Preparation and Characterization of New C_2- and C_1-Symmetric Nitrogen, Oxygen, Phosphorous, and Sulfur Derivatives and Analogs of TADDOL

Part II

TADDAMIN-Derived and Phosphorous-Containing Compounds

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TADDOL (= $\alpha,\alpha,\alpha',\alpha'$-Tetraaryl-1,3-dioxolane-4,5-dimethanol) and the corresponding dichloride are converted to TADDAMINs (= (4*S*,5*S*)-2,2,*N*,*N*′-tetramethyl-$\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-1,3-dioxolan-4,5-dimethanamines) (*Scheme 2*) and ureas, **12**–**15**, and to TADDOP derivatives with seven-membered O–P–O ester rings (*Schemes 3* and *4*). Cl/P-Replacement *via* the *Michaelis–Arbuzov* reaction (*Scheme 7*) on mono- and dichlorides, derived from TADDOL, are described. It was not possible to obtain phosphines with the P-atom attached to the benzhydrylic C-atom of the TADDOL skeleton (*Schemes 6* and *7*). The X-ray crystal structures (*Figs. 1* and *2*) of ten of the more than 30 new TADDOL derivatives are discussed. Full experimental details are presented.

1. Introduction. – As discussed in the previous paper [1a] of this series[5]) of publications on TADDOL (= $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanol) derivatives [1], the modification of the OH groups (HO → R–O, R–OSO_x, R–OPO_x) and their substitution by other heteroatoms (S, N, and P) in TADDOLs lead to a plethora of chiral compounds for possible new applications in organic synthesis. The previous report [1a] was focused on (mainly C_1-symmetrical) S-containing derivatives, and in the present report the preparation of hitherto unpublished (mainly C_2-symmetrical) N- and P-containing compounds derived from the parent TADDOL (**1**) is described. The methods used for the transformations are likely to be applicable to TADDOLs with geminal diaryl groups other than Ph and with substituents R other than Me at C(2) of the dioxolane ring. The key intermediate *en route* to C_1-symmetrical derivatives was the monochloride **2**, which is formed selectively under the conditions of the *Appel* reaction

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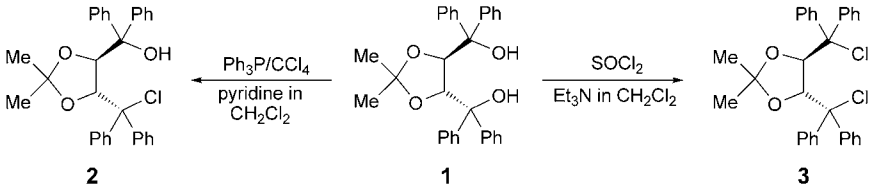
[5]) Part I: 'Compounds Containing One or Two Sulfur Substituents and Use in Cu-Catalyzed Enantioselective Conjugate Additions to Cyclic Enones' (p. 1239 of this issue); Part III: 'Some New Chiral *Brønsted* Acids for Organocatalysis and pK_a Values in MeO–$(CH_2)_2$–OH/H_2O – A Survey' (p. 1303 of this issue).

[1a][2][3]. The key intermediates for preparing C_2-symmetrical derivatives are the TADDOL (**1**) [4] itself or the dichloro derivation **3** [2][3] (*Scheme 1*). For the three compounds **1**–**3**, large-scale preparations have been described.

Scheme 1. *Preparation of the Chloro Alcohol* **2** *and of the Dichloro Derivative* **3** *from TADDOL* **1** [1a][2][3]



2 **1** **3**

2. TADDAMIN Derivatives. – The diamines **4** and **5** were prepared[6]) by heating in an autoclave the dichloro derivative **3** with NH_3 [5] or with $MeNH_2$, in the presence of NH_4Cl. Mixtures of the desired diamine and the *trans*-fused bicycles **6** and **7** are formed; the ratio depends on the reaction conditions (temperature, pressure, presence of excess NH_4Cl, see *Scheme 2* and *Exper. Part*); due to the strain of the *trans*-fused dioxa-aza-bicyclo[3.3.0]octane skeleton, there is partial hydrolysis of the acetonide group[7]) during chromatography on silica gel, with formation of the pyrrolidine-diol **8** (from **7**; *cf.* the *O*- and *S*-analogs **9**)[7]). Under optimized conditions, the ratios of mono- to bicyclic product are such that 60–65% of the TADDAMINs (=(4*S*,5*S*)-2,2,*N*,*N*′-tetramethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanamine)[8]) **4** and **5** can be isolated after chromatography of the crude product mixtures. Treatment of the dichloro compound with tenfold excess of $PhNH_2$ gave the *N*-Ph-substituted TADDAMIN **10** (*Scheme 2*).

In unsuccessful attempts to generate a chiral, TADDAMIN-derived carbene **A** – and transition metal complexes thereof [9] – from an orthoformic acid derivative of type **B** [10], or from a thiourea such as **11** (R = H) [11], we have also prepared the ureas **12a**, **13**, and the thiourea **12b**, as well as the compounds **14** and **15** obtained by benzylation at the S-atom; with *rac*-2-phenylethyl bromide, the two diastereoisomers (*R*)-**15** and (*S*)-**15** were formed in a 1:1 ratio, and one of them was isolated in pure crystalline form (see X-ray analysis in *Sect. 5*). The *N*-Ph-substituted TADDAMIN **10** could not be converted to a urea under various conditions. Finally, the TADDAMIN

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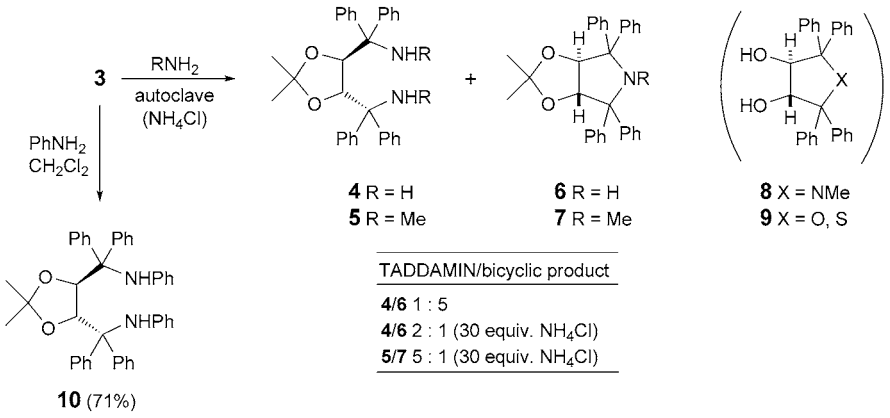
6) For the azido and thiocyanato route to the diamines **4** and **5**, see [2][3]. For a conversion of **4** to **5**, see also *Footnote 8*.

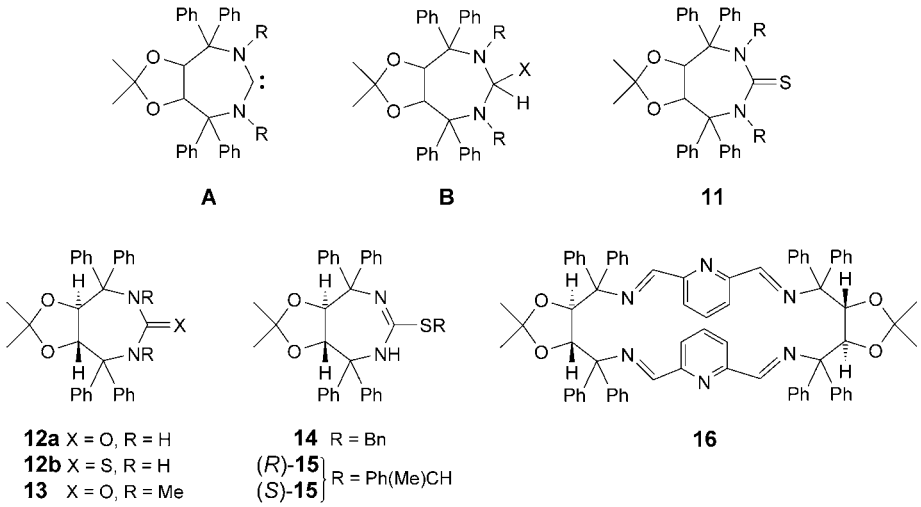
7) This has also been observed with the corresponding tetrahydrothiophene derivative [2] (*cf.* [6][7]).

8) The doubly lithiated TADDAMIN **5** was used to generate achiral Li-enolates (*cf.* of cyclohexanone), which, by way of coordination with the mono-lithio-TADDAMIN, reacted with electrophiles (aldehydes, nitro-olefines) to give chiral products of high diastereoisomer and enantiomer purity [8]; compound **5** was prepared for this investigation through the bis-formamide (R = CHO instead of Me in **5**) and $LiAlH_4$ reduction.

Scheme 2. *Preparation of the TADDAMINs* **4**–**8** *and* **10** *from the Dichloro Derivative* **3** *and* NH_3, $MeNH_2$, *or* $PhHN_2$. Optimization of the yields of diamines **4** and **5** by carrying out the reaction in the presence of excess NH_4Cl; no solvent was used. The heterocyclic diols **8** and **9** are formed by hydrolysis of the corresponding highly strained bicycles.

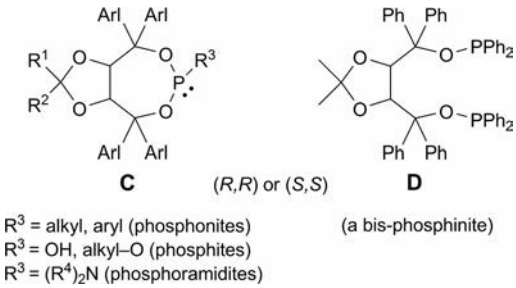


4 and pyridine-2,6-dicarbaldehyde were condensed (TsOH, molecular sieve (MS), in boiling toluene) to give the macrocycle **16** (67%), the crystals of which turned out to be one of the very few examples of an organic zeolite [12].



3. Phosphorous-Containing TADDOL Derivatives. – Since our first report on TADDOP derivatives of type **C** and **D**, and their use in enantioselective transition metal-catalyzed reactions [2][3][13], the compounds of type **C** have made a

remarkable *career* in many laboratories. This is demonstrated by the list of contents[9]) in a recent 32-page review article by *Lam* [14][10])[11]). Such TADDOP derivatives have, however, not only been employed in transition metal catalysis but also as stoichiometric reagents, for instance, for the preparation of β-amino phosphonates [20], or as kind of organocatalysts for a sophisticated cross benzoin reaction [21] (with type **C**, $R^3 = OH$).



Not surprisingly, all the phosphoramidites **17**, which we had prepared in the mid-1990s, have, with one exception, **17d**, now been described in the literature by other groups (see references in *Scheme 3*)[12]). Compounds **17** have a tendency to hydrolyze[13]) to phosphite **19**, which could be prepared from TADDOL and PCl_3 with aqueous workup in 81% yield[14]). Reactions of the intermediate TADDOP chloride with bulky amines (*cf.* 2,2,6,6-tetramethylpiperidin-4-one ethylene ketal, Ph_2NH, phenothiazine) did not lead to the corresponding compounds **17**; in one case, we isolated *ca.* 10% of the rather unstable compound **20** (with a P,P bond) from a reaction mixture[15]). Oxidation of the phosphoramidites **17** to the stable phosphoroxyamidites **18a**–**18f** (*Scheme 3*) was carried out with H_2O_2 (avoiding acidic conditions as with *m*-chloroperbenzoic acid).

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[9]) Hydrosilylations, hydroborations and diborations, hydrogenations, conjugate additions, allylic substitutions, nucleophilic allylations, cycloadditions, miscellaneous reactions [14].

[10]) For a comparison of TADDOP ligands with corresponding biaryl and BINOL derivatives in Rh-catalyzed multicomponent cycloadditions, see [15].

[11]) In some more or less randomly chosen papers published in 2011, the use of such phosphonites [16], phosphoramidites [17][18], and phosphites [19] is described for Pt-, Pd-, and Cu-catalyzed enantioselective diborations, direct arylations, conjugate allylations, 'diastereodivergent deracemization', and 1,4-additions of *Grignard* reagents, respectively.

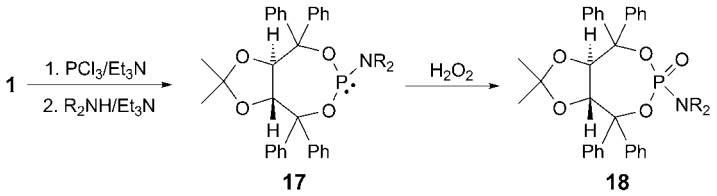
[12]) In the *Exper. Part*, we only present data differing from those published elsewhere; **17g** is commercially available; for **17**, R_2N = pyrrolidin-1-yl, there is an *Org. Synth.* procedure in preparation [22a]. For some spirocyclic phosphites and phosphonites, see [22b].

[13]) In the chromatographic purification (SiO_2) of the phosphoramidites **17**, we added some Et_3N to prevent this acid-catalyzed hydrolysis (see *Exper. Part*).

[14]) For previous preparations and an X-ray crystal structure of **19**, see [20] [21]. Although compounds of type **19** react as P-nucleophiles $(RO)_2P^{III}OH$, most of their crystal structures show a short P,O bond (*ca.* 1.45 Å) typical of a phosphate $(RO)_2P^{V}(O)H$ (search in the *Cambridge Crystallographic Data Base*).

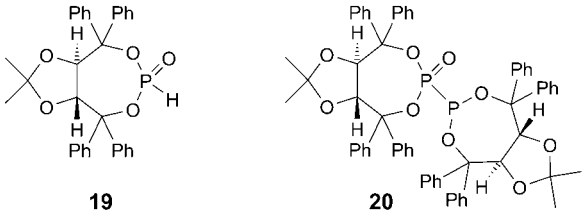
[15]) There is an *AB* system of signals in the ^{31}P-NMR spectrum at δ 158 (P^{III}) and 13.5 ppm (P^{V}). For full characterization of **20**, see *Exper. Part*.

Scheme 3. *Preparation of Phosphoramidites* **17**, *Phoshoroxyamidites* **18**, *and of the Phosphite* **19**, *and Isolation of the* P^{V}/P^{III} *Derivative* **20** *from TADDOL,* PCl_3, R_2NH, *and* H_2O_2



17 **18**

R [ref.]	**17** (yield [%])	**18** (yield [%])
$-(CH_2)_5-$ [23]	**a** (91)	**a** (71)
$-(CH_2)_2O(CH_2)_2-$ [24]	**b** (79)	**b** (59)
Bn [24]	**c** (69)	**c** (66)
Allyl	**d** (69)	**d** (72)
^{i}Pr [25]	**e** (88)	**e** (85)
Et [23b]	**f** (57)	**f** (80)
Me [26]	**g** (72)	
cHex [27]	**h** (79)	



19 **20**

Phosphonic and phosphoric acid derivatives of TADDOL have also been prepared by reaction of the Li_2-dialkoxide with $RPOCl_2$ (R = alkyl or Cl). As outlined in *Scheme 4*, the resulting primary products **21** and **23** can be used to prepare the phosphono-acetate **22** and the methyl ester **24**, the Na salt **25**, as well as the anhydride **26** of the phosphoric acid derivative. Obviously, these P^{V} compounds were prepared for testing stereoselective olefinations (*cf.* **21** and **22**) or phosphorylations (*cf.* **26**), which were, however, hitherto not seriously investigated[16]).

We also tried to prepare P-derivatives of the TADDAMIN **10** (*Scheme 5*), which was first treated with 2 equiv. of BuLi and then with a chloro- or dichlorophosphine. From the 'messy' product mixtures, the three compounds, **27**–**29**, could be isolated in pure form. Of the desired type of products with an N–P bond, only the methyl diazaphosphite **27** was found. The Ph_2PCl attacked the lithiated aniline moiety in the *para*-position to give the phosphine **28** and the diphosphine **29**. The crystal structure of compound **27** is shown in *Sect. 5*.

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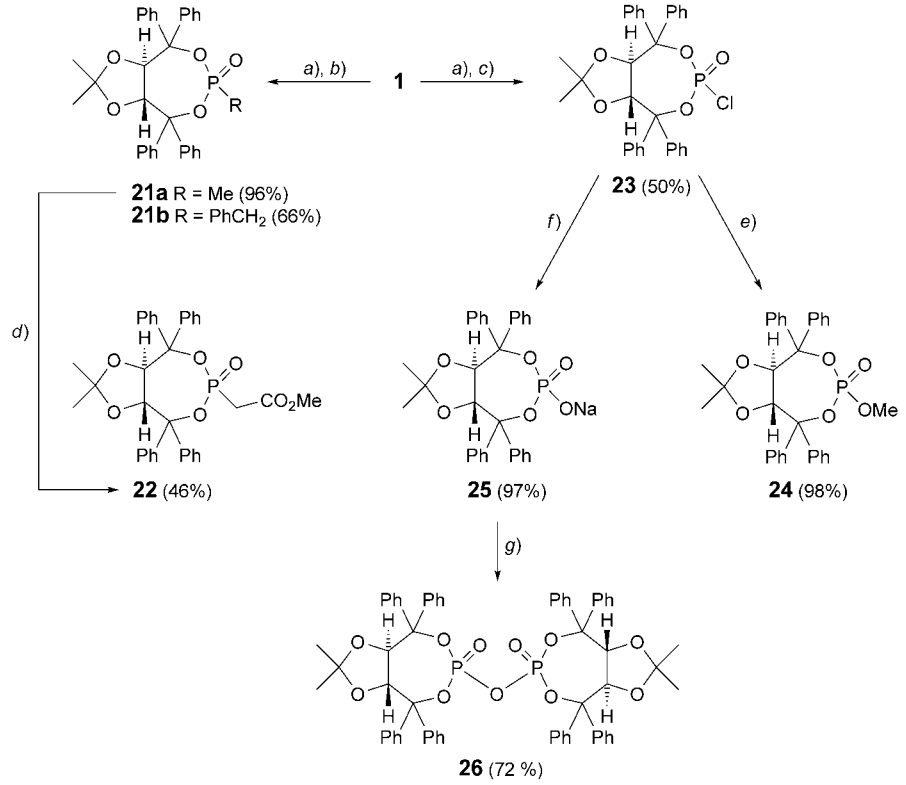
16) The retirement of the corresponding author *D. S.*, at the end of 2002 was accompanied by a dramatic reduction in the group size and by the necessity to decide which one of the research areas could be continued on small scale. The decision was made in favor of the investigation of peptides consisting of homologated proteinogenic amino acid residues [28].

Scheme 4. *TADDOP-P^V Derivatives* **21**–**26** *Prepared by Reaction of TADDOL with Phosphorylating Reagents and Subsequent Conversions.* The yields shown are those of purified, mostly recrystallized materials (see *Exper. Part*).

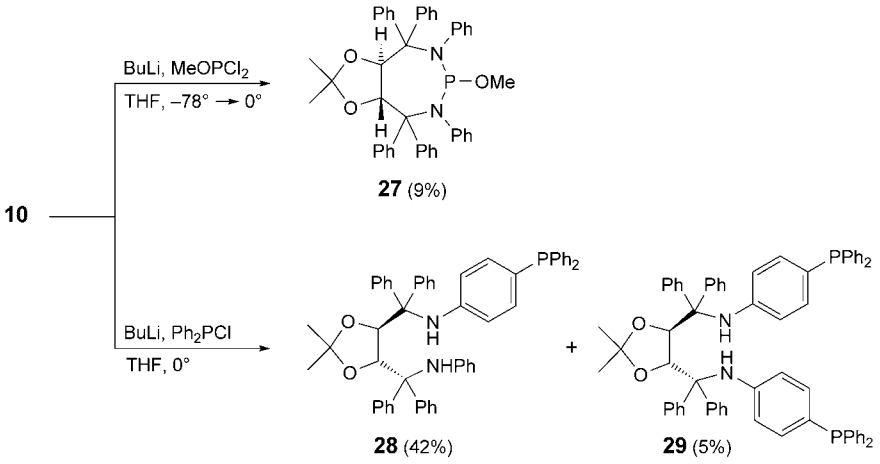


a) 2.2 equiv. of BuLi. *b*) $RPOCl_2$. *c*) $POCl_3$. *d*) **21a**, 4 equiv. of BuLi, then 4 equiv. of $NC–CO_2Me$, *e*) MeONa. *f*) NaOH/THF/H_2O. *g*) 1 equiv. of **23**/THF.

4. Results of Attempts to Replace the TADDOL OH Group(s) by R_2P Groups. – The successful application of DIOP (=(−)-2,2-dimethyl-4,5-bis[(diphenylphosphino)-methyl-1,3-dioxolone)-type ligands **E** in transition-metal chemistry [29] and the numerous uses of TADDOLs as ligands for *Lewis*-acidic metal centers [30] suggest that a C_2-symmetrical diphosphine **E** (*cf.* $R^1 = R^2 = R^4 = Ph$, $R^3 = Me$, 'TADDDP') or a C_1-symmetrical monophosphine **F** with a R_2P, and an amino or an alkoxy group might be excellent chiral ligands. Thus, we have undertaken an intensive investigation towards the preparation of phosphines of types **E** and **F**.

As outlined in *Scheme 6*, various starting materials **G**, reagents, and conditions were employed to test the possibility of forming C,P bonds either by nucleophilic (C–X + HPR_2 or metal–PR_2) or by electrophilic (C–metal + XPR_2) phosphinylation. In no case were we able to isolate a P-containing product, derived from TADDOL, from any of the reactions mixtures. What we did isolate were products of elimination: the dienes

Scheme 5. *Reactions of the TADDAMIN* **10** *with a Chloro- and Dichlorophosphine Derivative.* Besides the isolated and characterized products **27**–**29** many non-identified compounds were present in the crude reaction mixtures; from the reaction with Ph_2PCl, 30% of starting material **10** was recovered.



30[17]) and **32** [34], and the – optically active[18]) – epoxide **31** (*Scheme 6*); the butadiene could either have been formed by double elimination or by deoxygenation of the epoxide **31**, which, in turn, could have arisen from a process indicated in **H** (*Scheme 6*). Thus, the structural instability inherent to the TADDOL skeleton has reared its ugly head[19])[20])!

We than studied introductions of P substituents in the TADDOL scaffold by *Michaelis–Arbuzov* reactions [37], by using the dichloro compound **3**, the sulfate **34**, and the chloro methoxy derivative **35** [1a], and the phosphites $(MeO)_3P$, $(MeO)_2P$-Ph,or $MeOPPh_2$ (*Scheme 7*). The cyclic sulfate **34** was included in this investigation, because heterocyclic compounds of this type are known to undergo *O*,*P*-substitution with P-nucleophiles [38]. Compound **34** was prepared from the readily available sulfite **33** [3] by oxidation with $NaIO_4$ [39] (see also the crystal structure in *Sect. 5*). The reactions of the di- and monochloro derivatives **3** and **35**, respectively, with excess methyl phosphites required high temperatures and long reaction times to occur (120°/12 h). With the dichloride, cyclic phosphonate **36** and phosphinate **37** are formed in modest yields; a single diastereoisomer, **36**, and two diastereoisomers, (R_P)-**37** and (S_P)-**37** (in a ratio of 3:2), were isolated as products from the reaction with $(MeO)_3P$ and with $(MeO)_2PPh$, respectively. The configurations of the isomers **37** was assigned by an X-ray crystal-structure analysis of the (S_P)-isomer (see *Sect. 5*). The reaction of

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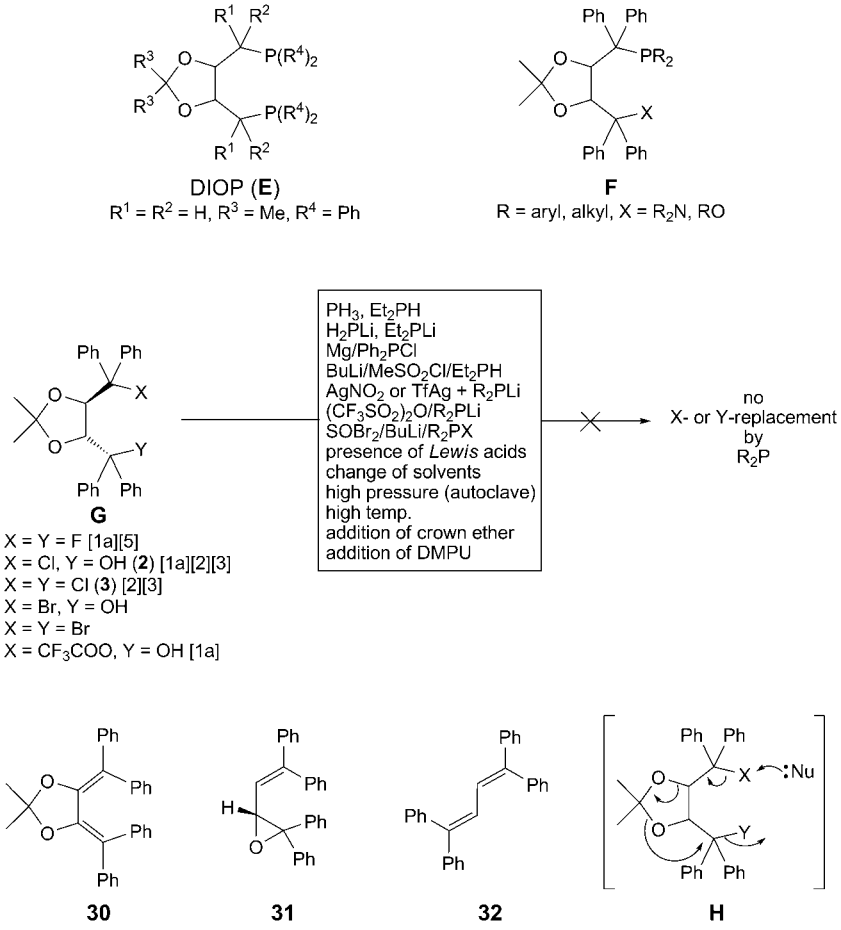
17) Yellow powder, isolated from the reaction of **G** (X = Y = Br) + **G** (X = Br, Y = OH) (ratio 2:1) with PH_3 pyridine in DMF in an autoclave; yield *ca.* 20%. Compound **30** has been isolated and characterized before from **3** by heating at 80° for 5 d in DMF [2].

18) The racemic form of **31** has been described before [35].

19) See also cationic rearrangements observed with the TADDOL carrying methoxyphenyl groups [36].

20) There might be a chance to prepare TADDDP derivatives by radical processes, the intermediates of which have a lower tendency to undergo rearrangements and/or eliminations.

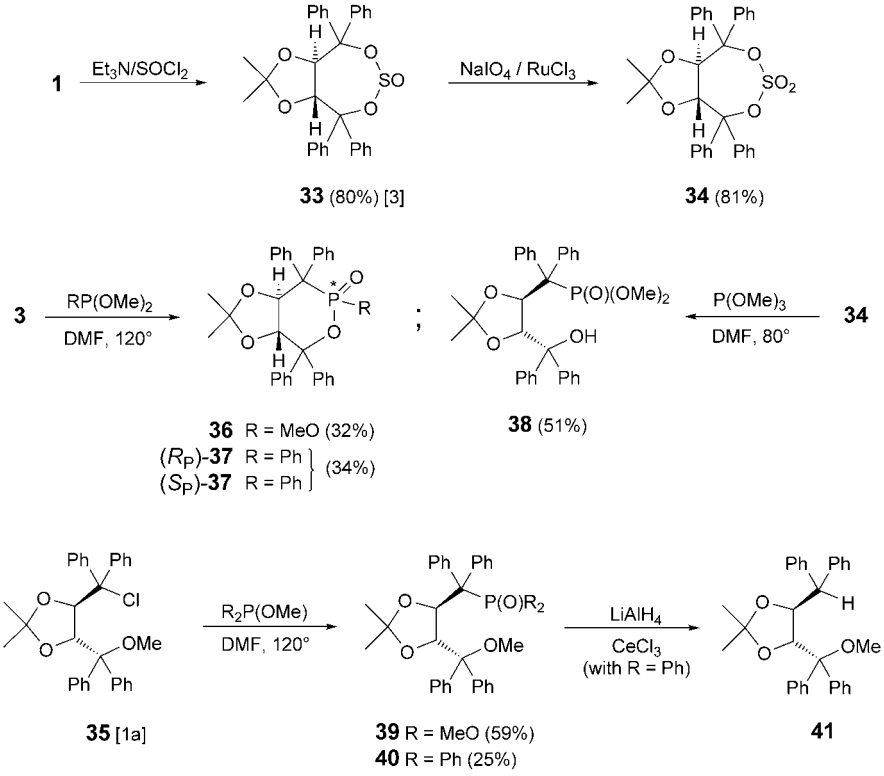
Scheme 6. *Phosphine Derivatives* **E** *and* **F** *with Structures Similar to That of TADDOL, and Attempted Reactions of F, Cl, Br, and Triflate Derivatives of TADDOL with Various* P^{III} *Reagents.* The dibromo derivative **G** (X = Y = Br) is rather unstable and could not be isolated in pure form (from **1** + $SOBr_2$/Et_3N); it was used in a mixture with the monobromo derivative **G** (X = Br, Y = OH). For the elimination products **30**–**32**, see *Footnotes 17* and *18*, and *Exper. Part.* In **H**, a generalized mechanistic picture is proposed for the formation of the tetraphenyl-butadiene monoepoxide **31**. A related double elimination of X and RO would lead to tetraphenyl-butadiene **32**, which could, however, also have been formed from **31**, by the known deoxygenation of epoxides with phosphines [31]. Solutions of $LiPH_2$ [32] and $LiPEt_2$ [33] in Et_2O were prepared according to literature procedures.



$(MeO)_3P$ with the cyclic sulfate took place at lower temperature (80°)[21]), which might be the reason why the monocyclic hydroxy phoshonate **38**, and not the bicyclic compound **36**, was isolated. Monocyclic products **39** and **40** were also accessible from the chloro methoxy derivative **35** (*vide infra* for the crystal structures of **38** and **39**).

[21]) ... it better had, because the sulfate **34** starts decomposing above *ca.* 95°!

Scheme 7. *Preparation of the Sulfate* **34** *and Cl/P- and SO_2O/P Replacements by the* Michaelis–Arbuzov *Reaction to Form P^V Analogs* **36**–**40** *of TADDOL with a Benzhydrylic C–P Bond.* Attempted deoxygenation to a phosphine leads to dephosphinylation.



Thus, we finally had replaced a TADDOL OH group by a P-containing substituent in the compounds **36**–**40**! To obtain a monodentate phosphine ligand of type **F** (*vide supra*; *Scheme 6*), we had, however, to remove an O- from the P-atom. This turned out to be impossible in all our experiments carried out with the methoxy phosphine oxide **40**, and employing almost 20 different reagents and conditions[22]). According to ^{31}P-NMR analyses, there were no P-containing compounds in the product mixtures. The only compound, which was sometimes obtained in good yields, was the product **41** of reductive removal of the P-atom. Thus, the weak benzhydrylic bond of the TADDOL-type skeleton has prevented success, again[20]).

5. X-Ray Crystal Structures. – The structures of ten of the compounds described in the previous sections are shown in *Figs. 1* (TADDAMIN derivatives) and *2* (P-containing compounds). Besides three monocyclic derivatives (**10** in *Fig. 1*, and **38**, **39**,

[22]) These include silanes, disilanes, $LiAlH_4$, $LiAlH_4/CeCl_3$, DIBAL-H, Cp_2ZrClH, BH_3, $BH_3/AlMe_3$, *Raney* Ni/H_2.

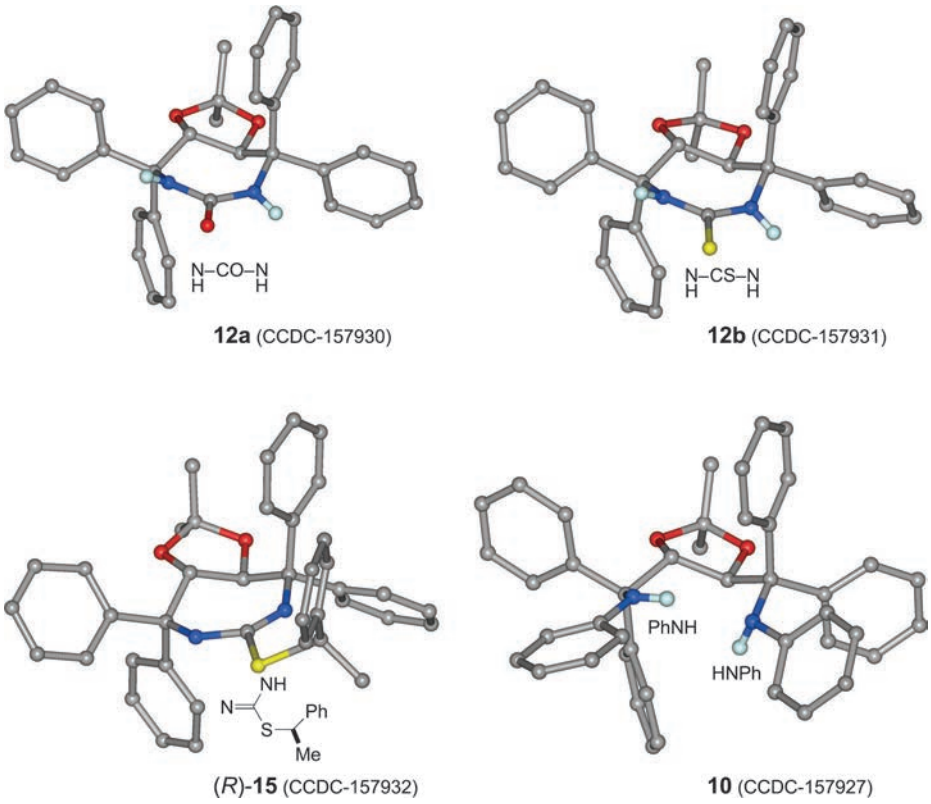


Fig. 1. *X-Ray crystal structures of TADDAMIN derivatives* **10**, **12a**, **12b**, *and* (R)-**15**

in *Fig. 2*), there are seven bicyclic ones, one [4.3.0] skeleton (**37** in *Fig. 2*) and six [5.3.0] skeletons (**12a**, **12b**, and **15** in *Fig. 1*, and **23**, **27**, and **34** in *Fig. 2*). In all but one structure, the characteristic TADDOL-type features are observed, with *quasi*-axial and *quasi*-equatorial Ph groups on the CPh_2 centers and antiperiplanar O–C–C–X conformations around the exocyclic C–C bonds. Only in the methoxy-phosphonate **39** (in *Fig. 2*), the $P(O)(OMe)_2$ group occupies the 'axial' position, with a *gauche*-relationship between the dioxolane O- and the P-atom (sterically and stereoelectronically favorable). In the other two monocyclic structures, the hydroxy-phosphonate **38** (*Fig. 2*) and the *N*,*N*′-diphenyl-TADDAMIN **10** (*Fig. 1*), there are H-bonds between the OH group and the P(O) O-atom in the first case, and between the anilino-NH group and the aniline N-atom in the second case[23]). In the structures **12a** and **12b** (*Fig. 1*), there is a deviation of the urea moieties from coplanarity, while, in the seven-membered ring of the 2-phenylethylsulfanyl-diazepin **15**, five ring atoms, more or less accurately, share a plane. The other three seven-membered rings, containing the sequences of atoms N–P–N

[23]) For a discussion of the delicate interplay between H-bonding, steric, and stereoelectronic effects that govern the conformation around the exocyclic dioxolane C–C bond in TADDOLs and their analogs, see [1a].

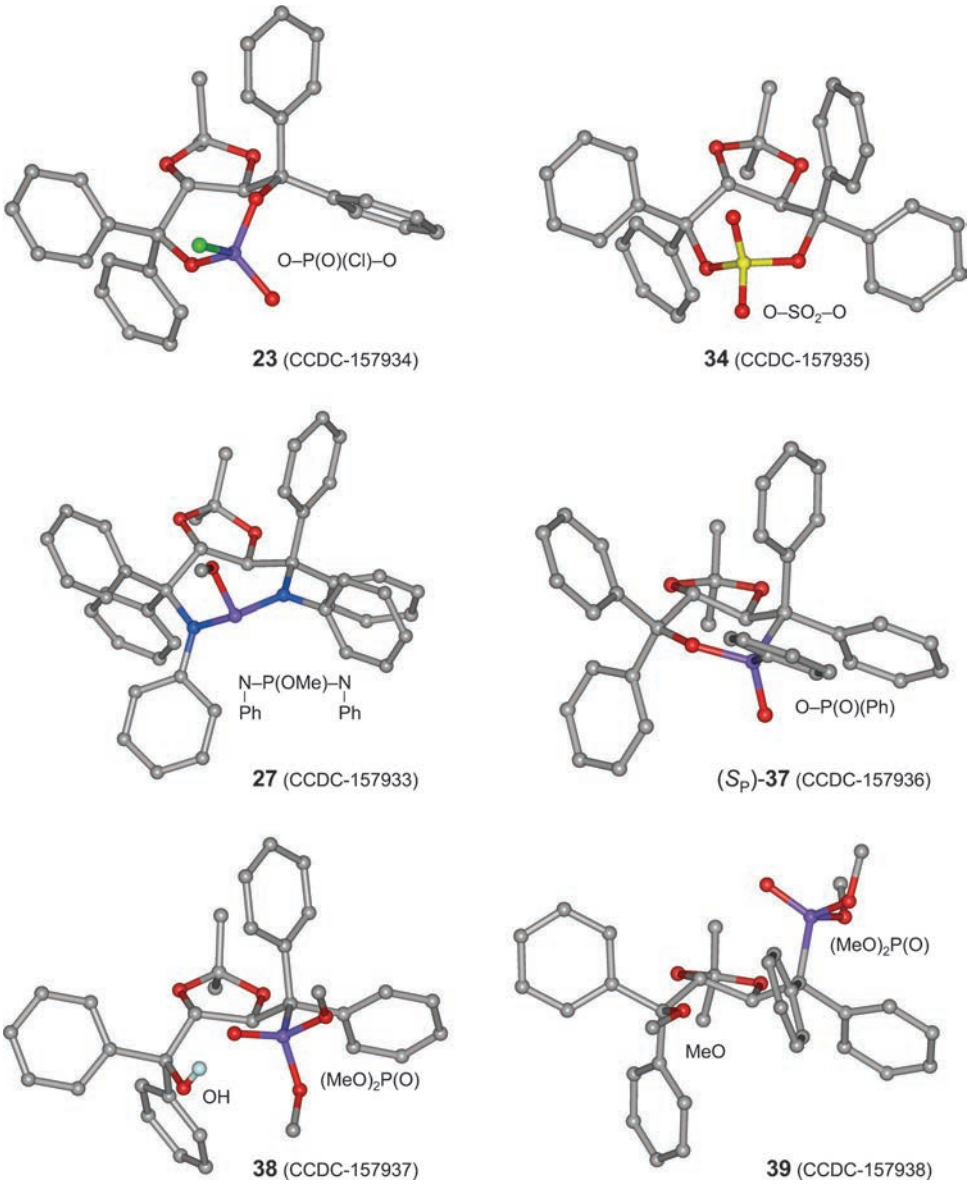


Fig. 2. *X-Ray crystal structures of the P-containing compounds* **23**, **27**, *and* **37**–**39**, *and of the sulfate* **34**

(**27**), O–P–O (**23**) and O–S–O (**34**) (*Fig. 2*), are strongly folded, and the oxa-phospha-cyclohexane ring in (S_P)-**37** exhibits a chair conformation with an axial P(O) O-atom and two axial Ph substituents (*Fig. 2*). In a metal complex of **27**, the two neighboring *N*-Ph groups (one *quasi*-axial, the other *quasi*-equatorial) will provide a strongly asymmetric environment; thus it would be worthwhile to improve the yield of the reaction of TADDAMIN **10** with phosphinylating reagents.

Of the 'formally' C_2-symmetrical TADDOL-derived compounds with bicyclo[3.3.0]octane, bicyclo[4.3.0]nonane, and bicyclo[5.3.0]decane skeletons (*Fig. 3*, top), described in the present series of papers [1] or in previous publications by us and others, essentially none has a geometrically exact C_2-structure in the crystal. Not only do different conformations around the C,Ph bonds lead to deviations from C_2-symmetry but also the conformations, *i.e.*, the folding of the rings, especially of the seven-membered rings (*Fig. 3*, bottom). On the other hand, the NMR spectra of these compounds are compatible with C_2-symmetry: there are, for instance, single signals for the Me H-atoms and for the bridgehead CH H-atoms in the ^{1}H-NMR spectra. Thus, at least on the NMR time scale, there is C_2-symmetry at ambient temperatures[24]).

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Experimental Part

1. *General. Abbreviations:* FC: flash chromatography; h.v.: high vacuum, 0.01 – 0.1 Torr. THF was freshly distilled over K before use. Et_3N was distilled over CaH_2. CH_2Cl_2 was used in *puriss.* quality. Solvents for workup and chromatography: pentane and hexane were distilled over P_4O_{10} or *Sikkon* (anh. $CaSO_4$; *Fluka*), AcOEt over *Sikkon*, Et_2O over KOH/$FeSO_4$, and CH_2Cl_2 over P_4O_{10}. PCl_3 was distilled before use. TADDOL and TADDOL derivatives were prepared according to literature procedures: TADDOL (**1**) [4], dichloride **3** [2][3], sulfite **33** [3], and chloride **35** [1a]. All other reagents were used as received from *Fluka* or *Aldrich*. All indicated reaction temp. were monitored with an internal thermometer (*Ebro-TTX-690* digital thermometer). Autoclaves used for reactions under high pressure: 80 (home-made, ETH Zürich), 240, and 450 ml (*Autoclave Engineers*); the pressure was monitored with a *Haenni-ED-510* apparatus (Piezoresitiver Druckmessumformer). TLC: *Macherey-Nagel Alugram SIL G/UV$_{254}$* or *Merck 60 F$_{254}$* silica-gel plates; detection by $UV_{254\,nm}$ light or I_2 or by dipping in/spraying with phosphomolybdic acid soln. [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot 4\,H_2O$ (10 g), H_2SO_4 (60 ml), H_2O (940 ml)], followed by heating. FC: *Fluka* silica gel 60 (0.040 – 0.063 mm), at *ca.* 0.3 bar. GC: *Carlo Erba Fractovap 4160* with *Carlo Erba DP 700 CE integrators* and *Macherey-Nagel FS-Hydrodex β-PM* cap. column (50 m × 0.25 mm i.d.) for enantiomer separations. M.p.: *Büchi-510* apparatus, uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter (10-cm, 1-ml cell), at r.t. IR spectra: *Perkin-Elmer-1620-FT-IR* spectrometer, in cm^{-1}. NMR Spectra: *Bruker AMX-500* (^{1}H: 500 and ^{13}C: 125 MHz), *AMX-400* (^{1}H: 400 and ^{13}C: 100 MHz), *Varian Gemini 300* (^{1}H: 300, ^{13}C: 75, and ^{19}F: 282 MHz), *Mercury 300* (^{1}H: 300 MHz, ^{13}C: 75, and ^{19}F: 282 MHz) or *Gemini 200* (^{1}H: 200, and ^{13}C: 50 MHz); chemical shifts (δ) in ppm downfield from TMS (δ 0.0) as internal standard; *J* values in Hz. MS: *VG Tribrid* (EI; 70 ev), *VG ZAB-2 SEQ* (FAB; 3-Nitrobenzyl alcohol matrix), *IonSpec Ultima* (FT-ICR-MALDI; 4.7 T; 2,5-

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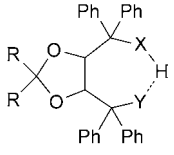
[24]) This is also true of the monocyclic compounds **i** with an intramolecular H-bond.



i

Dihydroxybenzoic acid matrix), *Bruker REFLEX* (TOF-MALDI; N_2 laser) or *Finnigan MAT TSQ 7000* (ESI) spectrometer; in *m/z* (% of basic peak). HR-MS: *IonSpec Ultima* (FT-ICR-MALDI; 4.7 T; 2,5-

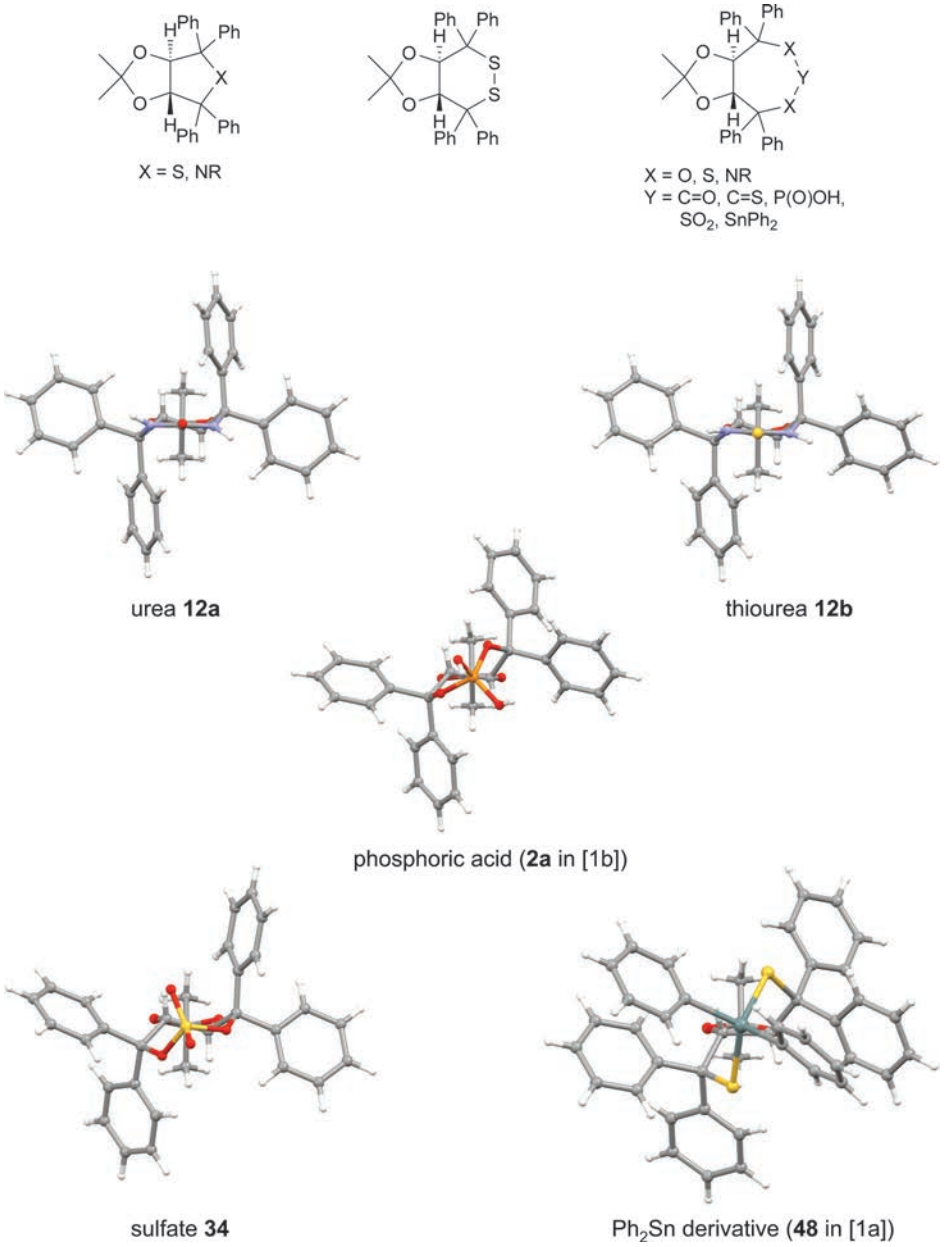


Fig. 3. *Different types of* C_2*-symmetrical bicyclic TADDOL derivatives and analogs* (*top*) *and view along the 'formal'* C_2 *axes in some of the corresponding crystal structures* (*bottom*). For the crystal structures with bicyclo[3.3.0] and -[5.3.0] skeletons, see the present paper and [1][3]; for the crystal structure of the cyclic disulfide with bicyclo[4.3.0] skeleton, see [2].

dihydroxybenzoic acid matrix). Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH Zürich.

2. *General Procedures. Preparation of the TADDAMINs* **4** *and* **5**, *and the Pyrrols* **6** *and* **7**. *General Procedure 1* (*GP 1*). Dichloro compound **3**, NH_4Cl (12.74 g, 240 mmol, 30 equiv.), and NH_3 (condensed at $-78°$) or $MeNH_2$ (25 ml, 0.8 mol) were placed in an autoclave, the mixture was heated to 100° (30 bar) and stirred for 2 d. The autoclave was cooled to r.t., and the excess NH_3 or $MeNH_2$ was vented. The crude product was dissolved in CH_2Cl_2/H_2O, and the aq. phase was neutralized with 1N HCl soln. The org. phase was washed with sat. aq. $NaHCO_3$ soln., H_2O, and sat. aq. NaCl soln., and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified.

Preparation of Urea-TADDOL Derivatives **12** and **13**. *General Procedure 2* (*GP 2*). *Caution: The following reactions should be carried out in a well-ventilated hood because of the toxicity of phosgene and thiophosgene.* In analogy to [40], a soln. of the appropriate TADDAMIN derivative (1 equiv.) in toluene (*ca.* 0.1M) was treated with Et_3N (2–3 equiv.) and cooled to 0°. Phosgene ($COCl_2$; 1 equiv.; 20% soln. in toluene) or thiophosgene (1 equiv.; neat) was added, and the mixture was stirred at 0° for 1.5 h. The mixture was warmed to r.t., washed quickly with H_2O, and the org. layer was separated and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified as indicated.

Preparation of Isothiourea-TADDOL Derivatives **14** *and* **15**. *General Procedure 3* (*GP 3*). To a soln. of thiourea derivative **12b** (1 equiv.) in DMF (0.08M) was added the appropriate alkyl bromide (1.0–1.3 equiv.) at r.t. After stirring for 7 h–7 d, sat. aq. $NaHCO_3$ soln. was added, the org. layer was separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. layers were washed with H_2O (3×), dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified as indicated.

Preparation of TADDOL-Derived Phosphoramidites **17a**–**17h**. *General Procedure 4* (*GP 4*). To a soln. of TADDOL **1** (1 equiv.) in CH_2Cl_2 (40 ml) was added Et_3N (2 equiv.) at $-50°$. After stirring for 5 min, PCl_3 (1 equiv.) was added dropwise over 15 min, which led to the formation of a white precipitate. The mixture was slowly warmed to $-20°$ (*ca.* 100 min), and then cooled to $-50°$ again. Et_3N (1 equiv.) and the appropriate amine (1 equiv.) were added consecutively, and the mixture was slowly warmed to r.t. After stirring at ambient temp. for further 12 h, sat. aq. NaCl soln. (50 ml) and sat. aq. $NaHCO_3$ soln. (5 ml) were added, the org. layer was separated, and the aq. layer was extracted with Et_2O (2×). The combined org. layers were dried ($MgSO_4$), and then the solvent was removed under reduced pressure. The crude product was purified as indicated.

Preparation of TADDOL-Derived Phosphoroxy Amidites **18a**–**18f**. *General Procedure 5* (*GP 5*). To a soln. of the appropriate phosphoramidite **17** (1 equiv.) in Et_2O (10 ml) was added 30% aq. H_2O_2 soln. (5–11 equiv.) ar r.t. The mixture was stirred for 12 h at ambient temp., and then sat. aq. NaCl soln. (10 ml) was added. The org. layer was separated, and the aq. layer was extracted with Et_2O (20 ml). The combined org. layers were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The crude product was purified by FC (3–4 drops of Et_3N added to 100 ml of solvent).

Preparation of P-Containing TADDOL Derivatives **36**–**40** *by* Michaelis–Arbuzov *Reaction. General Procedure 6* (*GP 6*). To a soln. of the appropriate TADDOL chloride or sulfate (1 equiv.) in DMF (0.1–4.5M) was added the indicated P compound (5–50 equiv.), and the mixture was stirred for 24 h at 80–120°. After cooling to r.t., the solvent was removed under reduced pressure (cooling trap!), and the residue was purified by FC.

3. *Preparation of the TADDAMINs* **4**–**8**, *and* **10**. *(4*S,5S*)-2,2-Dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanamine* (**4**) *and (3a*S,6*a*S*)-Tetrahydro-2,2-dimethyl-4,4,6,6-tetraphenyl-4*H*-1,3-dioxolo[4,5-*c*]pyrrole* (**6**). According to *GP 1*, **3** (5.00 g, 9.95 mmol) and NH_4Cl (15.94 g, 300 mmol, 30 equiv.) were placed in an autoclave (250 ml) under Ar. After cooling to $-78°$, 44 g of NH_3 were condensed in, and the mixture was heated to 100° (30 bar) and stirred for 2 d. The autoclave was cooled to r.t., and the excess NH_3 was vented. The crude product was dissolved in CH_2Cl_2/H_2O, and the aq. phase was neutralized with 1N HCl soln. The org. phase was washed with sat. aq. $NaHCO_3$ soln., H_2O, and sat. aq. NaCl soln, and dried ($MgSO_4$). The residue (**4**/**6** 2:1 by ^{1}H-NMR) was dissolved in Et_2O, whereby **4** (1.25g, 34%) precipitated as a colorless powder. The mother liquor was purified by FC (SiO_2 (100 g); Et_2O) to afford another crop of **4** (1.59 g, 34%). Total yield: 2.84 g (61%). $[\alpha]_D^{r.t.} = -43.1$ ($c = 0.98$,

$CHCl_3$) ([3]: $[\alpha]_D^{r.t.} = -42.96$ ($c = 0.68$, $CHCl_3$). The anal. data matched those reported in [2][3][5]. For anal. data of **6**, see below and [3].

(4S,5S)-N⁴,N⁵,2,2-Tetramethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanamine (**5**), *(3aS,6aS)-Tetrahydro-2,2,5-trimethyl-4,4,6,6-tetraphenyl-4H-1,3-dioxolo[4,5-c]pyrrole* (**7**), *and (3S,4S)-1-Methyl-2,2,5,5-tetraphenylpyrrolidine-3,4-diol* (**8**). According to *GP 1*, **3** (4.00 g, 7.96 mmol), NH_4Cl (12.74 g, 240 mmol), and $MeNH_2$ (25 ml, 0.8 mol) were placed in an autoclave (80 ml), the mixture was heated to 100° (30 bar) and stirred for 2 d. The autoclave was cooled to r.t., and the excess $MeNH_2$ was vented. The crude product was dissolved in CH_2Cl_2/H_2O, and the aq. phase was neutralized with 1N HCl soln. The org. phase was washed with sat. aq. $NaHCO_3$ soln., H_2O, and sat. aq. NaCl soln, and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified by FC (2 ×) (1. pentane/CH_2Cl_2 5:7; 100 g of SiO_2; 2. toluene/AcOEt 9:1; 150 g of SiO_2) to afford **5** (2.80 g, 62%), **7** (0.30 g, 8%), and **8** (0.23 g, 7%).

Data of **5**. M.p. 197–200° ([2]: M.p. 200–203°). The anal. data matched those of [2][3].

Data of **7**. White foam. R_f (pentane/CH_2Cl_2 5:7) 0.65. $[\alpha]_D^{r.t.} = -95.2$ ($c = 1.09$, $CHCl_3$). IR ($CHCl_3$): 3692*w*, 3087*w*, 3058*m*, 3007*s*, 2936*m*, 2803*w*, 1953*w*, 1813*w*, 1599*m*, 1493*m*, 1444*s*, 1383*s*, 958*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.22 (*s*, 2 Me); 2.40 (*s*, NMe); 4.82 (*s*, 2 CH); 7.13–7.16 (*m*, 4 arom. H); 7.22–7.32 (*m*, 16 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.7, 31.53 (Me); 70.09 (C); 81.73 (CH); 118.65 (C); 126.56, 127.08, 127.31, 127.93, 129.25, 129.47 (CH); 142.21, 142.82 (C). EI-MS: 461 (7, M^+), 384 (83), 362 (30), 346 (37), 207 (53), 196 (100), 194 (90), 179 (77), 167 (53), 118 (67). Anal. calc. for $C_{32}H_{31}NO_2$ (461.61): C 83.26, H 6.77, N 3.03; found: C 83.09, H 6.99, N 2.91.

Data of **8**. M.p. 192–195°. R_f (toluene/AcOEt 9:1) 0.85. $[\alpha]_D^{r.t.} = -52.4$ ($c = 0.94$, $CHCl_3$). IR ($CHCl_3$): 3555*m*, 3059*m*, 3007*s*, 2807*w*, 1962*w*, 1897*w*, 1815*w*, 1757*w*, 1598*w*, 1490*s*, 1443*s*, 1401*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.55–1.64 (*m*, 2 OH); 2.30 (*s*, Me); 4.65–4.71 (*m*, 2 CH); 7.08–7.11 (*m*, 4 arom. H); 7.25–7.39 (*m*, 16 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 30.10 (Me); 73.38 (C); 76.36 (CH); 127.21, 127.40, 127.60, 127.91, 129.89, 129.97 (CH); 142.91, 142.58 (C). FAB-MS: 421 (23, M^+), 420 (27), 419 (36), 360 (19), 345 (17), 344 (42), 343 (100), 209 (12), 208 (12), 197 (13), 196 (43), 195 (16), 179 (14), 167 (43), 165 (17), 148 (34), 117 (30).

(3aS,6aS)-Tetrahydro-2,2-dimethyl-4,4,6,6-tetraphenyl-4H-1,3-dioxolo[4,5-c]pyrrole (**6**). According to *GP 1*, **3** (15.0 g, 33.5 mmol) was placed in an autoclave (450 ml) and dissolved in THF (200 ml). The autoclave was cooled to −50°, NH_3 (65.0 g, 3.80 mol) was condensed in. The mixture was heated to 100° (39 bar) and stirred for 80 h. After cooling to r.t., excess NH_3 was vented, and the crude product was dissolved in CH_2Cl_2 (400 ml). After addition of H_2O (200 ml), the aq. phase was neutralized with 1N HCl soln. For better phase separation, sat. aq. NaCl soln. (100 ml) and CCl_4 (300 ml) were added. The org. phase was washed with H_2O (2 × 400 ml) and sat. aq. NaCl soln. (250 ml), and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford crude **6** (12.5 g, 83%). For further purification, a sample (5.00 g) was purified by FC (SiO_2 (800 g); pentane/Et_2O 35:1) and subsequent trituration with pentane (15 ml; 30 min under reflux and 1 h at r.t.) to yield anal. pure **6** (3.00 g). Colorless solid. M.p. 140–141° ([3]: M.p. 140–141°). $[\alpha]_D^{r.t.} = -230.9$ ($c = 1.01$, $CHCl_3$) ([3]: $[\alpha]_D^{r.t.} = -222.6$ ($c = 0.5$, $CHCl_3$)). The anal. data matched those of [3].

(4S,5S)-2,2-Dimethyl-N⁴,N⁵,α,α,α′,α′-hexaphenyl-1,3-dioxolane-4,5-dimethanamine (**10**). A soln. of **3** (5.55 g, 11.02 mmol) in CH_2Cl_2 (11 ml) was treated with $PhNH_2$ (10.0 ml, 109.6 mmol), and the mixture was stirred at r.t. for 16 h. The brown soln. was washed with H_2O, dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude product was purified by FC (SiO_2 (200 g); CH_2Cl_2), and subsequent trituration with Et_2O under reflux afforded **10** (4.81 g, 71%). Colorless crystals. M.p. 239–240°. R_f (CH_2Cl_2) 0.75. $[\alpha]_D^{r.t.} = -73.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3286*m*, 3061*m*, 3007*m*, 2935*w*, 1953*w*, 1828*w*, 1601*s*, 1496*s*, 1447*m*, 1372*m*, 1083*m*, 1064*m*, 891*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.91 (*s*, 2 Me); 4.28 (*s*, 2 CH); 5.94 (*s*, 2 NH); 6.27 (*d*, $J = 7.7$, 4 arom. H); 6.53 (*t*, $J = 2.6$, 2 arom. H); 6.81–6.84 (*m*, 4 arom. H); 7.07–7.15 (*m*, 6 arom. H); 7.32–7.34 (*m*, 4 arom. H); 7.42–7.48 (*m*, 6 arom. H); 7.78–7.80 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.7 (Me); 67.13 (C); 84.65 (CH); 107.48 (C); 116.84, 118.23, 126.65, 127.61, 127.81, 128.28, 128.74, 130.78 (CH); 139.04, 142.46, 145.02 (C). FAB-MS: 618 (8, $[M + 2]^+$), 617 (18, $[M + 1]^+$), 466 (6), 447 (10), 446 (25), 432 (35), 432 (100), 388 (8), 373 (9), 345 (11), 259 (11), 258 (33), 179 (8). Anal. calc. for $C_{43}H_{40}N_2O_2$ (616.81): C 83.73, H 6.54, N 4.54; found: C 83.69, H 6.65, N 4.50.

4. *Preparation of the TADDAMIN derivatives* **12**–**16** *and* **27**–**29**. *(3aS,8aS)-Hexahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-6*H-*1,3-dioxolo[4,5-*e*][1,3]diazepin-6-one* (**12a**). A soln. of **4** (2.10 g, 4.50 mmol) in toluene (60 ml) was treated with Et_3N (1.26 ml, 9.0 mmol) and phosgene (2.33 ml, 4.50 mmol; 20% soln. in toluene) according to *GP 2*. The crude product was dissolved in Et_2O, and **12a** (0.37 g) was precipitated by addition of pentane as a colorless solid. The solvent of the mother liquor was removed, and the residue was purified by FC (SiO_2 (180 g); pentane/Et_2O 1:2) to afford further **12a** (1.07 g). White foam. Total yield 1.44 g (64%). M.p. 224–225°. R_f (pentane/Et_2O 1:2) 0.32. $[\alpha]_D^{r.t.} = -100.6$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3394*m*, 3076*w*, 3007*m*, 2912*w*, 1953*w*, 1897*w*, 1810*w*, 1759*w*, 1598*w*, 1446*s*, 1493*m*, 1405*s*, 600*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.25 (*s*, 2 Me); 4.54 (*s*, 2 CH); 5.16 (*s*, 2 NH); 7.12–7.15 (*m*, 4 arom. H); 7.22–7.26 (*m*, 6 arom. H); 7.35–7.40 (*m*, 6 arom. H); 7.59–6.22 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.90 (Me); 65.94 (C); 79.14 (CH); 109.89 (C); 127.52, 127.72, 127.80, 128.05, 128.40, 128.59, 129.03 (CH); 140.83, 144.51, 160.20 (C). EI-MS: 490 (5, M^+), 390 (20), 237 (10), 207 (10), 182 (100). Anal. calc. for $C_{32}H_{30}N_2O_3$ (490.61): C 78.34, H 6.16, N 5.71; found: C 77.89, H 6.38, N 5.57.

*(3aS,8aS)-Hexahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-6*H-*1,3-dioxolo[4,5-*e*][1,3]diazepine-6-thione* (**12b**). A soln. of **4** (3.00 g, 6.46 mmol) in toluene (50 ml) was treated with Et_3N (2.70 ml, 19.40 mmol) and thiophosgene ($CSCl_2$; 0.50 ml, 6.52 mmol) according to *GP 2*. The crude product was triturated with Et_2O for 15 min to afford **12b** (1.03 g). After removing the solvent from the filtrate, the residue was triturated with Et_2O to afford further **12b** (0.40 g). Purification of the mother liquor by FC (SiO_2; Et_2O) afforded further **12b** (1.00 g). Total yield: 2.43 g (74%). Beige powder. M.p. >310°. R_f (pentane/Et_2O 2:3) 0.66. $[\alpha]_D^{r.t.} = -218.7$ ($c = 0.98$, $CHCl_3$). IR ($CHCl_3$): 3387*w*, 3059*w*, 2990*m*, 2046*m*, 1811*w*, 1734*w*, 1657*w*, 1599*m*, 1525*m*, 1612*s*, 1494*s*, 1446*s*, 1428*m*, 1381*m*, 1104*s*, 875*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.20 (*s*, 2 Me); 4.59 (*s*, 2 CH); 6.85 (*s*, 2 NH); 7.12–7.15 (*m*, 4 arom. H); 7.25–7.29 (*m*, 6 arom. H); 7.39–7.43 (*m*, 6 arom. H); 7.60–7.63 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.89 (Me); 70.53 (C); 77.91 (CH); 110.84 (C); 127.65, 127.98, 128.11, 128.52, 128.80, 129.29 (CH); 139.56, 143.32, 185.87 (C). FAB-MS: 1013 (22, $[2M + 1]^+$), 507 (100, $[M + 1]^+$), 237 (30), 179 (75). Anal. calc. for $C_{32}H_{30}N_2O_2S$ (506.67): C 75.86, H 5.97, N 5.53, S 6.33; found: C 75.90, H 6.51, N 5.58, S 6.35.

*(3aS,8aS)-Hexahydro-2,2,5,7-tetramethyl-4,4,8,8-tetraphenyl-6*H-*1,3-dioxolo[4,5-*e*][1,3]diazepin-6-one* (**13**). A soln. of **5** (95 mg, 0.19 mmol) in toluene (2.5 ml) was treated with Et_3N (26 ml, 9.0 mmol) and $COCl_2$ (100 ml, 0.19 mmol; 20% soln. in toluene) according to *GP 2*. The crude product was purified by FC (SiO_2 (40 g); pentane/Et_2O 1:2) to afford **13** (73 mg, 73%). White solid foam. Drying at 100° in h.v. for 3 h afforded **13**. Colorless solid. M.p. 162–163°. R_f (pentane/Et_2O 2:3) 0.66. $[\alpha]_D^{r.t.} = -136.4$ ($c = 0.94$, $CHCl_3$). IR ($CHCl_3$): 3671*w*, 3061*m*, 3007*s*, 2936*m*, 2635*w*, 2461*w*, 2256*w*, 1957*w*, 1750*s*, 1612*s*, 1493*s*, 1446*s*, 1337*s*, 600*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.94 (*s*, 2 Me); 2.46 (*s*, 2 NMe); 5.33 (*s*, 2 CH); 7.25–7.38 (*m*, 20 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.75, 37.54 (Me); 71.99 (C); 80.82 (CH); 111.74 (C); 127.19, 127.33, 127.76, 128.13, 128.68, 130.54 (CH); 140.28, 141.96, 164.84 (C). FAB-MS: 1037 (19, $[2M + 1]^+$), 519 (100, $[M + 1]^+$), 460 (30), 418 (17), 265 (25), 179 (48). Anal. calc. for $C_{34}H_{34}N_2O_3$ (518.66): C 78.74, H 6.61, N 5.40; found: C 78.58, H 6.81, N 5.38.

*(3aS,8aS)-3a,5,8,8a-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-6-[(phenylmethyl)sulfanyl]-4*H-*1,3-dioxolo[4,5-*e*][1,3]diazepine* (**14**). A soln. of **12b** (830 mg, 1.64 mmol) in DMF (20 ml) was treated with BnBr (0.25 ml, 2.1 mmol) according to *GP 3* for 7 h. Purification by FC (SiO_2 (40 g); pentane/Et_2O 5:1) afforded **14** (850 mg, 87%). White foam. For anal. purposes, a sample was crystallized from pentane/Et_2O by slow evaporation of the solvent. M.p. 202–204°. R_f (pentane/Et_2O 1:1) 0.84. $[\alpha]_D^{r.t.} = -142.5$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3385*w*, 3062*w*, 3008*m*, 1667*s*, 1600*w*, 1494*s*, 1445*s*, 1372*m*, 1096*s*, 1032*w*, 881*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*s*, Me); 1.05 (*s*, Me), 4.12 (*d*, $J = 13.7$, CH_2); 4.28 (*d*, $J = 13.7$, CH_2); 4.58 (*d*, $J = 9.05$, CH); 4.71 (*s*, NH); 4.76 (*d*, $J = 9.05$, CH); 7.16–7.30 (*m*, 21 arom. H); 7.35–7.38 (*m*, 2 arom. H); 7.50–7.52 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.8, 27.0 (Me); 36.9 (CH_2); 68.1, 71.4 (C); 77.8, 78.5 (CH); 110.5 (C); 126.3, 126.6, 126.8, 126.9, 127.42, 127.44, 127.5, 127.6, 127.8, 128.4, 128.5, 128.6, 129.0, 129.7, 130.2 (CH); 138.6, 140.9, 142.0, 145.2, 146.5, 148.8 (C). HR-MS: 597.2573 ($[M + H]^+$, $C_{39}H_{37}N_2O_2S^+$; calc. 597.2576 (−0.33 ppm)). MALDI-FT-ICR-MS: 597.3 (100, $[M + H]^+$), 546.3 (32). Anal. calc. for $C_{39}H_{36}N_2O_2S$ (596.79): C 78.49, H 6.08, N 4.69, S 5.37; found: C 78.60, H 6.37, N 4.75, S 5.44.

*(3aS,8aS)-3a,5,8,8a-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-6-[[(1*R*)- and (1*S*)-1-phenylethyl]-sulfanyl]-4*H-*1,3-dioxolo[4,5-*e*][1,3]diazepine* ((*R*)-**15** *and* (*S*)-**15**, resp.). A soln. of **12b** (2.0 g, 3.9 mmol)

in DMF (50 ml) was treated with 1-phenylethyl bromide (0.54 ml, 4.0 mmol) according to *GP 3* for 7 d. Purification by FC (3 ×; 1. SiO_2 (100 g); pentane/Et_2O 15:1; 2. SiO_2 (160 g); toluene/hexane 1:1; 3. SiO_2 (36 g); toluene/hexane 1:2) afforded diastereoisomerically enriched (*R*)-**15** (350 mg) and (*S*)-**15** (360 mg) besides a mixture of (*R*)-**15**/(*S*)-**15** (450 mg, 19%) and starting material **12b** (675 mg, 34%). Recrystallization from Et_2O afforded pure (*R*)-**15** (320 mg, 13%). Colorless crystals. Similarly, (*S*)-**15** (126 mg, 5%) was obtained by recrystallization from hexane. Colorless crystals. Total yield of **15**: 37%.

Data of (*R*)-**15**. M.p. 231–232°. R_f (toluene) 0.71. $[\alpha]_D^{r.t.} = -54.8$ ($c = 1.06$, $CHCl_3$). IR ($CHCl_3$): 3390*m*, 3064*w*, 3008*m*, 2926*w*, 1662*s*, 1600*w*, 1493*s*, 1474*s*, 1445*s*, 1372*m*, 1096*s*, 1029*w*, 960*w*, 880*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*s*, Me); 1.05 (*s*, Me); 1.52 (*d*, $J = 7.3$, Me); 4.59 (*d*, $J = 9.1$, CH); 4.66 (*d*, $J = 9.0$, CH); 4.66 (*s*, NH); 4.78 (*q*, $J = 7.3$, CH); 6.98–7.01 (*m*, 2 arom. H); 7.09–7.46 (*m*, 19 arom. H); 7.49–7.51 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$) 22.5, 26.8, 27.0 (Me); 45.9 (CH); 67.8, 71.4 (C); 77.9, 78.5 (CH); 110.5 (C); 126.3, 126.4, 126.7, 127.0, 127.4, 127.45, 127.49, 127.51, 127.8, 128.42, 128.45, 128.6, 128.7, 130.1 (CH); 141.2, 141.7, 144.1, 145.3, 146.8, 148.9 (C, N_2CS). HR-MS: 611.2728 ($[M+H]^+$, $C_{40}H_{39}N_2O_2S^+$; calc. 611.2732 (−0.65 ppm)). MALDI-FT-ICR-MS: 611.3 (7, $[M + H]^+$); 507.2 (79), 431.2 (19), 345.2 (42), 273.0 (100), 267.1 (29). Anal. calc. for $C_{40}H_{38}N_2O_2S$ (610.82): C 78.66, H 6.27, N 4.59, S 5.25; found: C 78.73, H 6.48, N 4.45, S 5.24.

Data of (*S*)-**15**. M.p. 197–198°. R_f (toluene) 0.59. $[\alpha]_D^{r.t.} = -264.7$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3386*w*, 3062*w*, 3007*m*, 1664*s*, 1600*w*, 1477*s*, 1445*s*, 1372*m*, 1172*s*, 1096*s*, 1028*w*, 960*w*, 880*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.85 (*s*, Me); 1.00 (*s*, Me); 1.70 (*d*, $J = 7.1$, Me); 4.52 (*d*, $J = 9.0$, CH); 4.66 (*q*, $J = 7.1$, CH); 4.66 (*s*, NH); 4.79 (*d*, $J = 9.0$, CH); 7.04–7.07 (*m*, 2 arom. H); 7.14–7.31(*m*, 21 arom. H); 7.49–7.52 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 22.4, 26.7, 27.0 (Me); 46.2 (CH); 68.2, 71.6 (C); 77.4, 78.2 (CH); 110.5 (C); 126.3, 126.6, 126.9, 127.3, 127.4, 127.5, 127.6; 127.7, 128.3, 128.56, 128.60, 129.7, 130.4 (CH); 140.8, 142.2, 143.3, 145.4, 146.2, 148.7 (C, N_2CS). HR-MS: 611.2725 ($[M+H]^+$, $C_{40}H_{39}N_2O_2S^+$; calc. 611.2732 (−1.1 ppm)). MALDI-FT-ICR-MS: 633.3 (8, $[M + Na]^+$), 611.3 (9, $[M + H]^+$); 507.2 (100), 431.2 (23), 345.2 (51), 267.1 (36). Anal. calc. for $C_{40}H_{38}N_2O_2S$ (610.82): C 78.66, H 6.27, N 4.59, S 5.25; found: C 78.44, H 6.39, N 4.60, S 5.26.

*(3a*S*,5*E*,12*E*,14a*S*,17a*S*,19*E*,26*E*,28a*S*)-3a,4,14,14a,17a,18,28,28a-Octahydro-2,2,16,16-tetramethyl-4,4,14,14,18,18,28,28-octaphenyl-7,11:25,21-dinitrilo-1,3-dioxolo[4,5-*c*][1,3]dioxolo[4,5-*p*][1,6,14,19]tetraazacyclohexacosine* (**16**). To a soln. of **4** (0.60 g, 1.3 mmol) in toluene (150 ml), in a 500-ml round-bottomed flask, equipped with a condenser and 4-Å molecular sieve (1 g) in the gas phase [41], was added pyridine-2,6-dicarbaldehyde (0.174 g, 1.3 mmol) and $TsOH \cdot H_2O$ (24 mg, 0.13 mmol). After 3 h heating under reflux, the solvent was evaporated, and the residue was dried under h.v. Purification by FC (alumina (75 g); pentane/Et_2O) yielded **16** (0.47 g, 67%). Colorless solid. M.p. 304–305°. R_f (alumina, pentane/Et_2O 1:1) 0.8. $[\alpha]_D^{r.t.} = -131.91$ ($c = 1.08$, $CHCl_3$). IR ($CHCl_3$): 3061*m*, 3007*s*, 2934*w*, 1642*s*, 1584*w*, 1566*w*, 1494*s*, 1445*s*, 1380*m*, 1334*m*, 1164*m*, 1071*s*, 1022*m*, 930*m*, 906*m*, 879*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.21 (*s*, Me); 0.91 (*s*, Me); 4.81 (*s*, CH); 6.28 (*s*, CH); 7.01–7.22 (*m*, 8 arom. H); 7.18 (*s*, CHN); 7.32–7.51 (*m*, 11 arom. H); 7.63–7.67 (*m*, 4 arom. H); 8.17 (*s*, CHN). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.3, 27.7 (Me); 75.7, 76.3 (C); 80.5, 80.8 (CH); 106.1, 114.0 (C); 120.9, 121.9, 126.4, 126.5, 126.9, 127.0, 127.1, 127.5, 127.8, 128.4, 128.8, 130.3, 131.3, 132.5, 136.5 (CH); 138.0, 141.6, 145.0, 145.9, 153.6, 155.3 (C); 156.9, 159.1 (CHN). MALDI-FT-ICR-MS: 1149.5 (100, $[M + Na]^+$); 1127.2 (25, $[M + H]^+$), 883.4 (65), 383.2 (91). Anal. calc. for $C_{76}H_{66}N_6O_4$ (1127.40): C 80.97, H 5.90, N 7.45; found: C 80.93, H 6.09, N 7.44.

*(3a*S*,8a*S*)-Hexahydro-6-methoxy-2,2-dimethyl-4,4,5,7,8,8-hexaphenyl-4*H*-1,3-dioxolo[4,5-*e*][1,3,2]diazaphosphepine* (**27**). To a soln. of **10** (1.54 g, 2.5 mmol) in THF (20 ml), BuLi (3.4 ml, 5.3 mmol) was added dropwise at −70°. The soln. was warmed to −10° (*ca.* 20 min), then cooled again to −70°, and $MeOPCl_2$ (0.27 ml, 0.28 mmol) was added. The dry ice was removed from the cooling bath, and the mixture was warmed slowly to r.t. (*ca.* 3 h) and stirred for further 2 h at r.t. The solvent was removed under reduced pressure, and the residue (dried under h.v.) was purified by FC (2 ×; 1. SiO_2 (75 g); hexane/Et_2O 10:1; 2. SiO_2 (18 g); hexane/Et_2O 20:1) to afford **27** (150 mg, 9%). Colorless solid. M.p. 142–143° (dec.). R_f (hexane/Et_2O 10:1) 0.5. $[\alpha]_D^{r.t.} = -15.0$ ($c = 0.78$, $CHCl_3$). IR ($CHCl_3$): 3062*m*, 3003*m*, 2935*m*, 1595*m*, 1488*s*, 1445*m*, 1381*m*, 1170*m*, 1075*s*, 1022*s*, 948*w*, 911*w*, 891*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.32 (*s*, Me); 0.51 (*s*, Me); 3.16 (*d*, ^3J (H,P) = 14.0, MeO); 5.89 (*d*, $J = 7.6$, CH); 6.29 (*d*, $J = 7.6$, CH); 6.78–7.37 (*m*, 26 arom. H); 7.68–7.70 (*m*, 2 arom. H); 7.92–7.94 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.7, 27.8, 54.6 (*d*, ^2J (C,P) = 36.1) (Me); 75.8 (*d*, $^2J = 7.5$), 79.3 (*d*, $^2J = 11.4$) (C); 81.1,

82.7 (CH); 111.3 (C); 116.9, 118.3, 122.4, 125.61, 125.65, 126.2, 126.3, 126.61, 126.64, 126.71, 126.73, 126.76, 126.84, 127.38, 127.44, 127.6, 127.8, 128.0, 128.1, 128.3, 128.8, 129.4, 130.5, 130.8, 132.0, 132.7, 132.8, 133.9 (CH); 140.5, 140.6, 143.8, 145.7, 146.0, 146.8, 147.0, 147.3 (C). ^{31}P-NMR (120 MHz, $CDCl_3$): 136.7. MALDI-FT-ICR-MS: 677.3 (100, $[M+H]^+$); 431.2 (24), 345.2 (37), 273.0 (29). Anal. calc. for $C_{44}H_{41}N_2O_3P$ (676.79): C 78.09, H 6.11, N 4.14, P 4.58; found: C 77.92, H 6.34, N 3.98, P 4.61.

*(4*S*,5*S*)-*N*^{4}*-[4-(Diphenylphosphino)phenyl]-2,2-dimethyl-*N*^{5}*,α,α,α′,α′-pentaphenyl-1,3-dioxolane-4,5-dimethanamine* (**28**) *and (4*S*,5*S*)-*N*^{4}*,*N*^{5}*-Bis[4-(diphenylphosphino)phenyl]-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanamine* (**29**). To a soln. of **10** (0.2 g, 0.32 mmol) in THF (2.6 ml) was added BuLi (0.5 ml, 0.75 mmol) at $-70°$. The soln. was warmed to 0°, stirred for further 1 h, and then $PClPh_2$ (0.22 ml, 1.6 mmol) was added at 0°. The red mixture was stirred for further 3 h at 0°, and the solvent was removed under reduced pressure. Purification of the residue by FC (SiO_2 (25 g); pentane/Et_2O 15:2) afforded, besides recovered **10** (50 mg, 25%), **28** (110 mg, 42%), and **29** (15 mg, 5%).

Data of **28**. R_f (pentane/Et_2O 5:1) 0.25. $[\alpha]_D^{rt} = -77.8$ ($c = 0.93$, $CHCl_3$). IR ($CHCl_3$): 3286*m* (br.), 3059*m*, 3007*m*, 2935*w*, 1597*s*, 1497*s*, 1447*m*, 1434*m*, 1391*m*, 1382*m*, 1324*m*, 1084*m*, 908*m*, 892*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*s*, Me); 0.92 (*s*, Me); 4.32 (*d*, $J = 8.0$, CH); 4.33 (*d*, $J = 8.0$, CH); 5.67 (br. *s*, NH); 6.22–6.24 (*m*, 2 arom. H, NH); 6.27–6.30 (*m*, 2 arom. H); 6.57 (*m*, 1 arom. H); 6.77–6.86 (*m*, 4 arom. H); 7.08–7.47 (*m*, 26 arom. H); 7.73–7.76 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.8, 26.9 (Me); 67.4, 67.5 (C); 84.5, 84.8 (CH); 107.8 (C); 117.1, 117.2, 117.5, 118.9, 126.95, 126.98, 127.9, 128.0, 128.1, 128.2, 128.4, 128.46, 128.52, 128.6, 129.1, 130.96, 131.01, 133.5, 133.8, 134.5, 134.8 (CH); 139.3, 139.6, 142.7, 145.2, 146.6 (C). ^{31}P-NMR (162 MHz, $CDCl_3$): −6.45. HR-MS: 801.3607 ($[M+H]^+$, $C_{55}H_{50}N_2O_2P^+$; calc. 801.3609 (−0.25 ppm)). MALDI-FT-ICR-MS: 839.3 (15, $[M+K]^+$), 801.4 (46, $[M+H]^+$), 573.1 (47), 481.2 (38), 442.2 (100), 273.0 (95). Anal. calc. for $C_{55}H_{49}N_2O_2P^+$ (800.98): C 82.47, H 6.17, N 3.50, P 3.87; found: C 82.30, H 6.37, N 3.54, P 3.70.

Data of **29**. White solid foam. R_f (pentane/Et_2O 5:1) 0.14. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.89 (*s*, Me); 4.39 (*s*, CH); 6.02 (br. *s*, NH); 6.24–6.28 (*m*, 4 arom. H); 6.79–6.85 (*m*, 4 arom. H); 7.10–7.41 (*m*, 36 arom. H); 7.70.-7.73 (m, 4 arom. H). HR-MS: 985.4053 ($[M+H]^+$, $C_{67}H_{59}N_2O_2P_2^+$; calc. 985.4052 (−0.10 ppm)). MALDI-FT-ICR-MS: 1039.4 (9), 985.4 (3, $[M+H]^+$), 458.2 (57), 442.4 (97), 273.0 (100).

5. *Preparation of the TADDOP Derivatives* **17**–**26**. *1-[(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl]piperidine* (**17a**). TADDOL (**1**; 1.50 g, 3.21 mmol) was treated with Et_3N (0.90 ml, 6.42 mmol) and PCl_3 (0.28 ml, 3.21 mmol), and then with Et_3N (0.45 ml, 3.21 mmol) and piperidine (0.32 ml, 3.21 mmol) according to *GP 4*. Washing the crude product (1.79 g) with ice-cold Et_2O (20 ml) afforded **17a** (1.69 g, 91%). For anal. purposes, a sample was purified by FC (hexane/CH_2Cl_2 1:3; 3–4 drops of Et_3N added to 100 ml of solvent). Colorless powder. M.p. 210–212°. $[\alpha]_D^{rt} = -151.4$ ($c = 1.13$, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3008*m*, 2937*m*, 2853*w*, 1600*w*, 1494*m*, 1447*m*, 1382*w*, 1372*m*, 1164*m*, 1086*w*, 1047*m*, 1036*s*, 1018*s*, 951*s*, 879*m*, 822*w*, 640*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.30 (*s*, Me), 1.33 (*s*, Me), 1.54–1.64 (*m*, 3 CH_2), 3.17–3.23 (*m*, NCH_2), 3.28–3.33 (*m*, NCH_2), 4.79 (*d*, $J = 8.4$, CH), 5.19 (*dd*, J(H,H) = 8.4, J(H,P) = 3.4, CH), 7.18–7.37 (*m*, 12 arom. H), 7.43–7.52 (*m*, 4 arom. H), 7.63–7.67 (*m*, 2 arom. H), 7.78–7.81 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.10, 25.20, 26.90, 26.95, 27.48, 44.74, 45.00, 81.08, 81.58, 82.21, 82.47, 82.61, 82.66, 111.56, 125.39, 127.05, 127.18, 127.23, 127.30, 127.46, 127.56, 127.72, 128.11, 128.32, 128.87, 128.93, 129.13, 142.05, 142.42, 146.78, 147.29. ^{31}P-NMR (122 MHz, $CDCl_3$): 138.15. FAB-MS: 580 (1, M^+), 384 (18), 326 (16), 238 (17), 237 (97), 236 (21), 208 (13), 207 (30), 180 (19), 179 (100). Anal. calc. for. $C_{36}H_{38}NO_4P$ (579.68): C 74.59, H 6.61, N 2.42; found: C 74.63, H 6.60, N 2.12. Anal. data match those in [23].

*4-[(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl]morpholine* (**17b**). TADDOL (**1**; 1.50 g, 3.21 mmol) was treated with Et_3N (0.90 ml, 6.42 mmol) and PCl_3 (0.28 ml, 3.21 mmol), and then with Et_3N (0.45 ml, 3.21 mmol) and morpholine (0.28 ml, 3.21 mmol) according to *GP 4*. Washing the crude product (1.80 g) with ice-cold Et_2O (20 ml) afforded **17b** (1.47 g, 79%). For anal. purposes, a sample was recrystallized from hexane/CH_2Cl_2 (2:1) at $-20°$. Colorless powder. M.p. 209–210° ([24]: M.p. 230°). $[\alpha]_D^{rt} = -159.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3062*w*, 3007*m*, 2964*w*, 2903*w*, 2857*w*, 1600*w*, 1494*m*, 1447*m*, 1383*m*, 1372*m*, 1346*w*, 1297*w*, 1256*m*, 1165*m*, 1110*s*, 1081*m*, 1050*s*, 1038*s*, 1013*m*, 956*s*, 916*m*, 879*s*, 826*m*, 640*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.32 (*s*, Me); 1.28 (*s*, Me); 3.18–3.24 (*m*, NCH_2); 3.25–3.37 (*m*, NCH_2); 3.68–3.72 (*m*, 2 OCH_2); 4.82 (*d*, $J = 8.4$,

CH); 5.19 (*dd*, *J*(H,H) = 8.4, *J*(H,P) = 3.4, CH); 7.19–7.40 (*m*, 12 arom. H); 7.46–7.49 (*m*, 2 arom. H); 7.56 (*dd*, *J* = 7.8, *J* = 1.9, 2 arom. H); 7.63 (*d*, *J* = 7.2, 2 arom. H); 7.74–7.77 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.35, 27.10, 27.45, 43.92, 44.24, 67.76, 67.89, 81.00, 81.38, 81.92, 82.27, 111.83, 127.06, 127.16, 127.32, 127.48, 127.63, 127.73, 128.05, 128.11, 128.62, 128.75, 128.84, 128.90, 141.60, 142.05, 142.78, 146.02, 146.36, 146.81. ^{31}P-NMR (122 MHz, $CDCl_3$): 138.13. FAB-MS: 1092 (9), 1064 (16), 1051 (12), 1049 (14), 1048 (23), 599 (16), 598 (32), 583 (42), 582 (100, M^+), 580 (19), 431 (21). Anal. calc. for $C_{35}H_{36}NO_5P$ (581.65): C 72.27, H 6.24, N 2.41; found: C 72.17, H 6.33, N 2.28. Anal. data match those in [24].

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl*-N,N-*bis(phenylmethyl)-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine* (**17c**). TADDOL (**1**; 2.82 g, 6.03 mmol) was treated with Et_3N (1.69 ml, 12.13 mmol) and PCl_3 (0.53 ml, 6.07 mmol), and then with Et_3N (0.84 ml, 6.06 mmol) and Bn_2NH (1.16 ml, 6.03 mmol) according to *GP 4*. Purification by FC (hexane/Et_2O 3 : 1; 3–4 drops of Et_3N added to 100 ml of solvent) afforded **17c** (2.88 g, 69%). Colorless powder. M.p. 190–192°. $[\alpha]_D^{rt.} = -63.3$ ($c = 0.98$, $CHCl_3$). IR ($CHCl_3$): 3062*w*, 3007*m*, 2934*w*, 1952*w*, 1892*w*, 1812*w*, 1601*w*, 1494*m*, 1447*s*, 1383*m*, 1372*w*, 1290*w*, 1165*m*, 1086*m*, 1049*s*, 1039*m*, 999*m*, 975*s*, 918*w*, 878*s*, 826*m*, 640*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.32 (*s*, Me); 1.33 (*s*, Me); 4.19 (*dd*, *J*(H,H) = 10.0, *J*(H,P) = 10.3, 2 CH_2); 4.87 (*d*, *J* = 8.4, CH); 5.34 (*dd*, *J*(H,H) = 8.4, *J*(H,P) = 3.4, CH); 7.21–7.48 (*m*, 16 arom. H); 7.70–7.73 (*m*, 2 arom. H); 7.86–7.89 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.33, 27.50, 47.88, 48.21, 81.69, 81.84, 81.97, 82.13, 82.42, 111.77, 127.04, 127.14, 127.20, 127.36, 127.46, 127.60, 127.72, 128.19, 128.32, 128.85, 129.03, 129.17, 129.34, 138.64, 141.78, 142.57, 146.52, 147.02. ^{31}P-NMR (122 MHz, $CDCl_3$): 139.19. FAB-MS: 691 (5, M^+), 690 (9), 496 (20), 438 (27), 432 (18), 431 (53), 374 (11), 373 (12), 345 (18), 265 (11), 238 (20), 237 (100), 207 (15), 179 (81). Anal. calc. for. $C_{45}H_{42}NO_4P$ (691.81): C 78.13, H 6.12; N 2.02; found: C 78.23, H 6.33, N 1.94. NMR and MS data match those in [23].

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl*-N,N-*diprop-2-en-1-yl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine* (**17d**). TADDOL (**1**; 3.00 g, 6.42 mmol) was treated with Et_3N (1.80 ml, 12.84 mmol) and PCl_3 (0.56 ml, 6.42 mmol), and then with Et_3N (0.90 ml, 6.42 mmol) and diallylamine (0.79 ml, 6.42 mmol) according to *GP 4*. Purification by FC (hexane/Et_2O 3 : 1; 3–4 drops of Et_3N added to 100 ml of solvent) afforded **17d** (2.63 g, 69%). Colorless powder. M.p. 118–119°. $[\alpha]_D^{rt.} = -123.3$ ($c = 1.05$, $CHCl_3$). IR (CHCl3): 3061*m*, 3008*s*, 1601*w*, 1494*m*, 1447*m*, 1384*w*, 1372*w*, 1166*m*, 1086*m*, 1050*s*, 1035*s*, 1018*s*, 945*m*, 882*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.28 (*s*, Me); 1.34 (*s*, Me); 3.44–3.88 (*m*, 2 NCH_2); 4.77 (*d*, *J* = 8.4, 1 H); 5.12–5.23 (*m*, 5 H); 5.74–5.89 (*m*, 2 H); 7.15–7.80 (*m*, 20 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.15; 27.50; 46.94; 47.21; 81.42; 81.77; 82.13; 82.40; 82.55; 111.57; 116.85; 127.10; 127.22; 127.36; 127.52; 127.59; 127.72; 128.12; 128.87; 128.93; 129.17; 136.32; 141.83; 142.44; 146.62; 147.18. ^{31}P-NMR (122 MHz, $CDCl_3$): 141.27. FAB-MS: 591 (12, M^+), 431 (100), 373 (21), 345 (36), 237 (54), 179 (50). Anal. calc. for $C_{37}H_{38}NO_4P$ (591.69): C 75.11, H 6.47, N 2.37; found: C 75.39, H 6.52, N 2.15.

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl*-N,N-*bis(1-methylethyl)-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine* (**17e**). TADDOL (**1**; 1.50 g, 3.21 mmol) was treated with Et_3N (0.90 ml, 6.42 mmol) and PCl_3 (0.28 ml, 3.21 mmol), and then with Et_3N (0.45 ml, 3.21 mmol) and $^iPr_2NH$ (0.46 ml, 3.21 mmol) according to *GP 4*. Purification of the crude product (1.85 g) by FC (hexane/Et_2O 3 : 1; 3–4 drops of Et_3N added to 100 ml of solvent) afforded **17e** (1.61 g, 88%). For anal. purposes, a sample was recrystallized from hexane/Et_2O (15 : 1) at −20°. Colorless powder. M.p. 169–170° ([25]: M.p. 174–175°). $[\alpha]_D^{rt.} = -107.0$ ($c = 1.15$, $CHCl_3$) ([25]: $[\alpha]_D^{rt.} = -83.4$ ($c = 0.7$, CH_2Cl_2)). IR ($CHCl_3$): 3066*w*, 3008*w*, 2970*m*, 2933*w*, 2874*w*, 1493*w*, 1459*w*, 1448*m*, 1396*w*, 1382*w*, 1364*w*, 1163*m*, 1130*w*, 1103*w*, 1085*m*, 1051*s*, 1042*s*, 1032*m*, 1006*m*, 982*s*, 918*w*, 878*m*, 819*w*, 652*w*, 636*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.24 (*s*, Me); 1.20 (*d*, *J* = 6.5, 2 Me); 1.25 (*d*, *J* = 6.5, 2 Me); 1.44 (*s*, Me); 3.98 (*sept.*, *J* = 6.5,2 NCH); 4.62 (*d*, *J* = 8.7, CH); 5.21 (*dd*, *J*(H,H) = 8.7, *J*(H,P) = 3.4, CH); 7.17–7.33 (*m*, 12 arom. H); 7.44–7.49 (*m*, 4 arom. H); 7.64 (*d*, *J* = 7.80, 2 arom. H); 7.84 (*d*, *J* = 8.1, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.05, 24.21, 24.27, 24.40, 25.09, 27.73, 44.11, 44.40, 80.74, 81.25, 82.30, 82.74, 83.06, 83.13, 111.00, 126.81, 126.93, 127.09, 127.16, 127.41, 127.48, 127.79, 128.71, 128.81, 129.13, 142.24, 142.99, 147.12, 147.67. ^{31}P-NMR (122 MHz, $CDCl_3$): 141.04. FAB-MS: 1190 (11), 1189 (13), 777 (16), 747 (19), 733 (14), 718 (11), 634 (12), 618 (23), 612 (67), 608 (17), 597 (95), 596 (100, $[M+1]^+$), 594 (88), 580 (36), 537 (66), 431 (80),

400 (97), 341 (49), 236 (69). Anal. calc. for $C_{37}H_{42}NO_4P$ (595.71): C 74.60, H 7.11, N 2.35; found: C 74.46, H 7.25, N 2.18. NMR and MS data match those in [25].

*(3aR,8a*R*)*-N,N-*Diethyltetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine* (**17f**). To a soln. of PCl_3 (0.28 ml, 3.21 mmol) in toluene (5 ml) was added Et_3N (0.90 ml, 6.42 mmol) at $-60°$ under Ar, and then a soln. of TADDOL (**1**; 1.50 g, 3.21 mmol) in toluene (15 ml) was added dropwise over 15 min. The mixture was stirred for further 45 min at $-60°$, then the cooling bath was removed, and the mixture was allowed to warm slowly to r.t. which led to the formation of a colorless precipitate. After cooling to $-40°$, Et_3N (0.45 ml, 3.21 mmol) and Et_2NH (0.33 ml, 3.21 mmol) were added consecutively. The mixture was warmed to r.t. and stirred for further 12 h at r.t. Workup according to *GP 4*. Purification of the crude product (1.59 g) by FC (hexane/Et_2O 3:1; 3–4 drops of Et_3N added to 100 ml of solvent) afforded **17f** (1.01 g, 57%). Colorless powder. M.p. 159–161°. IR ($CHCl_3$): 3061*w*, 3007*m*, 2934*w*, 2870*w*, 1599*w*, 1494*m*, 1447*s*, 1382*m*, 1165*m*, 1086*s*, 1052*s*, 1028*s*, 1012*s*, 942*m*, 918*w*, 878*s*, 822*w*, 640*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.30 (*s*, Me); 1.18 (*t*, 2 Me); 1.36 (*s*, Me); 3.20–3.33 (*m*, 2 CH_2); 4.78 (*d*, $J = 8.7$, CH); 5.21 (*dd*, J(H,H) = 8.7, J(H,P) = 3.4, CH); 7.18–7.37 (*m*, 12 arom. H); 7.45–7.52 (*m*, 4 arom. H); 7.62 (*d*, $J = 6.9$, 2 arom. H); 7.81 (*d*, $J = 6.9$, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.12, 15.15, 25.13, 27.51, 38.68, 38.97, 81.14, 81.26, 81.45, 82.18, 82.45, 82.61, 82.66, 111.43, 127.01, 127.07, 127.17, 127.23, 127.30, 127.43, 127.54, 127.65, 127.91, 128.07, 128.20, 128.32, 128.85, 128.923, 129.16, 142.02, 142.62, 146.86, 147.39. ^{31}P-NMR (122 MHz, $CDCl_3$): 142.04. FAB-MS: 569 (5), 568 (12, M^+), 432 (10), 431 (29), 373 (11), 372 (24), 345 (8), 314 (16), 265 (11), 238 (26), 237 (100), 207 (16), 179 (55).

*(3a*R*,8a*R*)-Tetrahydro-*N,N*,2,2-tetramethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine* (**17g**). TADDOL (**1**; 1.50 g, 3.21 mmol) was treated with Et_3N (0.90 ml, 6.42 mmol) and PCl_3 (0.28 ml, 3.21 mmol), and then with Et_3N (0.88 ml, 6.30 mmol), and a suspension of $Me_2NH \cdot HCl$ (0.36 g, 4.41 mmol) in CH_2Cl_2 (5 ml) according to *GP 4*. Purification of the crude product (1.62 g) by FC (hexane/CH_2Cl_2 1:2; 3–4 drops of Et_3N added to 100 ml of solvent) afforded **17g** (1.24 g, 72%). For anal. purposes, a sample was recrystallized (2×) from hexane/CH_2Cl_2 (3:1) at $-20°$. Colorless powder. M.p. 218–221° ([25a]: M.p. >220°). $[\alpha]_D^{r.t.} = -161.5$ ($c = 0.91$, $CHCl_3$) ([25a]: $[\alpha]_D^{r.t.} = -151$ ($c = 0.69$, $CHCl_3$)). IR ($CHCl_3$): 3061*w*, 3039*w*, 3008*m*, 2889*w*, 2839*w*, 1600*w*, 1498*m*, 1447*s*, 1383*m*, 1372*w*, 1292*w*, 1165*m*, 1086*m*, 1050*s*, 1000*m*, 976*s*, 918*w*, 879*s*, 825*m*, 640*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.32 (*s*, Me); 1.30 (*s*, Me); 2.76 (*d*, J(H,P) = 10.4, 2 Me); 4.85 (*d*, $J = 8.7$, CH); 5.21 (*dd*, J(H,H) = 8.7, J(H,P) = 2.9, CH); 7.21–7.51 (*m*, 16 arom. H); 7.53–7.65 (*m*, 2 arom. H); 7.72–7.79 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.35, 27.48, 35.10, 35.48, 81.13, 81.29, 81.95, 82.11, 82.49, 111.73, 127.03, 127.13, 127.25, 127.44, 127.67, 128.08, 128.59, 128.71, 128.81, 129.00, 141.86, 142.21, 146.56, 146.90. ^{31}P-NMR (122 MHz, $CDCl_3$): 140.04. FAB-MS: 540 (4, $[M + 1]^+$), 432 (6), 431 (19), 289 (7), 288 (9), 267 (6), 265 (12), 238 (11), 237 (47), 207 (17), 195 (12), 191 (10), 179 (100), 178 (51). Anal. calc. for $C_{33}H_{34}NO_4P$ (539.62): C 73.45, H 6.35, N 2.60; found: C 73.61, H 6.38, N 2.49. NMR and MS data match those in [25a][26].

*(3a*R*,8a*R*)*-N,N-*Dicyclohexyltetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine* (**17h**). TADDOL (**1**; 1.50 g, 3.21 mmol) was treated with Et_3N (0.90 ml, 6.42 mmol) and PCl_3 (0.28 ml, 3.21 mmol), and then with Et_3N (0.45 ml, 3.21 mmol) and dicyclohexylamine (0.63 ml, 3.21 mmol) according to *GP 4*. Purification of the crude product (2.12 g) by FC (hexane/Et_2O 3:1; 3–4 drops of Et_3N added to 100 ml of solvent) afforded **17h** (1.72 g, 79%). For anal. purposes, a sample was recrystallized from hexane/Et_2O (15:1) at $-20°$. Colorless powder. M.p. 192–194°. $[\alpha]_D^{r.t.} = -77.9$ ($c = 1.36$, $CHCl_3$) ([27]: $[\alpha]_D^{r.t.} = -60.6$ ($c = 1$, CH_2Cl_2)). IR ($CHCl_3$): 3064*w*, 3039*w*, 3002*w*, 2933*s*, 2853*s*, 1599*w*, 1493*m*, 1448*s*, 1383*m*, 1372*w*, 1163*s*, 1119*w*, 1084*m*, 1077*m*, 1050*s*, 1038*s*, 1021*s*, 981*s*, 918*w*, 877*s*, 854*w*, 822*m*, 650*w*, 640*w*, 611*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.23 (*s*, Me); 1.44 (*s*, Me); 1.29–1.49 (*m*, 10 H, CH_2); 1.77–1.89 (*m*, 10 H, CH_2); 3.42–3.58 (*m*, 2 H, NCH); 4.63 (*d*, $J = 8.7$, CH); 5.16 (*dd*, J(H,H) = 8.7, J(H,P) = 3.4, CH); 7.17–7.33 (*m*, 12 arom. H); 7.45 (*d*, $J = 7.5$, 4 arom. H); 7.63 (*d*, $J = 7.2$, 2 arom. H); 7.82–7.85 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.00, 25.51, 26.81, 26.91, 27.73, 34.94, 35.06, 35.19, 35.32, 53.57, 53.83, 80.65, 80.94, 81.13, 82.49, 82.87, 83.10, 83.16, 111.00, 126.78, 126.87, 127.10, 127.19, 127.32, 127.44, 127.54, 127.79, 128.62, 128.71, 129.03, 142.24, 142.81, 147.00, 147.51. ^{31}P-NMR (122 MHz, $CDCl_3$): 140.99. FAB-MS: 675 (1, M^+), 422 (5), 238 (12), 237 (61), 228 (7), 207 (12), 180 (17), 179 (100), 178 (18), 167 (37). Anal. calc. for $C_{43}H_{50}NO_4P$ (675.86): C 76.42, H 7.46, N 2.07; found: C 76.60, H 7.53, N 1.97. Anal. data match those in [27].

*1-[(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl]piperidine* (**18a**). Compound **17a** (150 mg, 0.26 mmol) was treated with H_2O_2 (0.04 ml, 1.31 mmol) according to *GP 5*. FC (hexane/CH_2Cl_2 1:3) afforded **18a** (109 mg, 71%). Colorless powder. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.59 (*s*, Me); 0.76 (*s*, Me); 1.48–1.53 (*m*, 3 CH_2); 3.01–3.09 (*m*, 2 NCH_2); 5.08 (*d*, *J* = 8.1, CH); 5.46 (*d*, *J* = 8.1, CH); 7.24–7.40 (*m*, 14 arom. H); 7.52–7.59 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.43, 25.73, 25.83, 26.59, 26.72, 78.30, 79.60, 84.78, 84.91, 88.94, 89.10, 113.13, 126.75, 127.10, 127.44, 127.79, 127.89, 128.05, 128.62, 129.73, 140.02, 140.08, 140.33, 140.52, 144.14, 145.06, 145.19. ^{31}P-NMR (122 MHz, $CDCl_3$): 0.65. FAB-MS: 1193 (10, $[2\,M]^+$), 1192 (14), 759 (5), 597 (10), 596 (23, M^+), 432 (37), 431 (100), 373 (17), 345 (24), 207 (11), 195 (15), 179 (25).

*4-[(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-6-oxido-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl]morpholine* (**18b**). Compound **17b** (180 mg, 0.31 mmol) was treated with H_2O_2 (0.10 ml, 3.26 mmol) according to *GP 5*. Purification of the crude product by recrystallization from hexane/CH_2Cl_2 3:1 at −20° afforded **18b** (110 mg, 59%). Colorless powder. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.63 (*s*, Me); 0.71 (*s*, Me); 3.00–3.07 (*m*, NCH_2); 3.13–3.21 (*m*, NCH_2); 3.57–3.64 (*m*, 2 OCH_2); 5.10 (*d*, *J* = 8.4, CH); 5.48 (*d*, *J* = 8.1, CH); 7.22–7.41 (*m*, 12 arom. H); 7.54–7.61 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.59, 44.60, 66.81, 78.26, 79.44, 85.20, 85.28, 89.57, 89.70, 113.48, 126.86, 127.20, 127.27, 127.69, 128.07, 128.20, 128.30, 128.62, 129.82, 132.91, 139.87, 140.16, 140.30, 143.93, 145.03. ^{31}P-NMR (122 MHz, $CDCl_3$): 0.30.

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-*N,N*-bis(phenylmethyl)-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine 6-Oxide* (**18c**). Compound **17c** (120 mg, 0.17 mmol) was treated with H_2O_2 (0.05 ml, 1.63 mmol) according to *GP 5*. FC (hexane/Et_2O 3:1) afforded **18c** (144 mg, 66%). Colorless powder. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.60 (*s*, Me); 0.80 (*s*, Me); 4.07 (*dd*, *J*(H,H) = 12.1, *J*(H,P) = 4.7, 2 CH_2); 5.13 (*d*, *J* = 8.1, CH); 5.65 (*d*, *J* = 8.1, CH); 7.17–7.46 (*m*, 26 arom. H); 7.58–7.61 (*m*, 2 arom. H); 7.74–7.77 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.46, 26.75, 48.64, 78.02, 79.35, 85.67, 85.75, 89.40, 89.51, 113.26, 127.17, 127.23, 127.35, 127.56, 127.64, 127.99, 128.09, 128.40, 128.66, 128.92, 130.03, 137.44, 137.47, 140.29, 144.09, 144.90. ^{31}P-NMR (122 MHz, $CDCl_3$): 2.38.

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-*N,N*-diprop-2-en-1-yl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine 6-Oxide* (**18d**). Compound **17d** (70 mg, 0.12 mmol) was treated with H_2O_2 (0.04 ml, 1.31 mmol) according to *GP 5*. FC (hexane/Et_2O 3:1) afforded **18d** (52 mg, 72%). Colorless powder. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.60 (*s*, Me); 0.75 (*s*, Me); 3.54–3.62 (*m*, 2 NCH_2); 5.05 (*d*, *J* = 8.1, CH); 5.09–5.20 (*m*, 2 CH_2); 5.49 (*d*, *J* = 8.1, CH); 5.68–5.79 (*m*, 2 CH); 7.19–7.39 (*m*, 12 arom. H); 7.49–7.66 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.59, 26.81, 48.08, 78.24, 79.41, 85.21, 85.32, 89.25, 89.46, 113.13, 117.51, 126.90, 127.10, 127.32, 127.48, 127.86, 127.98, 128.08, 128.78, 129.92, 134.43, 140.11, 140.52, 144.17, 145.00. ^{31}P-NMR (122 MHz, $CDCl_3$): 2.00.

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-*N,N*-bis(1-methylethyl)-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine 6-Oxide* (**18e**). Compound **17e** (70 mg, 0.12 mmol) was treated with H_2O_2 (0.04 ml, 1.31 mmol) according to *GP 5*. FC (hexane/Et_2O 3:1) afforded **18e** (61 mg, 85%). Colorless powder. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.57 (*s*, Me); 0.81 (*s*, Me); 1.15 (*d*, *J* = 6.9, Me); 1.23 (*d*, *J* = 6.9, Me); 3.35–3.47 (*m*, 2 NCH); 5.07 (*d*, *J* = 8.1, CH); 5.52 (*d*, *J* = 8.1, CH); 7.18–7.38 (*m*, 12 arom. H); 7.51–7.70 (*m*, 6 arom. H); 7.71–7.73 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.95, 22.30, 26.35, 26.77, 46.57, 78.26, 79.62, 84.86, 84.93, 88.58, 88.72, 112.80, 127.12, 127.18, 127.44, 127.72, 127.83, 127.90, 127.98, 128.50, 130.06, 140.58, 140.82, 140.97, 144.80, 145.59. ^{31}P-NMR (122 MHz, $CDCl_3$): −0.04. FAB-MS: 1224 (2, $[2\,M]^+$), 613 (28), 612 (67, M^+), 432 (35), 431 (100), 373 (19), 346 (15), 345 (31), 265 (17), 237 (18), 207 (30), 195 (32), 179 (50).

*(3a*R*,8a*R*)-*N,N*-Diethyltetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine 6-Oxide* (**18f**). Compound **17f** (100 mg, 0.18 mmol) was treated with H_2O_2 (0.05 ml, 1.63 mmol) according to *GP 5*. FC (hexane/Et_2O 3:1) afforded **18f** (82 mg, 80%). Colorless powder. M.p. 194–195°. $[\alpha]_D^{r.t.} = -229.7$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3050*w*, 3008*m*, 2935*w*, 1601*w*, 1448*m*, 1382*w*, 1364*w*, 1259*m*, 1167*w*, 1092*w*, 1064*w*, 1034*m*, 1019*s*, 960*w*, 916 *m*, 832*w*, 824*w*, 640*m*, 629*m*, 619*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.61 (*s*, Me); 0.75 (*s*, Me); 1.05 (*t*, *J* = 7.5, 2 Me); 3.08 (*m*, *J* = 6.5, 2 NCH); 5.11 (*d*, *J* = 8.3, CH); 5.52 (*d*, *J* = 8.3, CH); 7.20–7.39 (*m*, 14 arom. H); 7.50–7.57 (*m*, 4 arom. H); 7.64–7.73 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.96, 26.53, 26.72, 39.89, 39.95, 78.23, 79.48, 84.22, 84.93, 89.01, 89.04, 113.08, 127.01, 127.14, 127.17, 127.39, 127.49, 127.85, 127.93, 128.04, 128.07, 128.85,

130.08, 140.43, 140.71, 140.85, 144.53, 145.36, 145.47. ^{31}P-NMR (122 MHz, $CDCl_3$): 2.34. Anal. calc. for $C_{35}H_{38}NO_5P$ (583.65): C 72.03, H 6.56, N 2.40; found: C 72.11, H 6.57, N 2.34.

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin 6-Oxide* (**19**). To a soln. of TADDOL (**1**; 1.00 g, 2.14 mmol) in Et_2O (30 ml) was added pyridine (0.36 ml, 4.46 mmol) at $-15°$, and then PCl_3 (0.19 ml, 2.14 mmol) was added dropwise over 15 min. The mixture (which contained a colorless precipitate) was slowly warmed to r.t. (*ca.* 1 h) and stirred for further 2 h at r.t. Sat. aq. NaCl soln. (50 ml) and sat. aq. $NaHCO_3$ soln. (20 ml) were added, the org. layer was separated, and the aq. layer was extracted with Et_2O (2 × 30 ml). The combined org. layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by FC (hexane/CH_2Cl_2 1:3) to afford **19** (0.89 g, 81%). For anal. purposes, a sample was recrystallized from pentane/Et_2O 1:5 at $-20°$. Colorless powder. M.p. 181–183° ([25a]: M.p. 226–227° (dec.)). $[\alpha]_D^{r.t.} = -299.16$ ($c = 1.07$, $CHCl_3$; [25a]: $[\alpha]_D^{r.t.} = -289.9$ ($c = 1.56$, $CHCl_3$)). IR ($CHCl_3$): 3064*w*, 3008*m*, 2937*w*, 1600*w*, 1496*m*, 1448*s*, 1384*w*, 1374*w*, 1354*w*, 1270*s*, 1167*m*, 1092*s*, 1073*s*, 1054*s*, 1035*m*, 982*s*, 955*s*, 900*w*, 857*w*, 654*w*, 641*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.68 (*s*, Me); 0.88 (*s*, Me); 1.36 (*d*, $J = 5.3$, OH); 5.23 (*d*, $J = 8.1$, CH); 5.38 (*d*, $J = 8.1$, CH); 7.26–7.45 (*m*, 16 arom. H); 7.59–7.64 (*m*, 4 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 26.18, 26.65, 79.73, 79.98, 80.05, 88.56, 88.71, 114.30, 126.71, 126.81, 127.29, 127.44, 127.83, 127.92, 128.14, 128.24, 128.40, 128.62, 128.75, 138.84, 139.00, 139.19, 143.13, 143.57. ^{31}P-NMR (122 MHz, $CDCl_3$): −3.92. FAB-MS: 1027 (16), 1026 (26), 513 (1, M^+), 432 (40), 431 (100), 345 (18), 265 (11), 237 (59), 207 (44), 179 (79). Anal. calc. for $C_{31}H_{29}O_5P$ (512.55): C 72.65, H 5.70, P 6.04; found: C 72.60, H 5.88, P 5.93. Anal. data match those in [25a].

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-6-[(3a*R*,8a*R*)-tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl]-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin 6-Oxide* (**20**). To a soln. of TADDOL (**1**; 2.32 g, 4.96 mmol) and Et_3N (1.40 ml, 9.99 mmol) in CH_2Cl_2 (40 ml) under Ar at −50° was added slowly (15 min) PCl_3 (0.43 ml, 4.93 mmol). After warming up to −20° (100 min) and recooling to −50°, again Et_3N (0.68 ml, 4.85 mmol) and phenothiazin (0.97 g, 4.87 mmol) were added. After warming up to r.t., the mixture was stirred for further 72 h at r.t. During this period, a brownish precipitate was formed. For workup, the mixture was diluted with CH_2Cl_2 (100 ml), washed with sat. NaCl (50 ml) and sat. $NaHCO_3$ (5 ml), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification by FC (CH_2Cl_2, 1% Et_3N) afforded **20** (231 mg, 9%). Colorless powder. M.p. 171–173. IR ($CHCl_3$): 3061*w*, 3008*m*, 1600*w*, 1495*m*, 1448*s*, 1384*m*, 1377*w*, 1252*s*, 1165*m*, 1093*m*, 1086*m*, 1047*w*, 1030*m*, 997*s*, 919*m*, 878*m*, 838*w*, 641*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.21 (*s*, Me); 0.59 (*s*, Me); 0.95 (*s*, Me); 1.58 (*s*, Me); 4.71 (*d*, $J = 8.30$, CH); 5.25 (*d*, $J = 7.89$, CH); 5.43 (*quint.*, J(H,H) = 8.30, J(H,P) = 4.15, J(H,P) = 3.73, CH); 5.63 (*d*, $J = 7.89$, CH); 7.25–7.42 (*m*, 24 arom. H); 7.48–7.87 (*m*, 16 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.56, 26.33, 27.03, 27.73, 80.02, 80.11, 80.27, 83.03, 83.45, 80.60, 83.70, 84.05, 84.15, 84.24, 84.38, 84.70, 86.87, 87.16, 91.51, 91.88, 112.02, 113.64, 126.46, 127.16, 127.25, 127,38, 127.63, 127.73, 127.86, 128.02, 128.14, 128.33, 128.71, 129.25, 129.98, 139.31, 139.41, 139.50, 140.05, 140.46, 143.98, 144.33, 144.41, 144.87, 145.03, 145.73. ^{31}P-NMR (122 MHz, $CDCl_3$): 157.96 (*d*, J(P,P) = 189.98), 13.51 (*d*, J(P,P) = 189.98). FAB-MS: 1616 (1), 1552 (1), 1125 (1), 1024 (1), 1007 (1, M^+), 432 (39), 431 (100), 373 (15), 345 (21), 237 (26). MALDI-MS: 1029.6 ([M + Na]$^+$), 1045.6 ([M + O + Na]$^+$), 1061.7 ([M + O + K]$^+$).

*(3a*R*,8a*R*)-Tetrahydro-2,2,6-trimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin 6-Oxide* (**21a**). To a soln. of TADDOL (**1**; 2.33 g, 5.0 mmol) in THF (20 ml) was added BuLi (6.88 ml, 11.0 mmol) at −78°. The soln. was warmed to r.t. and stirred for 1 h, then cooled to −78° again, and $MeP(O)Cl_2$ (0.55 ml, 6.0 mmol) was added. The mixture was warmed to r.t. and stirred for 3.5 h. The solvent was removed under reduced pressure, and the residue purified by FC (hexane/EtOAc 2:1 → 1:1) to afford **21a** (2.54 g, 96%). Colorless solid. M.p. 240–242°. $[\alpha]_D^{r.t.} = -287.5$ ($c = 0.76$, $CHCl_3$). IR ($CHCl_3$): 3002*m*, 1495*m*, 1448*m*, 1373*w*, 1313*m*, 1166*m*, 1090*m*, 1056*s*, 1009*m*, 942*s*, 902*m*, 641*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.58 (*s*, Me); 0.65 (*s*, Me); 1.46 (*d*, $J = 18.1$, MeP); 5.21 (*d*, $J = 8.0$, CH); 5.51 (*d*, $J = 8.0$, CH); 7.21–7.41 (*m*, 14 arom. H); 7.46–7.49 (*m*, 2 arom. H); 7.54–7.61 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.2; 14.7; 26.6 (*d*, $J = 5.2$); 79.1 (*d*, $J = 2.3$); 79.7 (*d*, $J = 2.2$); 87.2 (*d*, $J = 8.6$); 88.7 (*d*, $J = 10.7$); 114.2; 126.8; 127.08; 127.14; 127.2; 127.58; 127.61; 128.18; 128.22; 128.3; 128.4; 129.2; 139.77; 139.82; 139.84; 140.0; 143.4; 144.16; 144.19. ^{31}P-NMR (162 MHz, $CDCl_3$): 22.2. MALDI-FT-ICR-MS:

549.2 (72, $[M + Na]^+$), 431 (70), 345 (77), 267 (82), 105 (100). Anal. calc. for $C_{32}H_{31}O_5P$ (526.57): C 72.99, H 5.93; found: C 73.01, H 6.12.

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-6-(phenylmethyl)-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin 6-Oxide* (**21b**). To a soln. of TADDOL (**1**; 1.87 g, 4.0 mmol) in THF (16 ml) was added BuLi (5.50 ml, 8.8 mmol) at $-78°$. The soln. was warmed to r.t. and stirred for 1 h, then cooled to $-78°$ again, and a soln. of $BnP(O)Cl_2$ (1.05 g, 5.0 mmol) in THF (4 ml) was added. The mixture was warmed to r.t. and stirred for 3 h. The mixture was diluted with AcOEt, the org. layer was washed with sat. aq. $NaHCO_3$ soln. (2 ×) and sat. aq. NaCl soln., dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. Recrystallization of the residue from hexane/AcOEt afforded **21b** (1.58 g, 66%). Colorless solid. M.p. 245–246°. $[\alpha]_D^{r.t.} = -220.1$ ($c = 0.84$, $CHCl_3$). IR ($CHCl_3$): 3063*w*, 3003*m*, 1495*m*, 1448*m*, 1373*m*, 1271*m*, 1166*m*, 1090*m*, 1055*s*, 1042*s*, 996*s*, 939*m*, 924*m*, 882*w*, 641*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.46 (*s*, Me); 0.77 (*s*, Me); 3.21–3.36 (*m*, CH_2); 4.95 (*d*, $J = 8.0$, CH); 5.46 (*d*, $J = 8.0$, CH); 6.86–6.89 (*m*, 2 arom. H); 7.05–7.08 (*m*, 2 arom. H); 7.11–7.31 (*m*, 12 arom. H); 7.32–7.42 (*m*, 7 arom. H); 7.50–7.65 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.4; 26.9; 35.6 (*d*, $J = 146.5$); 78.9 (*d*, $J = 2.6$); 79.4 (*d*, $J = 2.5$); 86.1 (*d*, $J = 8.4$); 90.3 (*d*, $J = 13.1$); 113.5; 126.58; 126.64; 127.0; 127.1; 127.2; 127.4; 127.56; 127.59; 128.0; 128.05; 128.06; 128.10; 128.29; 128.32; 128.7; 129.9; 130.0; 131.7; 131.8; 139.72; 139.73; 139.8; 139.9; 143.7; 144.66; 144.73. ^{31}P-NMR (162 MHz, $CDCl_3$): 19.9. MALDI-FT-ICR-MS: 625.2 (56, $[M + Na]^+$), 431 (33), 345 (48), 273 (65), 267 (58), 195 (100), 105 (52). Anal. calc. for $C_{38}H_{35}O_5P$ (602.67): C 75.73, H 5.85; found: C 75.77, H 5.87.

*Methyl (3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-acetate 6-Oxide* (**22**). To a soln. of **21a** (263 mg, 0.50 mmol) in THF (10 ml) was added BuLi (1.25 ml, 2.0 mmol) at $-78°$, and the mixture was stirred for 3.5 h. At the same temp., NCCOOMe (0.16 ml, 2.0 mmol) was added, and stirring continued for another 1 h before quenching the reaction with H_2O. The mixture was diluted with AcOEt, the org. layers were washed with sat. aq. K_2CO_3 soln. (2 ×) and sat. aq. NaCl soln., dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. FC of the residue (hexane/AcOEt 3:1 → 1:1) afforded **22** (134 mg, 46%). Colorless glass. $[\alpha]_D^{r.t.} = -244.0$ ($c = 0.77$, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 1740*s*, 1496*m*, 1448*m*, 1384*m*, 1273*s*, 1167*m*, 1117*m*, 1089*m*, 1055*s*, 1040*s*, 1010*s*, 942*m*, 642*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.57 (*s*, Me); 0.75 (*s*, Me); 3.00–3.19 (*m*, CH_2); 3.35 (*d*, $J = 0.5$, MeO); 5.22 (*d*, $J = 7.9$, CH); 5.49 (*d*, $J = 7.9$, CH); 7.22–7.40 (*m*, 14 arom. H); 7.46–7.61 (*m*, 6 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.5; 26.9; 36.0 (*d*, $J = 146.0$); 52.2; 79.0 (*d*, $J = 2.5$); 79.5 (*d*, $J = 2.5$); 87.5 (*d*, $J = 7.9$); 91.0 (*d*, $J = 11.9$); 114.1; 126.7; 127.2; 127.3; 127.70; 127.73; 128.1; 128.18; 128.23; 128.7; 129.6; 139.42; 139.44; 139.5; 139.7; 143.4; 144.07; 144.13; 165.6; 165.7. ^{31}P-NMR (162 MHz, $CDCl_3$): 12.6. MALDI-FT-ICR-MS: 607.2 (31, $[M + Na]^+$), 431 (18), 345 (16), 267 (16), 105 (17).

*(3a*R*,8a*R*)-6-Chlorotetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin 6-Oxide* (**23**). To a soln. of TADDOL (**1**; 2.33 g, 5.0 mmol) in THF (25 ml) was added BuLi (6.88 ml, 11.0 mmol) at $-78°$. The mixture was warmed to r.t. and stirred for 1 h, then again cooled to $-78°$ before addition of $POCl_3$ (0.60 ml, 6.50 mmol). The mixture was stirred for 3 h at $-78°$, the reaction was quenched with sat. aq. $NaHCO_3$ soln., and the mixture was diluted with Et_2O. The org. layer was washed with sat. aq. $NaHCO_3$ soln. (2 ×) and sat. aq. NaCl soln., dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The residue was purified by recrystallization from hexane/AcOEt to afford **23** (1.37 g, 50%). Colorless solid. M.p. 134° (dec.). $[\alpha]_D^{r.t.} = -319.9$ ($c = 0.67$, $CHCl_3$). IR: 3008*m*, 1496*m*, 1448*m*, 1374*m*, 1293*s*, 1167*m*, 1089*m*, 1055*m*, 1036*s*, 1019*s*, 998*s*, 654*m*, 641*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.58 (*s*, Me); 0.64 (*s*, Me); 5.33 (*d*, $J = 7.9$, CH); 5.38 (*d*, $J = 7.9$, CH); 7.25–7.44 (*m*, 16 arom. H); 7.56–7.61 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.5 (Me); 26.6 (Me); 78.6, 79.4, 91.6 (*d*, ^2J(C,P) = 10.8); 92.5 (*d*, ^2J(C,P) = 9.3); 115.1 (C); 126.6, 127.3, 127.5, 127.5, 128.1, 128.1, 128.3, 128.4, 128.5, 128.8, 128.8, 128.9, 138.6 (*d*, ^3J(C,P) = 11.4, C); 138.8 (*d*, ^3J(C,P) = 10.6, C); 141.4 (C); 142.1 (C). ^{31}P-NMR (162 MHz, $CDCl_3$): −9.1. ESI-MS (pos.): 564 (100, $[M + NH_4]^+$). ESI-MS (neg.): 577 (100, $[M + MeO]^-$). Anal. calc. for $C_{31}H_{28}O_5PCl$ (546.99): C 68.07, H 5.16; found: C 68.03, H 5.34.

*(3a*R*,8a*R*)-Tetrahydro-6-methoxy-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin 6-Oxide* (**24**). To a soln. of **23** (820 mg, 1.5 mmol) in THF (30 ml) was added a soln. of MeONa (160 mg, 3 mmol) in MeOH (5 ml). After stirring for 1 d at r.t., sat. aq. $NaHCO_3$ soln. was added, the org. layer was separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. layers were washed with sat. aq. NaCl soln., dried ($MgSO_4$), and concentrated under reduced pressure to

afford **24** (800 mg, 98%). White foam. M.p. 176–179°. $[\alpha]_D^{r.t.} = -235.5$ ($c = 0.52$, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 1496*m*, 1448*s*, 1384*m*, 1380*m*, 1279*s*, 1167*m*, 1037*s*, 1021*s*, 941*m*, 901*m*, 640*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.58 (*s*, Me); 0.73 (*s*, Me); 3.34 (*d*, $J = 11.8$, MeO); 5.25 (*d*, $J = 8.1$, CH); 5.32 (*d*, $J = 8.1$, CH); 7.23–7.42 (*m*, 16 arom. H); 7.54–7.58 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.4; 26.7; 54.4 (*d*, $J = 6.0$); 78.6; 79.6; 87.7 (*d*, $J = 6.5$); 88.1 (*d*, $J = 8.3$); 113.8; 126.9; 127.17; 127.22; 127.3; 127.71; 127.73; 128.21; 128.24; 128.4; 129.0; 129.1; 139.4; 139.5; 139.8; 139.9; 143.2; 143.3; 143.91; 143.93. ^{31}P-NMR (162 MHz, $CDCl_3$): −9.8. ESI-MS (pos.): 560 (100, $[M + NH_4]^+$). ESI-MS (neg.): 527 (100, $[M - Me]^-$).

*Sodium (3a*R,*8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-olate 6-Oxide* (**25**). To a soln. of **23** (0.5 g, 0.91 mmol) in THF (20 ml) were added H_2O (10 ml) and NaOH (91 mg, 2.3 mmol). After stirring for 10 h at r.t., the solvent was removed under reduced pressure, and then the residue was dissolved in AcOEt. The soln. was filtered and concentrated under reduced pressure to afford, after drying under h.v., **25** (490 mg, 97%). Colorless solid. M.p. 329–330° (dec.). $[\alpha]_D^{r.t.} = -153.2$ ($c = 1.05$, MeOH). IR (KBr): 3059*w*, 2989*w*, 2935*w*, 1636.3br. *m*, 1495*s*, 1447*s*, 1382*m*, 1372*m*, 1240br. *s*, 1166*s*, 1082*s*, 1057*s*, 1022*s*, 899*s*, 858*w*, 804*w*, 743*s*, 699*s*, 592*m*, 549*s*. ^{1}H-NMR (400 MHz, CD_3OD): 0.68 (*s*, Me); 5.30 (*s*, CH); 7.16–7.29 (*m*, 12 arom. H); 7.53–7.56 (*m*, 8 arom. H). ^{13}C-NMR (100 MHz, CD_3OD): 27.0 (Me); 82.1 (CH); 84.8 (*d*, ^2J (C,P) = 6.6), 113.0 (C); 127.9, 128.0, 128.08, 128.13, 128.4, 128.7, 130.4 (CH); 143.4, 143.5, 147.4, 147.5 (C). ^{31}P-NMR (120 MHz, CD_3OD): −7.57. MALDI-FT-ICR-MS: 573.1 (46, $[M + Na]^+$); 381.2 (100), 345.2 (44), 273.0 (94), 267.1 (92), 105.0 (51). ESI-MS (neg.): 527.2 $[M - Na]^-$.

*(3a*R,*8a*R,*3′a*R,*8′a*R*)-6,6′-Oxybis[tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin] 6,6′-Dioxide* (**26**). Compound **23** (125 mg, 0.23 mmol) and **25** (126 mg, 0.23 mmol) were dissolved in THF (2 ml), and the mixture was stirred for 3 d. The soln. (which contained a fine precipitate) was concentrated under reduced pressure, and the residue was recrystallized from CH_2Cl_2/hexane by slow evaporation of the solvent to afford **26** (170 mg, 72%). Colorless needles. M.p. 215–218°. $[\alpha]_D^{r.t.} = -266.9$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3008*m*, 2927*m*, 1496*m*, 1448*m*, 1394*w*, 1309*s*, 1167*w*, 1096*m* (br.), 1020*s*, 961*s*, 902*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.46 (*s*, Me); 0.74 (*s*, Me); 5.28 (*d*, $J = 8.0$, CH); 5.32 (*d*, $J = 8.0$, CH); 7.22–7.30 (*m*, 12 arom. H); 7.37–7.45 (*m*, 6 arom. H); 7.51–7.53 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.1, 26.8 (Me); 79.2, 79.4 (CH); 89.4 (*d*, ^2J(C,P) = 2.6), 90.0 (*d*, ^2J(C,P) = 4.3), 114.2 (C); 127.0, 127.2, 127.3, 127.5, 127.7, 127.8, 128.1, 128.3, 128.40, 128.41, 128.8, 128.9 (CH); 139.1, 142.1, 142.4 (C). ^{31}P-NMR (162 MHz, $CDCl_3$): −24.99. HR-MS: 1061.3193 ($[M + Na]^+$, $C_{62}H_{56}NaO_{11}P_2$; calc. 1061.3196 (−0.28 ppm)). MALDI-FT-ICR-MS: 1061.3 (10, $[M + Na]^+$); 431.2 (97), 345.2 (65), 273.0 (100), 200.9 (63). Anal. calc. for $C_{62}H_{56}O_{11}P_2$ (1039.05): C 71.67, H 5.43; found: C 71.23, H 5.65.

6. *Products* **31**, **32**, **34**, **36**–**41** *of Experiments Aimed at Preparation of C,P-Derivatives. (3*R*)-3-(2,2-Diphenylethenyl)-2,2-diphenyloxirane* (**31**). To a suspension of **3** in DMF (15 ml) under Ar, $LiPH_2$ (0.14g, 3.51 mmol) was added. The dark brown mixture was stirred for 10 min at r.t., 15 h at 80°, and again at r.t. for 13 h, then H_2O (degassed, 30 ml) and Et_2O (60 ml) were added. The org. layer was washed with aq. NaCl soln. and dried (Na_2SO_4), the solvent was removed under reduced pressure to afford **31** (0.32 g, 86%), which was recrystallized from acetone at −20°. Colorless powder. $[\alpha]_D^{r.t.} = -35.8$ ($c = 1.25$, $CHCl_3$). IR ($CHCl_3$): 3083*w*, 3062*m*, 3008*s*, 1952*w*, 1893*w*, 1812*w*, 1658*w*, 1600*m*, 1495*s*, 1447*s*, 1319*w*, 1280*w*, 1075*m*, 1030*m*, 941*w*, 910*w*, 628*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.91 (*d*, $J = 8.72$, CH); 5.52 (*d*, $J = 8.27$, CH); 7.09–7.56 (*m*, 20 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 64.24, 68.24, 124.02, 126.84, 127.16, 127.25, 127.70, 127.76, 127.86, 127.95, 128.14, 128.27, 128.36, 128.75, 130.14, 130.71, 137.57, 138.84, 140.71, 141.53, 148.40. FAB-MS: 374 (1, M^+), 372 (2), 358, (7), 344 (16), 270 (25), 269 (100), 191 (73). Anal. data match those of *rac*-**31** in [35].

1,1′,1″,1‴-(Buta-1,3-diene-1,4-diylidene)tetrakisbenzene (**32**). At r.t. in an autoclave (7 ml) under Ar, **3** (2.05g, 4.07 mmol) and $ZnCl_2 \cdot Et_2O$ (2 ml, 2.00 mmol) were mixed and cooled to −196°. PH_3 Gas was condensed in (4 × *ca.* 20 ml each, 20 bar), and the temp. was allowed to rise to r.t. within 3 h (12 bar); after further 16 h at r.t., the temp. was increased to 90° for 2 h (130 bar) and then kept at 70° for 16 h (70 bar). After flushing several times with N_2, the yellow suspension was washed with Et_2O (10 ml), CH_2Cl_2 (10 ml), H_2O (20 ml), and Et_2O (50 ml) to afford **32** (1.16 g, 80%). ^{1}H-NMR (200 MHz, $CDCl_3$): 6.80 (*s*, 2 CH); 7.15–7.27 (*m*, 10 arom. H); 7.30–7.44 (*m*, 10 arom. H).

*(3a*R*,8a*R*)-Tetrahydro-2,2-dimethyl-4,4,8,8-tetraphenyl-1,3-dioxolo[4,5-*e*][1,3,2]dioxathiepin 6,6-Dioxide* (**34**). Compound **33** [3] (3.05 g, 5.95 mmol) was dissolved in CCl_4/MeCN/H_2O (8:8:12 ml), and the mixture was cooled to 0°. $NaIO_4$ (2.60 g, 12.2 mmol) and $RuCl_3$ (15 mg, 0.07 mmol) were added, and the mixture was stirred at 0° for 6.5 h. CH_2Cl_2 (10 ml) was added, and the phases were separated. The aq. layer was extracted with CH_2Cl_2, and the combined org. layers were washed with ice-cooled H_2O and sat. aq. NaCl soln., and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford **34** (2.97 g, 95%) as black solid foam (pure according to ^{1}H-NMR). To remove the color, the product was dissolved in CH_2Cl_2 (30 ml), charcoal (*ca.* 5 g) was added, and the mixture was stirred for 1 h at r.t. After filtration through *Celite*, the resulting orange soln. was concentrated under reduced pressure, where upon crystallization occurred. Trituration of the beige solid with Et_2O (15 ml) for 2 h afforded **34** (2.55 g, 81%). Colorless solid. *Caution:* Sulfate **34** is very prone to hydrolysis on a TLC plate. It should be stored at −18°. M.p. >95° (dec.). $[\alpha]_D^{r.t.} = -67.5$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3062*w*, 2995*w*, 2941*w*, 1600*w*, 1496*m*, 1448*m*, 1407*s*, 1385*m*, 1375*w*, 1165*m*, 1090*m*, 1052*w*, 1029*w*, 976*m*, 958*m*, 881*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (*s*, 2 Me); 5.42 (*s*, 2 CH); 7.27–7.37 (*m*, 12 arom. H); 7.43–7.47 (*m*, 4 arom. H); 7.54–7.58 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.00 (Me); 80.17 (CH); 92.35, 111.97 (C); 126.90, 127.84, 128.29, 128.36, 128.45, 128.56 (CH); 137.78, 142.10 (C). ESI-MS (pos.): 1625 (4, $[3\,M + K + 2]^+$), 1609 (26, $[3\,M + Na + 2]^+$), 1095 (22, $[2\,M + K]^+$), 1079 (100, $[2\,M + Na]^+$), 1074 (7, $[2\,M + NH_4]^+$), 592 (18, $[M + MeCN + Na]^+$), 494 (8, $[M - SO_4 - 2 + MeCN + Na]^+$), 431 (14, $[M - SO_4 - 2]^+$). ESI-MS (neg.): 559 (8, $[M + H_2O + OH]^-$), 545 (100, $[M + OH]^-$), 527 (2, $[M - 1]^-$). Anal. calc. for $C_{31}H_{28}O_6S$ (528.62): C 70.44, H 5.34, S 6.07; found: C 70.33, H 5.45, S 6.03.

*(3a*R*,7a*R*)-Tetrahydro-6-methoxy-2,2-dimethyl-4,4,7,7-tetraphenyl-4*H*-1,3-dioxolo[4,5-*d*][1,2]oxaphosphorin 6-Oxide* (**36**). Compound **3** (500 mg, 0.99 mmol) was treated with $P(OMe)_3$ (2 ml, 17 mmol) in DMF (4 ml) at 120° according to *GP 6*. FC (SiO_2 (60 g); pentane/Et_2O 3:2) afforded **36** (170 mg, 32%). Colorless solid. M.p. 227–229°. R_f (hexane/AcOEt 2:1) 0.35. $[\alpha]_D^{r.t.} = -122.0$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 3450*w* (br.), 3063*w*, 3007*m*, 2955*w*, 1600*w*, 1495*m*, 1448*m*, 1384*m*, 1375*m*, 1258*s*, 1171*m*, 1128*m*, 1095*s*, 1077*m*, 1056*s*, 985*s*, 947*m*, 926*m*, 912*m*, 892*w*, 874*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.79 (*s*, Me); 1.69 (*s*, Me); 2.87 (*d*, ^3J(H,P) = 10.9, Me); 4.24 (*dd*, $J = 10.0$, ^4J(H,P) = 0.7, CH); 5.33 (*dd*, $J = 10.0$, ^3J(H,P) = 1.2, CH); 7.16–7.35 (*m*, 12 arom. H); 7.47–7.53 (*m*, 4 arom. H); 7.56–7.60 (*m*, 2 arom. H); 7.87–7.91 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 25.88, 27.38, 53.53 (*d*, ^2J(C,P) = 8.0) (Me); 58.83 (*d*, ^1J(C,P) = 117.8) (C); 75.49 (*d*, J(C,P) = 2.6), 80.79 (*d*, J(C,P) = 5.4) (CH); 85.85 (*d*, ^2J(C,P) = 8.4), 111.58 (C); 125.29, 126.81, 126.99, 127.02, 127.11, 127.39, 127.53, 127.55, 127.62, 127.99, 128.09, 128.11, 129.13, 129.19, 132.19, 132.29 (CH) (C,P couplings!); 137.36 (*d*, J(C,P) = 2.3), 139.57 (*d*, J(C,P) = 8.9), 140.24, 144.31 (*d*, J(C,P) = 8.7) (C). ^{31}P-NMR (121 MHz, $CDCl_3$): 21.26. MALDI-FT-ICR-MS: 549.2 (24, $[M + Na]^+$), 491.1 (7), 469.2 (11), 455.2 (19), 451.1 (17), 437.2 (18), 431.2 (20), 397.2 (88), 373.2 (41), 355.1 (100). HR-MS: 549.1774 ($[M + Na]^+$, $C_{32}H_{31}NaO_5P^+$; calc. 549.1801 (−4.9 ppm)). Anal. calc. for $C_{32}H_{31}O_5P$ (526.57): C 72.99, H 5.93; found: C 72.97, H 6.13.

*(3a*R*,6*R*,7a*R*)- and (3a*R*,6*S*,7a*R*)-Tetrahydro-2,2-dimethyl-4,4,6,7,7-pentaphenyl-4*H*-1,3-dioxolo[4,5-*d*][1,2]oxaphosphorin 6-Oxide* ((R_P)-**37** and (S_P)-**37**, resp.). Compound **3** (250 mg, 0.50 mmol) was treated with $PhP(OMe)_2$ (0.4 ml, 2.52 mmol) in DMF (4 ml) at 120° according to *GP 6*. FC (SiO_2 (20 g); pentane/Et_2O 8:2 → Et_2O) afforded (R_P)-**37** (61 mg, 22%) and (S_P)-**37** (35 mg, 12%). Colorless solids.

Data of (R_P)-**37**. M.p. 208–210°. R_f (hexane/AcOEt 2:1) 0.37. $[\alpha]_D^{r.t.} = -189.9$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3404br. *w*, 3064*w*, 2991*m*, 2935*w*, 1599*w*, 1495*m*, 1448*m*, 1438*w*, 1384*m*, 1374*w*, 1170*m*, 1126*m*, 1108*s*, 1094*s*, 1036*w*, 1005*s*, 989*s*, 935*w*, 924*w*, 905*m*, 865*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.62 (*s*, Me); 1.58 (*s*, Me); 4.91 (*dd*, $J = 10.0$, J(H,P) = 0.6, CH); 5.49 (*dd*, $J = 10.0$, J(H,P) = 0.8, CH); 6.85–7.13 (*m*, 8 arom. H); 7.16–7.40 (*m*, 11 arom. H); 7.61–7.66 (*m*, 4 arom. H); 7.69–7.75 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 25.77, 27.41 (Me); 61.75 (*d*, ^1J(C,P) = 73.2) (C); 76.29 (*d*, J(C,P) = 7.1), 80.23 (*d*, J(C,P) = 7.8) (CH); 87.46 (*d*, ^2J(C,P) = 10.3), 112.15 (C); 125.46, 126.81, 126.85, 126.88, 126.91, 127.04, 127.17, 127.67, 127.91, 127.95, 128.11, 128.35, 129.54, 129.61, 130.95, 130.98, 131.95, 132.05, 133.46, 133.53 (CH) (C,P couplings!); 130.81 (*d*, ^1J(C,P) = 138.4), 138.28 (*d*, J(C,P) = 4.1), 140.26 (*d*, J(C,P) = 2.3), 140.68 (*d*, J(C,P) = 3.4), 145.03 (*d*, J(C,P) = 4.1) (C). ^{31}P-NMR (121 MHz, $CDCl_3$): 37.90. MALDI-FT-ICR-MS: 611.2 (3, $[M + K]^+$), 595.2 (26, $[M + Na]^+$), 455.2 (10), 431.2 (13), 397.2 (100), 357.2 (9), 330.1

(49), 321.1 (16). HR-MS: 595.1981 ([M + Na]$^+$, $C_{37}H_{33}NaO_4P^+$; calc. 595.2008 (−4.5 ppm)). Anal. calc. for $C_{37}H_{33}O_4P$ (572.64): C 77.61, H 5.81; found: C 77.66, H 5.97.

Data of (S_P)-**37**. M.p. 239–240° (dec.). R_f (hexane/AcOEt 2:1) 0.25. $[\alpha]_D^{r.t.} = -124.8$ ($c = 0.69$, $CHCl_3$). IR ($CHCl_3$): 3426*w* (br.), 3058*w*, 2991*m*, 1600*w*, 1496*m*, 1449*m*, 1437*w*, 1383*m*, 1374*w*, 1170*m*, 1116*m*, 1094*s*, 1075*m*, 1034*w*, 1102*m*, 981*s*, 940*m*, 921*w*, 903*m*, 864*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.92 (*s*, Me); 1.42 (*s*, Me); 4.64 (*d*, J = 9.8, CH); 5.58 (*dd*, J = 9.8, J(H,P) = 1.9, CH); 7.02–7.56 (*m*, 19 arom. H); 7.61–7.67 (*m*, 2 arom. H); 7.78–7.87 (*m*, 2 arom. H); 7.91–7.97 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.23, 26.75 (Me); 62.34 (*d*, ^1J(C,P) = 75.6) (C); 74.22, 79.14 (*d*, J(C,P) = 4.9) (CH); 90.11 (*d*, ^2J(C,P) = 8.6), 110.76 (C); 125.70, 126.83, 126.93, 127.20, 127.23, 127.48, 127.65, 127.91, 128.03, 128.20, 128.28, 128.38, 128.61, 129.92, 129.98, 132.64, 132.75, 134.32, 134.45 (CH) (C,P couplings!); 130.10 (*d*, ^1J(C,P) = 136.7), 138.02, 139.33, 140.30 (*d*, J(C,P) = 6.1), 145.66 (*d*, J(C,P) = 7.3) (C). ^{31}P-NMR (121 MHz, $CDCl_3$): 35.37. MALDI-FT-ICR-MS: 611.2 (7, [M + K]$^+$), 595.2 (64, [M + Na]$^+$), 455.2 (9), 431.2 (21), 397.2 (100), 357.2 (9), 330.1 (45), 321.1 (12). HR-MS: 595.1966 ([M + Na]$^+$, $C_{37}H_{33}NaO_4P^+$; calc. 595.2008 (−7.1 ppm)).

Dimethyl P-*[{(4*R,*5*R*)-5-[(Hydroxy)(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}(diphenyl)methyl]phosphonate* (**38**). Sulfate **34** (250 mg, 0.47 mmol) was treated with $P(OMe)_3$ in DMF (3 ml) at 80° according to *GP 6*. FC (SiO_2 (70 g); pentane/Et_2O 8:2 → pentane/Et_2O 1:1) and subsequent precipitation from CH_2Cl_2/hexane afforded **38** (136 mg, 51%). Colorless solid. M.p. 234–237°. R_f (hexane/AcOEt 8:2) 0.43. $[\alpha]_D^{r.t.} = -117.6$ ($c = 1.09$, $CHCl_3$). IR ($CHCl_3$): 3324br. *m*, 3062*w*, 3007*m*, 2956*m*, 2853*w*, 1600*w*, 1495*m*, 1447*m*, 1380*w*, 1370*w*, 1166*m*, 1056*s*, 1035*s*, 875*w*, 830*w*, 658*w*, 632*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.25 (*s*, Me); 0.51 (*s*, Me); 3.55 (*d*, ^3J(H,P) = 10.9, Me); 3.64 (*d*, ^3J(H,P) = 10.6, Me); 5.26 (*dd*, J = 6.0, ^4J(H,P) = 0.6, CH); 5.81 (*dd*, J = 6.0, ^3J(H,P) = 2.4, CH); 5.99 (br. *s*, OH); 7.17–7.34 (*m*, 12 arom. H); 7.44–7.51 (*m*, 4 arom. H); 7.55–7.60 (*m*, 2 arom. H); 7.71–7.76 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.14, 27.99, 53.40 (*d*, ^2J(C,P) = 8.0), 54.72 (*d*, ^2J(C,P) = 7.3) (Me); 60.32 (*d*, ^1J(C,P) = 131.7) (C); 78.45 (*d*, J(C,P) = 7.4) (CH); 78.49 (C); 83.27 (CH); 111.49 (C); 126.84, 126.85, 126.89, 126.92, 127.01, 127.04, 127.13, 127.32, 127.34, 127.57, 127.84, 129.48, 131.69, 131.74, 132.73, 132.81 (CH) (C,P couplings!); 137.19 (*d*, ^2J(C,P) = 2.1), 139.45 (*d*, ^2J(C,P) = 10.0), 143.66, 149.34 (C). ^{31}P-NMR (121 MHz, $CDCl_3$): 28.50. MALDI-FT-ICR-MS: 597.2 (3, [M + K]$^+$), 581.2 (100, [M + Na]$^+$), 483.2 (6), 431.2 (8), 373.2 (31), 355.1 (9), 341.1 (6), 305.1 (11), 298.1 (25), 289.1 (41). HR-MS: 581.2054 ([M + Na]$^+$, $C_{33}H_{35}NaO_6P^+$; calc. 581.2063 (−1.5 ppm)). Anal. calc. for $C_{33}H_{35}O_6P$ (558.61): C 70.96, H 6.32; found: C 70.92, H 6.48.

Dimethyl P-*[{(4*R,*5*R*)-5-[(methoxy)(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}(diphenyl)methyl]phosphonate* (**39**). Compound **35** [1a] (1.45 g, 2.91 mmol) was treated with $P(OMe)_3$ (3.5 ml, 30 ml) in DMF (10 ml) at 120° according to *GP 6*. The residue was dissolved in CH_2Cl_2 (15 ml), the soln. was washed with H_2O, and the org. layer was separated (tedious phase separation!). The aq. layer was extracted with CH_2Cl_2 (3×), the combined org. layers were washed with H_2O and sat. aq. NaCl soln., dried (Na_2SO_4), and concentrated under reduced pressure. The crude product (1.88 g) was triturated with Et_2O (*ca.* 10 ml) to afford **39** (990 mg, 59%). Slightly beige powder. For anal. purposes, a sample was purified by FC (pentane/Et_2O 4:1 → Et_2O). Colorless powder. M.p. 225–226°. R_f (hexane/AcOEt 4:1) 0.14. $[\alpha]_D^{r.t.} = -3.2$ ($c = 1.11$, $CHCl_3$). IR ($CHCl_3$): 3389br. *w*, 3059*w*, 3002*m*, 2953*m*, 2850*w*, 1600*w*, 1494*m*, 1445*m*, 1380*w*, 1370*w*, 1170*m*, 1080*s*, 1035*s*, 909*w*, 881*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.80 (*s*, Me); 1.35 (*s*, Me); 2.08 (*s*, MeO); 3.39 (*d*, ^3J(H,P) = 10.9, Me); 3.65 (*d*, ^3J(H,P) = 10.8, Me); 4.67 (*dd*, ^3J(H,P) = 18.7, J = 7.7, CH); 5.56 (*d*, J = 7.7, CH); 7.10–7.16 (*m*, 2 arom. H); 7.21–7.35 (*m*, 14 arom. H); 7.55–7.60 (*m*, 2 arom. H); 7.67–7.72 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.30, 27.67, 51.38, 52.93 (*d*, ^2J(C,P) = 7.9), 53.35 (*d*, ^2J(C,P) = 7.3) (Me); 60.75 (*d*, ^1J(C,P) = 134.8) (C); 80.62 (*d*, J(C,P) = 5.9), 81.99 (*d*, J(C,P) = 6.5) (CH); 84.22, 108.58 (C); 126.64, 126.66, 126.72, 126.84, 126.88, 126.90, 127.27, 127.40, 127.48, 129.84, 131.10, 131.43, 131.49, 132.37, 132.45 (CH) (C,P couplings!); 137.61, 138.94, 140.48, 140.56 (C). ^{31}P-NMR (121 MHz, $CDCl_3$): 28.66. MALDI-FT-ICR-MS: 611.2 (5, [M + K]$^+$), 595.2 (75, [M + Na]$^+$), 373.2 (5), 298.1 (100). Anal. calc. for $C_{34}H_{37}O_6P$ (572.64): C 71.31, H 6.51; found: C 71.24, H 6.63.

*[{(4*R,*5*R*)-5-[(Methoxy)(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}(diphenyl)methyl](diphenyl)phosphorane Oxide* (**40**). Compound **34** (250 mg, 0.50 mmol) was treated with $Ph_2P(OMe)$ (450 mg, 2.1 mmol) in DMF (4 ml) at 120° according to *GP 6*. FC (SiO_2 (50 g); pentane/Et_2O 4:1 → Et_2O) and subsequent trituration with Et_2O afforded **40** (85 mg, 25%). Colorless powder. M.p. 183–

199°. R_f (hexane/AcOEt 4:1) 0.2. $[\alpha]_D^{r.t.} = -57.3$ ($c = 1.57$, $CHCl_3$). IR ($CHCl_3$): 3326*w* (br.), 3058*m*, 2988*m*, 2827*w*, 1600*w*, 1495*m*, 1447*m*, 1437*m*, 1382*m*, 1372*m*, 1166*s*, 1091*s*, 1064*s*, 1036*w*, 1001*w*, 976*w*, 908*w*, 869*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.70 (*s*, Me); 0.97 (*s*, Me); 2.05 (*s*, MeO); 4.98–5.02 (*m*, CH); 5.37 (*d*, $J = 7.7$, CH); 6.97–7.81 (*m*, 30 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.05, 27.23, 51.07 (Me); 62.96 (*d*, ^1J(C,P) = 60.7) (C); 80.35 (*d*, ^3J(C,P) = 8.0), 82.02 (*d*, ^2J(C,P) = 4.2) (CH); 83.99, 108.03 (C); 126.39, 126.79, 126.88, 127.00, 127.02, 127.10, 127.22, 127.33, 127.40, 127.50, 129.79, 130.33, 130.35, 130.48, 130.50, 131.01, 132.70, 132.75, 133.17, 133.20, 133.25, 133.30, 133.37 (CH) (C,P couplings!); 134.14 (*d*, ^1J(C,P) = 93.8), 134.57 (*d*, ^1J(C,P) = 90.9), 135.75, 137.72, 137.91 (*d*, ^2J(C,P) = 5.2), 140.54 (C). ^{31}P-NMR (121 MHz, $CDCl_3$): 36.30. MALDI-FT-ICR-MS: 700.3 (2, $[M + K]^+$), 687.3 (84, $[M + Na]^+$), 431.2 (20), 390.1 (100), 368.1 (14). Anal. calc. for $C_{44}H_{41}O_4P$ (664.78): C 79.50, H 6.22; found: C 79.67, H 6.27.

*(4*S*,5*R*)-4-(Diphenylmethyl)-5-[(methoxy)(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane* (**41**). To a suspension of $CeCl_3$ (128 mg, 0.52 mmol) in THF (10 ml), **40** (150 mg, 0.22 mmol) and $LiAlH_4$ (20 mg, 0.52 mmol) were added consecutively at r.t. After stirring for 2.5 h (TLC control), 1N aq. NaOH soln. (1 ml), H_2O (8 ml) and Et_2O (10 ml) were added. The org. layer was separated, and the aq. layer was extracted with Et_2O. The combined org. layers were washed with sat. aq. NaCl soln., dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by FC (SiO_2 (20 g); pentane/Et_2O 4:1) to afford **41** (45 mg, 45%). White foam. M.p. 73–78°. R_f (hexane/AcOEt 2:1) 0.73. $[\alpha]_D^{r.t.} = -19.1$ ($c = 1.06$,

Table 1. *Crystallographic Data for* **10**, **12a**, **12b**, *(*R*)-*__15__, *and* **23**

	10	**12a**	**12b**	(*R*)-**15**	**23**
Formula	$C_{43}H_{40}N_2O_2$	$C_{32}H_{30}N_2O_3^+O_{0.25}$	$C_{32}H_{30}N_2O_2S$	$C_{40}H_{38}N_2O_2S$	$C_{31}H_{28}ClO_5P$
Formula weight [g/mol]	616.81	494.58	506.64	610.78	546.95
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71069	0.71069	1.54178	1.54178	1.54184
Source	MoK_α	MoK_α	CuK_α	CuK_α	CuK_α
Crystal dimensions [mm]	0.4 × 0.3 × 0.3	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.1	0.5 × 0.3 × 0.1	0.4 × 0.3 × 0.2
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	orthorhombic
Space group	$P2_1$	$P2_12_12$	$P2_1$	$P1$	$P2_12_12_1$
θ Range [°]	$1.9 < \theta < 26.0$	$1.8 < \theta < 25.0$	$4.3 < \theta < 50.0$	$4.4 < \theta < 50$	$3.7 < \theta < 65.0$
a [Å]	9.472(1)	16.003(4)	8.30(1)	8.826(6)	9.671(4)
b [Å]	16.287(2)	14.252(2)	15.53(3)	10.090(9)	16.355(8)
c [Å]	11.194(2)	11.517(1)	10.34(2)	10.687(7)	17.239(4)
α [°]	90	90	90	68.84(6)	90
β [°]	99.82(1)	90	93.8(2)	80.04(5)	90
γ [°]	90	90	90	68.62(7)	90
V [Å^3]	1701.6(3)	2626.7(8)	1330(4)	825(1)	2727(2)
Z	2	4	2	1	4
ρ_{calc} [g cm^{-3}]	1.204	1.251	1.265	1.229	1.332
μ [mm^{-1}]	0.073	0.081	1.327	1.157	2.119
Total reflections measured	3635	2616	1441	1703	2663
Independent reflections	3459	2616	1441	1703	2637
Reflections observed	2451	1506	1383	1682	2139
No. of variables	584	366	335	407	343
Criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
Final R [%]	3.56	4.81	3.48	3.67	9.62
wR_2 [%]	9.90	14.94	9.41	8.96	28.38
Goodness-of-fit	1.093	1.137	1.012	1.123	2.343
$\Delta\rho$ (max, min) [e Å^{-3}]	0.138, −0.175	0.414, −0.232	0.154, −0.199	0.239, −0.217	0.641, −0.663
CCDC No.	157927	157930	157931	157932	157934

$CHCl_3$). IR ($CHCl_3$): 3060*m*, 3007*m*, 2938*m*, 2832*w*, 1949*w*, 1885*w*, 1813*w*, 1652*m*, 1598*m*, 1494*s*, 1445*s*, 1383*s*, 1373*m*, 1326*w*, 1264*s*, 1177*w*, 1135*s*, 1072*s*, 1033*w*, 990*w*, 867*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.02 (*s*, Me); 1.23 (*s*, Me); 3.18 (*s*, MeO); 3.24 (s, 1 H); 4.53–4.60 (*m*, 2 H); 7.09–7.35 (*m*, 18 arom. H); 7.42–7.47 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.96, 27.03 (Me); 51.76 (CH); 54.04 (Me); 79.41, 81.06 (CH); 83.49, 108.97 (C); 125.95, 126.41, 127.39, 127.56, 127.62, 128.09, 128.16, 128.66, 128.75, 129.93, 131.41 (CH); 140.27, 141.32, 142.80, 144.19 (C). MALDI-FT-ICR-MS: 487.2 (52, $[M + Na]^+$), 413.3 (14, $[M - O_2CMe_2 + Na]^+$), 357.2 (6), 279.1 (8), 273.0 (100, matrix), 263.1 (29), 219.1 (22), 180.1 (24). HR-MS: 487.2232 ($[M + Na]^+$, $C_{32}H_{32}NaO_3^+$; calc. 487.2244 (−2.5 ppm)).

7. *X-Ray Data*. See *Tables 1* and *2*.

Table 2. *Crystallographic Data for* **27**, **34**, *(*S_P*)*-**37**, **38**, *and* **39**

	27	**34**	(*S*$_P$)-**37**	**38**	**39**
Formula	$C_{44}H_{41}N_2O_3P$	$C_{31}H_{28}O_6S$	$C_{37}H_{33}O_4P$	$C_{33}H_{35}O_6P$	$C_{34}H_{37}O_6P$
Formula weight [g/mol]	676.76	528.59	572.60	558.58	572.61
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	1.54178	0.71073
Source	MoK_α	MoK_α	MoK_α	CuK_α	MoK_α
Crystal dimensions [mm]	0.4 × 0.3 × 0.2	0.5 × 0.4 × 0.3	0.4 × 0.2 × 0.2	0.2 × 0.1 × 0.1	0.4 × 0.2 × 0.2
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
θ Range [°]	$1.8 < \theta < 20.0$	$1.8 < \theta < 20.0$	$1.7 < \theta < 21.6$	$3.5 < \theta < 50.0$	$1.9 < \theta < 20.0$
a [Å]	10.657(4)	10.592(9)	9.661(5)	9.010(8)	11.683(7)
b [Å]	15.164(4)	16.26(2)	14.801(6)	16.45(2)	17.77(1)
c [Å]	11.728(4)	16.09(2)	21.172(6)	19.77(2)	18.373(8)
α [°]	90	90	90	90	90
β [°]	107.96(2)	107.76(7)	90	90	90
γ [°]	90	90	90	90	90
V [Å^3]	1803(1)	2639(5)	3027(2)	2925(5)	2956(3)
Z	2	4	4	4	4
ρ_{calc} [g cm^{-3}]	1.247	1.331	1.256	1.267	1.287
μ [mm^{-1}]	0.120	0.167	0.130	1.187	0.138
Total reflections measured	1907	2710	1989	1735	1604
Independent reflections	1785	2595	1989	1735	1604
Reflections observed	1515	2304	1517	1469	1316
No. of variables	493	690	382	362	371
Criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Final R [%]	2.52	2.63	2.69	10.16	2.83
wR_2 [%]	5.64	5.70	5.31	23.10	5.93
Goodness-of-fit	0.810	0.957	0.761	1.066	0.918
$\Delta\rho$ (max, min) [e Å^{-3}]	0.107, −0.106	0.103, −0.171	0.097, −0.114	0.630, −0.569	0.111, −0.134
CCDC No.	157933	157935	157936	157937	157938

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