH₃); δ_C (50.3 MHz, CDCl₃) 145.9 (d, $J=9.2$ Hz, POC=CH), 135.8 (*ipso*-Ph), 127.9, 127.8, 125.4 (Ph), 117.5 (d, $J=6.0$ Hz, POC=CH), 72.8, 72.7 (d, $J=6.0$ Hz, CH(CH₃)₂), 28.1 (CH₂), 23.6, 23.5, 23.3, 23.2 (CH(CH₃)₂), 22.2 (CH₂), 13.7 (CH₃); δ_P (81.0 MHz, CDCl₃) -7.3 ; MS (CI-isobutane): m/z (%) 327 (100) [M+H]⁺, 183 (20). Anal. calcd for C₁₇H₂₇O₄P (326.37): C, 62.56; H, 8.34; P, 9.49. Found: C, 61.90; H, 8.48; P, 10.05%.

4.1.8. Phosphoric acid bis-(4-methoxy-phenyl) ester 1-phenyl-pent-1-enyl ester 2h. Single isomer, yellowish oil (78%); R_f 0.70 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3060, 3028, 2983, 2909, 1660, 1495, 1275, 1130, 1052, 1031, 979; δ_H (200 MHz, CDCl₃) 7.50–7.46 (2H, m, Ph), 7.29–7.26 (3H, m, Ph), 7.02 (4H, d, $J=9.0$ Hz, 4-MeO–C₆H₄O), 6.78 (4H, d, $J=9.1$ Hz, 4-MeO–C₆H₄O), 5.63 (1H, dt, $J=7.4$, 1.8 Hz, C=CH), 3.76 (6H, s, OCH₃), 2.23 (2H, dq, $J=7.4$, 2.6 Hz, C=CCH₂), 1.44 (2H, sext, $J=7.3$ Hz, CH₂CH₂CH₃), 0.89 (3H, t, $J=7.3$ Hz, C=CCH₂CH₂CH₃); δ_C (50.3 MHz, CDCl₃) 156.9 (*ipso*-Ph), 152.5 (d, $J=9.0$ Hz, *ipso*-4-MeO–C₆H₄O), 144.4 (d, $J=9.0$ Hz, POC=CH), 128.2, 125.6 (Ph, 4-MeO–C₆H₄O), 121.0 (d, $J=4.7$ Hz, POC₆H₄–MeO), 118.3 (d, $J=6.2$ Hz, POC=CH), 114.6 (4-MeO–C₆H₄O), 55.6 (CH₃O), 28.1, 22.3 (CH₂), 13.8 (CH₃); δ_P (81.0 MHz, CDCl₃) -15.99 ; MS (CI-isobutane): m/z (%) 455 (100) [M+H]⁺; calcd for C₂₅H₂₇O₆P [M]⁺: 454.1545; found [M]⁺: 454.1542.

4.1.9. Phosphoric acid 1,2-diphenyl-vinyl ester diethyl ester 2i.^{17a,24} The mixture *E/Z* isomers (1/10), yellowish oil (75%); R_f 0.33 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2988, 2845, 1667, 1495, 1410, 1370, 1270, 1020, 980; δ_H (200 MHz, CDCl₃) 7.69–7.62 (4H, m, Ph), 7.45–7.09 (6H, m, Ph), 6.72 (1H, d, $J=2.7$ Hz, C=CH, 'E'), 6.41 (1H, d, $J=1.2$ Hz, C=CH, 'Z'), 4.22–4.06 (4H, m, OCH₂CH₃, 'E'), 4.05–3.78 (4H, m, OCH₂CH₃, 'Z'), 1.30 (6H, dt, $J=7.0$, 1.1 Hz, OCH₂CH₃, 'E'), 1.11 (6H, dt, $J=7.1$, 1.2 Hz, OCH₂CH₃, 'Z'); δ_C (50.3 MHz, CDCl₃) 145.2 (d, $J=9.0$ Hz, POC=CH), 136.3 (*ipso*-Ph), 134.5 (d, $J=6$ Hz, *ipso*-Ph), 129.0, 128.3, 127.5, 127.0, 126.3 (Ph), 117.2 (d, $J=8.4$ Hz, POC=CH, 'E'), 116.0 (d, $J=7.0$ Hz, POC=CH, 'Z'), 64.3 (d, $J=6.1$ Hz, POCH₂CH₃), 15.9 (d, $J=7.6$ Hz, POCH₂CH₃); δ_P (81.0 MHz, CDCl₃) -6.08 (Z), -5.5 (E); MS (CI-isobutane): m/z (%) 333 (100) [M+H]⁺, 105 (18).

4.1.10. Phosphoric acid diethyl ester 1-(4-methoxy-phenyl)-propenyl ester 2j.²⁵ Single isomer, yellow oil (85%); R_f 0.25 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2980, 2961, 1667, 1505, 1260, 1022, 1007, 814; δ_H (200 MHz, CDCl₃) 7.44–7.41 (2H, 5 lines, Ar), 6.86–6.81 (2H, 6 lines, Ar), 5.52 (1H, dq, $J=7.0$, 2.0 Hz, C=CH), 4.06 (4H, dsxt, $J=7.1$, 1.8 Hz, OCH₂CH₃), 3.80 (3H, s, OCH₃), 1.86 (3H, dd, $J=7.0$, 3.0 Hz, C=CCH₃), 1.25 (6H, t, $J=7.0$ Hz, OCH₂CH₃); δ_C (50.3 MHz, CDCl₃) 144.3 (d, $J=9.0$ Hz, POC=CH), 140.5 (*ipso*-Ar), 127.8, 125.2 (Ar), 112.9 (d, $J=6.0$ Hz, POC=CH), 114.7 (Ar), 64.4 (d, $J=5.5$ Hz, POCH₂CH₃), 52.8 (CH₃O), 14.9 (d, $J=6.6$ Hz, POCH₂CH₃), 11.8 (CH₃); δ_P (81.0 MHz, CDCl₃) -4.37 ; MS (EI, 15 eV): m/z (%) 300 (50) [M]⁺, 155 (22), 146 (100).

4.1.11. Phosphoric acid 3,4-dihydro-naphthalen-1-yl ester diethyl ester 5a.²⁶ Yellow oil (85%); R_f 0.37 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2949, 2888, 2835, 1650, 1470, 1270, 1162, 1038, 952, 737; δ_H (200 MHz, CDCl₃) 7.42–7.38 (1H, m, Ph), 7.23–7.07 (3H, m, Ph), 5.87 (1H, dt, $J=4.6$, 1.7 Hz, C=CH), 4.19 (4H, 2q, $J=7.4$ Hz, OCH₂CH₃), 2.78 (2H, t, $J=7.4$ Hz, CH₂), 2.33–2.42 (2H, m, CH₂), 1.33 (6H, t, $J=7.1$ Hz, OCH₂CH₃); δ_C (50.3 MHz, CDCl₃) 144.8 (d, $J=7.7$ Hz, POC=CH), 136.2 (C^{4a}-Ar), 130.1 (d, $J=6.5$ Hz, C^{8a}-Ar), 127.8, 127.0, 126.1, 121.0 (Ar), 110.3 (d, $J=3.7$ Hz, POC=CH), 64.1 (d, $J=5.9$ Hz, POCH₂CH₃), 27.0, 21.6 (CH₂), 15.8 (d, $J=6.5$ Hz, POCH₂CH₃); δ_P (81.0 MHz, CDCl₃) -5.7 ; MS (CI-isobutane): m/z (%) 283 (10) [M+H]⁺, 157 (100); calcd for C₁₄H₁₉O₄P [M]⁺: 282.1020; found [M]⁺: 282.1016.

4.1.12. Phosphoric acid 3,4-dihydro-naphthalen-1-yl ester diphenyl ester 5b. Yellowish oil (86%); R_f 0.70 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3068, 2939, 1649, 1590, 1488, 1299, 1187, 1083, 956, 765; δ_H (200 MHz, CDCl₃) 7.41–7.12 (14H, m, PhO, Ar), 6.01 (1H, dt, $J=4.6$, 2.0 Hz, C=CH), 2.83 (2H, t, $J=8.0$ Hz, CH₂), 2.37–2.49 (2H, m, CH₂); δ_C (50.3 MHz, CDCl₃) 150.4 (d, $J=7.5$ Hz, *ipso*-PhO), 145.1 (d, $J=8.2$ Hz, POC=CH), 136.3 (C^{4a}-Ar), 129.8 (C^{8a}-Ar), 129.6, 128.1, 127.6, 126.3, 125.3, 121.3 (PhO, Ar), 120.0 (d, $J=4.9$ Hz, POPh), 111.4 (d, $J=4.0$ Hz, POC=CH), 27.0, 21.8 (CH₂); δ_P (81.0 MHz, CDCl₃) -17.0 ; MS (CI-isobutane): m/z (%) 379 (40) [M+H]⁺, 251 (100). Anal. calcd for C₂₂H₁₉O₄P (378.36): C, 69.84; H, 5.06; P, 8.18. Found: C, 69.40; H, 5.01; P, 8.04%.

4.1.13. Phosphoric acid 8,9-dihydro-7H-benzocyclohepten-5-yl ester diethyl ester 5c. Yellowish oil (79%); R_f 0.32 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3060, 2983, 2932, 2861, 1648, 1449, 1272, 1119, 1030, 972, 903, 771; δ_{H} (200 MHz, CDCl_3) 7.57–7.52 (1H, m, Ph), 7.29–7.14 (3H, m, Ph), 6.08 (1H, dt, $J=6.4$, 2.5 Hz, C=CH), 4.19 (4H, dq, $J=7.5$, 3.0 Hz, OCH_2CH_3), 2.72 (2H, t, $J=6.2$ Hz, CH_2), 2.08–2.02 (4H, m, CH_2), 1.29 (6H, t, $J=7.1$ Hz, OCH_2CH_3); δ_{C} (50.3 MHz, CDCl_3) 146.4 (d, $J=8.8$ Hz, POC=CH), 142.3 ($\text{C}^{9\text{a}}$ -Ar), 135.4 (d, $J=4.7$ Hz, $\text{C}^{4\text{a}}$ -Ar), 129.8, 129.2, 127.6, 126.9 (Ar), 117.1 (d, $J=4.7$ Hz, POC=CH), 65.1 (d, $J=6.0$ Hz, POCH_2CH_3), 34.3, 32.6, 25.5 (CH_2), 16.9 (d, $J=6.8$ Hz, POCH_2CH_3); δ_{P} (81.0 MHz, CDCl_3) –5.4; MS (CI-isobutane): m/z (%) 297 (100) $[\text{M}+\text{H}]^+$, 155 (8). Anal. calcd for $\text{C}_{15}\text{H}_{21}\text{O}_4\text{P}$ (296.30): C, 60.80; H, 7.14; P, 10.45. Found: C, 60.55; H, 7.33; P, 10.34%.

4.1.14. Phosphoric acid 1,2-dihydro-phenanthren-4-yl ester diethyl ester 5d. Yellowish oil (85%); R_f 0.20 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2957, 2924, 2869, 1688, 1460, 1279, 1260, 1090, 799; δ_{H} (200 MHz, CDCl_3) 8.63 (1H, dt, $J=8.5$, 1.2 Hz, Ar), 7.79–7.67 (2H, m, Ar), 7.49–7.27 (3H, m, Ar), 6.14 (1H, dt, $J=5.6$, 2.4 Hz, C=CH), 4.10 (4H, dq, $J=7.1$, 1.7 Hz, OCH_2CH_3), 2.92–2.84 (2H, m, CH_2), 2.38–2.26 (2H, m, CH_2), 1.23 (6H, dt, $J=7.1$, 1.1 Hz, OCH_2CH_3); δ_{C} (50.3 MHz, CDCl_3) 147.4 (d, $J=8.0$ Hz, POC=CH), 137.3 (C^{IV} -Ar), 133.4 (C^{IV} -Ar), 129.8 (C^{IV} -Ar), 128.8, 128.5, 126.0, 124.8 (Ar), 119.2 (C^{IV} -Ar), 113.4 (d, $J=4.7$ Hz, POC=CH), 64.4 (d, $J=5.9$ Hz, POCH_2CH_3), 29.8, 22.6 (CH_2), 16.1 (d, $J=6.5$ Hz, POCH_2CH_3); δ_{P} (81.0 MHz, CDCl_3) –5.96; MS (CI-isobutane): m/z (%) 333 (100) $[\text{M}+\text{H}]^+$, 155 (8). Anal. calcd for $\text{C}_{18}\text{H}_{21}\text{O}_4\text{P}$ (332.33): C, 65.05; H, 6.37; P, 9.32. Found: C, 65.56; H, 6.12; P, 9.02%.

4.1.15. Phosphoric acid diethyl ester 2-methyl-3H-inden-1-yl ester 5e. Yellow oil (87%); R_f 0.5 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3047, 2983, 2911, 1647, 1463, 1395, 1300, 1136, 1051, 983, 911, 763; δ_{H} (200 MHz, CDCl_3) 7.43–7.13 (4H, m, Ar), 4.26 (4H, dq, $J=7.2$, 1.4 Hz, OCH_2CH_3), 3.29 (2H, d, $J=4.4$ Hz, CH_2), 2.14 (3H, d, $J=2.9$ Hz, CH_3), 1.37 (6H, t, $J=7.1$ Hz, OCH_2CH_3); δ_{C} (50.3 MHz, CDCl_3) 143.2 (d, $J=7.7$ Hz, POC=CCH₃), 139.8 (d, $J=3.6$ Hz, $\text{C}^{7\text{a}}$ -Ar), 139.7 ($\text{C}^{3\text{a}}$ -Ar), 126.5 (d, $J=6.3$ Hz, POC=CCH₃), 126.1, 124.5, 123.7, 117.6 (Ar), 64.4 (d, $J=6.0$ Hz, POCH_2CH_3), 38.7 (CH_2), 15.9 (d, $J=6.7$ Hz, POCH_2CH_3), 12.1 (CH_3); δ_{P} (81.0 MHz, CDCl_3) –5.19; MS (CI-isobutane): m/z (%) 283 (100) $[\text{M}+\text{H}]^+$, 256 (16). Anal. calcd for $\text{C}_{14}\text{H}_{19}\text{O}_4\text{P}$ (282.27): C, 59.57; H, 6.78; P, 10.97. Found: C, 59.51; H, 7.02; P, 10.78%.

4.1.16. Phosphoric acid diphenyl ester 2-methyl-3H-inden-1-yl ester 5f. White solid, mp 67 °C (68%); R_f 0.66 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3050, 2932, 1657, 1441, 1353, 1274, 1167, 1031, 967, 898, 721; δ_{H} (200 MHz, CDCl_3) 7.42–7.13 (14H, m, Ar, PhO), 3.31 (2H, d, $J=4.5$ Hz, CH_2), 2.07 (3H, d, $J=3.0$ Hz, CH_3); δ_{C} (50.3 MHz, CDCl_3) 150.5 (d, $J=7.5$ Hz, POPh), 143.2 (d, $J=9.9$ Hz, POC=CCH₃), 139.7 ($\text{C}^{3\text{a}}$ -Ar), 139.2 (d, $J=2.1$ Hz, $\text{C}^{7\text{a}}$ -Ar), 129.6 (PhO), 127.2 (d, $J=6.7$ Hz, POC=CCH₃), 126.3 (Ar), 125.4 (PhO), 124.8, 123.4 (Ar),

120.0 (d, $J=4.8$ Hz, POPh), 117.6 (Ar), 38.8 (CH_2), 12.0 (CH_3); δ_{P} (81.0 MHz, CDCl_3) –16.8; MS (CI-isobutane): m/z (%) 379 (100) $[\text{M}+\text{H}]^+$, 95 (8). Anal. calcd for $\text{C}_{22}\text{H}_{19}\text{O}_4\text{P}$ (378.36): C, 69.84; H, 5.06; P, 8.18. Found: C, 69.92; H, 5.12; P, 7.97%.

4.2. Syntheses of racemic α -hydroxy ketones 4 and 7

4.2.1. Epoxidation procedure.²⁷

4.2.1.1. Phosphoric acid diethyl ester 2-phenyl-3-methyl-oxiranyl ester 3a. To a solution of enol phosphate **2a** (810 mg, 3 mmol) in methylene chloride (30 mL) was added a solution of *m*-chloroperbenzoic acid (1 g, 6 mmol) in CH_2Cl_2 (30 mL) at –20 °C, with stirring. The reaction mixture was stirred at this temperature until enol phosphate disappeared (monitored by TLC). Then the reaction mixture was washed with sodium thiosulfate (10%, 2×10 mL), saturated NaHCO_3 (2×5 mL), and water (10 mL) and dried (MgSO_4). Evaporation of solvent afforded the crude epoxide **3a**. Colorless oil (755 mg, 88%); R_f 0.54 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2987, 2885, 2807, 1450, 1274, 1167, 1064, 1028, 699; δ_{H} (200 MHz, CDCl_3) 7.52–7.47 (2H, m, Ph), 7.40–7.33 (3H, m, Ph), 4.07, 4.06 (4H, 2q, $J=7.3$ Hz, OCH_2CH_3), 3.04 (1H, dq, $J=5.3$, 1.9 Hz, $\text{POCOC}(\text{H})\text{CH}_3$), 1.56 (3H, d, $J=5.3$ Hz, $\text{POCOC}(\text{H})\text{CH}_3$), 1.26 (3H, dt, $J=7.1$, 1.1 Hz, OCH_2CH_3), 1.16 (3H, dt, $J=7.1$, 1.1 Hz, OCH_2CH_3); δ_{C} (50.3 MHz, CDCl_3) 136.1 (*ipso*-Ph), 128.9, 127.9, 125.3 (Ph), 88.6 (d, $J=9.0$ Hz, $\text{POCOC}(\text{H})\text{CH}_3$), 68.8 (d, $J=6.7$ Hz, $\text{POCOC}(\text{H})\text{CH}_3$), 64.0 (d, $J=5.9$ Hz, POCH_2CH_3), 15.8 (t, $J=6.5$ Hz, POCH_2CH_3), 10.0 (CH_3); δ_{P} (81.0 MHz, CDCl_3) –3.97; MS (CI-isobutane): m/z (%) 287 (100) $[\text{M}+\text{H}]^+$, 211 (38), 151 (34), 135 (16); calcd for $\text{C}_{13}\text{H}_{19}\text{O}_5\text{P}$ $[\text{M}]^+$: 286.0970; found $[\text{M}]^+$: 286.0962.

4.2.1.2. Phosphoric acid diphenyl ester 2-phenyl-3-methyl-oxiranyl ester 3b. Yellow oil (74%); R_f 0.61 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3068, 2910, 1588, 1491, 1395, 1312, 1214, 1128, 1092, 959, 773; δ_{H} (200 MHz, CDCl_3) 7.53–7.05 (15H, m, Ph, OPh), 3.11 (1H, dq, $J=5.3$, 1.9 Hz, $\text{POCOC}(\text{H})\text{CH}_3$), 1.54 (3H, d, $J=5.3$ Hz, $\text{POCOC}(\text{H})\text{CH}_3$); δ_{C} (50.3 MHz, CDCl_3) 156.7 (d, $J=7.0$ Hz, *ipso*-PhO), 135.3 (*ipso*-Ph), 129.6, 128.3, 125.4 (Ph, PhO), 120.1 (d, $J=4.4$ Hz, POPh), 87.8 (d, $J=9.0$ Hz, $\text{POCOC}(\text{H})\text{CH}_3$), 72.2 (d, $J=6.7$ Hz, $\text{POCOC}(\text{H})\text{CH}_3$), 17.1 (CH_3); δ_{P} (81.0 MHz, CDCl_3) –15.3; MS (CI-isobutane): m/z (%) 383 (100) $[\text{M}+\text{H}]^+$, 289 (4); calcd for $\text{C}_{21}\text{H}_{19}\text{O}_5\text{P}$ $[\text{M}]^+$: 382.0970; found $[\text{M}]^+$: 382.0965.

4.2.1.3. Phosphoric acid diethyl ester 2-phenyl-3-ethyl-oxiranyl ester 3c. Colorless oil (85%); R_f 0.5 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2967, 1449, 1259, 1031, 816, 699; δ_{H} (200 MHz, CDCl_3) 7.50–7.45 (2H, m, Ph), 7.40–7.33 (3H, m, Ph), 4.07, 4.06 (4H, 2q, $J=7.3$ Hz, OCH_2CH_3), 2.85 (1H, dt, $J=6.2$, 1.9 Hz, $\text{POCOC}(\text{H})\text{CH}_2$), 1.87 (2H, quint, $J=7.2$ Hz, $\text{POCOC}(\text{H})\text{CH}_2$), 1.24 (3H, t, $J=7.1$ Hz, OCH_2CH_3), 1.14 (3H, t, $J=7.1$ Hz, OCH_2CH_3), 1.09 (3H, t, $J=7.3$ Hz, $\text{POCOC}(\text{H})\text{CH}_2\text{CH}_3$); δ_{C} (50.3 MHz, CDCl_3) 136.1 (*ipso*-Ph), 128.8, 128.1, 125.7 (Ph), 86.3 (d, $J=8.8$ Hz, $\text{POCOC}(\text{H})\text{CH}_2$), 67.3 (d, $J=6.9$ Hz, $\text{POCOC}(\text{H})\text{CH}_2$), 63.9 (d, $J=5.7$ Hz, POCH_2CH_3), 20.8 (CH_2), 15.7 (t, $J=6.6$ Hz, POCH_2CH_3), 9.8 (CH_3); δ_{P} (81.0 MHz, CDCl_3) –4.29; MS (CI-isobutane): m/z (%)

301 (100) [M+H]⁺, 155 (12), 149 (8); calcd for C₁₄H₂₁O₅P [M]⁺: 300.1126; found [M]⁺: 300.1119.

4.2.1.4. Phosphoric acid diphenyl ester 2-phenyl-3-ethyl-oxiranyl ester 3d. Yellow oil (80%); *R_f* 0.7 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3032, 2990, 1595, 1460, 1297, 1187, 946, 790; δ_{H} (200 MHz, CDCl₃) 7.51–7.04 (2H, m, Ph), 7.36–7.09 (13H, Ph, OPh), 2.93 (1H, dt, *J*=6.2, 2.1 Hz, POCOC(H)CH₂), 1.83 (2H, quint, *J*=7.5 Hz, POCOC(H)CH₂), 1.04 (3H, t, *J*=7.5 Hz, CH₃); δ_{C} (50.3 MHz, CDCl₃) 156.7 (d, *J*=7.0 Hz, *ipso*-PhO), 134.4 (*ipso*-Ph), 129.7, 129.1, 128.3, 127.9, 125.8 (Ph, PhO), 125.0 (d, *J*=4.8 Hz, POPh), 86.8 (d, *J*=8.5 Hz, POCOC(H)CH₂), 68.2 (d, *J*=6.7 Hz, POCOC(H)CH₂), 20.2 (CH₂), 13.5 (CH₃); δ_{P} (81.0 MHz, CDCl₃) –15.48; MS (CI-isobutane): *m/z* (%) 397 (100) [M+H]⁺, 155 (12), 149 (10), 95 (15); calcd for C₂₂H₂₁O₅P [M]⁺: 396.1126; found [M]⁺: 396.1119.

4.2.1.5. Phosphoric acid 2,2-dimethyl-propyl ester 2-phenyl-3-ethyl-oxiranyl ester 3e. Colorless oil (30%); *R_f* 0.55 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2952, 2901, 1460, 1310, 1225, 1165, 885; δ_{H} (200 MHz, CDCl₃) 7.58–7.41 (2H, m, Ph), 7.39–7.27 (3H, m, Ph), 3.68 (4H, d, *J*=4.6 Hz, OCH₂C(CH₃)₃), 2.87 (1H, dt, *J*=5.0, 2.0 Hz, POCOC(H)CH₂), 1.92 (2H, q, *J*=7.6 Hz, POCOC(H)CH₂), 1.11 (3H, t, *J*=7.5 Hz, CH₂CH₃), 0.93, 0.86 (18H, 2×s, C(CH₃)₃); δ_{C} (50.3 MHz, CDCl₃) 133.2 (*ipso*-Ph), 128.5, 128.1, 127.5, 126.1 (Ph), 83.1 (d, *J*=8.0 Hz, POCOC(H)CH₂), 78.4 (t, *J*=7.0 Hz, POCH₂), 67.1 (t, *J*=7.0 Hz, POCOC(H)CH₂), 32.3 (d, *J*=6.7 Hz, C(CH₃)₃), 25.9 (C(CH₃)₃), 21.2 (CH₂), 15.5 (CH₃); δ_{P} (81.0 MHz, CDCl₃) –4.06; MS (CI-isobutane): *m/z* (%) 385 (100) [M+H]⁺, 239 (40); calcd for C₂₀H₃₃O₅P [M]⁺: 384.2065; found [M]⁺: 384.2057.

4.2.1.6. Phosphoric acid diethyl ester 2-phenyl-3-propyl-oxiranyl ester 3f. Colorless oil (90%); *R_f* 0.3 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2970, 2860, 1498, 1244, 1052, 997, 756; δ_{H} (200 MHz, CDCl₃) 7.52–7.45 (2H, m, Ph), 7.42–7.28 (3H, m, Ph), 4.07, 4.06 (4H, 2q, *J*=7.3 Hz, OCH₂CH₃), 2.90 (1H, dt, *J*=6.0, 2.0 Hz, POCOC(H)CH₂), 1.91–1.80 (2H, m, POCOC(H)CH₂), 1.56 (2H, sext, *J*=7.3 Hz, CH₂CH₂), 1.26 (3H, dt, *J*=7.1, 1.1 Hz, OCH₂CH₃), 1.16 (3H, dt, *J*=7.0, 1.1 Hz, OCH₂CH₃), 1.01 (3H, t, *J*=7.3 Hz, CH₂CH₂CH₃); δ_{C} (50.3 MHz, CDCl₃) 136.1 (*ipso*-Ph), 128.9, 128.3, 125.8 (Ph), 85.2 (d, *J*=8.8 Hz, POCOC(H)CH₂), 66.4 (d, *J*=7.0 Hz, POCOC(H)CH₂), 63.9 (d, *J*=5.4 Hz, POCH₂CH₃), 29.3, 19.1 (CH₂), 15.9 (t, *J*=6.6 Hz, POCH₂CH₃), 13.8 (CH₃); δ_{P} (81.0 MHz, CDCl₃) –3.93; MS (CI-isobutane): *m/z* (%) 315 (100) [M+H]⁺, 155 (10); calcd for C₁₅H₂₃O₅P [M]⁺: 314.1283; found [M]⁺: 314.1281.

4.2.1.7. Phosphoric acid diisopropyl ester 2-phenyl-3-propyl-oxiranyl ester 3g. Colorless oil (83%); *R_f* 0.5 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2975, 2901, 2877, 1460, 1305, 1270, 1035, 983, 701; δ_{H} (200 MHz, CDCl₃) 7.52–7.48 (2H, m, Ph), 7.46–7.34 (3H, m, Ph), 4.60 (2H, septet, *J*=6.3 Hz, OCHCH₃), 2.88 (1H, dt, *J*=6.0, 1.8 Hz, POCOC(H)CH₂), 1.93–1.81 (2H, m, POCOC(H)CH₂), 1.57 (2H, sext, *J*=7.1 Hz, CH₂CH₂), 1.27 (3H, dd, *J*=6.1, 4.0 Hz, OCHCH₃), 1.12 (3H, d, *J*=6.0 Hz, OCHCH₃), 1.00 (3H, t, *J*=7.3 Hz, CH₃); δ_{C} (50.3 MHz, CDCl₃) 136.1

(*ipso*-Ph), 128.8, 128.3, 127.8, 125.4 (Ph), 87.3 (d, *J*=8.5 Hz, POCOC(H)CH₂), 72.8 (d, *J*=6.0 Hz, POCH(CH₃)₂), 64.4 (d, *J*=7.2 Hz, POCOC(H)CH₂), 29.3 (CH₂), 23.5, 23.4, 23.25, 23.2 (CH(CH₃)₂), 20.1 (CH₂), 13.8 (CH₃); δ_{P} (81.0 MHz, CDCl₃) –6.09; MS (CI-isobutane): *m/z* (%) 343 (100) [M+H]⁺, 183 (16); calcd for C₁₇H₂₇O₅P [M]⁺: 342.1596; found [M]⁺: 342.1593.

4.2.1.8. Phosphoric acid bis-(4-methoxy-phenyl) ester 2-phenyl-3-propyl-oxiranyl ester 3h. Yellow oil (55%); *R_f* 0.57 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2961, 1503, 1253, 1185, 1035, 967, 833; δ_{H} (200 MHz, CDCl₃) 7.51–7.43 (2H, m, Ph), 7.35–7.26 (3H, Ph), 7.09–6.95 (4H, m, 4-MeOC₆H₄O), 6.82–6.75 (4H, m, 4-MeOC₆H₄O), 3.77 (6H, s, OCH₃), 2.94 (1H, dt, *J*=6.0, 1.9 Hz, POCOC(H)CH₂), 1.77 (2H, q, *J*=7.0 Hz, POCOC(H)CH₂), 1.49 (2H, sext, *J*=7.4 Hz, CH₂CH₂CH₃), 0.96 (3H, t, *J*=7.4 Hz, CH₃); δ_{C} (50.3 MHz, CDCl₃) 156.8 (*ipso*-4-MeO-C₆H₄O), 135.7 (*ipso*-Ph), 129.1, 128.6, 128.3, 126.0 (Ph, 4-MeOC₆H₄O), 120.9 (d, *J*=4.8 Hz, POC₆H₄-OMe), 114.5 (4-MeOC₆H₄O), 87.5 (d, *J*=8.3 Hz, POCOC(H)CH₂), 66.3 (d, *J*=7.0 Hz, POCOC(H)CH₂), 55.5 (CH₃O), 29.3, 19.2 (CH₂), 13.7 (CH₃); δ_{P} (81.0 MHz, CDCl₃) –14.78; MS (CI-isobutane): *m/z* (%) 471 (100) [M+H]⁺, 311 (12); calcd for C₂₅H₂₇O₇P [M]⁺: 470.1494; found [M]⁺: 470.1487.

4.2.1.9. Phosphoric acid diethyl ester 2-phenyl-3-phenyl-oxiranyl ester 3i. Colorless oil (55%); *R_f* 0.55 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2983, 2870, 1456, 1394, 1271, 1165, 1035; δ_{H} (200 MHz, CDCl₃) 7.64–7.60 (2H, m, Ph), 7.58–7.52 (2H, m, Ph), 7.51–7.29 (6H, m, Ph), 3.97 (1H, s, POCOC(H)Ph), 3.88 (4H, dq, *J*=7.1, 2.9 Hz, OCH₂CH₃), 1.14, 1.13 (6H, dt, *J*=7.1, 0.6 Hz, OCH₂CH₃); δ_{C} (50.3 MHz, CDCl₃) 133.5 (*ipso*-Ph), 129.3, 129.1, 128.7, 128.6 (Ph), 81.1 (d, *J*=8.0 Hz, POCOC(H)Ph), 80.2 (d, *J*=7.6 Hz, POCOC(H)Ph), 64.2 (d, *J*=5.4 Hz, POCH₂CH₃), 15.9 (t, *J*=6.6 Hz, POCH₂CH₃); δ_{P} (81.0 MHz, CDCl₃) –4.04; MS (CI-isobutane): *m/z* (%) 349 (100) [M+H]⁺, 333 (10), 243 (16), 195 (40), 155 (74); calcd for C₁₈H₂₁O₅P [M]⁺: 348.1126; found [M]⁺: 348.1121.

4.2.1.10. Phosphoric acid 2,3-dihydro-1*aH*-1-oxa-cyclopropa[*a*]naphthalen-7*b*-yl ester diethyl ester 6a. Yellowish oil (88%); *R_f* 0.25 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 2970, 2870, 1450, 1410, 1285, 1150, 1070, 1053, 980; δ_{H} (200 MHz, CDCl₃) 7.30–7.27 (3H, m, Ar), 7.14–7.09 (1H, m, Ar), 4.40 (1H, d, *J*=3.0 Hz, POCOC(H)CH₂), 4.20 (4H, dq, *J*=7.1, 0.6 Hz, OCH₂CH₃), 2.80–2.52 (2H, m, CH₂), 2.43–2.30 (1H, m, CH₂), 1.87 (1H, ddd, *J*=14.8, 12.9, 6.1 Hz, CH₂), 1.36, 1.35, 1.34, 1.33 (6H, 4t, *J*=7.1 Hz, OCH₂CH₃); δ_{C} (50.3 MHz, CDCl₃) 131.7 (C^{IV}-Ar), 130.3 (C^{IV}-Ar), 129.8, 129.4, 127.8, 127.3 (Ar), 79.1 (d, *J*=6.0 Hz, POCOCH), 64.4 (d, *J*=6.0 Hz, POCH₂CH₃), 63.4 (d, *J*=5.0 Hz, POCOCH), 30.9, 27.4 (CH₂), 15.9 (d, *J*=6.6 Hz, POCH₂CH₃); δ_{P} (81.0 MHz, CDCl₃) –6.09; MS (CI-isobutane): *m/z* (%) 299 (100) [M+H]⁺, 283 (20), 155 (36); calcd for C₁₄H₁₉O₅P [M]⁺: 298.0970; found [M]⁺: 298.0964.

4.2.1.11. Phosphoric acid 2,3-dihydro-1*aH*-1-oxa-cyclopropa[*a*]naphthalen-7*b*-yl ester diphenyl ester 6b. Orange oil (52%); *R_f* 0.66 (1:1 petroleum ether–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 3030, 2896, 1591, 1456, 1217, 1128, 1042, 908,

735; δ_{H} (200 MHz, CDCl_3) 8.07–8.02 (1H, m, Ar), 7.55–7.47 (1H, m, Ar), 7.39–7.09 (12H, m, Ar, Ph), 4.39 (1H, d, $J=2.8$ Hz, $\text{POCOC}(H)\text{CH}_2$), 2.85–2.55 (2H, m, CH_2), 2.48–2.36 (1H, m, CH_2), 1.87 (1H, ddd $J=14.1$, 13.1, 6.1 Hz, CH_2); δ_{C} (50.3 MHz, CDCl_3) 150.4 (d, $J=7.0$ Hz, *ipso*-OPh), 136.5 (C^{IV} -Ar), 129.7 (C^{IV} -Ar), 129.6 (OPh), 128.2, 128.0, 127.3, 127.0 (Ar), 125.4 (OPh), 120.4 (OPh), 82.8 (d, $J=6.4$ Hz, POCOCH), 66.5 (d, $J=4.0$ Hz, POCOCH), 30.8, 27.3 (CH_2); δ_{P} (81.0 MHz, CDCl_3) –17.3; MS (EI): m/z (%) 394 (4) $[\text{M}]^+$, 300 (44), 250 (66), 144 (46), 94 (100); calcd for $\text{C}_{22}\text{H}_{19}\text{O}_5\text{P}$ $[\text{M}]^+$: 394.0970; found $[\text{M}]^+$: 394.0969.

4.2.1.12. Phosphoric acid diethyl ester 1a,2,3,4-tetrahydro-1-oxa-benzo[*a*]cyclopropa[*c*]cyclohepten-8b-yl ester 6c. Yellow oil (60%); R_f 0.45 (1:1 petroleum ether–EtOAc); $\nu_{\text{max}}/\text{cm}^{-1}$ 2995, 2880, 1440, 1310, 1270, 1160, 1038, 980; δ_{H} (200 MHz, CDCl_3) 7.77–7.71 (1H, m, Ph), 7.31–7.25 (3H, m, Ph), 3.91 (4H, m, OCH_2CH_3), 3.31 (1H, ddd, $J=13.9$, 12.1, 6.3 Hz, $\text{POCOC}(H)\text{CH}_2$), 2.73–2.67 (2H, m, CH_2), 2.08–1.90 (4H, m, CH_2), 1.29, 1.28 (6H, 2t, $J=7.1$ Hz, OCH_2CH_3); δ_{C} (50.3 MHz, CDCl_3) 137.8 (C^{4a} -Ar), 132.6 (C^{8a} -Ar), 129.6, 129.3, 128.7, 126.7 (Ar), 84.2 (d, $J=6.1$ Hz, POCOCH), 64.1 (d, $J=5.4$ Hz, POCH_2CH_3), 60.6 (d, $J=4.6$ Hz, POCOCH), 30.7, 27.0, 22.6 (CH_2), 15.7 (d, $J=4.8$ Hz, POCH_2CH_3); δ_{P} (81.0 MHz, CDCl_3) –6.23; MS (CI-isobutane): m/z (%) 313 (100) $[\text{M}+\text{H}]^+$, 297 (18), 155 (16); calcd for $\text{C}_{15}\text{H}_{21}\text{O}_5\text{P}$ $[\text{M}]^+$: 312.1126; found $[\text{M}]^+$: 312.1128.

4.2.2. Hydrolysis of epoxides 3 and 6.

4.2.2.1. 2-Hydroxy-1-phenyl-1-propan-1-one 4a.^{5a} To a solution of **3a** (755 mg, 2.64 mmol) in diethyl ether (10 mL), trifluoroacetic acid (2 mL) in water (10 mL) was added with stirring at 5 °C. The reaction was stirred and monitored by TLC. After 24–48 h the reaction mixture was diluted with chloroform, washed with saturated NaHCO_3 and water and dried (MgSO_4). After removal of the solvent the crude product was purified by column chromatography with petroleum ether/EtOAc as an eluent (5:1 v/v) to give 309 mg (78% yield) of product as colorless liquid; R_f 0.52 (2:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CDCl_3) 7.95–7.91 (2H, m, Ph), 7.63–7.46 (3H, m, Ph), 5.16 (1H, q, $J=7.0$ Hz, CH (OH)), 3.04 (1H, br s, OH), 1.45 (3H, d, $J=7.0$ Hz, CH_3); MS (CI-isobutane): m/z (%) 151 (100) $[\text{M}+\text{H}]^+$, 133 (16), 123 (32).

4.2.2.2. 2-Hydroxy-1-phenyl-1-butan-1-one 4c.^{5a} Colorless liquid; yield 76%; R_f 0.69 (2:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CDCl_3) 7.93–7.88 (2H, m, Ph), 7.66–7.57 (1H, m, Ph), 7.53–7.45 (2H, m, Ph), 5.16 (1H, dd, $J=6.8$, 3.8 Hz, CH (OH)), 3.70 (1H, br s, OH), 1.85 (1H, qdd, $J=7.4$, 7.0, 3.8 Hz, CH_2), 1.61 (1H, septet, $J=7.0$ Hz, CH_2), 0.93 (3H, t, $J=7.4$ Hz, CH_3); MS (CI-isobutane): m/z (%) 165 (100) $[\text{M}+\text{H}]^+$, 147 (10), 136 (18).

4.2.2.3. 2-Hydroxy-1-phenyl-1-pentan-1-one 4f.²⁸ Colorless liquid; yield 55%; R_f 0.75 (1:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CDCl_3) 7.91–7.88 (2H, 2 lines, Ph), 7.60–7.44 (3H, m, Ph), 5.07 (1H, dd, $J=6.7$, 3.2 Hz, CH (OH)), 3.66 (1H, br s, OH), 1.81 (1H, dq, $J=3.2$,

5.9 Hz, CH_2), 1.60–1.34 (3H, m, $\text{HCH}-\text{CH}_2$), 0.89 (3H, t, $J=7.0$ Hz, CH_3); δ_{C} (50.3 MHz, CDCl_3) 202.1 ($\text{C}=\text{O}$), 133.6 (*ipso*-Ph), 133.8, 128.7, 128.4 (Ph), 72.8 ($\text{CH}(\text{OH})$), 37.8, 18.1 (CH_2), 13.7 (CH_3); MS (CI-isobutane): m/z (%) 179 (100) $[\text{M}+\text{H}]^+$, 163 (16), 105 (10).

4.2.2.4. 2-Hydroxy-1,2-diphenyl-ethanone 4i.²⁹ White solid, mp 135 °C; yield 73%; R_f 0.62 (1:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CD_3OD) 7.98–7.93 (2H, m, Ph), 7.56–7.26 (8H, m, Ph), 6.11 (1H, s, CH (OH)), 4.87 (1H, br s, OH); MS (CI-isobutane): m/z (%) 213 (100) $[\text{M}+\text{H}]^+$, 195 (74).

4.2.2.5. 2-Hydroxy-1-(4-methoxyphenyl)-propan-1-one 4j.³⁰ Colorless liquid; yield 48%; R_f 0.5 (1:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CDCl_3) 7.91 (2H, d, $J=8.9$ Hz, Ph), 6.96 (2H, d, $J=8.9$ Hz, Ph), 5.10 (1H, q, $J=7.0$ Hz, CH (OH)), 3.88 (3H, s, OCH_3), 3.25 (1H, br s, OH), 1.43 (3H, d, $J=7.0$ Hz, CH_3); MS (CI-isobutane): m/z (%) 181 (100) $[\text{M}+\text{H}]^+$, 163 (16), 135 (20).

4.2.2.6. 2-Hydroxy-3,4-dihydro-2H-naphthalen-1-one 7a.²⁹ Colorless liquid; yield 68%; R_f 0.49 (1.5:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CDCl_3) 8.10–7.97 (1H, m, Ph), 7.62–7.31 (3H, m, Ph), 4.40 (1H, dd, $J=13.4$, 5.4 Hz, CH (OH)), 3.99 (1H, br s, OH), 3.26–2.97 (2H, m, CH_2), 2.60–2.48 (1H, m, CH_2), 2.04 (1H, ddd, $J=17.4$, 12.5, 5.3 Hz, CH_2); MS (CI-isobutane): m/z (%) 163 (100) $[\text{M}+\text{H}]^+$, 157 (36), 145 (32).

4.2.2.7. 6,7,8,9-Tetrahydro-6-hydroxy-5H-benzocyclohepten-5-one 7c.³¹ Colorless liquid; yield 60%; R_f 0.55 (1:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CDCl_3) 7.95–7.90 (1H, m, Ph), 7.50–7.22 (3H, m, Ph), 4.50 (1H, dd, $J=10.0$, 5.4 Hz, $\text{CH}(\text{OH})$), 4.00 (1H, br s, OH), 3.03–2.90 (2H, m, CH_2), 2.53–2.33 (1H, m, CH_2), 2.30–2.09 (1H, m, CH_2), 1.90–1.59 (2H, m, CH_2); MS (CI-isobutane): m/z (%) 177 (100) $[\text{M}+\text{H}]^+$, 157 (36), 145 (32).

4.2.2.8. 2,3-Dihydro-3-hydroxy-1H-phenanthren-4-one 7d. Dark yellow oil; yield 66%; R_f 0.58 (1:1 petroleum ether–EtOAc); $\nu_{\text{max}}/\text{cm}^{-1}$ 3454, 2962, 1664, 1260, 1089, 1021, 800; δ_{H} (200 MHz, CDCl_3) 9.35 (1H, d, $J=8.6$ Hz, Ar), 7.97 (1H, d, $J=8.4$ Hz, Ar), 7.83 (1H, d, $J=8.1$ Hz, Ar), 7.66 (1H, dd, $J=7.4$, 8.1 Hz, Ar), 7.53 (1H, t, $J=7.4$ Hz, Ar), 7.31 (1H, d, $J=8.4$ Hz, Ar), 4.48 (1H, dd, $J=5.0$, 13.6 Hz, $\text{CH}-\text{OH}$), 4.31 (1H, br s, OH), 3.99 (1H, ddd, $J=4.3$, 13.0, 17.3 Hz, CH_2), 3.20 (1H, dd, $J=4.0$, 17.5 Hz, CH_2), 2.61 (1H, dd, $J=5.8$, 6.1 Hz, CH_2), 2.16 (1H, ddd, $J=4.8$, 12.8, 17.5 Hz, CH_2); δ_{C} (50.3 MHz, CDCl_3) 201.6 ($\text{C}=\text{O}$), 146.5 (C^{IV} -Ar), 135.0 (Ar), 132.5 (C^{IV} -Ar), 131.2 (C^{IV} -Ar), 129.1 (Ar), 128.4 (Ar), 126.7 (Ar), 126.2 (Ar), 125.8 (Ar), 124.8 (C^{IV} -Ar), 73.8 (CHOH), 32.2 (CH_2), 29.1 (CH_2); MS (CI-isobutane): m/z (%) 213 (100) $[\text{M}+\text{H}]^+$; calcd for $\text{C}_{14}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 213.0916; found $[\text{M}+\text{H}]^+$: 213.0910.

4.2.2.9. 2-Hydroxy-2-methyl 1-indanone 7e.³² White solid, mp 49 °C; yield 65%; R_f 0.54 (1:1 petroleum ether–EtOAc); δ_{H} (200 MHz, CDCl_3) 7.77 (1H, d, $J=7.6$ Hz, Ph), 7.67 (1H, m, Ph), 7.49–7.36 (2H, m, Ph), 3.27 (2H, s, CH_2), 2.48 (1H, br s, OH), 1.44 (3H, s, CH_3); MS (CI-isobutane): m/z (%) 163 (100) $[\text{M}+\text{H}]^+$, 145 (16).

4.3. General procedure for asymmetric oxidation

To a stirred solution of NaOCl (4 mL, 7 equiv) and phosphate buffer (4 mL, pH=11) the mixture of appropriate enol phosphate (1.1 mmol, 1 equiv), 4-phenylpyridine *N*-oxide (PPNO) (30 mol %), and (salen) Mn(III) complex **1** (7 mol %) in 4 mL CH₂Cl₂ was added at –10 °C. The stirring of the reaction mixture was continued at 0 °C for 18 h (the reaction was monitored by TLC), *n*-hexane (40 mL) was added, organic layer was separated, washed with distilled water and dried (MgSO₄). Evaporation of solvent afforded crude epoxide, which was diluted with Et₂O and treated with CF₃COOH in H₂O (10 mL) at 0 °C. Stirring was continued until TLC analysis revealed the complete consumption of epoxide. Then the mixture was washed with NaHCO₃, CHCl₃ was added, the organic layer was separated, washed with water and dried. After removal of the solvent the residue was subjected to silica gel column chromatography with hexane–ethyl acetate (3:1 v/v) as the eluent, to afford pure, optically active α -hydroxy ketones **4** and **7**. Spectral data of **4** and **7** as described.

4.3.1. Determination of the enantiomeric purity of compounds 4 and 7. The enantiomeric ratios were determined by HPLC analysis on Chiralcel OD column. All runs were carried out at room temperature.

4.3.1.1. HPLC conditions for compounds 4 (Table 2 in text). *S*-(–)-**4a** Entry 1: 5% *i*-PrOH in hexane, 0.4 mL/min; *t*_R [min] 17.3 (*S*), *t*_R [min] 19.8 (*R*), absolute configuration of product determined by comparison of sign of optical rotation to the literature value (*S*)-**4a**: [α]_D²⁰ –82.7 (*c* 3.6, CHCl₃); lit. [α]_D²⁰ –80.9 (*c* 2.0, CHCl₃), ee=95%;^{33a} [α]_D²⁰ –58.3 (*c* 2.0, CHCl₃), ee=62%.^{33b}

R-(+)-**4a**, Entry 2: 5% *i*-PrOH in hexane, 0.4 mL/min; *t*_R [min] 17.7 (*S*), *t*_R [min] 20.1 (*R*), [α]_D²⁰ +65.4 (*c* 0.75, CHCl₃); lit. (*R*)-**4a**: [α]_D²⁰ +81.0 (*c* 1.5, CHCl₃);³⁰ [α]_D²⁰ +82.2 (*c* 2.0, CHCl₃), ee=96%.³⁴

S-(–)-**4c** Entry 3: 4% *i*-PrOH in hexane, 0.4 mL/min; *t*_R [min] 14.7 (*S*), *t*_R [min] 17.8 (*R*), [α]_D²⁰ –29.3 (*c* 1.1, CHCl₃); lit. (*S*)-**4c**: [α]_D²⁰ –30.78 (*c* 2.24, CHCl₃), ee=95% was determined by Eu(hfc)₃ NMR shift reagent of acetate derivative.^{33a}

R-(+)-**4c** Entry 4: 4% *i*-PrOH in hexane, 0.4 mL/min; *t*_R [min] 14.5 (*S*), *t*_R [min] 19.0 (*R*), [α]_D²⁰ +40.54 (*c* 0.3, CHCl₃).

S-(–)-**4c** Entry 5: [α]_D²⁰ –3.8 (*c* 0.5, CHCl₃).

S-(–)-**4f** Entry 6: 3% *i*-PrOH in hexane, 0.3 mL/min; *t*_R [min] 16.1 (*S*), *t*_R [min] 22.5 (*R*), [α]_D²⁰ –14.0 (*c* 0.3, CHCl₃); lit.³⁵ (*S*)-acetate derivative of **4f**: [α]_D²⁰ +1.9 (*c* 0.8, acetone), (*R*)-acetate derivative of **4f**: [α]_D²⁰ –2.3 (*c* 0.5, acetone), ee=50%.

S-(–)-**4f** Entry 7: 3% *i*-PrOH in hexane, 0.3 mL/min; *t*_R [min] 18.8 (*S*), *t*_R [min] 24.5 (*R*), [α]_D²⁰ –19.9 (*c* 2.4, CHCl₃).

R-(+)-**4f** Entry 8: 3% *i*-PrOH in hexane, 0.3 mL/min; *t*_R [min] 19.7 (*S*), *t*_R [min] 23.3 (*R*), [α]_D²⁰ +17.3 (*c* 1.3, CHCl₃).

S-(+)-**4i** Entry 9: 5% *i*-PrOH in hexane, 0.4 mL/min; *t*_R [min] 38.5 (*S*), *t*_R [min] 57.6 (*R*), [α]_D²⁰ +138.4 (*c* 0.25, CHCl₃); lit. (*S*)-**4i**: [α]_D²⁰ +114.9 (*c* 1.5, acetone), ee=95%.³³

S-(–)-**4j** Entry 10: 0.25% *i*-PrOH in hexane, 0.3 mL/min; *t*_R [min] 221.6 (*S*), *t*_R [min] 215.5 (*R*), [α]_D²⁰ –30.7 (*c* 0.87, CHCl₃); lit. (*S*)-**4j**: [α]_D²⁰ –33.4 (*c* 1.05, MeOH).³⁰

4.3.1.2. HPLC conditions for compounds 7 (Table 3 in text). *S*-(–)-**7a** Entry 1: 0.5% *i*-PrOH in hexane, 0.5 mL/min; *t*_R [min] 31.9 (*S*), *t*_R [min] 29.3 (*R*), [α]_D²⁰ –16.6 (*c* 0.35, CHCl₃); lit.^{4a} (*S*)-**7a**: [α]_D²⁰ –8.6 (*c* 1.0, CH₂Cl₂), ee=99%, (kinetic resolution, HPLC-Chiralcel OB-H).

S-(–)-**7a** Entry 2: 0.5% *i*-PrOH in hexane, 0.5 mL/min; *t*_R [min] 31.9 (*S*), *t*_R [min] 29.4 (*R*), [α]_D²⁰ –12.0 (*c* 0.2, CHCl₃).

S-(+)-**7c** Entry 3: 2.25% *i*-PrOH in hexane, 0.3 mL/min; *t*_R [min] 32.6 (*S*), *t*_R [min] 28.1 (*R*), absolute configuration of product determined by comparing circular dichroism (CD) spectrum of the purified α -hydroxy ketone **7c** to the CD spectrum of (*S*)-2-hydroxy tetralone **7a**, [α]_D²⁰ +44.2 (*c* 4.4, CHCl₃); lit.²⁹ *R*-**7c** ([α]_D²⁰ +72.5 (*c* 1.0, EtOH)) at 94% ee, [(CHIRALPAK AD (20% *i*-PrOH in hexane, 0.8 mL/min)], *t*_R [min] 20.9 (*S*), *t*_R [min] 15.5 (*R*); lit.³¹ 95% ee (Chiral SFC AD, 10% MeOH/CO₂, 1.5 mL/min, *t*_R [min] 7.1 (*S*), *t*_R [min] 9.5 (*R*)).

R-(+)-**7d** Entry 4: 5% *i*-PrOH in hexane, 0.4 mL/min, *t*_R [min] 34.3 (*S*), *t*_R [min] 45.2 (*R*), absolute configuration of product determined by comparing circular dichroism (CD) spectrum of the purified α -hydroxy ketone **7d** to the CD spectrum of (*S*)-2-hydroxy tetralone **7a**, [α]_D²⁰ +17.5 (*c* 0.4, CHCl₃).

R-(+)-**7e** Entry 5: hexane–EtOH–*i*-PrOH (98:1.6:0.4 v/v), 0.2 mL/min, *t*_R [min] 65.9 (*S*), *t*_R [min] 74.3 (*R*), absolute configuration of product determined by comparison of sign of optical rotation to the literature value [α]_D²⁰ +19.8 (*c* 3.1, CHCl₃); lit.^{32a} (*R*)-**7e**: [α]_D²⁰ +33.4 (*c* 1.4, CHCl₃) at 78% ee (chiral GC); lit.^{32b} (*R*)-**7e**: [α]_D²⁵ +20.0 (*c* 2.0, MeOH) at 81% ee; (*S*)-**7e**: [α]_D²⁵ –22.7 (*c* 1.62, MeOH) at 85% ee, (Daicel Chiralcel OB-H, 35% *i*-PrOH in hexane, 1.5 mL/min, *t*_R [min] 8.2 (*S*), *t*_R [min] 4.2 (*R*)).

R-(+)-**7e** Entry 6: hexane–EtOH–*i*-PrOH (98:1.6:0.4 v/v), 0.2 mL/min, *t*_R [min] 63.5 (*S*), *t*_R [min] 71.5 (*R*), [α]_D²⁰ +7.5 (*c* 0.48, CHCl₃).

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Supplementary data

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