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Chiral base promoted enantioselective rearrangement of organophosphorus epoxides

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Abstract—*Cinchona* alkaloids serve as effective chiral bases for enantioselective rearrangement of 3,4-epoxyphospholane oxides resulting in the formation of P,C-chirogenic 4-hydroxy-2-phospholene derivatives with up to 52% ee. A stereochemical course of the epoxide rearrangement involving *anti* β-proton abstraction is proposed. 3,4-Epoxy-1-phospholane-borane rearranges to 4-hydroxy-2-phospholene-borane of 55% ee on treatment with *sec*-BuLi/sparteine base system.

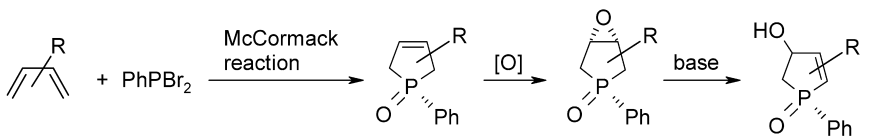
Asymmetric rearrangements of achiral epoxides to enantiomerically enriched allylic alcohols by the action of chiral lithium bases has emerged as one of the most useful methodologies in the field of asymmetric synthesis.[1] It is widely accepted that these rearrangements proceed via initial lithium coordination to the epoxy oxygen followed by abstraction of a *syn* β-proton.[2] In the last two decades, since the pioneering work of Whitesell and Felman,[3] a number of successful strategies based on this transformation have been developed for targeted synthesis of cyclic and acyclic enantiopure compounds containing carbon stereogenic centers.[1,4,5]

In the course of our research programme directed towards the synthesis of P,C-stereogenic monophosphines[6] we wanted to utilize 3-phospholene epoxide derivatives easily available on a large scale by oxidation of 1-phenyl-3-phospholene 1-oxide derivatives. These epoxides open a convenient way to the synthesis of phosphorus stereogenic center embedded in the frame of a five-membered ring containing endocyclic allylic functionality in its structure (Scheme 1).[7]

1. Synthesis of 3,4-epoxy-1-phenylphospholane 1-oxide derivatives

1-Phenyl-3-phospholene 1-oxide (**1**), 3-methyl-1-phenyl-3-phospholene 1-oxide (**2**) and 3,4-dimethyl-1-phenyl-3-phospholene 1-oxide (**3**) were prepared by the McCormack reaction according to the known procedure[8,9] involving addition of dibromophenylphosphine to 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene, respectively. 2-Methyl-1-phenyl-3-phospholene 1-oxide (**4**) and 2,5-dimethyl-1-phenyl-3-phospholene 1-oxide (**5**) were prepared by regioselective alkylation of **1**.[10]

Phospholenes **1**–**5** were converted into epoxides by treatment with *m*-chloroperbenzoic acid in refluxing chloroform (Scheme 2) according to procedures described by Arbuzov[11a] and by Quin[11b] who reported that the peracid oxidation of 3-phospholene oxides occurred at only one face of the ring and gave a single epoxide stereoisomer. This methodology was utilized by Bodalski[12] who described a preparation of 3,4-epoxy-1-phenylphospholane 1-oxide (**6**). As expected, epoxidations of **2**–**5**, under the same



Scheme 1.

Keywords: phospholenes; epoxides; enantioselective rearrangement.
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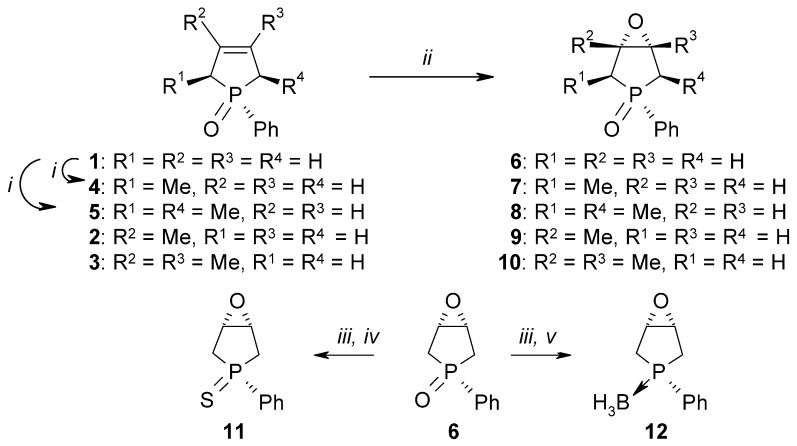


Scheme 2. *Reagents and conditions*: (i) (a) LDA, (b) MeI; (ii) *m*-CPBA; (iii) $PhSiH_3$; (iv) S_8; (v) BH_3×THF.

conditions were completely stereoselective and led cleanly to epoxides **7**–**10**. 3,4-Epoxy-1-phenylphospholane 1-sulfide (**11**) and 3,4-epoxy-1-phenylphospholane 1-borane (**12**) were prepared by reduction of **6** with phenylsilane[13] followed by treatment with powdered sulfur or borane–THF complex, respectively (Scheme 2). The expected retention of configuration at phosphorus in the reduction step was confirmed by X-ray analysis of **12** (Fig. 1).

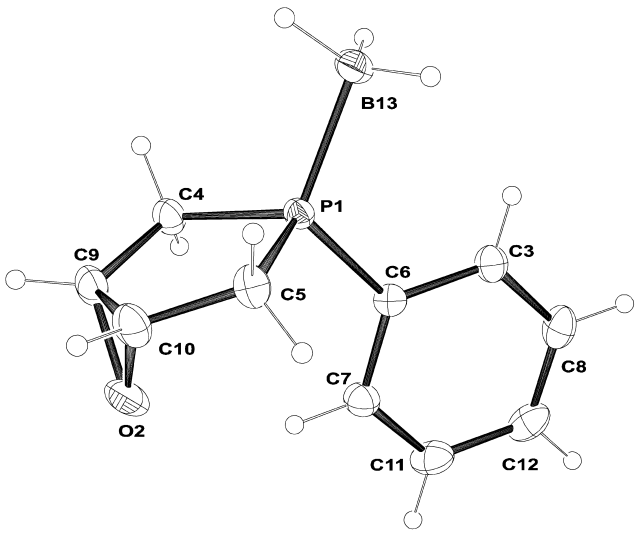
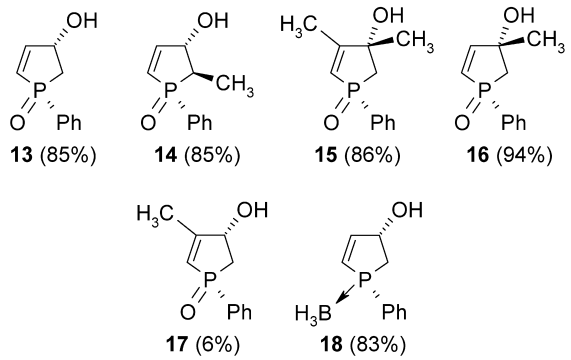


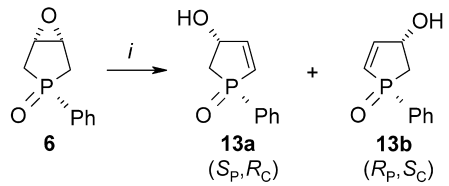
Figure 1. X-Ray diffraction structure (ORTEP) of compound **12**.

2. Rearrangement of 3,4-epoxy-1-phenylphospholane 1-oxide derivatives

It was already known that epoxide **6** rearranges efficiently to racemic 4-hydroxy-1-phenyl-2-phospholene 1-oxide (**13**) in the presence of triethylamine in refluxing ethanol.[11a,12] We used the same procedure for the synthesis of racemic 4-hydroxy-5-methyl-1-phenyl-2-phospholene 1-oxide (**14**) and 3,4-dimethyl-4-hydroxy-1-phenyl-2-phospholene 1-oxide (**15**) starting from epoxides **7** and **10**, respectively. The rearrangement of epoxide **9** led to the formation of 4-hydroxy-4-methyl-1-phenyl-2-phospholene 1-oxide (**16**) as the main product but a minor amount of regioisomer **17** (6%) was also detected in this reaction. Epoxide **8** was completely unaffected by triethylamine, whereas sulfide **11** was decomposed under the reaction conditions. Because alkylamines effectively decompose the phosphorus–boron bond,[14] to obtain alcohol **18** *sec*-BuLi/TMEDA in THF solution was used to promote the desired rearrangement of the epoxide **12**.



We expected that the use of a chiral base in lieu of triethylamine would render the studied rearrangement asymmetric and would result in an efficient production of **13**–**18** in enantiomerically enriched forms. The asymmetric version of this rearrangement was first studied with **6** as a model phospholene epoxide (Scheme 3).



Scheme 3. *Reagents and conditions*: (i) chiral base, cf Table 1.

Treatment of the model epoxide **6** with chiral lithium base systems such as LDA/*S*-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine (79, 0% op),[15] *sec*-BuLi/sparteine (71, 0% op), *n*-BuLi/sparteine (53, 0% op), LDA/sparteine (68, 0% op) or *n*-BuLi/bis(*S*-1-phenylethyl)amine (61, 8% op), known as very effective catalysts for enantioselective epoxide rearrangement reactions,[16,17] afforded the desired hydroxyphospholene **13** in good chemical yields but with only very little or even no induction. Similar results were obtained when quinine/LDA and quinidine/*n*-BuLi were used as bases (chemical yields: 29 and 54%; ees: 0 and 8%, respectively). All reactions were performed in THF solution

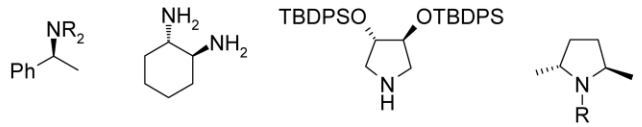
Table 1. Rearrangement of **6** in the presence of chiral bases

Entry	Base (equiv.)/solvent	Temperature (°C)	Time	Isolated yield (%)	Dominating enantiomer	$[\alpha]_D^{20}$ ($CHCl_3$)	Optical purity (%)[a]
1	**19** (3.0)/EtOH	20	60 d	54	**13b**	−12, *c* 1.0	7
2	**20** (3.0)/EtOH	20	3 d	57	–	–	0
3	**21** (0.5)/EtOH	20	27 d	64	–	–	0
4	**22** (0.5)/CH_2Cl_2	80	5 d	38	**13a**	+10, *c* 1.0	6
5	**23** (0.5)/EtOH	80	70 h	55	–	–	0
6	**24** (0.5)/EtOH	80	70 h	55	**13b**	−12, *c* 1.0	7
7	Quinine (0.5)/CH_2Cl_2	55	5 d	25	**13a**	+36, *c* 1.0	19
8	Quinine (1.0)/CH_2Cl_2	20	90 d	60	**13a**	+34, *c* 1.1	18
9	Cinchonidine (0.5)/CH_2Cl_2	60	2 d	19	**13a**	+11, *c* 1.0	6
10	Cinchonidine (1.0)/CH_2Cl_2	20	90 d	62	**13a**	+39, *c* 0.8	21
11	Cinchonine (0.5)/CH_2Cl_2	60	2 d	13	**13b**	−39, *c* 1.0	21
12	Cinchonine (1.0)/CH_2Cl_2	20	90 d	77	**13b**	−87, *c* 0.9	47
13	Quinidine (0.5)/CH_2Cl_2	60	2 d	22	**13b**	−50, *c* 1.0	27
14	Quinidine (0.5)/CH_2Cl_2	20	90 d	41	**13b**	−96, *c* 0.3	52
15	Quinidine (1.0)/CH_2Cl_2	20	90 d	72	**13b**	−72, *c* 1.5	39
16	Sparteine (1.0)/CH_2Cl_2	20	90 d	78	–	–	0
17	Brucine (1.0)/CH_2Cl_2	20	90 d	40	–	–	0
18	*O*-acetyl quinidine (1.0)/CH_2Cl_2	20	90 d	0	–	–	–

[a] Ops were determined by comparison of optical rotation values with the known value for pure S_P,R_C-(+)-**13a** ($[\alpha]_D^{20}$=+184.8, *c* 1.98 in chloroform)[12] and for products of entries 10 and 14 were additionally confirmed by ^{1}H NMR measurements in the presence of the Kagan's shift reagent.[19]

at −78°C. Due to extremely low solubility of epoxide **6** in diethyl ether no reactions were observed in this solvent. Attempted rearrangement of epoxide **6** in the presence of *n*-BuLi/bis(*S*-1-phenylethyl)amine and equimolar amount of LiCl in THF solution at −100°C[18] caused decomposition of the starting material.

Next, a series of chiral free amines **19**–**24**, brucine, sparteine and a set of four *Cinchona* alkaloids were used as bases to promote the rearrangement of **6**. The results of this screening are presented in Table 1. Bases **19**–**24** (entries 1–6), as well as sparteine (entry 16) and brucine (entry 17), gave unexpectedly poor results in terms of asymmetric induction.



19: R = Me **20**: R = H **21** **22** **23**: R = H **24**: R = Bn

Much more promising results were obtained when *Cinchona* alkaloids were used as free amine catalysts for the studied rearrangement of **6**. The test reactions with these bases were carried out at 20 or 60°C using 0.5 or 1.0 equiv. of base in ethanol or in methylene chloride (which proved to be a better solvent) and were typically kept for prolonged times in order to achieve higher conversions.

As shown in Table 1, the highest optical purities of alcohol **13** were obtained for the reactions performed in the presence of quinidine (52% op, entry 14) and cinchonine (47% op, entry 12) which both favored the formation of (−)-**13b**. The two quasi-enantiomeric bases, quinine and cinchonidine, afforded predominantly (+)-**13a** (entries 7–10). *O*-Acetylated quinidine was completely ineffective (entry 18).

Analogous asymmetric rearrangements of chiral non-symmetrically substituted phospholene epoxides **7** and **9** could potentially serve for kinetic resolutions of the racemic substrates. Table 2 shows results obtained for the rearrangement of epoxides **7** and **9** in the presence of *Cinchona* alkaloids. Even though very long reaction times (90–120 days) were applied for these substrates, their conversions were usually low or moderate at most. In addition, the desired kinetic resolution process was also found poorly efficient. Treatment of **7** with cinchonine gave allylic

Table 2. Rearrangement of the epoxides **7** and **9** in the presence of alkaloid bases in dichloromethane solution at 20°C

Entry	Base (equiv.)	Epoxide	Recovered epoxide (%) (% ee)	Isolated yield (%)	$[\alpha]_D^{20}$ ($CHCl_3$)	% ee[a] of the product	Configuration[b]
1	Cinchonine (1.0)	**7**	33 (9)[c]	55	−7.3, *c* 1.0	3	R_PS_C
2	Quinidine (1.0)	**7**	40 (12)[c]	55	−7.6, *c* 1.1	8	R_PS_C
3	Quinidine (0.5)	**7**	77 (4)[c]	19	−19.5, *c* 0.6	12	R_PS_C
4	Quinine (1.0)	**7**	76 (n.d.)	23	N.d.	2	R_PS_C
5	Cinchonidine (1.0)	**7**	96 (n.d.)	Traces	–	–	–
6	Cinchonidine (1.0)	**9**	79[d] (n.d.)	12[d]	–	25	S_PR_C
7	Quinine (1.0)	**9**	78[d] (n.d.)	13[d]	–	36	S_PR_C
8	Cinchonine (1.0)	**9**	79[d] (7)[e]	13[d]	–	35	R_PS_C
9	quinidine (1.0)	**9**	59[d] (14)[e]	35[d]	–	36	R_PS_C

[a] Ees were determined by ^{1}H NMR in the presence of the Kagan's shift reagent.[19]
[b] Postulated configuration of alcohols **14** (from epoxide **7**) or **16** (from epoxide **9**).
[c] Ees were determined by ^{1}H NMR in the presence of (−)-*O*,*O*′-dibenzoyl-L-tartaric acid as chiral shift reagent.[20]
[d] Inseparable mixture of recovered epoxide **9** and allylic alcohol **16**. Composition of the mixtures were determined by HPLC (LiChrospher 100 RP-18, methanol–water, 40:60 as eluent). In all cases proportion of **16**/**17** was about 94:6.
[e] Ees were determined by ^{31}P NMR in the presence of (−)-*O*,*O*′-dibenzoyl-L-tartaric acid as chiral shift reagent.[20]

alcohol **14** with 3% ee only (9% ee of the recovered **7**). Similar reaction with quinidine (0.5 equiv.) afforded **14** with 12% ee (4% ee of the recovered **7**) but the chemical yield was low. Equimolar amount of quinidine increased the chemical yield to 55%, however, the enantiomeric purity of the product was lowered to 8% (12% ee of the recovered **7**).

Rearrangement of epoxide **9** in the presence of *Cinchona* alkaloids yielded allylic alcohol **16** with much better enantioselectivity (25–36% ee), but the chemical yields were again low (12–13%) and reached 35% only in the presence of quinidine.

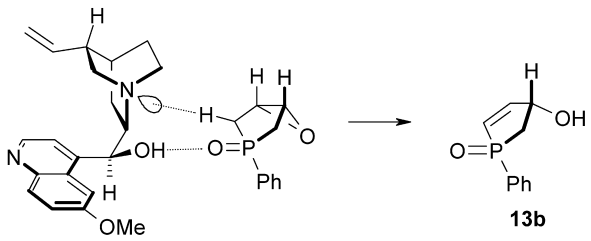
Treatment of epoxides **8**, **10** and **11** with quinidine at room temperature as described above, gave only recovered starting material and no epoxide ring opening was observed.

Based on literature precedents on the enantioselective deprotonation of phosphine–boranes by *sec*-BuLi/sparteine at low temperature[21] we treated epoxy phosphine–borane **12** with this base system in THF at −78°C. The formation of the expected alcohol **18** with 83% yield was observed but the product was found to be racemic. By comparison, the same reaction carried out in diethyl ether at −78°C[22] afforded allylic alcohol **18** with $[\alpha]_D^{20}=-72.1$ (*c* 0.32, chloroform). For determination of its enantiomeric purity (−)-**18** obtained above was treated with DABCO followed by hydrogen peroxide oxidation[23] and gave oxide **13b** with 55% ee (determined by ^{31}P NMR in the presence of the Kagan's shift reagent).[19]

3. Determination of configuration and proposed mechanism for phospholene epoxide ring rearrangement in the presence of *Cinchona* alkaloids

Absolute configuration of allylic alcohol **13** was determined by comparison of optical rotation value with the available enantiomer of **13a** of known configuration (S_PR_C).[12] Additionally we have found that ^{1}H NMR spectroscopy of **13b** in the presence of (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-1-phenylethylamine (Kagan's shift reagent)[24] shows strong H-2 proton deshielding ($\Delta\delta$ −21.9 Hz)[25] by comparison with the appropriate signal for **13a**. According to the above H-2 proton shift and the unidirectional shift observed for the series of 2-phospholene 1-oxide derivatives of known configuration,[19] we could tentatively assign the R_PS_C configuration to the dominating stereoisomer of **14** ($\Delta\delta$ −11.8 Hz for H-2 proton). Similarly, for rearrangement of epoxide **9** in the presence of cinchonine and quinidine the formation of (R_PS_C)-**16** ($\Delta\delta$ −13.1 Hz for H-2 proton) was preferred whereas in the presence of cinchonidine and quinine (S_PR_C)-**16** prevailed.

The above stereochemical results and the failure of chiral lithium amide bases to induce asymmetry in the studied rearrangement of epoxyphospholene oxides are most likely to result from the effects of the Ph–P═O functionality present in the substrate structure. It has been already demonstrated that Ph–P═O group in five-membered rings facilitates abstraction of adjacent protons which are *syn* to phosphoryl oxygen.[26] It is also well known that basic phosphoryl oxygen is an efficient donor site for protons and



Scheme 4. Preferred quinidine approach to epoxide **6**.

metal cations.[27] It is thus reasonable to assume that in the studied case the rearrangement process is initiated by coordination of the alkaloid molecule to epoxide **6** through hydrogen bonding between alkaloid hydroxyl and phosphoryl functionalities as shown in Scheme 4.

In the next step, the anchored base abstracts the more easily accessible one of the two enantiotopic β-protons *anti* to epoxide oxygen depending on the stereochemistry of the alkaloid molecule. The absolute configurations of **13b**, prevailing in the reactions catalyzed by quinidine and cinchonine, and of **13a**, formed predominantly in the reactions with quinine and cinchonidine, are in accord with the proposed picture.

In line with the above proposal is also an additional observation that the corresponding epoxy phospholene sulfide **11** unable to participate in similar hydrogen bonding, failed to undergo the rearrangement under the same conditions.

In summary, we have demonstrated that the asymmetric rearrangement of phospholene epoxides can be used to generate a phosphorus stereogenic center in the cyclic five-membered ring system. *Cinchona* alkaloids are the most effective catalysts for the rearrangements of epoxy phospholene oxides and, unlike the lithium amide bases, are most likely to operate in the studied system via the mechanism involving *anti* β-proton abstraction. For the rearrangement of epoxy phospholene–borane the highest enantioselectivity (55% ee) has been achieved with *sec*-BuLi/sparteine base system as a promoter.

4. Experimental

Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a stream of argon prior to use. Other solvents were purified and dried according to literature methods. TLC was performed on Silica Gel HF-254 and column chromatography on Silica Gel 230–400 mesh (Merck). NMR spectra were recorded with a Bruker AM-500 (500 MHz) spectrometer in deuterochloroform ($CDCl_3$) with Me_4Si as internal standard. High resolution mass spectra (HR-MS) were measured with AMD-604 mass spectrometer. Optical rotations were measured with a JASCO DIP-360 automatic polarimeter. IR spectra were recorded on Perkin–Elmer 1640 FT-IR spectrophotometer.

4.1. X-Ray structure determination of 12

Suitable crystals were grown from an ethyl ether solution.

Table 3. Crystal data and structure refinement for **12**

Empirical formula	$C_{40}H_{56}B_4O_4P_4$
Formula weight	767.97
Temperature (K)	293(2)
Wavelength (Å)	1.54184
Crystal system, space group	Monoclinic, *P*21/*a*
Unit cell dimensions	
a (Å)	10.414
b (Å)	8.497
c (Å)	11.889
α (°)	90
β (°)	99.50
γ (°)	90
Volume (Å^3)	1037.5
Z, calculated density (mg/m^3)	1, 1.229
Absorption coefficient (mm^{-1})	1.979
F(000)	408
Crystal size (mm)	0.49×0.28×0.245
θ-range for data collection (°)	3.77–73.98
Limiting indices	$0\leq h\leq 12$
	$0\leq k\leq 10$
	$-14\leq l\leq 14$
Reflections collected/unique	1633/1633 [R_{int}=0.0000]
Refinement method	Full-matrix least-squares on F_2
Data/restraints/parameters	1633/0/139
Goodness-of-fit on F_2	1.054
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0430, wR_2=0.1153
R indices (all data)	R_1=0.0430, wR_2=0.1153
Extinction coefficient	0.0148(16)
Largest diff. peak and hole (e Å^{-3})	0.432 and −0.365

The measurement was run on a Nonius BV MACH3 diffractometer. The structure was solved by the SHELXS-86[28] and refined with the SHELXS-97[29] programs. Crystallographic data reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as a supplementary material number CCDC 212774 (Tables 3 and 4).

4.1.1. 2-Methyl-1-phenyl-3-phospholene 1-oxide (4).[10a] To a solution of a freshly prepared LDA (2.1 mM) cooled to −78°C 1-phenyl-3-phospholene 1-oxide (**1**, 356 mg, 2.0 mM) was added and stirred for 10 min. Methyl iodide (284 mg, 2.0 mM) was added and stirring was continued for 1 h at −78°C. Water (five drops) was added and solvents were evaporated to dryness. Column chromatography (hexane–ethyl acetate–methanol, 5:3:1 as eluent) of the residue gave 227 mg (59%) of the title compound as thick colourless syrup. ν_{max} (film): 1437, 1186, 1113, 721, 697, 558 cm^{-1}. HR-MS(EI) calcd for $C_{11}H_{13}OP$ $(M)^+$: 192.0704. Found: 192.0700.

Table 4. Selected bond lengths (Å) and angles (°) for **12**

P(1)–B(13)	1.917(3)
P(1)–C(4)	1.833(2)
P(1)–C(5)	1.833(2)
P(1)–C(6)	1.807(2)
O(2)–C(9)	1.440(3)
O(2)–C(10)	1.443(4)
C(4)–C(9)	1.495(3)
C(9)–C(10)	1.460(4)
C(5)–C(10)	1.498(3)
C(6)–P(1)–B(13)	114.12(11)
C(4)–P(1)–B(13)	113.44(13)
C(5)–P(1)–B(13)	113.79(13)
C(4)–P(1)–C(5)	95.89(11)
C(9)–O(2)–C(10)	60.86(17)
O(2)–C(9)–C(10)	59.67(17)
O(2)–C(10)–C(9)	59.47(18)
B(13)–P(1)–C(4)–C(9)	−127.0(2)
B(13)–P(1)–C(5)–C(10)	126.48(19)
B(13)–P(1)–C(6)–C(3)	8.4(2)
P(1)–C(4)–C(9)–C(10)	5.9(3)
P(1)–C(5)–C(10)–C(9)	−5.5(3)
C(4)–C(9)–C(10)–C(5)	−0.3(4)
C(4)–P(1)–C(5)–C(10)	7.6(2)
C(5)–P(1)–C(4)–C(9)	−7.8(2)
C(6)–P(1)–C(4)–C(9)	103.74(19)
C(6)–P(1)–C(5)–C(10)	−105.76(19)
P(1)–C(4)–C(9)–O(2)	−60.4(3)
C(4)–P(1)–C(6)–C(3)	137.36(18)

4.1.2. 2,5-Dimethyl-1-phenyl-3-phospholene 1-oxide (5). To a solution of a freshly prepared LDA (5.0 mM) cooled to −78°C 1-phenyl-3-phospholene 1-oxide (**1**, 356 mg, 2.0 mM) was added and stirred for 10 min. Methyl iodide (4.26 g, 30 mM) was added and stirring was continued for 1 h at −78°C. Water (five drops) was added and solvents were evaporated to dryness. Column chromatography (hexane–ethyl acetate–methanol, 5:3:1 as eluent) of the residue gave 341 mg (83%) of the title compound as colourless syrup. ^{1}H NMR ($CDCl_3$), δ 5.96 (dd, 2H, $J_{H,P}$=27.7 Hz, J=0.7 Hz, H-3,4), 2.76 (m, 2H, H-2,5), 1.36 (dd, 6H, $J_{H,P}$=14.8 Hz, $J_{Me,2(5)}$=7.5 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ 134.40 (d, $J_{C,P}$=100.0 Hz), 133.38 (d, $J_{C,P}$=13.8 Hz, C-3,4), 131.68 (d, $J_{C,P}$=2.6 Hz), 129.81 (d, $J_{C,P}$=9.0 Hz), 128.56 (d, $J_{C,P}$=11.1 Hz), 37.83 (d, $J_{C,P}$=66.9 Hz, C-2,5), 14.14 (d, $J_{C,P}$=4.2 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 55.15. ν_{max} (film): 1437, 1185, 1113, 744, 718, 697, 562 cm^{-1}. HR-MS(EI) calcd for $C_{12}H_{15}OP$ $(M)^+$: 206.0860. Found: 206.0863.

4.2. General procedure for the synthesis of 3,4-epoxy-1-phenylphospholane 1-oxide derivatives

To a solution of 1-phenyl-3-phospholene 1-oxide derivative (2.0 mM) in chloroform (10 mL) *m*-chloroperbenzoic acid (3.0 mM) was added. The reaction mixture was refluxed for 12 h, washed with sat. $NaHCO_3$, 10% aq. $Na_2S_2O_3$, dried (Na_2SO_4) and evaporated to dryness. Column chromatography (hexane–ethyl acetate–methanol, 5:3:1 as eluent) of the residue yielded pure epoxide.

4.2.1. 3,4-Epoxy-2-methyl-1-phenylphospholane 1-oxide (7). Yield 73%. Mp: 93–95°C. ^{1}H NMR ($CDCl_3$), δ 3.73 (m, 1H, $J_{H,P}$=27.4 Hz, $J_{3,4}$=3.0 Hz, H-4), 3.53 (dd, 1H, $J_{H,P}$=24.5 Hz, H-3), 2.57 (d, 1H, $J_{5,5'}$=16.5 Hz, H-5), 2.49 (q, 1H, $J_{Me,2}$=7.9 Hz, H-2), 2.38 (ddd, 1H, J=18.1, 2.6 Hz, H-5′), 1.40 (dd, 3H, $J_{H,P}$=14.6 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ 133.14 (d, $J_{C,P}$=93.2 Hz), 131.71 (d, $J_{C,P}$=2.9 Hz), 131.03 (d, $J_{C,P}$=10.3 Hz), 128.43 (d, $J_{C,P}$=12.2 Hz), 59.60 (d, $J_{C,P}$=8.0 Hz, C-3 or C-4), 53.51 (d, $J_{C,P}$=5.1 Hz, C-4 or C-3), 34.50 (d, $J_{C,P}$=66.0 Hz, C-2), 31.56 (d, $J_{C,P}$=63.6 Hz, C-5), 9.96 (d, $J_{C,P}$=5.0 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 61.13. ν_{max} (film): 1438, 1235, 1175, 1110, 816, 739, 564 cm^{-1}. HR-MS(EI) calcd for $C_{11}H_{13}O_2P$ $(M)^+$: 208.0653. Found: 208.0646.

4.2.2. 3,4-Epoxy-2,5-dimethyl-1-phenylphospholane 1-oxide (8). Yield 71%. Mp: 83–86°C. ^{1}H NMR ($CDCl_3$), δ 3.50 (d, 2H, $J_{H,P}$=25.4 Hz, H-3,4), 2.54 (q, 2H, $J_{Me,2}$=$J_{Me,5}$=7.9 Hz, H-2,5), 1.38 (dd, 6H, $J_{H,P}$=14.2 Hz, 2×CH_3). ^{13}C NMR ($CDCl_3$), δ 132.14 (d, $J_{C,P}$=2.7 Hz), 131.65 (d, $J_{C,P}$=9.7 Hz), 128.91 (d, $J_{C,P}$=11.7 Hz), 59.77 (d, $J_{C,P}$=8.8 Hz, C-3,4), 34.90 (d, $J_{C,P}$=64.0 Hz, C-2,5), 11.15 (d,

$J_{C,P}$=5.2 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 62.58. ν_{max} (film): 1453, 1438, 1182, 1108, 814, 718, 563 cm^{-1}. HR-MS(EI) calcd for $C_{12}H_{15}O_2P$ $(M)^+$: 222.0810. Found: 222.0803.

4.2.3. 3,4-Epoxy-3-methyl-1-phenylphospholane 1-oxide (9). Yield 83%. Mp: 69–71°C (lit.[30] Mp: 89°C). ^1H NMR ($CDCl_3$), δ 3.57 (dd, 1H, J=2.3, 27.6 Hz, H-4), 2.54 (m, 3H, H-2,5,5′), 2.37 (dd, 1H, J=16.5, 18.1 Hz, H-2′), 1.59 (d, 3H, J=0.5 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ 132.97 (d, $J_{C,P}$=95.6 Hz), 131.79 (d, $J_{C,P}$=3.0 Hz), 130.97 (d, $J_{C,P}$=10.4 Hz), 128.43 (d, $J_{C,P}$=12.4 Hz), 61.96 (d, $J_{C,P}$=6.2 Hz, C-3), 60.49 (d, $J_{C,P}$=2.9 Hz, C-4), 36.51 (d, $J_{C,P}$=67.0 Hz, C-2 or C-5), 33.50 (d, $J_{C,P}$=65.8 Hz, C-5 or C-2), 20.39 (d, $J_{C,P}$=10.2 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 59.34. ν_{max} (film): 1438, 1393, 1227, 1190, 1154, 913, 748 cm^{-1}. HR-MS(EI) calcd for $C_{11}H_{13}O_2P$ $(M)^+$: 208.0653. Found: 208.0645.

4.2.4. 3,4-Epoxy-3,4-dimethyl-1-phenylphospholane 1-oxide (10). Yield 79%. Mp: 148–150°C. ^1H NMR ($CDCl_3$), δ 2.63 (dd, 2H, $J_{H,P}$=3.5 Hz, J_{HCH}=16.5 Hz, H-2,5), 2.41 (dd, 2H, $J_{H,P}$=18.6 Hz, H-2′,5′), 1.53 (d, 6H, $J_{H,P}$=1.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ 132.97 (d, $J_{C,P}$=95.8 Hz), 131.72 (d, $J_{C,P}$=2.8 Hz), 131.011 (d, $J_{C,P}$=10.2 Hz), 128.38 (d, $J_{C,P}$=12.1 Hz), 65.75 (d, $J_{C,P}$=4.6 Hz, C-3,4), 38.29 (d, $J_{C,P}$=67.6 Hz, C-2,5), 17.61 (d, $J_{C,P}$=11.4 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 50.96. ν_{max} (film): 1438, 1251, 1207, 1179, 1144, 1108, 1028, 879, 756 cm^{-1}. HR-MS(EI) calcd for $C_{12}H_{15}O_2P$ $(M)^+$: 222.0810. Found: 222.0804.

4.2.5. 3,4-Epoxy-1-phenylphospholane 1-sulfide (11). A mixture of 3,4-epoxy-1-phenylphospholane 1-oxide (**6**, 400 mg, 2.06 mM) toluene (2 mL) and phenylsilane (1.7 mM) was heated at 110°C (oil bath temperature) for 3 h under an argon atmosphere. Solvents were evaporated. The residue was dissolved in benzene (2 mL) and powdered sulfur (120 mg) was added. Suspension was stirred overnight at room temperature. Column chromatography (hexane–ethyl acetate, 7:3) afforded 412 mg (95%) of the title compound. Mp: 65–66°C. ^1H NMR ($CDCl_3$), δ 3.85 (dm, 2H, J=0.6, 1.8, 26.6 Hz, H-3,4),2.93 (dd, 2H, J=2.1, 16.6 Hz, H-2,5),2.63 (m, 2H, H-2′,5′). ^{13}C NMR ($CDCl_3$), δ 131.98 (d, $J_{C,P}$=74.6 Hz), 131.72 (d, $J_{C,P}$=11.5 Hz), 131.57 (d, $J_{C,P}$=3.1 Hz), 128.38 (d, $J_{C,P}$=12.6 Hz), 56.33 (s, C-3,4), 39.44 (d, $J_{C,P}$=52.2 Hz, C-2,5). ^{31}P NMR ($CDCl_3$), δ 61.66. ν_{max} (film): 1434, 1396, 1105, 955, 841, 740 cm^{-1}. HR-MS(EI) calcd for $C_{10}H_{11}OPS$ $(M)^+$: 210.0268. Found: 210.0261.

4.2.6. 3,4-Epoxy-1-phenylphospholane 1-borane (12). 3,4-Epoxy-1-phenylphospholane 1-oxide (**6**, 970 mg, 5.0 mM) was reduced as described for **11** and to the solution of free phosphine in toluene (3 mL) borane–THF complex (5.0 mM) was added. Column chromatography (hexane–ethyl acetate, 9:1) gave 835 mg (87%) of the title compound. Mp: 94–95°C. ^1H NMR ($CDCl_3$), δ 3.78 (d, 2H, J=17.9 Hz, H-3,4), 2.55 (dd, 2H, J=5.8, 16.2 Hz, H-2,5), 2.45 (dd, 2H, J=5.1, 16.2 Hz, H-2′,5′), 0.0–1.4 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$), δ 133.11 (d, $J_{C,P}$=10.3 Hz), 131.44 (d, $J_{C,P}$=2.5 Hz), 129.14 (d, $J_{C,P}$=49.9 Hz), 128.65 (d, $J_{C,P}$=10.2 Hz), 58.07 (d, $J_{C,P}$=4.4 Hz, C-3,4) 29.43 (d, $J_{C,P}$=34.9 Hz, C-2,5). ^{31}P NMR ($CDCl_3$), δ 34.05 (dd, J=45.5, 103.7 Hz). ν_{max} (film): 2374, 1400, 1066 cm^{-1}. HR-MS(EI) calcd for $C_{10}H_{11}OP$ $(M-BH_3)^+$: 178.0547. Found: 178.0545.

4.3. General procedure for the rearrangement of the phospholene epoxides in the presence of triethylamine

A mixture of phospholene epoxide (0.5 mM), ethanol (96%, 5 mL) and triethylamine (0.4 mL) was heated at 100°C in a tube with screw cap for 24–70 h. Solvents were evaporated. Column chromatography (hexane–ethyl acetate–methanol, 5:3:1) of the residue yielded 4-hydroxy-1-phenyl-2-phospholene 1-oxide derivative.

4.3.1. 4-Hydroxy-5-methyl-1-phenyl-2-phospholene 1-oxide (14). Yield 85%. Mp: 118–120°C. ^1H NMR ($CDCl_3$), δ 7.09 (ddd, 1H, $J_{H,P}$=44.3, $J_{3,2}$=8.5, $J_{3,4}$=1.6 Hz, H-3), 6.25 (ddd, 1H, $J_{H,P}$=21.3, $J_{2,4}$=0.9 Hz, H-2), 4.78 (m, 2H, H-4, OH), 2.06 (m, 1H, H-5), 1.37 (dd, 3H, $J_{H,P}$=15.3 Hz, $J_{Me,5}$=7.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ 156.14 (d, $J_{C,P}$=14.5 Hz, C-2), 132.24 (d, $J_{C,P}$=98.5 Hz), 132.13 (d, $J_{C,P}$=2.8 Hz), 131.00 (d, $J_{C,P}$=10.7 Hz), 128.65 (d, $J_{C,P}$=12.2 Hz), 125.87 (d, $J_{C,P}$=85.0 Hz, C-3), 80.04 (d, $J_{C,P}$=21.5 Hz, C-4), 41.44 (d, $J_{C,P}$=71.9 Hz, C-5), 9.97 (d, $J_{C,P}$=1.9 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 55.67. ν_{max} (film): 1438, 1163, 1081, 749, 728 cm^{-1}. HR-MS(EI) calcd for $C_{11}H_{13}O_2P$ $(M)^+$: 208.0653. Found: 208.0650.

4.3.2. 4-Hydroxy-3,4-dimethyl-1-phenyl-2-phospholene 1-oxide (15). Yield 86%. Mp: 197–198°C. ^1H NMR ($CDCl_3$), δ 5.81 (m, 1H, $J_{H,P}$=21.7 Hz, H-2), 2.39 (m, 2H, H-5,5′), 2.08 (m, 3H, CH_3), 1.63 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ 169.13 (d,$J_{C,P}$=17.8 Hz, C-3), 132.95 (d, $J_{C,P}$=100.5 Hz), 131.73 (d, $J_{C,P}$=2.8 Hz), 131.09 (d, $J_{C,P}$=10.7 Hz), 128.44 (d, $J_{C,P}$=12.2 Hz), 120.70 (d, $J_{C,P}$=94.1 Hz, C-2), 79.70 (d, $J_{C,P}$=13.9 Hz, C-4), 43.74 (d, $J_{C,P}$=69.2 Hz, C-5), 29.31 (d, $J_{C,P}$=4.0 Hz, CH_3), 15.51 (d, $J_{C,P}$=19.1 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 48.78. ν_{max} (film): 1438, 1168, 1137, 1103, 745 cm^{-1}. HR-MS(EI) calcd for $C_{12}H_{15}O_2P$ $(M)^+$: 222.0810. Found: 222.0801.

4.3.3. 4-Hydroxy-4-methyl-1-phenyl-2-phospholene 1-oxide (16). Quantitative yield (contains approximately 6% of 4-hydroxy-3-methyl-1-phenyl-2-phospholene 1-oxide, **17**). ^1H NMR ($CDCl_3$), δ 6.90 (dd, 1H, $J_{H,P}$=45.8 Hz, $J_{3,2}$=8.1 Hz, H-3), 6.15 (dd, 1H, $J_{H,P}$=22.4 Hz, H-2), 2.34 (m, 2H, H-5,5′), 1.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ 157.65 (d, $J_{C,P}$=17.2 Hz, H-2), 132.44 (d, $J_{C,P}$=99.2 Hz), 131.97 (d, $J_{C,P}$=2.8 Hz), 131.02 (d, $J_{C,P}$=11.2 Hz), 128.57 (d, $J_{C,P}$=12.3 Hz), 125.44 (d, $J_{C,P}$=87.7 Hz, H-3), 78.76 (d, $J_{C,P}$=15.2 Hz, H-4), 42.02 (d, $J_{C,P}$=70.3 Hz, H-5), 30.74 (d, $J_{C,P}$=4.1 Hz, CH_3). ^{31}P NMR ($CDCl_3$), δ 58.93. ν_{max} (film): 1438, 1157, 1104, 746 cm^{-1}. HR-MS(EI) calcd for $C_{11}H_{13}O_2P$ $(M)^+$: 208.0653. Found: 208.0658.

4.3.4. 4-Hydroxy-1-phenyl-2-phospholene 1-borane (18). To a solution of sparteine (47 mg, 0.2 mM) in THF (8 mL) cooled to −78°C *sec*-butyllithium (1.2 mM) was added and stirred for 30 min. 3,4-Epoxy-1-phenylphospholane 1-borane (**12**, 192 mg, 1.0 mM) in THF (2 mL) was added and stirred at −78°C for 2 h. Few drops of water were added, solvents were evaporated to dryness and product was separated by column chromatography (hexane–ethyl

acetate, 7:3 as eluent) to afford 160 mg (83%) of the title compound as colourless wax. ^{1}H NMR ($CDCl_3$), δ 6.81 (ddd, 1H, $J_{H,P}$=33.3 Hz, $J_{2,3}$=7.7 Hz, $J_{2,4(3,4)}$=2.3 Hz, H-2 or H-3), 6.23 (ddd, 1H, $J_{H,P}$=29.0 Hz, $J_{2,4(3,4)}$=1.3 Hz, H-2 or H-3), 5.23 (m, 1H, H-4), 2.77 (ddd, 1H, $J_{H,P}$=7.7 Hz, $J_{5,5'}$=15.0 Hz, $J_{5,4}$=1.1 Hz, H-5), 2.05 (ddd, 1H, $J_{H,P}$= 12.0 Hz, $J_{5',4}$=3.8 Hz, H-5′), 0.00–1.80 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$), δ 149.69 (d, $J_{C,P}$=7.1 Hz, C-3), 132.45 (d, $J_{C,P}$=10.3 Hz), 131.80 (d, $J_{C,P}$=2.6 Hz), 129.08 (d, $J_{C,P}$= 47.6 Hz), 128.80 (d, $J_{C,P}$=10.1 Hz), 125.98 (d, $J_{C,P}$= 48.6 Hz, C-2), 75.47 (d, $J_{C,P}$=4.6 Hz, C-4), 34.07 (d, $J_{C,P}$=35.6 Hz, C-5). ^{31}P NMR ($CDCl_3$), δ 38.56 (m). ν_{max} (KBr): 2377, 1438, 1313, 1113, 745 cm^{-1}. HR-MS(EI) calcd for $C_{10}H_{11}OP$ $(M\text{-}BH_3)^+$: 178.0547. Found: 178.0542.

The same reaction carried out in Et_2O solution and in the presence of *sec*-BuLi/sparteine complex (1.05 equiv.) gave (−)-**18** with 73% yield and $[\alpha]_D^{20}$=−72.1 (*c* 0.32, chloroform).

4.4. Transformation of (−)-18 into 13b

(−)-**18** obtained above (70 mg, 0.36 mM) and DABCO (125 mg, 1.1 mM) in benzene (2 mL) was heated at 40–45°C for 24 h. Then the whole mixture was evaporated to dryness at 40°C under reduced pressure (1 mmHg), dissolved in benzene (1 mL) and stirred overnight with 15% H_2O_2, evaporated and purified by column chromatography (hexane–*iso*-propyl alcohol, 1:1 as eluent) to yield 63 mg (89%) of the title compound.

4.5. General procedure for the rearrangement of the phospholene epoxide 6 in the presence of chiral lithium amides

To a solution of chiral amine (see text, 0.55 mM) in THF (4 mL) cooled to −78°C alkyllithium (see text, 0.5 mM) was added and stirred for 15 min. A solution of **6** (97 mg, 0.5 mM) in THF (1 mL) was added and stirred for additional 2 h at −78°C, quenched by addition of water (0.5 mL) and purified by column chromatography (hexane–*iso*-propyl alcohol, 1:1 as eluent).

4.6. General procedure for the rearrangement of the phospholene epoxides in the presence of *Cinchona* alkaloids

To a solution of phospholene epoxide (0.5 mM) in dichloromethane (1 mL) quinidine (0.25 mM) was added and kept at room temperature for 90–120 days. Solvents were evaporated. Column chromatography (hexane–*iso*-propyl alcohol, 1:1 or hexane–ethyl acetate–methanol, 5:3:1 as eluent) of the residue yielded 4-hydroxy-1-phenyl-2-phospholene 1-oxide derivatives (Tables 1 and 2).

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