2,4-Dioxa-7-aza-, 2,4-Dioxa-8-aza-, and 2,4-Dioxa-9-aza-3-phosphadecalins as Rigid Acetylcholine Mimetics: Syntheses and Characterization

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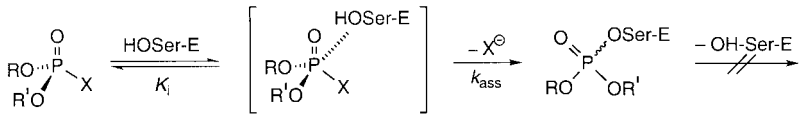
Phosphorylation of suitable piperidine precursors yielded a series of novel decalin-type O,N,P-heterocycles. The title compounds, P(3)-axially and P(3)-equatorially X-substituted, *cis*- and *trans*-configurated 2,4-dioxa-7-aza-, 2,4-dioxa-8-aza-, and 2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-oxides (X = Cl, F, 4-nitrophenoxy, and 2,4-dinitrophenoxy), are configuratively fixed and conformationally constrained P-analogues of acetylcholine and as such represent acetylcholine (7-aza and 9-aza isomers) or γ-homo-acetylcholine mimetics (8-aza isomers). Being irreversible inhibitors of acetylcholinesterase (AChE), the compounds are considered to be suitable probes for the investigation of the stereochemical course of the inhibition reaction by ^{31}P-NMR spectroscopy. Moreover, the design of these mimetics will enable studies of molecular interactions with AChE, in particular, the recognition conformation of acetylcholine.

1. Introduction. – The acute toxicity of organophosphorus compounds is mainly due to their inhibitory action on acetylcholinesterase and related serine hydrolases such as chymotrypsin (*Scheme 1*) [1]. Hence, the exact knowledge of the chemical reaction mechanisms is the prerequisite for the understanding of organophosphorus poisoning and its prophylaxis and therapy. Since the phosphorylated enzymes are considered to represent stable transition-state analogues [2], organophosphorus compounds are unique active-site probes of serine hydrolases and enable direct ^{31}P-NMR spectroscopic studies of the inhibited enzyme species [3].

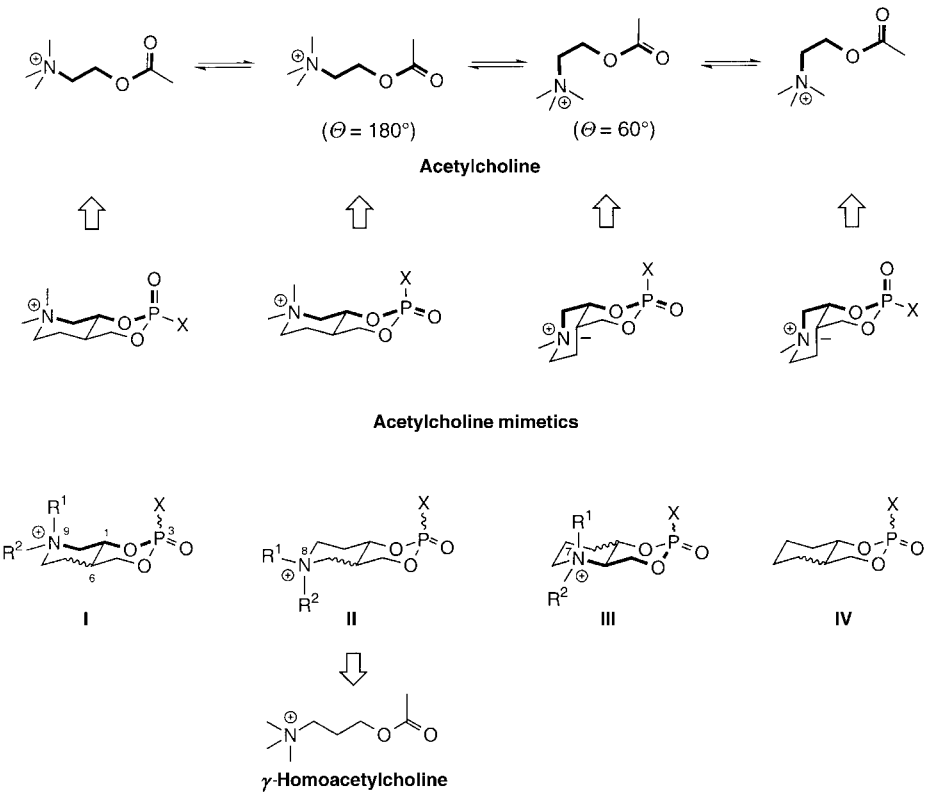
Scheme 1. E = Enzyme: Serine hydrolase, *e.g.* chymotrypsin ,acetylcholinesterase



E = Enzyme: Serine hydrolase, *e.g.*, chymotrypsin, acetylcholinesterase

As a result of recent investigations of the regio- and stereochemical pathways of the irreversible inhibition of serine hydrolases with configuratively fixed and conformationally restricted organophosphates, we had reported on the inhibition of δ-chymotrypsin with the enantiomerically pure 3-epimers of 3-(2,4-dinitrophenoxy)-substituted *cis*- and *trans*-configurated 2,4-dioxa-3-phosphabicyclo[4.4.0]decane 3-oxides (= hexahydro-4*H*-1,3,2-benzodioxaphosphorin 3-oxides **IV** (*Scheme 2*)) [4–6]. According to kinetic measurements, all *trans*-compounds inhibited the enzyme

Scheme 2



For each structural type (**I**–**IV**): *cis*-, *trans*-, axially and equatorially *P*-substituted isomers.
X = electron withdrawing group, *e.g.*, F, Cl, 4-nitrophenoxy, 2,4-dinitrophenoxy, or amino acid derivatives (model compounds).
R^1, R^2 = : (*tert*-amines, free bases), H, Me, Ph CH_2; $R^1 = R^2$ or $R^1 \neq R^2$.

irreversibly, the (S_P)-enantiomers reacting significantly faster. In the *cis*-series, only the (−)-enantiomer of the equatorially substituted 3-epimer was an irreversible inhibitor. The decisive stereochemical experiments were designed so that the enzyme and the inhibitors reacted in stoichiometric amounts to monitor the inhibition reaction directly by ^{31}P-NMR spectroscopy. The results have evidenced that the irreversible inhibition of δ-chymotrypsin follows different stereochemical pathways yielding diastereoisomeric phosphorylated derivatives of δ-chymotrypsin. Depending on the isomer, neat inversion (*trans*, X−P axial), inversion and retention (*trans*, X−P equatorial) [4], and neat retention (*cis*, X−P equatorial) [5] of the configuration at the P-atom took place. This result clearly showed the unexpected dependence of an enzyme's stereochemical pathway on the structure of the substrate. The covalent nature of the enzyme−P bond was later established by means of a deuterated inhibitor ((±)-*trans*-3-(2,4-dinitrophenoxy)-(1,5,5-$^2H_3$)-2,4-dioxa-3-phosphabicyclo[4.4.0]decane 3-oxide),

where ^{1}H-correlated ^{31}P{^{2}H}-NMR spectra of the enzyme–inhibitor adduct revealed a cross signal of the Ser^{195}-H_2 with the P-atom of the inhibitor [6].

Similar experiments with acetylcholinesterase (AChE) were not successful [7]. Although kinetics revealed the organophosphates **IV** to be potent irreversible inhibitors of AChE, only complex, not clearly interpretable ^{31}P-NMR spectra of the inhibited enzyme could be obtained when the inhibitors were applied in excess[1]). This fact might be mainly due to postinhibitory phenomena [8] with concomitant loss of the stereochemical information[2]). These findings prompted us to search for more-suitable inhibitors that would bind more tightly to AChE and are less prone to hydrolysis and dealkylation [8]. For this purpose, the novel O,N,P-heterocycles of the types **I**, **II**, and **III** (*Scheme 2*) seemed promising compounds, and their syntheses were envisaged. As exemplified in the generalized *Scheme 2*, the 9-, 8-, or 7-aza-3-phosphadecalins **I**, **II**, and **III** are configuratively fixed and conformationally constrained P-analogues of acetylcholine. Representing acetylcholine (see **I** and **III**) or γ-homoacetylcholine mimetics (see **II**), these novel organophosphates are considered to be better suited for the attempted ^{31}P-NMR investigations. Moreover, the design of these mimetics will enable studies of molecular interactions with AChE, in particular the recognition conformation of acetylcholine [9–12][3]).

2. Syntheses of the Acetylcholine Mimetics of Type I and II (9- and 8-Aza-3-phosphadecalins). – 2.1. *General.* As outlined in *Scheme 3*, the synthesis of both compound types principially follows the same protocols, the main difference being the significantly different chemical and physical behaviors of the individual isomers. Keysteps in the syntheses of the starting 3-hydroxypiperidine-4-methanols **4** and **8** and 4-hydroxypiperidine-3-methanols **6** and **10** (*Scheme 3*) are the generation of a favorable ratio of the *cis*/*trans*-isomers that are formed by the reduction of the oxopiperidinecarboxylates **1** [10][14] and **2** [11][14] and, in particular, efficient separation methods. For these purposes, the procedures in [10][11][14] had to be modified and optimized [15–17]. The 8- and 9-aza-3-phosphadecalins **19**–**26** (*Fig. 1*) and **35**–**42** (*Fig. 2*) are prepared by cyclization of the corresponding hydroxypiperidinemethanol with the appropriate P-reagent (according to the desired substituent X), thus affording a ratio of the P-epimers of *ca.* 1:1)[4]). In all cases, the formation of both epimers (**a** = axial, **b** = equatorial) is evidenced by ^{31}P-NMR spectroscopy [4][5][19] (see *Sect. 4*). However, when X = Cl and X = 2,4-dinitrophenoxy, only the respective axial epimers could be isolated, as the equatorial ones rapidly epimerize during workup. The *N*-benzyl-*N*-methylammonium compounds **27**–**29**, **31**–**33** (*Fig. 1*), **43**–**45**, and **47**–**49** (*Fig. 2*) are prepared by methylating the respective *N*-benzyl derivatives with methyl trifluoromethanesulfonate (TfOMe) in abs. $CHCl_3$ or MeCN and are isolated as inseparable *N*-epimer mixtures. The final target *N*,*N*-dimethylammonium

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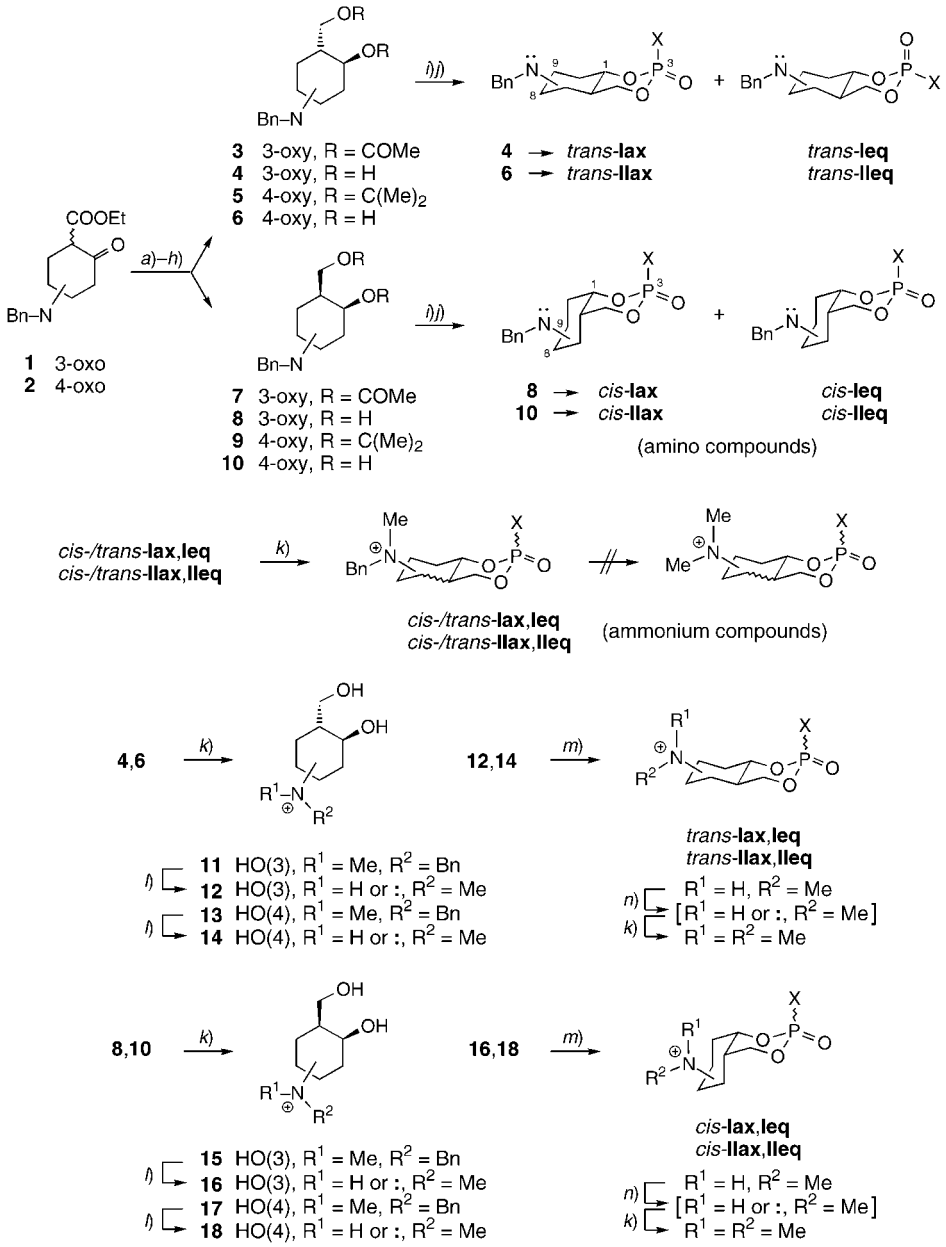
[1]) Compared to δ-chymotrypsin, AChE is a far more complex enzyme, and stoichiometric inhibiton was *a priori* not considered to provide reliable results.

[2]) For exper. details and tentative interpretations of the results, see [7].

[3]) This topic is discussed in one of our following papers [13].

[4]) The alternative way *via* nucleophilic reactions at the corresponding phosphorochloridates (prepared by cyclization of the hydroxypiperidinemethanols with $POCl_3$), showed strong diastereoselectivity in favor of the axial epimers; therefore, the equatorial epimers could be isolated in only minor amounts, see also [18].

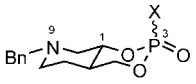
Scheme 3. *Synthesis of the Type-***I** *and Type-***II** *Compounds*

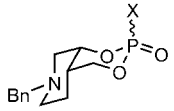


X = Cl, F, 4-$NO_2C_6H_4O$, 2,4-$(NO_2)_2C_6H_3O$; $Me(CF_3SO_3^-)$ as counter-ion (ammonium compounds).

a) $NaBH_4$, MeOH, 0° (*cis/trans ca.* 3:2 from **1**). *b*) $NaBH_4$, ^{i}PrOH, r.t., then $LiAlH_4$, Et_2O, r.t. (*cis/trans ca.* 1:1 from **2**). *c*) Ac_2O, pyridine, r.t. *d*) Chromatography (SiO_2, hexane/AcOEt → **3** + **7**). *e*) 2N NaOH/MeOH, 40° → **4** + **8**. *f*) $(Me)_2C(OMe)_2$, TsOH, CH_2Cl_2, 50°. g) Chromatography (SiO_2, hexane/Et_2O → **5** + **9**). *h*) 1N HCl, 60° → **6** + **10**. *i*) $Cl_2P(O)X$, Et_3N, CH_2Cl_2 or Et_2O, 0°. *j*) Chromatography (SiO_2, hexane/Et_2O or hexane/AcOEt). *k*) CF_3SO_3Me, $CHCl_3$, r.t. *l*) H_2, Pd/C, EtOH, r.t. *m*) $Cl_2P(O)X$, $CHCl_3$, 80°. *n*) 2N NaOH/sat. NaCl/$CHCl_3$, extraction, < 1 min (!), r.t.

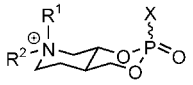
congeners (*e.g.*, **30a**; *Fig. 1*) could not be prepared as expected after hydrogenolysis of the corresponding *N*-benzyl-*N*-methylammonium compounds (*e.g.*, **29a**; *Fig. 1*) and methylation of the intermediate *N*-methylazaphosphadecalins. The X-substituent at the P-atom was either removed or reduced, and the equatorial derivatives were completely epimerized. Moreover, being very strong bases, the *N*-methylazaphosphadecalins could not be deprotonated easily, and their high nucleophilicity resulted in uncontrollable reactivity. Therefore the *N*,*N*-dimethylammonium compounds had to be prepared from the respective hydroxy-1-methylpiperidinemethanols **12**, **16**, **14**, and **18** (*Scheme 3*) *via* the 3-X-substituted 8- or 9-methyl-2,4-dioxa-8- or -9-aza-3-phosphabicyclo[4.4.0]decane 3-oxides followed by methylation (TfOMe) of the latter *in situ*. Due to their physical and chemical characteristics, the ammonium compounds could not be purified, and the reaction conditions had to be chosen so that either the pure component or the by-products preciptitated. The characterized compounds are compiled in the *Figs. 1–3*.

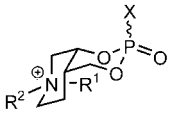




19a,**b** X = F
20a X = Cl
21a,**b** X = 4-$NO_2C_6H_4O$
22a,**b** X = 2,4-$(NO_2)_2C_6H_3O$

23a,**b** X = F
24a X = Cl
25a,**b** X = 4-$NO_2C_6H_4O$
26a,**b** X = 2,4-$(NO_2)_2C_6H_3O$



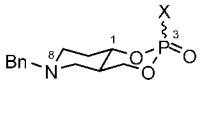


27a X = Cl, R^1 = Me, R^2 = Bn
28a,**b** X = 4-$NO_2C_6H_4O$, R^1 = Me, R^2 = Bn
29a X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = Me, R^2 = Bn
30a,**b** X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = R^2 = Me

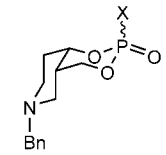
31a X = Cl, R^1 = Me, R^2 = Bn
32a,**b** X = 4-$NO_2C_6H_4O$, R^1 = Me, R^2 = Bn
33a X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = Me, R^2 = Bn
34a,**b** X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = R^2 = Me

Fig. 1. *Prepared 9-aza-actylcholine mimetics* (*Type* **I**)

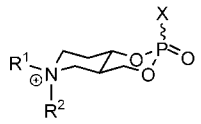
2.2. *9-Azaphosphadecalins* (*trans*- and *cis*-**Iax**,**Ieq**, *Scheme 3*, *Fig. 1*) [14–16]. Modifying the procedures in [10][13], ethyl 1-benzyl-3-oxopiperidine-4-carboxylate (**1**) was reduced ($NaBH_4$, MeOH, 0°), the resulting *ca.* 2:3 mixture of the hydroxypiperidinemethanols **4**/**8** were acetylated and the diacetates **3**/**7** separated by column chromatography (*Scheme 3*). Saponification of the pure diastereoisomers **3** and **7** afforded the *trans*- and *cis*-1-benzyl-3-hydroxypiperidine-4-methanols **4** and **8**, respectively. Reaction with selected phosphoric trihalides or phosphorodichloridates ($Cl_2P(O)X$, X = Cl, F, 4-$(NO_2)C_6H_4O$, 2,4-$(NO_2)_2C_6H_3O$) and chromatographic separation of the epimer mixtures gave the respective 3-X-substituted *cis*- and *trans*-9-benzyl-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-oxides **19**–**26**. Methylation (TfOMe) of the latter yielded the corresponding *N*-benzyl-*N*-methylammonium compounds **27**–**29** and **31**–**33**. The target *N*,*N*-dimethylammonium trifluoromethane-



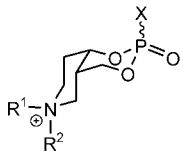
35a,**b** X = F
36a X = Cl
37a,**b** X = 4-$NO_2C_6H_4O$
38a,**b** X = 2,4-$(NO_2)_2C_6H_3O$



39a,**b** X = F
40a X = Cl
41a,**b** X = 4-$NO_2C_6H_4O$
42a,**b** X = 2,4-$(NO_2)_2C_6H_3O$

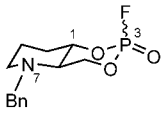


43a X = Cl, R^1 = Bn, R^2 = Me
44a,**b** X = 4-$NO_2C_6H_4O$, R^1 = Bn, R^2 = Me
45a X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = Bn, R^2 = Me
46a,**b** X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = Bn, R^2 = Me

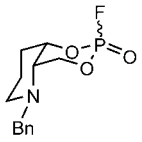


48a X = Cl, R^1 = Me, R^2 = Bn
48a,**b** X = 4-$NO_2C_6H_4O$, R^1 = Me, R^2 = Bn
49a X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = Me, R^2 = Bn
50a,**b** X = 2,4-$(NO_2)_2C_6H_3O$, R^1 = R^2 = Me

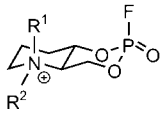
Fig. 2. *Prepared 8-aza-acetylcholine mimetics* (*Type* **II** *γ-homoacetylcholine*)



59a,**b**



60a,**b**



61 R^1 = Me, R^2 = Bn
62 R^1 = R^2 = Me
65 R^1 = R^2 = H

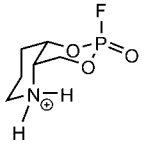


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Fig. 3. *Prepared 7-aza-acetylcholine mimetics* (*Type* **III**)

sulfonates **30a** and **34a**[5]) were prepared from the 3-hydroxy-1-methylpiperidine-4-methanols **12** and **16** that had been obtained after methylation (TfOMe) of **4** and **8** to yield the *N*-benzyl-*N*-methylammonium salts **11** and **13**, respectively, followed by hydrogenolysis. Cyclization of **12** and **16** with 2,4-dinitrophenyl phosphorodichloridate and methylation (TfOMe) finally furnished **30a** and **34a**.

2.3. *8-Azaphosphadecalins* (*trans-* and *cis-***IIax**,**IIeq**, *Scheme 3, Fig. 2*) [15–17]. Similarly, modifying the procedures of [11][14], ethyl 1-benzyl-4-oxopiperidine-3-carboxylate (**2**) was reduced ($NaBH_4$, ^{i}PrOH, room temperature, then $LiAlH_4$, Et_2O,

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[5]) Kinetic investigations showed that both the 2,4-dinitrophenoxy-substituted *N*-benzyl-*N*-methylammonium and *N,N*-dimethylammonium compounds are only weak reversible inhibitors of AChE of comparable strength ($K_i \approx$ *ca.* 10^{-6} M) [15][16]. Due to this finding, together with the fact that the preparation of the *N,N*-dimethylammonium compounds was not satisfyingly reproducible, only selected congeners have been characterized [16].

0°), the resulting *ca.* 1:1 mixture **6**/**10** of the hydroypiperidinemethanols was transformed into the acetonides **5**/**9** that could easily be separated by column chromatography. Hydrolysis of the pure diastereoisomers **5** and **9** afforded the *trans*- and *cis*-1-benzyl-4-hydroxypiperidine-3-methanols **6** and **10**. The γ-homoacetylcholine mimetics **35**–**42**, the respective *N*-benzyl-*N*-methylammonium trifluoromethanesulfonates **43**–**45** and **47**–**49**, as well as the target *N*,*N*-dimethylammonium compounds **46a** and **50a**[5]) were prepared as described above. The latter were obtained after cyclization of the respective 4-hydroxy-1-methylpiperidine-3-methanols **14** and **18** with 2,4-dinitrophenyl phosphorodichloridate and methylation (TfOMe).

3. Synthesis of the Acetylcholine Mimetics of Type III (7-Aza-3-phospadecalins). – 3.1. *General*. Starting from the 3-hydroxypiperidine-2-methanols **52** and **58**, the 7-aza-3-phosphadecalins were made analogously to the 8- and 9-aza compounds as described above [21]. But the syntheses of **52** and **58** were not as straightforward. Though their precursor ethyl 1-benzyl-3-oxopiperidine-2-carboxylate (=ethyl 1-benzyl-3-oxopipecolate; **55**) is accessible as the kinetic product of the *Dieckmann* condensation of ethyl 4-[benzyl(2-ethoxy-2-oxoethyl)amino]butanoate [15], its preparation is not satisfactory[6]). As a consequence, we followed the alternative route depicted in *Scheme 4*. In the course of our work with the acetylcholine mimetics of the types **I** and **II**, it became evident that almost all of the chloro-, (4-nitrophenoxy)-, and (2,4-dinitrophenoxy)-azaphosphadecalins were only weak reversible inhibitors of AChE [15][16] (see [also 13]). Moreover, due to facile epimerization of the chloro- and (2,4-dinitrophenoxy)-substituted compounds, the equatorial epimers of only the 4-nitrophenoxy derivatives could be isolated and characterized. In contrast to this finding, the corresponding phosphorofluoridates turned out to be well suited for our purposes. They are irreversible inhibitors of AChE, and both epimers of all three types are accessible, a fact that allows cross-link comparisons of their inhibition characterisics. For these reasons, only the fluoridates for the type-**III** congeners were synthesized [21]. Unfortunately, in spite of extensive exploration, all attempts to reliably prepare the *N*,*N*-dimethylammonium derivatives were not successful in this series. In particular, the protocol elaborated for the 8- and 9-aza isomers was not applicable. Since kinetic investigations exhibited no significant difference between the free bases and the ammonium compounds [16][21] (see also [13]), only the corresponding *N*-benzyl derivatives of the type-**III** acetylcholine mimetics were characterized.

3.2. *7-Azaphosphadecalins* (*trans*- and *cis*-**IIIax**,**IIIeq**, *Scheme 4*, *Fig. 3*) [21]. The key 3-hydroxypiperidine-2-methanols **52** and **58** were prepared by hydrogenation (Rh/Alox, 60 bar H_2, pH 3) and *in situ* benzylation of 3-hydroxypyridine-2-methanol (**51**). The predominantly resulting *cis*-hydroxypiperidinemethanol **52** was transformed into the pivaloate **53**[7]) and the latter oxidized (*Swern*) to afford the 3-oxopiperidine-2-

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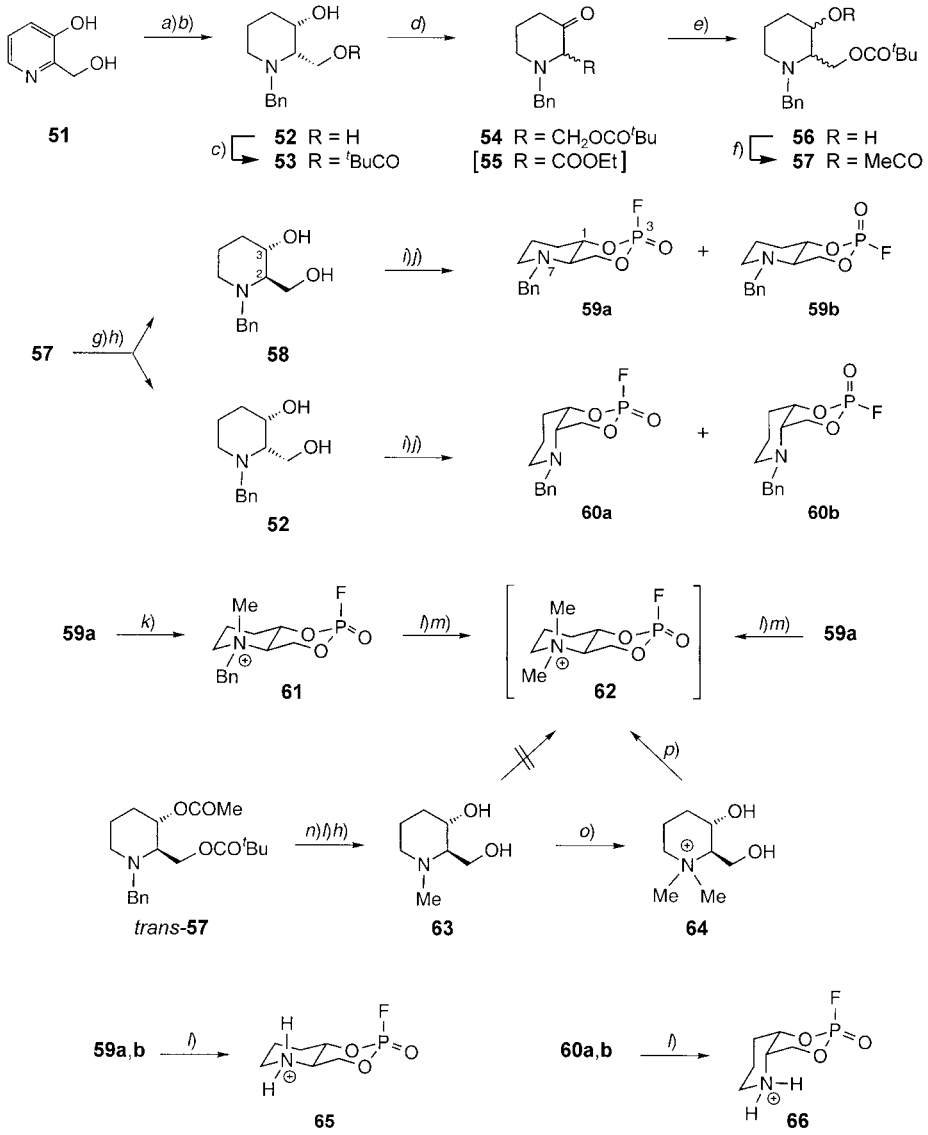
[6]) The thermodynamic product is ethyl 1-benzyl-3-oxopiperidine-4-carboxylate (**1**). Ethyl 1-benzyl-3-oxopiperidine-2-carboxylate (**55**) was accidentally isolated in 44% yield [15]. However, the procedure was not reproducible, and in spite of ample attempts to optimize the reaction conditions in favor of **55**, the yield never exceeded an unsatisfactory 30% (see also [20]). Moreover, **55** underwent a *retro*-reaction on storage for a while, yielding 1-benzylpyrrolidin-2-one.

[7]) The combination of both the acetic and pivalic acid esters was the most appropriate for an efficient chromatographic separation.

Scheme 4. *Synthesis of the Type-***III** *Compounds*



a) H_2, Rh/Alox, 60 bar, H_2O, pH 3, 35°. *b*) BnBr, K_2CO_3, EtOH, reflux. *c*) ^{t}BuCOCl, pyridine, −20°. *d*) $(COCl)_2$, DMSO, CH_2Cl_2, −60° (from **53**). *e*) $NaBH_4$, EtOH, −15° (*cis/trans ca.* 1:1 from **54**). *f*) Ac_2O, pyridine, r.t. g) Chromatography (SiO_2, hexane/AcOEt). *h*) KOH, EtOH/H_2O, r.t. *i*) $Cl_2P(O)X$, Et_3N, CH_2Cl_2 or Et_2O, 0°. *j*) Chromatography (SiO_2, hexane/Et_2O or hexane/AcOEt). *k*) CF_3SO_3Me, MeCN, 100°. *l*) H_2, Pd/C, EtOH, r.t. *m*) CF_3SO_3Me, Li_2CO_3, MeCN, sonication, r.t. *n*) CF_3SO_3Me (neat), sonication, r.t. *o*) CF_3SO_3Me, $CHCl_3$, r.t. *p*) $Cl_2P(O)F$, THF, r.t.

methyl pivaloate **54** that was reduced ($NaBH_4$, EtOH, $-15°$) to yield a *ca.* 1:1 mixture of the 3-hydroxy pivaloates **56**. Acetylation[7]), chromatographic separation of **57**, and saponification of the pure diastereoisomers furnished the *cis*- and *trans*-1-benzyl-3-hydroxypiperidine-2-methanols **52** and **58**. The 3-fluoro-7-aza-3-phosphadecalins **59a**,**b** and **60a**,**b** were obtained after cyclization with phosphoric dichloride fluoride [22] and chromatographic separation of the *P*-epimers. Experiments to prepare the corresponding ammonium compounds were performed with the *trans*-isomers since **59a** was the most-stable substrate in the series. The *N*-benzyl-*N*-methylammonium derivative **61** that was obtained after usual methylation of **59a** could be hydrogenolyzed and methylated *in situ* under special conditions (TfOMe, Li_2CO_3, sonication) to afford the *N*,*N*-dimethylammonium derivative **62** as a main component of a mixture[8]). But the product was only tentatively characterized by virtue of the ^{13}C- and ^{31}P-NMR signals anticipated for **62**. A similarly meager result was obtained when *trans*-3-hydroxy-2-(hydroxymethyl)-1,1-dimethyl-piperidinium (**64**) was cyclized with the phosphorus reagent. Though the *N*,*N*-dimethylammonium derivative **62** could be evidenced, the compound was again present in a inseparable mixture[8])[9]). In contrast, the protocol for the types **I** and **II**, *i.e.*, starting from 3-hydroxy-1-methylpiperidine-2-methanol (**63**), was not successful at all, and the target **62** could not be isolated. As demonstrated for **59b** and **60b**, hydrogenolytic removal of the *N*-benzyl group always resulted in quantitative epimerization at the P-atom, and only the axially substituted secondary ammonium salts **65** and **66** could be isolated. Generally, the outcome of all these *N*-alkylations is heavily dependent on the individual conditions and – most significantly – on both the reaction and workup time. In spite of ample exploration, we were not able to establish a reliable procedure to synthesize the target *N*,*N*-dimethylammonium compounds of the type-**III** acetylcholine mimetics.

4. Spectroscopic Properties. – The spectral characteristics of the novel azaphosphadecalins are very similar to those of the type-**IV** compounds, and all the structures can be assigned unequivocally. In particular, the ^{31}P-NMR spectra are most meaningful and exhibit the same essential features as discussed in [4][5][19]. Normally, the ^{31}P-NMR resonance of the axial epimer is shifted upfield with respect to the equatorial one[10]), and the magnitude of $^3J(P,H)$ in the ^1H-coupled ^{31}P-NMR is indicative of the conformation of the heterocyclic ring[11]). Due to the anomeric effect, electronegative substituents X occupy the stereoelectronically favored axial position. As a conse-

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[8]) Depending on the individual reaction conditions, the predominant products are *trans*-3-chloro-2-(chloromethyl)-1,1-dimethylpiperidinium chloride and phosphorofluoridic acid ($POF(OH)_2$) besides *N*-methyl- and *N*-demethylamines in variable concentrations. Obviously, the liberated chloride from $POCl_2F$ easily undergoes nucleophilic substitution reactions in the nonaqueous medium. In the course of all the trials, we encountered a series of surprising results that are not discussed further in this context. Although insufficient, the procedures indicated in the *Exper. Part* gave the best results and were reproducible to some extent.

[9]) Probably also the equatorial epimer is present (see *Exper. Part*).

[10]) The magnitude of the chemical shift difference ($\Delta\delta = \delta_{eq} - \delta_{ax}$) is indirectly proportional to the electronegativity of the P-substituent; we found a typical range of *ca.* 0.5–7 ppm [4][5][7].

[11]) The axial epimers show $^3J(P,H_{ax}-C(5)) \approx 0$ and $^3J(P,H_{eq}-C(5)) \approx 25$ Hz, whereas the equatorial ones have $^3J(P,H_{ax}-C(5)) \approx {}^3J(P,H_{eq}-C(5)) \approx 10-15$ Hz. Hence, the axial epimers exhibit a *d*-type and the equatorial ones a *m*-type splitting pattern.

quence, axially substituted cyclic phosphates adopt the chair and its equatorial counterparts a twist-boat conformation. Surprisingly, the ^{31}P-NMR chemical shifts of the fluoridates of the *cis*-series do not follow the general rule mentioned above and display an inverse behavior ($\Delta\delta < 0$)[12]). This finding can be explained by the F-atom being the substituent with the strongest electronegativity, and the enhanced flexibility of the *cis*-fused decalins allows facile conformational changes to render the anomeric effect most operative[13]).

5. Remarks. – The presented report summarizes the results of extensive preparative efforts during several years. Although the compounds look very similar, each isomer has individual, significantly different physical and chemical properties that cannot be anticipated, and each compound has to be treated adequately. Despite their pronounced reactivity, the *N*-benzyl derivatives of the acetylcholine mimetics **I** and **III** as well as the γ-homoacetylcholine mimetics **II** can well be handled. Unresolved problems are caused by the cationic compounds, especially the original target *N*,*N*-dimethylammonium congeners that constitute the real acetylcholine mimetics. Though the *N*-benzyl-*N*-methyl cations are accessible, the respective *N*-methyl-azaphosphadecalins cannot be isolated. Being highly basic and nucleophilic intermediates, they are extremely reactive substances that have to be transformed *in situ*. The quaternary ammonium salts proved to be rather tedious to handle. They are very hygroscopic and significantly more reactive than the free amines, and the fact that they cannot be purified is an additional drawback. Moreover, the equatorially substituted epimers are not accessible when a catalytic hydrogenation step is involved. Although not all of the congeners originally aimed at could be synthesized, the phosphorofluoridates of the types **I**, **II**, and **III**, *i.e.*, **19a**,**b**, **23a**,**b**, **35a**,**b**, **39a**,**b**, **59a**,**b** and **60a**,**b**, constitute a consistent set of closely related acetylcholinesterase inhibitors that enabled cross-linked investigations [13].

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Experimental Part

1. *General.* Continuous extraction of H_2O-soluble compounds (hydroxypiperidinemethanols, *etc.*) with Et_2O, from the H_2O soln. sat. with NaCl. The organophosphorus compounds were handled in a glove box (*Mecaplex* type *2201*) under dry N_2. Handling of volatile F-compounds in glassware with *Teflon* junctions; care must be taken when cleaning such glassware: prior to contact with alcohols (generation of dialkyl phosphorofluoridates), soaking in aq. NaOH soln. is indispensable. pH Determinations: *Knick Portamess 762 Calimatic*, *Mettler InLab-423-S7* electrode; calibration: *Mettler* standard buffers pH 4.01 and pH 7.00; electrolyte: *Mettler* standard, 3M KCl sat. with AgCl; measurements at 22°, accuracy $\pm$0.02 pH units. TLC: *Merck 60* F_{254} silica-gel plates; detection by UV_{254} light, by spraying with 'mostain' soln. ($(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ (40 g), $Ce(SO_4)_2$ (0.8 g), 10% H_2SO_4 soln. (800 ml)) and heating (blue spots) or *Schlittler*'s reagent (soln. *A:* H_2PtCl_6 (1 g), H_2O (6 ml), 2N HCl (20 ml); soln. *B:* KI (22.5 g) in H_2O (250 ml); soln. $A + B$ diluted to 1000 ml). Standard column chromatography (CC): alumina *90* (63–200 μm, *Merck 101097*, act. II–III) or silica gel *60* (40–63 μm, *Merck 109385*); CC of the hydrolytically labile azaphosphadecalins on modified silica gel *60*

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12) The same holds for the fluoridates of the type-**IV** *cis*-compounds [13].

13) For a discussion of conformational analysis, see a following paper [23].

(15–40 μm, *Merck. 115111*): silica gel (200 g) was washed with 1N HCl, thoroughly neutralized with H_2O, and reactivated by stepwise washing with EtOH and hexane and drying at 120° (pH of a 10% aq. slurry, 5.6), adsorbent/substance *ca.* 15–30:1, all separations within *ca.* 15 min (!). M.p.: *Mettler FP 5/52*; not corrected. UV: *Perkin-Elmer Lambda-9-* UV/VIS/NIR spectrophotometer, *Hewlett-Packard 8452A* diode-array spectrophotometer; λ_{max} (log ε) in nm. IR: *Perkin-Elmer 1600*-FT-IR, *Perkin-Elmer Paragon-1000PC*-FT-IR spectrometer; in cm^{-1}. ^1H-, ^{13}C-, and ^{31}P-NMR: *Bruker AC-300* or *ARX-300* (300.0, 75.4, and 121.4 MHz, resp.), *AMX-400* (400.0, 100.6, and 161.9 MHz, resp.), *DRX-500* (500.0, 125.7, and 202.4 MHz, resp.), *AMX-600* or *DRX-600* (600.0, 150.9, and 242.9 MHz, resp.; at 564.5 MHz for ^{19}F) spectrometers; chemical shifts δ in ppm rel. to the assigned solvent (Me_4Si as internal, H_3PO_4 (85% in D_2O) as external standard (0 ppm), coupling constants J in Hz; all assignments based on extensive interpretations of ^1H-, $^1H\{^{19}F\}$-, $^1H\{^{31}P\}$-, $^1H,^1H$-COSY, $^1H,^1H$-, $^1H,^{19}F$-NOESY, $^{13}C\{^1H\}$-, DEPT90, DEPT135, $^1H,^{13}C$-COSY (HSQC), $^1H,^{13}C$- (HMBC), ^{19}F-, ^{31}P-, and $^{31}P\{^1H\}$-NMR experiments; complex spin systems are interpreted according to 1st-order approximation, although, in several complex cases, the intensities show higher-order spectra; the signals are characterized according to their appearance and the relative intensities of the individual lines (*i.e.*, $ddd \neq dt$, although, in the latter case, three different coupling partners may be present, too). The specification of H_{ax} and H_{eq} in the phosphadecalins is strictly valid only for compounds adopting double-chair conformations, *i.e.*, for all compounds with axial X at the P-atom; for reasons of simplicity, this terminology is maintained also for the compounds with equatorial X, although the O,P-heterocyclic moiety adopts non-chair conformations. Due to the flexibility of the latter and the concomitant coalescence phenomena, high-field NMR spectra are often less resolved than expected. GC/MS: *Hewlett-Packard HP-5980* series *II* (GC), *HP-5971 MSD* (mass-selective detector, EI; 70 eV), column *HP-5*, 25 m × 0.2 mm, 0.33 μm; injector 180°, detector 330°; temp. program: 150° (2 min), 100°–240° (rate 30°/min), 290° (5 min). MS: *Varian MAT 112s*, *Varian MAT 90*, electron impact (EI), 70 eV; *Varian MAT 7011*, *Finnigan MAT SSQ 700*, chemical ionization (CI) with NH_3, unless otherwise stated; *Finnigan MAT TSQ 7000*, electrospray ionization (ESI).

2. *Piperidine Precursors* **3**–**18** (*for 9- and 8-Azaphosphadecalins* **I** *and* **II** (*Scheme 3*). *(±)*-trans- *and (±)*-cis-*1-Benzyl-3-hydroxypiperidine-4-methanol* (**4** and **8** resp.). A soln. of ethyl 1-benzyl-3-oxopiperidine-4-carboxylate hydrochloride (**1**; 10 g; *Aldrich. 14,320-O*) in MeOH (200 ml) was added dropwise to $NaBH_4$ (25 g) under vigourous stirring (*KPG*) at 0° [10]. After completing the addition, stirring of the heterogeneous mixture was continued at r.t. (20 h). H_2O (200 ml) was added, the mixture stirred for another 5 h at r.t., when MeOH was removed and the residue subjected to continuous extraction. After workup and drying (30°/0.05 Torr), **4**/**8** *ca.* 2:3 (GC) was obtained as a yellow oil (7.32 g, 98%). An aliquot (2 g) was subjected to CC (alumina, 2% MeOH/CH_2Cl_2): *cis*-isomer **8** (1.1 g), followed by the *trans*-isomer **4** (0.6 g). As this separation was not easily reproducible, crude **4**/**8** (4 g) was dissolved in anh. pyridine (20 ml) and Ac_2O (10 ml) and kept at r.t. (15 h). Usual workup afforded the mixture of the diacetates **3** and **7** (5.5 g, 99%). CC (SiO_2, hexane/AcOEt 2:3) gave a neat separation of *(±)*-trans-*1-benzyl-3-(acetyloxy)piperidine-4-methanol acetate* (**3**; 2.2 g) from the later eluting *(±)*-cis-*1-benzyl-3-(acetyloxy)piperidine-4-methanol acetate* (**7**; 3.0 g), both as yellowish, viscous oils.

Data of **3**: R_f (hexane/AcOEt 2:1) 0.44. IR ($CHCl_3$): 3030*w*, 2951*w*, 2810*w*, 2769*w*, 2360*m*, 2341*w*, 1733*s*, 1653*w*, 1466*w*, 1455*w*, 1370*m*, 1248*s*, 1115*w*, 1031*m*, 606*w*. ^1H-NMR (300 MHz, $CDCl_3$): 7.31–7.23 (*m*, H–C(2′) to H–C(6′)); 4.81 (*dt*, $^3J(3,2ax) = {}^3J(3,4) = 9.8$, $^3J(3,2eq) = 4.7$, H–C(3)); 4.03 (*AB* of *ABX*, not resolved, CH_2OCOMe); 3.54, 3.48 (*AB*, $^2J = 13.3$, PhCH_2); 3.09 (*m*, *dd*-like, $^2J = 1$, H_{eq}–C(2)); 2.81 (*m*, *dt*-like, $^2J = 11.2$, H_{eq}–C(6)); 2.04, 2.02 (each *s*, COMe); 1.96–1.87 (*m*, H_{ax}–C(2), H_{ax}–C(6)); 1.78–1.73 (*m*, H–C(4), H_{eq}–C(5)); 1.53 (*m*, *dq*-like, $w_{1/2} \approx 25$, H_{ax}–C(5)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 170.9, 170.2 (COMe); 137.8 (C(1′); 128.8 (C(3′), C(5′)); 128.2 (C(2′), C(6′)); 127.0 (C(4′)); 70.2 (C(3)); 64.6 (C(2)); 62.4 (C(6)); 56.7 (PhCH_2); 52.1 (CH_2OCOMe); 40.2 (C(4)); 27.1 (C(5)); 20.9, 20.7 (CO*Me*). CI-MS: 307 (17, $[M+2H]^+$), 306 (100, $[M+H]^+$).

Data of **7**: R_f (hexane/AcOEt 2:1) 0.26. IR ($CHCl_3$): 3030*m*, 2950*m*, 2807*m*, 2360*w*, 1732*s*, 1494*w*, 1454*m*, 1370*s*, 1248*s*, 1150*w*, 1107*w*, 1040*s*, 977*w*, 947*w*, 854*w*, 693*w*, 607*w*. ^1H-NMR (300 MHz, $CDCl_3$): 7.30–7.23 (*m*, H–C(2′) to H–C(6′)); 5.00 (br. *s*, $w_{1/2} \approx 10$, H–C(4)); 4.03 (*A* of *ABX*, $^2J = 11.0$, $^3J = 8.3$, CH_AOCOMe); 3.99 (*B* of *ABX*, $^2J = 11.0$, $^3J = 6.3$, CH_BOCOMe); 3.60, 3.50 (*AB*, $^2J = 13.4$, PhCH_2); 3.03 (*m*, *dd*-like, $^2J = 11$, H_{eq}–C(2)); 2.90 (*m*, *dt*-like, $^2J = 11.3$, H_{eq}–C(6)); 2.1–2.0 (*m*, H_{ax}–C(2)); 2.09, 2.02 (each *s*, COMe); 1.90 (*m*, $w_{1/2} \approx 25$, H_{ax}–C(6)); 1.71 (*m*, *q*-like, CH_2(5)); 1.55 (*X* of *ABX*, *dt*-like, $w_{1/2} \approx 20$, H–C(4)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 170.9, 170.6 (*C*OMe); 137.6 (C(1′); 128.8 (C(3′), C(5′)); 128.1 (C(2′), C(6′)); 127.0 (C(4′)); 67.8 (C(3)); 64.4 (C(2)); 62.4 (C(6)); 55.4 (PhCH_2); 52.2 (CH_2OCOMe); 37.6 (C(4)); 24.0 (C(5)); 21.0, 20.7 (CO*Me*). CI-MS: 307 (18, $[M+2H]^+$), 306 (100, $[M+H]^+$).

Saponification (2N NaOH in MeOH, 40°, TLC control) of **3** (2.2 g) and **7** (3.2 g) and continuous extraction afforded **4** (1.50 g, 97%) and **8** (2.20 g, 96%), both as colorless crystals.

Data of **4**: M.p. 111–112°. IR (KBr): 3379*s* (br.), 3091*s* (br.), 2909*s*, 2818*s*, 2362*m*, 1496*m*, 1444*m*, 1410*m*, 1366*s*, 1351*m*, 1294*m*, 1251*m*, 1204*m*, 1138*m*, 1102*s*, 1055*s*, 1003*s*, 956*s*, 874*m*, 789*m*, 759*s*, 705*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.33–7.26 (*m*, H–C(2′) to H–C(6′)); 3.78–3.66 (*m*, CH_2OH, H–C(3)); 3.56, 3.51 (*AB*, ^2J = 13.0, PhCH_2); 3.00 (*ddd*, ^2J = 10.5, ^3J(6eq,5ax) = 4.5, ^3J(6eq,5eq) = 1.5, H_{eq}–C(6)); 2.84 (*dd*, ^2J = 10.0, ^3J(2eq,3ax) = 4.0, H_{eq}–C(2)); 2.00 (*dt*, $^2J = {}^3J$(6ax,5ax) = 10.5, ^3J(6eq,5ax) = 2.5, H_{ax}–C(6)); 1.96 (*t*, $^2J = {}^3J$(2ax,3ax) = 10.0, H_{ax}–C(2)); 1.60–1.55 (*m*, CH_2(5)); 1.30 (*X* of *ABX*, *dq*-like, $w_{1/2} \approx 20$, H–C(4)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 139.0 (C(1′)); 130.7 (C(3′), C(5′)); 129.6 (C(2′), C(6′)); 128.4 (C(4′)); 73.5 (C(3)); 68.5 (CH_2OH); 64.1 (PhCH_2); 61.4 (C(2)); 54.0 (C(6)); 45.7 (C(4)); 27.5 (C(5)). CI-MS: 222 (100, $[M+H]^+$). See also [10][14].

Data of **8**: M.p. 82–84°. IR (KBr): 3375*s* (br.), 3085*s* (br.), 2916*s*, 2820*s*, 2362*m*, 1496*m*, 1468 *m*, 1410*m*, 1366*m*, 1340*m*, 1294*m*, 1251*m*, 1203*m*, 1132*m*, 1099*s*, 1046*s*, 1027*s*, 1008*s*, 956*s*, 921*m*, 775*m*, 759*s*, 705*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.25 (*m*, H–C(2′) to H–C(6′)); 3.95 (*s*, $w_{1/2} \approx 8$, H–C(3)); 3.74 (*A* of *ABX*, ^2J = 10.9, ^3J = 4.2, CH_AOH); 3.67 (*B* of *ABX*, ^2J = 10.9, ^3J = 5.7, CH_BOH); 3.528, 3.532 (*AB*, ^2J = 13.0, PhCH_2); 2.98–2.87 (*m*, H_{eq}–C(2), H_{eq}–C(6), OH); 2.19 (*dd*, ^2J = 11.5, ^3J(2ax,3) = 1.5, H_{ax}–C(2)); 2.05 (*ddd*, ^2J = 13.5, ^3J(6ax,5ax) = 9.5, ^3J(6eq,6ax) = 3.0, H_{ax}–C(6)); 1.81 (*X* of *ABX*, *dq*-like, $w_{1/2} \approx 20$, H–C(4)); 1.57–1.46 (*m*, *t*-like, CH_2(5)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 137.8 (C(1′)); 128.8 (C(3′), C(5′)); 128.1 (C(2′), C(6′)); 127.0 (C(4′)); 66.9 (C(3)); 64.7 (CH_2OH); 62.4 (PhCH_2); 59.4 (C(2)); 52.6 (C(6)); 41.3 (C(4)); 22.8 (C(5)). CI-MS: 222 (100, $[M+]^+$). See also [10][14].

(±)-trans- *and (±)*-cis-*1-Benzyl-4-hydroxypiperidine-3-methanol* (**6** and **10**) Ethyl 1-benzyl-4-oxopiperidine-3-carboxylate hydrochloride (**2**; 12 g; *Aldrich 49,597-2*) was dissolved in sat. Na_2CO_3 soln. (100 ml) and extracted with Et_2O. After workup, the resulting free base (9.7 g, 92%) was dissolved in ^{i}PrOH (15 ml), added dropwise to a suspension of anh. Na_2CO_3 (1.5 g) and $NaBH_4$ (1.95 g) in ^{i}PrOH (35 ml), and stirred at r.t. (3 h). Then 1N HCl (150 ml) was added and the mixture stirred at 40° (30 min), set to pH 10 with sat. Na_2CO_3 soln., and extracted with Et_2O. The resulting crude *cis*-/*trans*-4-hydroxy esters (7.5 g, 77%; *ca.* 1:1 (GC), not further characterized) in Et_2O (30 ml) were added to $LiAlH_4$ (2.1 g) in Et_2O (30 ml) at *ca.* 5° over 20 min, and the suspension was stirred at r.t. (2 h). Then 2,2′,2″-nitrilotris[ethanol] (8 g) was added slowly at *ca.* 5°, and after 30 min, H_2O (2 ml) was added and the mixture stirred for 15 h at r.t. The resulting suspension was filtered over *Celite* and afforded, after drying at 30°/0.05 Torr, crude **6**/**10** *ca.* 1:1 (GC) as a yellow oil (6.6 g, 99%). CC (alumina, several solvents) of **6**/**10** or CC (silica gel) of the corresponding diacetates was feasible but resulted in only moderate resolution. Therefore, the corresponding acetonides were prepared: 2,2-dimethoxypropane (25 g), $TsOH \cdot H_2O$ (5.5 g) and crude **6**/**10** (6.6 g) in CH_2Cl_2 (50 ml) were stirred at 50° for 30 min (TLC control). After workup (evaporation of the solvent, addition of sat. Na_2CO_3 soln. (pH 10), extraction with Et_2O, drying), **5**/**9** 1:1 (GC) (7.2 g, 93%) was obtained. CC (SiO_2, hexane/Et_2O 1:1 → Et_2O) of an aliquot (6 g) gave a neat separation of trans-*(1*RS*,6*SR*)-8-benzyl-3,3-dimethyl-2,4-dioxa-8-azabicyclo[4.4.0]decane* (= trans-*6-benzylhexahydro-2,2-dimethyl-4*H-*1,3-dioxino[5,4-c]pyridine,* **5**; 2.8 g) from the later eluting cis-*(1*RS*,6*RS*)-8-benzyl-3,3-dimethyl-2,4-dioxa-8-azabicyclo[4.4.0]decane* (= cis-*6-benzyl-hexahydro-2,2-dimethyl-4*H-*1,3-dioxino[5,4-c]pyridine;* **9**; 3.0 g), both as colorless crystals.

Data of **5**: R_f (AcOEt) 0.42. M.p. 59.5–60°. IR (KBr): 3033*w*, 2998m, 2937s, 2905*m*, 2873*m*, 2804s, 2756*m*, 1495*w*, 1454*m*, 1362*m*, 1339*m*, 1310*w*, 1270*m*, 1258*m*, 1240*w*, 1219*m*, 1199*s*, 1169*s*, 1131*m*, 1116*m*, 1102*s*, 1061*s*, 1031*m*, 972*m*, 934*m*, 901*w*, 862*s*, 793*m*, 748*s*, 701*s*, 626*w*, 542*w*, 530*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.32–7.27 (4 H), 7.26–7.23 (1 H) (each *m*, H–C(2′) to H–C(6′)); 3.64 (*A* of *ABX*, ^2J = 11.3, ^3J(5eq,6) = 4.8, H_{eq}–C(5)); 3.57 (*B* of *ABX*, ^2J = 11.3, ^3J(5ax,6) = 11.3, H_{ax}–C(5)); 3.52, 3.47 (*AB*, ^2J = 13.0, PhCH_2); 3.51 (*dt*, ^3J(1,6) = ^3J(1,10ax) = 10.5, ^3J(1,10eq) = 4.5, H–C(1)); 2.96 (*dquint.*, ^2J = 11.9, ^3J(9eq,10ax) = 2.6, ^3J(9eq,10eq) = ^4J(9eq,7eq) = 1.3, H_{eq}–C(9)); 2.66 (*ddd*, ^2J = 11.1, ^3J(7eq,6) = 3.4, ^4J(7eq,9eq) = 1.3, H_{eq}–C(7)); 2.11 (*dt*, $^2J = {}^3J$(9ax,10ax) = 11.9, ^3J(9ax,10e) = 2.9, H_{ax}–C(9)); 1.89 (*X* of *ABX*, ^3J(6,5ax) = 11.3, ^3J(6,7ax) = 11.1, ^3J(6,1) = 10.5, ^3J(6,5eq) = 4.8, H–C(6)); 1.75 (*m*, *dq*-like, ^2J = 11.5, ^3J(10eq,1) ≈ ^3J(10eq,9ax) ≈ ^3J(10eq,9eq) = 4.5, H_{eq}–C(10)); 1.70 (*m*, *dq*-like, $^2J \approx {}^3J$(10ax,1) ≈ ^3J(10ax,9ax) = 11.5 ^3J(10ax,9eq) = 2.6, H_{ax}–C(10)); 1.67 (*t*, $^2J = {}^3J$(7ax,6) = 11.1, H_{ax}–C(7)); 1.46 (*s*, Me_{ax}–C(3)); 1.40 (*s*, Me_{eq}–C(3)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 138.2 (C(1′)); 128.9 (C(3′), C(5′)); 128.2 (C(2′)), C(6′)); 127.0 (C(4′)); 89.9 (C(3)); 72.6 (C(1)); 62.9 (C(5)); 62.7 (C(13)); 52.7; (C(7)); 52.3 (C(9)); 39.8 (C(6)); 31.4 (C(10)); 29.9 (Me_{eq}–C(3)); 19.3 (Me_{ax}–C(3)). EI-MS: 261 (1, $M^{+\cdot}$), 246 (7, $[M-Me]^+$), 203 (9), 174 (3), 146 (7), 132 (7), 119 (16), 112 (24), 106 (27), 91 (100, $PhCH_2^+$), 84 (8), 65 (12), 56 (11).

Data of **9**: R_f (AcOEt) 0.14. M.p. 45.5–46°. IR (KBr): 3060*w*, 3022*w*, 2988*m*, 2943*m*, 2916*s*, 2874*m*, 2815*m*, 1495*w*, 1467*w*, 1454*m*, 1432*w*, 1401*w*, 1378*m* 1366*s*, 1328*w*, 1318*w*, 1292*w*, 1279*w*, 1240*m*, 1222*s*, 1204*s*, 1167*m*, 1130*m*, 1104*s*, 1091*s*, 1060*m*, 1006*m*, 987*w*, 931*w*, 918*w*, 854*w*, 790*w*, 765*w*, 740*m*, 697*m*, 647*w*, 614*w*, 518*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.33–7.27 (4 H), 7.26–7.23 (1 H) (each *m*, H–C(2′) to H–C(6′)); 4.13 (*q*,

$^3J(1,10eq) = {}^3J(1,10ax) = {}^3J(1,6) = 2.7$, H–C(1)); 4.06 (*A* of *ABX*, $^2J = 12.0$, ^3J(5eq,6) = 3.2, H_{eq}–C(5)); 3.54, 3.45 (*AB*, $^2J = 13.0$, PhCH_2); 3.46 (*B* of *ABX*, $^2J = 12.0$, ^3J(5ax,6) ≈ 1, H_{ax}–C(5)); 2.62 (*t*, $^2J = {}^3J$(7ax,6) = 11.2, H_{ax}–C(7)); 2.61 (*dq*-like, not resolved, $^2J = 11.3$, H_{eq}–C(9)); 2.53 (*ddd*, $^2J = 11.2$, ^3J(7eq,6) = 4.7, ^4J(7eq,9eq) = 1.0, H_{eq}–C(7)); 2.28 (*ddd*, $^2J = 11.3$, ^3J(9ax,10ax) = 13.6, ^3J(9ax,10eq) = 2.8, H_{ax}–C(9)); 1.82 (*m*, *ddt*-like, $^2J \approx {}^3J$(10ax,9ax) = 13.8, ^3J(10ax,6) ≈ ^3J(10ax,9eq) = 4.0, H_{ax}–C(10)); 1.69 (*dq*, $^2J = 13.8$, ^3J(10eq,9ax) = ^3J(10eq,9eq) = ^3J(10eq,1) = 2.7, H_{eq}–C(10)); 1.60 (*X* of *ABX*, *m*, $w_{1/2} \approx 20$, H–C(6)); 1.44 (*s*, Me_{ax}–C(3)); 1.40 (*s*, Me_{eq}–C(3)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 138.9 (C(1′)); 129.2 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.0 (C(4′)); 98.4 (C(3)); 64.5 (C(1)); 63.7 (Ph*C*H$_2$); 63.2 (C(5)); 51.7 (C(7)); 48.1 (C(9)); 34.6 (C(6)); 31.4 (C(10)); 30.0 (Me_{eq}–C(3)); 19.0 (Me_{ax}–C(3)). EI-MS: 261 (5, $M^{+\bullet}$), 246 (3, $[M - Me]^+$), 202 (4), 203 (4), 174 (30), 172 (16), 158 (11), 146 (4), 120 (10), 91 (100, $PhCH_2^+$), 82 (7), 65 (12), 56 (4).

Hydrolysis of **3** and **7** was performed by suspending **3** or **7** (each 1.65 g) in H_2O/1N HCl 1:1 (15 ml) and stirring at 60° for 2 h (TLC control). Workup afforded **6** (1.30 g, 93%) and **10** (1.30 g, 93%), both as colorless crystals.

Data of **6**: M.p. 71–73°. IR ($CHCl_3$): 3379*s* (br.), 3007*s*, 2945*s*, 2808*s*, 1454*m*, 1365*m*, 1342*m*, 1092*s*, 1074*m*, 1046*s*, 1027*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34–7.23 (*m*, H–C(2′) to H–C(6′)); 3.64 (*AB* of *ABX*, *d*-like, CH_2OH); 3.61 (*dt*, $^3J(4,3) \approx {}^3J(4,5ax) \approx 8$, $^3J(4,5eq) = 4.5$, H–C(4)); 3.495, 3.49 (*AB*, $^2J = 13.0$, PhCH_2); 2.80 (*m*, *t*-like, $w_{1/2} \approx 25$, H_{eq}–C(2), H_{eq}–C(6)); 2.06 (*dt*, $^2J = {}^3J$(6ax,5ax) = 11.5, ^3J(6ax,5eq) = 3.7, H_{ax}–C(6)); 1.94–1.73 (*m*, H_{ax}–C(2), H–C(3), H_{eq}–C(5)); 1.64 (*dq*, $^2J = {}^3J$(5ax,4) = ^3J(5ax,6ax) = 11.5, ^3J(5ax,6eq) = 3.7, H_{ax}–C(5)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 137.6 (C(1′)); 129.1 (C(3′), C(5′)); 128.2 (C(2′), C(6′)); 127.1 (C(4′)); 72.9 (C(4)); 65.3 (CH_2OH); 62.7 (Ph*C*H$_2$); 53.8 (C(2)); 51.3 (C(6)); 44.5 (C(3)); 33.5 (C(5)). CI-MS: 222 ($[M + H]^+$). See also [14].

Data of **10**: M.p. 135–136°. IR (KBr): 3357*s* (br.), 3066*s* (br.), 2953*s*, 2940*s*, 2859*s*, 2818*s*, 2360*s*, 1498*s*, 1472*s*, 1458*s*, 1423*m*, 1297*s*, 1266*s*, 1146*s*, 1118*s*, 1073*s*, 1058*s*, 1021*s*, 998*s*, 971*s*, 790*s*, 747*s*, 700*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32–7.25 (*m*, H–C(2′) to H–C(6′)); 4.04 (*m*, $w_{1/2} \approx 12$, H–C(4)); 3.90 (*A* of *ABX*, $^2J = 11.0$, $^3J = 3.5$, CH_AOH); 3.86 (*B* of *ABX*, $^2J = 11.0$, $^3J = 5.5$, CH_BOH); 3.49 (*s*, PhCH_2); 2.9–2.7 (br. *s*, 2 OH); 2.67–2.63 (*m*, H_{eq}–C(2), H_{eq}–C(6)); 2.44 (br. *d*-like, $w_{1/2} \approx 25$, H_{ax}–C(2)); 2.37 (*m*, $w_{1/2} \approx 25$, H_{ax}–C(6)); 1.93–1.82 (*m*, H–C(3), CH_2(5)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 137.6 (C(1′)); 128.9 (C(3′), C(5′)); 128.2 (C(2′), C(6′)); 127.0 (C(4′)); 69.0 (C(4)); 64.0 (*C*H$_2$OH); 63.0 (Ph*C*H$_2$); 53.3 (C(2)); 49.8 (C(6)); 41.4 (C(3)); 32.5 (C(5)). CI-MS: 222 ($[M + H]^+$). See also [14].

(±)-trans- *and (±)*-cis-*1-Benzyl-3-hydroxy-4-(hydroxymethyl)-1-methylpiperidinium Trifluoromethanesulfonates* (**11** and **15**, resp.). Methyl trifluoromethanesulfonate (300 µl) was added to a soln. of **4** (520 mg) in $CHCl_3$ (15 ml), heated with a fan (*ca.* 1 min) and kept at r.t. (2 h) when a yellowish oil separated. After decanting the solvent, washing the residue with $CHCl_3$, and drying (50°/0.05 Torr), pure **11** (850 mg, 94%) was obtained. Colorless viscous oil. ^{1}H- and ^{13}C-NMR: mixture of *N*-epimers (Me_{ax}/Me_{eq} *ca.* 2.5:1).

Analogous methylation of **8** (440 mg) afforded **15** (750 mg, 98%), mixture of *N*-epimers (Me_{ax}/Me_{eq} *ca.* 5:1). Colorless viscous oil.

Data of **11**: IR (KBr): 3550–3200*m*, 2934*w*, 2360*w*, 1699*w*, 1653*w*, 1558*w*, 1458*m*, 1259*s*, 1225*m*, 1165*m*, 1064*w*, 1029*s*, 881*w*, 767*w*, 705*m*, 639*s*, 574*w*, 518*m*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 7.79–7.72 (2 H), 7.65–7.56 (3 H) (each *m*, H–C(2′) to H–C(6′)); 4.93, 4.90 (each *s*, PhCH_2), 4.47, 4.20 (*dt*, $^3J(3,2ax) = {}^3J(3,4) = 10.3$, $^3J(3,2eq) = 4.5$, H–C(3)); 3.90–3.20 (*m*, CH_2OH, H_{eq}–C(2), H_{eq}–C(6), OH); 3.43, 3.28 (each *s*, MeN); 2.20–1.81 (*m*, H_{ax}–C(2), H_{ax}–C(6), CH_2(4)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): 133.3 (C(3′), C(5′)); 130.6, 130.5 (C(4′)); 128.6 (C(2′), C(6′)); 127.0 (C(1′)); 121.4 (*q*, ^1J(C,F) = 220, *C*F_3SO_3); 71.6, 70.7 (Ph*C*H$_2$); 64.6 (C(3)); 62.3, 61.2, 60.9, 60.6, 59.3 (*C*H$_2$OH, C(2), C(6)); 45.9, 43.4 (MeN); 29.2 (C(4)); 20.8, 19.5 (C(5)). CI-MS: 236 (6, $M^{+\bullet}$), 222 (100, $[M + H - Me]^+$)).

Data of **15**: IR (KBr): 3600–3450*m*, 2948*w*, 2360*w*, 1700*w*, 1684*w*, 1653*w*, 1558*w*, 1540*w*, 1481*m*, 1457*w*, 1277*s*, 1225*s*, 1165*m*, 1092*w*, 1029*s*, 1004*m*, 919*w*, 882*w*, 764*m*, 707*m*, 639*s*, 574*m*, 517*m*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 7.70–7.57 (2 H), 7.56–7.50 (3 H) (each *m*, H–C(2′) to H–C(6′)); 4.77, 4.74 (*AB*, $^2J = 13$, C$H_2C_6H_5$); 4.57, 4.45 (each br. *s*, $w_{1/2} \approx 10$, H–C(3)); 4.23 (*dd*, $^2J = 12.1$, ^3J(2eq,3) = 2.8, H_{eq}–C(2)); 3.88 (*dd*, $^2J = 13.9$, ^3J(6eq,5ax) = 2.9, H_{eq}–C(6)); 3.83–3.49 (*m*, CH_2OH, OH, H_{ax}–C(2), H_{ax}–C(6)); 3.36 (*s*, MeN); 2.60 (*m*, *q*-like, $w_{1/2} \approx 20$, H–C(4)); 1.92 (*m*, *t*-like, $w_{1/2} \approx 20$, CH_2(5)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): 133.4 (C(3′), C(5′)); 130.5 C(4′)); 128.9 (C(2′), C(6′)); 127.3 (C(1′)); 121.1 (*q*, ^1J(C,F) = 221, *C*F_3SO_3); 72.6, 71.7 (Ph*C*H$_2$); 64.6, 64.1 (C(3)); 62.5, 62.2 (CH_2OH, C(2)); 60.4, 59.6 (C(6)); 47.3, 39.6 (MeN); 30.1, 29.1 (C(4)); 18.8, 18.4 (C(5)). CI-MS: 236 (10, $M^{+\bullet}$), 222 (100, $[M + H - Me]^+$), 146 (8, $[M - Bn]^+$).

(±)-trans- *and (±)*-cis-*1-Benzyl-4-hydroxy-3-(hydroxymethyl)-1-methylpiperidinium Trifluoromethanesulfonates* (**13** and **17**, resp.). As described for **11** and **15**, with **6** (1.6 g) or **10** (1.1 g): **13** (2.7 g, 97%), mixture of *N*-

epimers (Me_{ax}/Me_{eq} *ca.* 2:1), and **17** (1.9 g, 99%), mixture of *N*-epimers (Me_{ax}/Me_{eq} *ca.* 3:1), resp., both as yellowish viscous oils.

Data of **13**: ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 7.71–7.69 (2 H), 7.57–7.53 (each *m*, H–C(2′) to H–C(6′)); 4.79 (*AB*, not resolved, PhCH_2); 4.25, 4.15 (each *ddd*, $^3J(4,3ax) = {}^3J(4,5) = 10.5$, $^3J(4,3eq) = 5.4$, H–C(4)); 3.98–3.23 (*m*, CH_2OH, H_{eq}–C(2), H_{eq}–C(6)); 3.30, 3.26 (each *s*, MeN); 2.61–1.87 (*m*, H_{ax}–C(2), CH_2(3), H_{ax}–C(6)). ^{13}C-NMR $(CD_3)_2CO$): 133.3, 132.9 (C(3′), C(5′)); 130.5 (C(4′)); 129.2, 129.1 (C(2′), C(6′)); 127.4, 127.3 (C(1′)); 121.1 (*q*, ^1J(C,F) = 220, CF_3SO_3); 71.2, 71.0 (PhCH_2); 68.6, 65.6 (C(4)); 61.6, 60.9, 60.7, 59.9, 59.7, 59.1 (CH_2OH, C(2), C(6)); 44.7, 44.2 (MeN); 40.7, 34.6 (C(5)); 28.6, 28.2 (C(3)). CI-MS: 236 (9, $M^{+\cdot}$), 222 (100, $[M + H - Me]^+$).

Data of **17**: ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 7.8–7.5 (*m*, H–C(2′) to H–C(6′)); 4.90, 4.84 (*AB*, $^2J = 11.3$, PhCH_2), 4.89 (*s*, PhCH_2); 4.39 (br. *s*, $w_{1/2} \approx 10$, H–C(4)); 4.29 (*dd*, $^2J = 12.5$, ^3J(6eq,5) = 3, H_{eq}–C(6)); 3.98 (*dd*, $^2J = {}^3J$(6ax,5) = 12.5, H_{ax}–C(6)); 3.75–3.42 (*m*, CH_2OH, CH_2(2)); 3.31, 3.24 (each *s*, MeN); 2.89–1.80 (*m*, H–C(3), CH_2(5)). ^{13}C-NMR ($(CD_3)_2CO$): 133.4, 132.8 (C(3′), C(5′)); 131.3, 129.1 (C(4′)), 128.9 (C(2′), C(6′)); 127.2 (C(1′)); 120.9 (*q*, ^1J(C,F) = 220, CF_3SO_3); 71.2, 68.4 (PhCH_2); 61.1 (C(4)); 60.5 (CH_2OH); 56.5 (2C), 54.5, 54.0 (C(2), C(6)); 52.3, 44.4 (MeN); 28.9 (2C), 25.5, 25.3 (C(3), (C(5)). CI-MS: 236 (2, $M^{+\cdot}$), 222 (100, $[M + H - Me]^+$).

(±)-trans- *and* (±)-cis-*3-Hydroxy-1-methylpiperidine-4-methanol* (**12** and **16**, resp.; free amines). A soln. of **11** (770 mg) in EtOH (15 ml) and 10% Pd/C (530 mg) was hydrogenolyzed by gentle stirring under a slight pressure of H_2 (rubber balloon, 15 h). The catalyst was removed by filtration over *Celite*, the residue washed with EtOH, the filtrate evaporated, and the residue dissolved in 2N NaOH. Continuous extraction yielded **12** (185 mg, 64%) as a colorless, viscous oil.

Analogous treatment of **15** (1.52 g) afforded **16** (350 mg, 61%) as a yellowish powder.

Data of **12**: IR (KBr): 3609*w*, 3482*m*, 3007*m*, 2942*s*, 2795*m*, 1602*w*, 1466*m*, 448*m*, 1381*m*, 1348*w*, 1251*m*, 1140*m*, 1090*m*, 1072*m*, 1049*m*, 1012*m*, 986*m*, 916*m*, 835*m*, 695*w*, 657*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.74 (*dt*, ^3J(3,2ax) = ^3J(3,4) = 11, ^3J(3,2eq) = 4.5), H–C(3)); 3.68–3.62 (*AB* of *ABX*, not resolved, CH_2OH); 2.96 (*ddd*, $^2J = 10.5$, ^3J(2eq,3) = 4.5, ^4J(3eq,4) = 1.5, H_{eq}–C(2)); 2.77 (*m*, *dt*-like, $^2J = 11$, H_{eq}–C(6)); 2.28 (*s*, MeN); 1.93 (*dt*, $^2J = {}^3J$(6ax,5ax) = 11.6, ^3J(6ax,5eq) = 2.7, H_{ax}–C(6)); 1.84 (*dd*, $^2J = {}^3J$(2ax,3) = 10.5, H_{ax}–C(2)); 1.62–1.56 (*m*, H–C(4), H_{eq}–C(5)); 1.30 (*ddt*, $^2J = {}^3J$(5ax,4) = ^3J(5ax,6ax) = 12.5, ^3J(5ax,6eq) = 4, H_{ax}–C(5)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 72.0 (C(3)); 67.2 (CH_2OH); 62.3 (C(2)); 54.8 (C(6)); 45.9 (*N*-Me); 43.8 (C(4)); 26.2 (C(5)). EI-MS: 145 (80, $M^{+\cdot}$), 128 (11, $[M - 2\,H - Me)]^+$), 114 (29), 101 (17), 96 (31), 86 (11), 71 (46), 70 (18), 58 (100).

Data of **16**: M.p. 103–104°. IR (KBr): 3361*s*, 3061*m*, 2940*s*, 2918*s*, 2846*m*, 201*m*, 1450*m*, 1406*m*, 1379*m*, 1360*m*,1325*m*, 1308*m*, 1263*m*, 1206*m*, 1183*m*, 1140*m*, 1099*m*, 1074*m*, 1044*m*, 1022*s*, 1009*s*, 971*w*, 956*w*, 922*m*, 891*m*, 816*w*, 760*m*, 668*w*, 530*w*, 501*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.96 (br. *s*, $w_{1/2} \approx 10$, H–C(3)); 3.68 (*AB* of *ABX*, not resolved, CH_2OH); 3.34–3.19 (br., 2 OH); 2.86 (*m*, *t*-like, H_{eq}–C(2), H_{eq}–C(6)); 2.26 (*s*, MeN); 2.08 (*dd*, $^2J = 11.5$, ^3J(2ax,3) = 1.1, H_{ax}–C(2)); 1.96 (*dd*, $^2J = {}^3J$(6ax,5ax) = 12, ^3J(6ax,5eq) = 2.5, H_{ax}–C(6)); 1.76 (*ddt*, $^2J = {}^3J$(5ax,6ax) = ^3J(5ax,4) = 12, ^3J(5ax,6eq) = 3.5, H_{ax}–C(5)); 1.30 (*ddt*, $^2J = {}^3J$(5ax,4) = ^3J(5ax,6ax) = 12.5, ^3J(5ax,6eq) = 4, H_{ax}–C(5)). 1.52–1.44 (*m*, H–C(4), H_{eq}–C(5)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 67.1 (C(3)); 66.3 (CH_2OH); 61.8 (C(2)); 55.1 (C(6)); 46.0 (MeN); 40.7 (C(4)); 22.8 (C(5)). CI-MS: 146 (84, $[M + H]^+$). EI-MS: 145 (84, $M^{+\cdot}$), 128 (12, $[M - 2\,H - Me)]^+$), 114 (20), 101 (20), 96 (24), 86 (14), 71 (40), 70 (14), 58 (100).

(±)-trans- *and (±)*-cis-*4-hydroxy-1-methylpiperidine-3-methanol* (**14** and **18**, resp.; free amines). As described for **12** and **16**, with **13** (1.25 g) or **17** (1.60 g): **14** (390 mg, 83%) and **18** (526 mg, 85%), resp., both as colorless viscous oils.

Data of **14**: ^{1}H-NMR (300 MHz, $CDCl_3$): 4.05 (br., 2 OH); 3.69 (*A* of *ABX*, $^2J = 10.8$, $^3J = 7$, CH_AOH); 3.65 (*B* of *ABX*, $^2J = 10.8$, $^3J = 4.5$, CH_BOH); 3.48 (*dt*, $^3J(4,3) = {}^3J(4,5ax) = 9.5$, $^3J(4,5eq) = 4.5$, H–C(4)); 2.81 (*m*, $w_{1/2} \approx 20$, H_{eq}–C(2), H_{eq}–C(6)); 2.25 (*s*, MeN); 2.04–1.59 (*m*, H_{ax}–C(2), H–C(3), CH_2(5), H_{ax}–C(6)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 74.4 (C(4)); 64.8 (CH_2OH); 56.4, 53.9 (C(2), C(6)); 45.8 (C(3)); 45.0 (MeN); 33.9 (C(5)). CI-MS: 146 (100, $[M + H]^+$), 145 (27, $M^{+\cdot}$), 144 (20, $[M - H]^+$).

Data of **18**: ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 4.24 (*m*, *q*-like, $^3J(4,3) \approx {}^3J(4,5ax) \approx {}^3J(4,5eq) \approx 3.5$, H–C(4)); 4.00 (*A* of *ABX*, $^2J = 10.8$, $^3J = 6.0$, CH_AOH); 3.93 (*B* of *ABX*, $^2J = 10.8$, $^3J = 6.0$, CH_BOH); 2.69 (*m*, $w_{1/2} \approx 25$, H_{eq}–C(2), H_{eq}–C(6)); 2.38 (*s*, MeN); 2.38–2.33 (*m*, H_{ax}–C(2), H_{eq}–C(5), H_{ax}–C(6)); 2.13 (*X* of *ABX*, *m*, $w_{1/2} \approx 18$, H–C(3)); 2.01 (*m*, *q*-like, H_{ax}–C(5)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): 66.5 (C(4)); 63.2 (CH_2OH); 54.8, 51.7 (C(2), C(6)); 46.5 (C(3)); 43.5 (MeN); 33.4 (C(5)). CI-MS: 146 (100, $[M + H]^+$), 145 (25, $M^{+\cdot}$), 144 (16, $[M - H]^+$).

3. *Piperidine Precursors* **52**–**54**, **56**–**58**, **63**, *and* **64** (*for 7-Azaphosphadecalins* (*Scheme 4*), **III**). *(±)*-trans- *and (±)*-cis-*1-Benzyl-3-hydroxypiperidine-2-methanol* (**58** and **52**, resp.) and *(±)*-cis-*1-Benzyl-3-hydroxypiper-*

idin-2-yl-methyl 2,2-Dimethylpropanoate (**53**). A soln. of 3-hydroxypyridine-2-methanol hydrochloride (5.0 g; *Aldrich H3,153-0*; techn. 85%) in H_2O (30 ml; pH 3.0 (HCl)) was hydrogenated for 18 h over 5% Rh/Alox (1.16 g) at 35°, 60 bar H_2. The catalyst was removed by filtration over *Celite*. To the filtrate, H_2O (50 ml), Na_2CO_3 (7.0 g), EtOH (80 ml), and benzyl bromide (3.5 ml) were added, and the mixture was refluxed for 30 min. After evporation of EtOH, the aq. phase was extracted with Et_2O and dried to afford crude **52** (5.25 g, 77%) containing *ca.* 6% of **58** (by ^{1}H- and ^{13}C-NMR).

To a soln. of crude **52** (9.60 g) in pyridine (25 ml), a soln. of pivaloyl chloride (5.61 ml) in pyridine (25 ml) was added dropwise at −30°, and the mixture was kept at −20° for 2 d. After evaporation, the residue was dissolved in CH_2Cl_2, the soln. washed with 2N NaOH (30 ml) and evaporated, and the residue dried at 50°/0.05 Torr to afford crude **53** (12.8 g, 97%) as a brownish oil. CC (SiO_2, hexane/AcOEt 2:1) of an aliquot (2 g) yielded pure **53** (1.85 g). Colorless solid. M.p. 58°. R_f (AcOEt) 0.51. IR (film): 3467*m* (br.), 3085*w*, 3062*w*, 3027*w*, 2958*s*, 2936*s*, 2871*m*, 2801*m*, 2724*w*, 1729*s*, 1603*w*, 1540*w*, 1495*m*, 1480*s*, 1453*s*, 1397*m*, 1366*m*, 1284*s*, 1228*m*, 1161*s*, 1073*m*, 1029*m*, 1001*m*, 983*m*, 960*w*, 940*w*, 911*w*, 868*w*, 841*w*, 802*w*, 771*w*, 737*m*, 699*m*, 626*w*, 571*w*, 548*w*, 539*w*, 523*w*, 511*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32–7.22 (*m*, H–C(2′) to H–C(6′)); 4.37 (*d*, ^3J = 5.1, CH_2OC-OCMe$_3$); 3.99, 3.26 (*AB*, ^2J = 13.6, PhCH_2); 3.93 (*m*, *quint.*-like, $w_{1/2} \approx 10$, H–C(3)); 2.71 (*ddt*, ^2J = 11.8, ^3J(6eq,5ax) = ^3J(6eq,5eq) = 3.7, ^4J = 1.2, H_{eq}–C(6)); 2.63 (*dd*, ^3J(2,3) = 2.2, ^3J = 5.1, H–C(2)); 2.03 (*ddd*, ^2J = 11.8, ^3J(6ax,5ax) = 10.3, ^3J(6ax,5eq) = 3.3, H_{ax}–C(6)); 1.82–1.63 (*m*, H_{eq}–C(4), H_{eq}–C(5)); 1.57–1.39 (*m*, H_{ax}–C(4), H_{ax}–C(5)); 1.21 (*s*, *Me*$_3$C). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 178.3 (*C*OCMe$_3$); 139.2 (C(1′)); 128.5 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.0 (C(4′)); 67.9 (C(3)); 65.0 (C(2)); 64.5 (*C*H$_2$OCOCMe$_3$); 58.2 (Ph*C*H$_2$); 51.4 (C(6)); 38.7 (Me$_3$*C*); 30.9 (C(4)); 27.1 (*Me*$_3$C); 20.6 (C(5)). EI-MS: 305 (1, $M^{+\cdot}$), 190 (100), 91 (71, $PhCH_2^+$), 57 (14). Anal. calc. for $C_{18}H_{27}NO_3$ (305.45): C 69.41, H 8.41, N 4.03; found: C 68.93, H 8.22, N 4.00.

[(±)-1-Benzyl-3-oxopiperidin-2-yl]methyl 2,2-Dimethylpropanoate (**54**). Crude **53** (12.8 g) in CH_2Cl_2 (33 ml) was added to a soln. of $(COCl)_2$ (4.30 ml) and DMSO (6.54 ml) in CH_2Cl_2 (33 ml) at −78° and the mixture was stirred at −60° for 10 min. Then Et_3N (28 ml) was added, and the mixture was warmed to r.t. within 20 min and further stirred at r.t. for 20 min. After drying at 35°/0.05 Torr, the residue was dissolved in 2N NaOH and extracted with Et_2O. Rapid CC (SiO_2, AcOEt) afforded **54** (12.2 g, 96%). Colorless oil that quickly decomposed at r.t. in air. R_f (AcOEt) 0.62. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32–7.22 (*m*, H–C(2′) to H–C(6′)); 4.61 (*A* of *ABX*, ^2J = 11.7, ^3J = 5.0, CH_AOCOCMe$_3$); 4.34 (*B* of *ABX*, ^2J = 11.7, ^3J = 4.7, CH_BOCOCMe$_3$); 3.92, 3.58 (*AB*, ^2J = 13.6, PhCH_2); 3.32 (*X* of *ABX*, ^3J(2,H_A) = 5.0, ^3J (2,H_B) = 4.7, H–C(2)); 3.02 (*dt*, ^2J = 11.8, ^3J = 6.6, 4.5, H_{eq}–C(6)); 2.62–2.34 (*m*, 3 H); 1.95 (*m*, *sext.*-like, $w_{1/2} \approx 20$, 2 H); 1.20 (*s*, *Me*$_3$C). ^{13}C-NMR (300 MHz, $CDCl_3$): 207.8 (C(3)); 178.1 (*C*OCMe$_3$); 138.2 (C(1′)); 128.6 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.2 (C(4′)); 69.6 (C(2)); 61.4 (*C*H$_2$OCOCMe$_3$); 58.3 (Ph*C*H$_2$); 47.4 (C(6)); 38.6 (Me$_3$*C*); 38.3 (C(4)); 27.1 (*Me*$_3$C); 23.2 (C(5)). EI-MS: 301 (1, $[M-2H]^+$), 201 (25), 188 (28), 160 (43), 91 (100, $PhCH_2^+$), 57 (26).

(±)-trans- *and (±)*-cis-*3-(Acetyloxy)-1-benzylpiperidine-2-yl-methyl 2,2-Dimethylpropanoate* (*trans*- and *cis*-**57**, resp.). To a soln. of **54** (12.2 g) in EtOH (200 ml) was added $NaBH_4$ (2.85 g) in portions keeping the temp. below −10° (6 portions within 1 h). After workup (addition of 10% H_2SO_4 soln. (140 ml), stirring at r.t. (15 min), evaporation of EtOH, addition of conc. NaOH soln. extraction with Et_2O, drying (K_2CO_3), and evaporation, drying at 50°/0.05 Torr yielded *cis*/*trans*-**56** (12.3 g, 96%) as a yellow oil. Acetylation (Ac_2O (17 ml) in pyridine (50 ml), r.t., 15 h) of **56** (11.05 g) and usual workup afforded *cis*-/*trans*-**57** 1:1 (12.4 g, 99%) as a brownish oil. CC (SiO_2, hexane/AcOEt 87:13) gave a neat separation of *trans*-**57** (5.41 g, 43%), colorless solid, from the later eluting *cis*-**57** (5.16 g, 41%), colorless oil.

Data of trans-**57**: M.p. 51°. R_f (hexane/AcOEt 4:1) 0.25. IR (film): 3085*w*, 3063*w*, 3028*w*, 2961*s*, 2873*m*, 2801*m*, 1731*s*, 1603*w*, 1495*m*, 1481*m*, 1454*m*, 1398*m*, 1368*m*, 1315*w*, 1282*s*, 1241*s*, 1155*s*, 1109*m*, 1072*m*, 1055*m*, 1036s, 985*m*, 947*w*, 924*w*, 845*w*, 804*w*, 770*w*, 738*m*, 699*m*, 603*w*, 584*w*, 526*m*, 510*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.24–7.14 (*m*, H–C(2′) to H–C(6′)); 4.80 (*ddd*, ^3J(3,4ax) = 8.3, ^3J(3,2) = 7.5, ^3J(3,4eq) = 4.4, H–C(3)); 4.29 (*A* of *ABX*, ^2J = 12.2, ^3J = 3.7, CH_AOCOCMe$_3$); 4.19 (*B* of *ABX*, ^2J = 12.2, ^3J = 4.1, CH_BOCOCMe$_3$); 3.97, 3.32 (*AB*, ^2J = 13.7, PhCH_2); 2.67 (*m*, $w_{1/2} \approx 20$, H_{eq}–C(6)); 2.61 (*X* of *ABX*, ^3J(2,H_B) = 4,1, ^3J(2,H_A) 3.7, ^3J(2,3) = 7.6, H–C(2)); 2.11–2.02 (*m*, H_{ax}–C(6)); 2.00 (*s*, COMe); 2.00–1.91, 1.64–1.54 (2 *m*, H_{eq}–C(4), H_{eq}–C(5)); 1.49–1.32 (*m*, H_{ax}–C(4), H_{ax}–C(5)); 1.14 (*s*, Me$_3$C). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 178.3 (*C*OCMe$_3$); 170.2 (*C*OMe); 139.5 (C(1′)); 128.4 (C(3′), C(5′)); 128.2 (C(2′), C(6′)); 126.7 (C(4′)); 69.8 (C(3)); 63.4 (C(2)); 60.5 (*C*H$_2$OCOCMe$_3$); 57.8 (Ph*C*H$_2$); 50.1 (C(6)); 38.8 (Me$_3$*C*); 28.6 (C(4)); 27.1 (*Me*$_3$C); 21.7 (C(5)); 21.2 (CO*Me*). EI-MS: 347 (1, $M^{+\cdot}$), 287 (3, $[M-AcOH]^+$), 232 (100), 91 (52, $PhCH_2^+$). Anal. calc. for $C_{20}H_{29}NO_4$ (347.4): C 69.41, H 8.41, N 4.03; found: C 68.99, H 8.03, N 3.93.

Data of cis-**57**: R_f (AcOEt/hexane 1:4) 0.20. IR (film): 3062*w*, 3027*w*, 2970*s*, 2869*m*, 2798*m*, 2721*w*, 1732*s*, 1603*w*, 1495*m*, 1481*m*, 1453*m*, 1398*m*, 1369*s*, 1316*w*, 1284*s*, 1239*s*, 1155*s*, 1123*m*, 1112*m*, 1067*m*, 1049*m*, 1030*m*, 982*w*, 965*w*, 939*w*, 911*w*, 855*w*, 808*w*, 769*w*, 739*m*, 699*m*, 651*w*, 606*w*, 585*w*, 543*m*, 511*s*, 503*s*. ^{1}H-NMR (300 MHz,

$CDCl_3$): 7.32–7.20 (*m*, H–C(2′) to H–C(6′)); 5.09 (*dt*, $^3J(3,4ax) = 8.3$, $^3J(3,4eq) = {}^3J(3,2) = 4.4$, H–C(3)); 4.50 (*A* of *ABX*, $^2J = 11.6$, $^3J = 6.4$, CH_AOCOCMe$_3$), 4.22 (*B* of *ABX*, $^2J = 11.6$, $^3J = 4.4$, CH_BOCOCMe$_3$); 3.79, 3.68 (*AB*, $^2J = 14.0$, PhCH_2); 3.14 (*X* of *ABX*, $^3J(2,H_A) = 6.4$, $^3J(2,H_B) = 4.4$, $^3J(2,3) = 4.4$, H–C(2)); 2.60 (*ddd*, $^2J = 12.5$, $^3J = 8.9$, 3.1, H_{eq}–C(6)); 2.38–2.29 (*m*, H_{ax}–C(6)); 2.07 (*s*, COMe); 1.75–1.45 (*m*, CH_2(4), CH_2(5)); 1.20 (*s*, Me$_3$C). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 178.3 (COCMe$_3$); 170.3 (*C*OMe); 139.2 (C(1′)); 128.4 (C(3′), C(5′)); 128.2 (C(2′), C(6′)); 126.9 (C(4′)); 70.5 (C(3)); 60.6 (*C*H$_2$COCMe$_3$); 60.4 (C(2)); 58.9 (Ph*C*H$_2$)); 47.1 (C(6)); 38.6 (Me$_3$*C*); 27.1 (*Me*$_3$C); 26.8 (C(4)); 22.1 (C(5)); 21.2 (CO*Me*). EI-MS: 347 (1, $M^{+\bullet}$), 287 (1, $[M - AcOH]^+$), 232 (100), 91 (55, $PhCH_2^+$). Anal. calc. for $C_{20}H_{29}NO_4$ (347.4): C 69.41, H 8.41, N 4.03; found: C 68.93, H 8.22, N 4.00.

Saponification of *trans*- or *cis*-**57** (each 4.00 g) in EtOH (20 ml) with KOH (5.0 g) in H_2O (20 ml) at r.t. (30 min), usual workup and bulb-to-bulb distillation at 150°/0.05 Torr gave *(±)*-trans-*1-benzyl-3-hydroxypiperidine-2-methanol* (**58**; 2.54 g, 99%) and *(±)*-cis-*1-benzyl-3-hydroxypiperidine-2-methanol* (**52**; 2.54 g, 99%), resp., both as colorless crystals.

Data of **58**: M.p. 80°. R_f (AcOEt) *ca.* 0.18 (tailing). IR (KBr): 3304*s* (br.), 3218*s* (br.), 3063*m*, 3029*m*, 2925*s*, 2896*m*, 2855*m*, 2805*s*, 2785*s*, 2715*w*, 1603*w*, 1494*m*, 1480*w*, 1453*m*, 1443*m*, 1399*m*, 1381*m*, 1354*w*, 1321*m*, 1275*w*, 1252*w*, 1223*w*, 1179*w*, 1157*w*, 1119*s*, 1107*s*, 1070*s*, 1037*s*, 1027*m*, 1013*s*, 1001*m*, 969*w*, 932*w*, 923*w*, 906*w*, 875*w*, 850*w*, 797*w*, 738*s*, 695*s*, 624*w*, 576*w*, 541*w*, 508*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.34–7.22 (*m*, H–C(2′) to H–C(6′)); 4.04, 3.37 (*AB*, $^2J = 13.6$, PhCH_2); 4.01 (*A* of *ABX*, $^2J = 11.3$, $^3J = 3.0$, CH_AOH), 3.91 (*B* of *ABX*, $^2J = 11.3$, $^3J = 4.5$, CH_BOH); 3.76 (*ddd*, $^3J(3,4ax) = 9.3$, $^3J(3,2) = 7.6$, $^3J(3,4eq) = 4.5$, H–C(3)); 2.83 (*br. s*, 2 OH); 2.78 (*dt*, $^2J = 11.9$, $^3J(6eq,5ax) = {}^3J(6eq,5eq) = 4.2$, H_{eq}–C(6)); 2.29 (*X* of *ABX*, $^3J(2,H_B) = 4.5$, $^3J(2,H_A) = 3.0$, $^3J(2,3) = 7.5$, H–C(2)); 2.13 (*ddd*, $^2J = 11.9$, $^3J(6ax,5ax) = 10.5$, $^3J(6ax,5eq) = 3.0$, H_{ax}–C(6)); 1.95 (*m*, *dq*-like, $^2J = 11.5$, $^3J(4eq,3) = 4.5$, $^3J(4eq,5ax) \approx {}^3(4eq,5eq) = 4.2$, H_{eq}–C(4)); 1.65 (*m*, *dquint.*-like, $^2J = 11.5$, $^3J(5eq,6eq) = 4.2$, $^3J(5eq,6ax) \approx {}^3J(5eq,4ax) = 3.0$ H_{eq}–C(5)); 1.43 (*m*, *tt*-like, $^2J = 11.5$, $^3J(5ax,6ax) \approx {}^3J(5ax,4ax) = 10.5$, $^3J(5ax,6eq) = 4.2$, H_{ax}–C(5)); 1.39 (*m*, *tt*-like, $^2J = 11.5$, $^3J(4ax,5ax) = 10.5$, $^3J(4ax,3) = 9.3$, $^3J(4ax,5eq) = 3.0$, H_{ax}–C(4)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 138.8 (C(1′)); 128.9 (C(3′), C(5′)); 128.5 (C(2′), C(6′)); 127.2 (C(4′)); 68.0 (C(3)); 67.9 (C(2)); 59.1 (*C*H$_2$OH); 58.2 (Ph*C*H$_2$); 51.0 (C(6)); 32.5 (C(4)); 22.2 (C(5)). EI-MS: 221 (<1, $M^{+\bullet}$), 190 (45, $[M - CH_2OH]^+$), 91 (100, $PhCH_2^+$), 65 (15). Anal. calc. for $C_{13}H_{19}NO_2$ (221.3): C 70.56, H 8.65, N 6.33; found: C 70.50, H 8.22, N 5.95.

Data of **52**: M.p. 60.5°. R_f (AcOEt) *ca.* 0.18 (tailing). IR (film): 3383*s* (br.), 3085*w*, 3061*m*, 3027*m*, 2936*s*, 2801*s*, 1602*w*, 1585*w*, 1495*m*, 1452*s*, 1367*m*, 1266*w*, 1221*m*, 1186*w*, 1116*m*, 1065*s*, 1028*s*, 989*m*, 955*m*, 916*w*, 885*w*, 842*w*, 796*w*, 737*s*, 699*s*, 525*s*, 504*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.36–7.30 (3 H), 7.29–7.22 (2 H) (each *m*, H–C(2′) to H–C(6′)); 4.19, 3.52 (*AB*, $^2J = 13.4$, PhCH_2); 4.05 (*m*, not resolved, H–C(3)); 4.01 (*A* of *ABX*, $^2J = 11.6$, $^3J = 5.6$, CH_AOH); 3.88 (*B* of *ABX*, $^2J = 11.6$, $^3J = 4.0$, CH_BOH); 2.99 (br. *s*, 2 OH); 2.75 (*dt*, $^2J = 11.7$, $^3J(6eq,5ax) = {}^3J(6eq,5eq) = 4.7$, H_{eq}–C(6)); 2.49 (*X* of *ABX*, $^3J(2,H_A) = 5.6$, $^3J(2,H_B) = 4.0$, $^3J(2,3) = 2.5$, H–C(2)); 2.10 (*ddd*, $^2J = 11.7$, $^3J(6ax,5ax) = 9.7$, $^3J(6ax,5eq) = 3.3$, H_{ax}–C(6)); 1.84–1.65 (*m*, H_{eq}–C(4), H_{eq}–C(5)); 1.59–1.44 (*m*, H_{ax}–C(4), H_{ax}–C(5)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 139.0 (C(1′)); 128.7 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.0 (C(4′)); 69.2 (C(3)); 64.9 (C(2)); 61.8 (CH_2OH); 57.8 (Ph*C*H$_2$)); 50.8 (C(6)); 30.9 (C(4)); 20.4 (C(5)). EI-MS: 221 (1, $M^{+\bullet}$), 190 (100, $[M - CH_2OH]^+$), 91 (91, $PhCH_2^+$), 65 (15). Anal. calc. for $C_{13}H_{19}NO_2$ (221.3): C 70.56, H 8.65, N 6.33; found: C 69.97, H 8.17, N 5.96.

(±)-trans-*3-Hydroxy-1-methylpiperidine-2-methanol* (**63**). Methyl trifluoromethanesulfonate (265 µl) was added to *trans*-**57** (168 mg). The flask was sonicated at r.t. (5 min) to homogenize the mixture when colorless drops began to separate; the reaction was complete within 30 min. After washing the residue with $CHCl_3$ and drying at 50°/0.05 Torr, the crude product was hydrogenolyzed in EtOH (2 ml) with 10% Pd/C (100 mg) by vigorous stirring under a slight pressure of H_2 (rubber balloon, 1 h). The catalyst was removed by filtration over *Celite*, the residue washed with EtOH, the filtrate evaporated, and the resulting viscous oil dissolved in a soln. of KOH (290 mg) in EtOH/H_2O 1:1 (2.5 ml) and stirred at r.t. (45 min). Continuous extraction afforded **63** (64 mg, 63%). Colorless viscous oil that slowly solidified. M.p. 75°. R_f (AcOEt) 0.06. IR (film): 3374*m* (br.), 2939*s*, 2859*m*, 2794*s*, 2712*w*, 1461*m*, 1449*m*, 1425*w*, 1373*w*, 1347*w*, 1303*w*, 1279*m*, 1227*w*, 1203*w*, 1181*w*, 1127*m*, 1065*s*, 1023*s*, 977*w*, 924*w*, 852*w*, 811*w*, 732*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 3.98 (*A* of *ABX*, $^2J = 11.6$, $^3J = 2.1$, CH_AOH); 3.81 (*B* of *ABX*, $^2J = 11.6$, $^3J = 4.1$, CH_BOH); 3.68 (*ddd*, $^3J(3,4ax) = 11.7$, $^3J(3,2) = 8.9$, $^3J(3,4eq) = 4.7$, H–C(3)); 3.52 (br. *s*, 2 OH); 2.81 (*m*, *d*-like, $w_{1/2} \approx 15$, $^2J = 11.3$, H_{eq}–C(6)); 2.32 (*s*, MeN); 2.13 (*dt*, $^2J = {}^3J(6ax,5ax) = 11.3$, $^3J(6ax,5eq) = 3.7$, H_{ax}–C(6)); 2.01 (*m*, *dq*-like, $^2J = 11.7$, $^3J(4eq,3) = 4.7$, $^3J(4eq,5ax) \approx {}^3J(4eq,5eq) \approx 4.5$, H_{eq}–C(4)); 1.79 (*X* of *ABX*, $^3J(2,H_B) = 4.1$, $^3J(2,H_A) = 2.1$, $^3J(2,3) = 8.9$, H–C(2)); 1.71–1.50 (*m*, CH_2(5)); 1.31 (*m*, *dq*-like, $^2J \approx {}^3J(4ax,3) \approx {}^3J(4ax,5ax) = 11.7$, $^3J(4ax,5eq) = 2.0$, H_{ax}–C(4)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 70.4 (C(2)); 67.8 (C(3)); 59.1 (*C*H$_2$OH); 56.2 (C(6)); 42.6 (MeN); 33.3 (C(4)); 23.1 (C(5)). EI-MS: 145 (<1, $M^{+\bullet}$), 128 (<1, $[M - OH]^+$), 114 (100, $[M - CH_2OH]^+$), 86 (17).

(±)-trans-*3-Hydroxy-2-(hydroxymethyl)-1,1-dimethylpiperidinium Trifluoromethanesulfonate* (**64**). Methyl trifluoromethanesulfonate (330 µl) in $CHCl_3$ (1 ml) was added to a soln. of **63** (303 mg) in $CHCl_3$ (1 ml) at r.t. (10 min) when a yellowish oil separated. After decanting the solvent and washing the residue twice with $CHCl_3$, drying at 50°/0.05 Torr gave pure **64** (640 mg, 99%). Colorless viscous oil. IR (film): 3447*m* (br.), 2853*w*, 1701*w*, 1485*m*, 1459*m*, 1422*w*, 1369*w*, 1252*s*, 1225*s*, 1163*s*, 1112*m*, 1187*m*, 1067*m*, 1053*m*, 1029*s*, 998*w*, 869*w*, 947*m*, 907*w*, 845*w*, 807*w*, 759*w*, 640*m*, 579*w*. ^{1}H-NMR (600 MHz, $(CD_3)_2CO$): 4.34 (*A* of *ABX*, $^2J = 13.9$, $^3J = 2.0$, CH_AOH); 4.24–4.18 (*B* of *ABX*, $^2J = 14$, $^3J = 4.5$, and *m*, not resolved, CH_BOH, H–C(3)); 3.66 (*ddt*, $^2J = 12.7$, $^3J(6eq,5ax) = {}^3J(6eq,5eq) = 3.8$, ^4J (6eq,4eq) = 1.3, H_{eq}–C(6)); 3.60 (*dt*, $^2J = {}^3J(6ax,5ax) = 12.4$, $^3J(6ax,5eq) = 3.5$, H_{ax}–C(6)); 3.47 (*s*, Me_{eq}–N); 3.31 (*X* of *ABX*, $^3J(2,H_B) = 4.5$, $^3J(2,H_A) = 2.0$, $^3J(2,3) = 9.5$, H–C(2)); 3.30 (*s*, Me_{ax}–N); 2.22–2.18 (*m*, *dq*-like, H_{eq}–C(4)); 2.15–2.09, 2.03–1.98 (2 *m*, $CH_2(5)$); 1.68 (*ddt*, $^2J = 12.6$, $^3J(4ax,3) = {}^3J(4ax,5ax) = 10.5$, $^3J(4ax,5eq) = 4.7$, H_{ax}–C(4)). ^{13}C-NMR (150.9 MHz, $(CD_3)_2CO$): 121.9 (*q*, $^1J(C,F) = 321$, *C*–F_3SO_3); 77.2 (C(2)); 66.3 (C(6)); 63.5 (C(3)); 56.9 (CH_2OH); 55.8 (Me_{eq}–N); 47.4 (Me_{ax}–N); 31.8 (C(4)); 19.1 (C(5)). CI-MS: 147 (7, $M^{+\cdot}$), 146 (100, $[M + H - Me]^+$).

4. *Phosphorus Heterocycles* **19**–**50**, **59**–**62**, **65**, *and* **66** (*Figs. 1–3*). *General Procedures.* 4.1. *Cyclizations.* To the soln. of the hydroxypiperidinemethanol (1 equiv.) and Et_3N (2 equiv.) in anh. CH_2Cl_2 prepared at 0° in a glove box under N_2, the respective phosphorus reagent (1 equiv.) in anh. CH_2Cl_2 was added, and the mixture was stirred at 0° (1 min to 6 h, according to the reactivity; TLC control). The volatile components were evaporated, and the residue was dissolved in the appropriate solvent and purified by CC (SiO_2, pH 5.6; see *General*). In most cases, the axial epimer was eluted faster, although there were exceptions (**37a**,**b**, **39a**,**b**, **60a**,**b**). Yields of pure compounds were generally *ca.* 20% per epimer, depending on several parameters, the most important ones being the reactivity of the starting materials and the rate of epimerization of the products (4-nitrophenoxy < F ≪ 2,4-dinitrophenoxy < Cl). Therefore, both the reaction, separation, and workup times as well as the ratio adsorbent/substance had to be optimized for each individual preparation. The axial epimers were stable when stored as such (< 0°, Ar), but in soln. they slowly decomposed. Although being reasonably stable when stored as such (< 0°, Ar), the equatorial epimers gradually epimerized.

4.2. *Phosphorus Reagents.* 4-Nitrophenyl phosphorodichloridate is commercially available (*Aldrich 15,540-3*). The 2,4-dinitrophenyl phosphorodichloridate was prepared according to [24]: $POCl_3$ (5 ml), anh. NaCl (7 mg), and 2,4-dinitrophenol were heated under reflux (*ca.* 120°) in a glove box under N_2 (48 h). After filtration and distilling off excess $POCl_3$ (bulb-to-bulb), the viscous residue crystallized (1.87 g, 92%). The product consisted of $Cl_2P(O)OC_6H_3(NO_2)_2$ (85%, ^{31}P-NMR ($CDCl_3$): 5.0) and $ClP(O)[OC_6H_3(NO_2)_2]_2$ (15%, ^{31}P-NMR($CDCl_3$): –6.5) and was not purified further.

$POCl_2F$ was prepared according to [22]: $POCl_3$ (100 g) and dry, finely crystalline NH_4F (48 g; *Fluka 09737*, *puriss. p.a.*) were heated at 110° for 15 h in a flask fitted with a condenser. The volatile fluorinated compounds passing through the condenser ($POCl_2F$ (b.p. 54°) $POClF_2$ (b.p. 3°) and POF_3 (b.p. –40°)) were trapped at –78°. The mixture from the cold trap was fractionally distilled (*Vigreux*, 50 cm) to afford $POCl_2F$ as a colorless liquid (11.6 g, 13%). B.p. 52°. ^{31}P-NMR ($CDCl_3$): 1.80 (*d*, $^1J(P,F) = 1191$). The compound was stable for a long period when stored in the refrigerator and handled in a rigourously dry atmosphere, see also *General*.

4.3. N-*Benzyl*-N-*methylammonium Trifluoromethanesulfonates* **27**–**29**, **31**–**33**, **43**–**45**, *and* **47**–**49**. They were prepared by adding methyl trifluoromethanesulfonate (neat, 1.1 equiv.) to the soln. of the respective *N*-benzyl compound in abs. $CHCl_3$ or MeCN in a dry flask under dry N_2 and heating with a fan to homogenize (*ca.* 1–2 min). The mixture was stirred at r.t. until viscous yellowish drops began to separate. After completion of the reaction (1–2 h; TLC control) the supernatant was decanted, the oily residue washed twice with the respective solvent, evaporated, and dried at 50°/0.05 Torr to afford the quaternary ammonium compounds.

4.4. N,N-*Dimethylammonium Trifluoromethanesulfonates* **30a**, **34a**, **46a**, *and* **50a**. They were prepared from the corresponding hydroxy-1-methylpiperidinemethanols **12**, **16**, **14**, and **18**, resp., *via* the 3-(2,4-dinitrophenoxy)-8- or -9-methyl-2,4-dioxa-8- or -9-aza-3-phosphabicyclo[4.4.0]decane 3-oxides (not isolated, preparation as described above). The crude products were dissolved in $CHCl_3$, shaken (< 1 min!) with an ice-cold soln. of sat. NaCl/2N NaOH (pH > 11) and extracted with $CHCl_3$. The org. phase was washed with H_2O to neutrality, dried (Na_2SO_4), filtered, and evaporated and the residue dried at 30°/0.05 Torr to afford the crude free amines as yellowish oils. The deprotonation reaction and the workup procedure must be performed as quickly as possible since the yields strongly depended on the speed of operation. Methylation of the crude free amines as described above afforded the *N*,*N*-dimethylammonium compounds. Special conditions had to be applied to the 7-azaphosphadecalins as their reaction characteristics were significantly different from the 8- and 9-aza series (see below, compounds **61** and **62**). All the cationic compounds are very hygroscopic, more reactive than the free amines, and quite tedious to handle.

5. *2,4-Dioxa-9-aza-3-phosphadecalins* **19**–**34** *of Type* **I**. *(1*RS,*3*SR,*6*RS*)-9-Benzyl-3-fluoro-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**19a**). Colorless viscous oil (34%). R_f (Et_2O) 0.18. IR ($CHCl_3$): 2951*m*, 2928*m*, 2816*m*, 2774*m*, 1952*w*, 1877*w*, 1825*w*, 1602*w*, 1495*m*, 1468*m*, 1454*m*, 1444*m*, 1334*s*, 1306*m*, 1160*m*, 1096*s*, 1072*s*, 1045*s*, 1009*s*, 982*s*, 933*m*, 899*s*, 882*s*, 858*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.27–7.19 (*m*, H–C(2′) to H–C(6′)); 4.30 (*A* of *ABX*–*P*, ^2J = 11.2, ^3J(5eq,P) = 24.3, ^3J(5eq,6) = 4.4, H_{eq}–C(5)); 4.24 (*td*, ^3J(1,6) = ^3J(1,10ax) = 10.9, ^3J(1,10eq) = 4.2, H–C(1)); 4.10 (*B* of *ABX*–*P*, ^2J = ^3J(5ax,6) = 11.2, H_{ax}–C(5)); 3.53, 3.51 (*AB*, ^2J = 13.1, Ph*C*H_2); 3.11 (*ddd*, ^2J = 10.5, ^3J(10eq,1) = 4.2, ^4J(10eq,8eq) = 1.5, (H_{eq}–C(10)); 2.85 (*dquint.*-like, ^2J = 11.5, ^3J(8eq,7ax) ≈ ^3J(8eq,7eq) = 4.3, ^4J(8eq,10eq) = 1.5, H_{eq}–C(8)); 2.09 (*t*, ^2J = ^3J(10ax,1) = 10.5, H_{ax}–C(10)); 2.02 (*ddd*, ^2J = 11.5, ^3J(8ax,7ax) = 12.4, ^3J(8ax,7eq) = 4.0, H_{ax}–C(8)); 1.92 (*X* of *ABX*–*P*, *qt*-like, $w_{1/2}$ ≈ 25, H–C(6)); 1.59 (*dq*, ^2J = 12.4, ^3J(7eq,6) ≈ ^3J(7eq,8ax) ≈ ^3J(7eq,8eq) ≈ 4, H_{eq}–C(7)); 1.23 (*qd*, ^2J = ^3J(7ax,6) = ^3J(7ax,8ax) = 12.4, ^3J(7ax,8eq) = 4.3, H_{ax}–C(7)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.3 (C(1′)); 128.8 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.4 (C(4′)); 80.6 (*d*, ^2J(1,P) = 6.4, C(1)); 73.7 (*d*, ^2J(5,P) = 7.5, C(5)); 62.1 (Ph*C*H_2); 56.6 (*d*, ^3J(10,P) = 11.9, C(10)); 51.7 (C(8)); 39.6 (*d*, ^3J(6,P) = 6.3, C(6)); 24.3 (C(7)). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −16.5 (*dd*, ^1J(P,F) = 1008, ^3J(P,H_{eq}–C(5)) = 24.3). EI-MS: 285 (7, $M^{+\bullet}$), 194 (9, [*M* − $PhCH_2$]$^+$); 171 (18), 160 (23), 91 (100, $PhCH_2^+$), 65 (19). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.45, H 5.58, N 4.83.

*(1*RS,*3*RS,*6*RS*)-9-Benzyl-3-fluoro-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**19b**). Colorless prisms (32%). M.p. 88–92°. R_f (Et_2O) 0.09. IR ($CHCl_3$): 2950*m*, 2930*m*, 2815*m*, 2773*m*, 1952*w*, 1878*w*, 1820*w*, 1711*w*, 1602*w*, 1494*m*, 1474*m*, 1468*m*, 1454*m*, 1332*s*, 1302*m*, 1159*m*, 1103*m*, 1053*s*, 1013*s*, 980*s*, 897*s*, 879*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.36–7.24 (*m*, H–C(2′) to H–C(6′)); 4.50–4.37 (*A* of *ABX*–*P* and *m*, not resolved, H_{eq}–C(5), H–C(1)); 4.21 (*B* of *ABX*–*P*, ^2J = ^3J(5ax,P) = ^3J(5ax,6) = 10.5, ^4J(5ax,F) = 4.0, H_{ax}–C(5)); 3.59, 3.585 (*AB*, ^2J = 13.2, Ph*C*H_2); 3.22 (*ddd*, ^2J = 10.6, ^3J(10eq,1) = 4.6, ^4J(10eq,8eq) = 1.5, H_{eq}–C(10)); 2.91 (*dquint.*-like, ^2J = 11.6, ^3J(8eq,7ax) ≈ ^3J(8eq,7eq) = 4.0, ^4J(8eq,10eq) = 1.5, H_{eq}–C(8)); 2.15 (*X* of *ABX*–*P*, *qt*-like, $w_{1/2}$ ≈ 25, H–C(6)); 2.13–2.03 (*m*, H_{ax}–C(8), H_{ax}–C(10)); 1.70 (*dq*, ^2J = 12.3, ^3J(7eq,6) ≈ ^3J(7eq,8ax) ≈ ^3J(7eq,8eq) ≈ 4, H_{eq}–C(7)); 1.33 (*qd*, ^2J = ^3J(7ax,6) = ^3J(7ax,8ax) = 12.3, ^3J(7ax,8eq) = 4.3, H_{ax}–C(7)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.1 (C(1′)); 128.8 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.4 (C(4′)); 80.2 (*d*, ^2J(1,P) = 5.3, C(1)); 73.6 (*d*, ^2J(5,P) = 7.2, C(5)); 62.0 (Ph*C*H_2); 56.9 (*d*, ^3J(10,P) = 8.9, C(10)); 51.5 (C(8)); 38.4 (*d*, ^3J(6,P) = 13.1, C(6)); 24.3 (C(7)). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −15.9 (*dt*, ^1J(P,F) = 1002, ^3J(P,H_{ax}–C(5)) = ^3J(P,H_{eq}–C(5)) = 10.5). EI-MS: 285 (9, $M^{+\bullet}$), 194 (5, [*M* − $PhCH_2$]$^+$), 171 (11), 160 (21), 91 (100, $PhCH_2^+$), 65 (12). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.63, H 5.88, N 5.04.

*(1*RS,*3*SR,*6*RS*)-9-Benzyl-3-chloro-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**20a**)[14]. Slightly yellow oil (78%). IR ($CHCl_3$): 3361*w* (br.), 2934*m*, 2497*m*, 1474*m*, 1469*m*, 1319*s*, 1254*m*, 1146*m*, 1095*s*, 1047*s*, 1014*s*, 987*m*, 972*s*, 946*m*, 938*m*, 796*s*, 753*s*, 697*s*, 570*s*, 558*s*, 525*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.29–7.18 (*m*, H–C(2′) to H–C(6′)); 4.29 (*A* of *ABX*–*P*, ^2J = 11.3, ^3J(5eq,P) = 28.5, ^3J(5eq,6) = 4.4, H_{eq}–C(5)); 4.28 (*m*, not resolved, H–C(1)); 4.11 (*B* of *ABX*–*P*, ^2J = ^3J(5ax,6) = 11.3, ^3J(5ax,P) = 2.3, H_{ax}–C(5)); 3.525, 3.52 (*AB*, ^2J = 13, Ph*C*H_2); 3.09 (*ddd*, ^2J = 10.5, ^3J(10eq,1) = 4.5, ^4J(10eq, 8eq) = 1.5, H_{eq}–C(10)); 2.86 (*dquint.*-like, ^2J = 11.5, ^3J(8eq,7ax) ≈ ^3J(8eq,7eq) ≈ 4.5, ^4J(8eq,10eq) = 1.5, H_{eq}–C(8)); 2.11 (*t*, ^2J = ^3J(10ax,1) = 10.3, H_{ax}–C(10)); 2.06–1.92 (*m*, H–C(6), H_{ax}–C(8)); 1.59 (*dq*, ^2J = 12.5, ^3J(7eq,6) = 4.0, ^3J(7eq,8ax) = ^3J(7eq,8eq) = 2.5, H_{eq}–C(7)); 1.59 (*dq*-like, ^2J = 12.5, ^3J(7eq,6) ≈ ^3J(7eq,8ax) ≈ ^3J(7eq,8eq) ≈ 4, H_{eq}–C(7)); 1.26 (*qd*, ^2J = ^3J(7ax,6) = ^3J(7ax,8ax) = 12.5, ^3J(7ax,8eq) = 4.2, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 137.0 (C(1′)); 128.8 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.4 (C(4′)); 80.6 (*d*, ^2J(1,P) = 7.3, C(1)); 73.5 (*d*, ^2J(5,P) = 8.3, C(5)); 62.1 (Ph*C*H_2); 56.4 (*d*, ^3J(10,P) = 12.7, C(10)); 51.6 (C(8)); 39.7 (*d*, ^3J(6,P) = 6.6, C(6)); 24.2 (C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −2.4 (*d*, ^3J(P,H_{eq}–C(5)) = 28.5). CI-MS: 321 (9, [*M*(^{37}Cl) + NH_4]$^+$), 319 (27, [*M*(^{35}Cl) + NH_4]$^+$), 304 (32, [*M*(^{37}Cl) + H]$^+$), 302 (100, [*M*(^{35}Cl) + H]$^+$), 244 (19), 235 (20), 219 (46), 218 (85).

*(1*RS,*3*SR,*6*RS*)-9-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**21a**). Yellow viscous oil (32%). IR ($CHCl_3$): 3005*w*, 2950*w*, 2860*w*, 2815*w*, 1614*m*, 1593*m*, 1526*s*, 1493*m*, 1348*s*, 1304*m*, 1160*m*, 1094*m*, 1040*s*, 1008*s*, 978*s*, 934*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.25 (*AA′* of *AA′BB′*, *J* = 9.2, H–C(3′), H–C(5′)); 7.41 (*BB′* of *AA′BB′*, *J* = 9.2, H–C(2′), H–C(6′)); 7.39–7.26 (*m*, H–C(2″) to H–C(6″)); 4.36 (*A* of *ABX*–*P*, ^2J = 10.9, ^3J(5eq,P) = 23.5, ^3J(5eq,6) = 4.4, H_{eq}–C(5)); 4.35 (*m*, not resolved,

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[14]) There is no evidence of the presence of the equatorially substituted epimer when the phosphorylation is performed under standard conditions. However, at low temperatures and short reaction times (< 0°, *ca.* 1 min), the product shows a concomitant, paramagnetically shifted ^{31}P-NMR signal that can be tentatively assigned to the equatorial epimer.

H–C(1)); 4,19 (*B* of *ABX–P*, $^2J = {}^3J(5ax,6) = 11.1$, $^3J(5ax,P) < 1$, H_{ax}–C(5)); 3.59 (*s*, PhCH_2); 3.18 (*ddd*, $^2J = 10.3$, $^3J(10eq,1) = 4.5$, $^4J(10eq, 8eq) = 1.5$, H_{eq}–C(10)); 2.94 (*dquint.*-like, $^2J = 11.5$, $^3J(8eq,7ax) \approx {}^3J(8eq,7eq) \approx 4.5$, $^4J(8eq,10eq) = 1.5$, H_{eq}–C(8)); 2.20 (*t*, $^2J = {}^3J(10ax,1) = 10.3$, H_{ax}–C(10)); 2.14–1.99 (*m*, H–C(6), H_{ax}–C(8)); 1.68 (*dq*-like, $^2J = 12.5$, $^3J(7eq,6) \approx {}^3J(7eq,8ax) \approx {}^3J(7eq,8eq) \approx 4.5$, H_{eq}–C(7)); 1.32 (*qd*, $^2J = {}^3J(7ax,6) = {}^3J(7ax,8ax) = 12.5$, $^3J(7ax,8eq) = 4.3$, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 155.4 (*d*, $^2J(1',P) = 6.1$, C(1')); 144.6 (C(4')); 137.1 (C(1'')); 128.8 (C(3''), C(5'')); 128.2 (C(2''), C(6'')); 127.2 (C(4'')); 125.6 (C(3'), C(5')); 120.0 (*d*, ^3J(2' and 6',P) = 5.4, C(2'), C(6')); 80.3 (*d*, $^2J(1,P) = 6.9$, C(1)); 73.2 (*d*, $^2J(5,P) = 7.8$, C(5)); 62.1 (Ph*C*H_2); 56.7 (*d*, $^3J(10,P) = 11.4$, C(10)); 51.7 (C(8)); 39.7 (*d*, $^3J(6,P) = 6.5$, C(6)); 24.2 (C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −14.6 (br. *d*, $^3J(P,H_{eq}$–C(5)) = 23.5). CI-MS: 405 (100, $[M+H]^+$).

*(1*RS*,3*RS*,6*RS*)-9-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**21b**). Slightly yellow powder (25%). IR ($CHCl_3$): 2927*w*, 1615*m*, 1594*s*, 1526*s*, 1494*m*, 1467*w*, 1348*s*, 1291*s*, 1248*s*, 1160*s*, 1098*s*, 1073*m*, 1047*s*, 1005*s*, 976*s*, 936*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.24 (*AA'* of *AA'BB'*, *J* = 9.3, H–C(3'), H–C(5')); 7.37 (*BB'* of *AA'BB'*, *J* = 9.3, H–C(2'), H–C(6')); 7.39–7.26 (*m*, H–C(2'') to H–C(6'')); 7.37–7.26 (*m*, H–C(2'') to H–C(6'')); 4.49 (*tdd*, $^3J(1,6) \approx {}^3J(1,10ax) \approx 10$, $^3J(1,10eq) = 4.5$, $^4J(1,P) = 1.5$, H–C(1)); 4.40 (*A* of *ABX–P*, $^2J = 10.8$, $^3J(5eq,P) = 15.5$, $^3J(5eq,6) = 5.0$, H_{eq}–C(5)); 4.30 (*B* of *ABX–P*, $^2J = {}^3J(5ax,6) = 10.8$, $^3J(5ax,P) = 6.5$, H_{ax}–C(5)); 3.62, 3.56 (*AB*, $^2J = 13.2$, PhCH_2); 3.21 (*ddd*, $^2J = 10.5$, $^3J(10eq,1) = 4.5$, $^4J(10eq,8eq) = 1.5$, H_{eq}–C(10)); 2.92 (*dquint.*-like, $^2J = 11.5$, $^3J(8eq,7ax) \approx {}^3J(8eq,7eq) = 4.0$, $^4J(8eq,10eq) = 1.5$, H_{eq}–C(8)); 2.01–2.12 (*m*, H–C(6), H_{ax}–C(8), H_{ax}–C(10); 1.68 (*dq*-like, $^2J = 13.1$, $^3J(7eq,6) \approx {}^3J(7eq,8ax) \approx {}^3J(7eq,8eq) \approx 4$, H_{eq}–C(7)); 1.35 (*qd*, $^2J = {}^3J(7ax,6) = {}^3J(7ax,8ax) = 13.1$, $^3J(7ax,8eq) = 4.3$, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 155.2 (*d*, $^2J(1',P) = 6.2$, C(1')); 144.3 (C(4')); 137.2 (C(1'')); 128.7 (C(3''), C(5'')); 128.2 (C(2''), C(6'')); 127.3 (C(4'')); 125.5 (C(3'), C(5')); 120.6 (*d*, ^3J(2' and 6',P) = 5.5, C(2'), C(6')); 79.3 (*d*, $^2J(1,P) = 65.4$, C(1)); 72.9 (*d*, $^2J(5,P) = 6.8$, C(5)); 62.0 (Ph*C*H_2); 56.9 (*d*, $^3J(10,P) = 10.2$, C(10)); 51.7 (C(8)); 39.0 (*d*, $^3J(6,P) = 9.5$, C(6)); 25.0 (C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −12.1 (*dd*, $^3J(P,H_{eq}$–C(5)) = 15.5, $^3J(P,H_{ax}$–C(5)) = 6.5). CI-MS: 405 (100, $[M+H]^+$).

*(1*RS*,3*SR*,6*RS*)-9-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**22a**). Slightly yellow foam (29%). IR ($CHCl_3$): 3065*w*, 3030*w*, 2927*w*, 2815*m*, 1609*s*, 1593*m*, 1541*s*, 1485*m*, 1455*m*, 1347*s*, 1318*s*, 1265*s*, 1159*m*, 1095*m*, 1070*s*, 1037*s*, 981*s*, 936*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.77 (*dd*, $^4J(3',5') = 2.8$, $^5J(3',6') = 1.2$, H–C(3')); 8.38 (*dd*, $^3J(5',6') = 9.2$, $^4J(5',3') = 2.8$, H–C(5')); 8.02 (*d*, $^3J(6',5') = 9.2$, $^5J(6',3') = 1.2$, H–C(6')); 7.29–7.18 (*m*, H–C(2'') to H–C(6'')); 4.43 (*td*, $^3J(1,6) = {}^3J(1,10ax) = 10.2$, $^3J(1,10eq) = 4.5$, H–C(1)); 4.33 (*AB* of *ABX–P*, $^2J \approx {}^3J(5ax,6) \approx 11$, $^3J(5eq,P) = 25$, $^3J(5eq,6) \approx 5$, CH_2(5)); 3.52, 3.515 (*AB*, $^2J = 13.4$, PhCH_2)); 3.09 (*ddd*, $^2J = 10.5$, $^3J(10eq,1) = 5.5$, $^4J(10eq, 8eq) = 1.3$, H_{eq}–C(10)); 2.87 (*dquint.*-like, $^2J = 11.5$, $^3J(8eq,7ax) \approx {}^3J(8eq,7eq) \approx 4.5$, $^4J(8eq,10eq) = 1.5$, H_{eq}–C(8)); 2.11 (*t*, $^2J = {}^3J(10ax,1) = 10.5$, H_{ax}–C(10)); 2.06–1.97 (*m*, H–C(6), H_{ax}–C(8)); 1.62 (*dq*-like, $^2J = 13.0$, $^3J(7eq,6) \approx {}^3J(7eq,8ax) \approx {}^3J(7eq,8eq) \approx 4.5$, H_{eq}–C(7)); 1.33 (*qd*, $^2J = {}^3J(7ax,6) = {}^3J(7ax,8ax) = 13.0$, $^3J(7ax,8eq) = 4.3$, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 148.3 (*d*, $^2J(1',P) = 5.6$, C(1')); 145.1 (C(4')); 141.9 (*d*, $^3J(2',P) = 7.5$, C(2')); 137.2 (C(1'')); 128.9 (C(5')); 128.8 (C(2''), C(6'')); 128.3 (C(3''), C(5'')); 127.2 (C(4'')); 122.8 (*d*, $^3J(6',P) = 2.2$, C(6'));121.7 (C(3')); 80.9 (*d*, $^2J(1,P) = 7.0$, C(1)); 73.8 (*d*, $^2J(5,P) = 7.9$, C(5)); 62.1 (Ph*C*H_2); 56.8 (*d*, $^3J(10,P) = 11.6$, C(10)); 51.7 (C(8)); 39.9 (*d*, $^3J(6,P) = 6.7$, C(6)); 24.2 (*d*, $^4J(7,P) = 1$, C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −15.4 (br. *d*, $^3J(P,H_{eq}$–C(5)) = 25). CI-MS: 450 (100, $[M+H]^+$).

*(1*RS*,3*RS*,6*RS*)-9-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**22b**)[15]). Yellow viscous oil (*ca.* 10%). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −14.7 (*m*, $w_{1/2} \approx 35$).

*(1*RS*,3*SR*,6*SR*)-9-Benzyl-3-fluoro-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**23a**). Colorless oil (24%). R_f (Et_2O) 0.13. IR ($CHCl_3$): 2953*s*, 2812*s*, 2768*s*, 1955*w*, 1877*w*, 1816*w*, 1758*w*, 1601*w*, 1586*w*, 1495*s*, 1454*s*, 1444*s*, 1371*s*, 1337*s*, 1272*s*, 1168*s*, 1125*s*, 1092*s*, 1075*s*, 1026*s*, 981*s*, 881*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.33–7.24 (*m*, H–C(2') to H–C(6')); 4.70 (*m*, $w_{1/2} \approx 6$, H–C(1)); 4.56 (*A* of *ABX–P*, $^2J = 11.4$, $^3J(5ax,6) = 2.5$, H_{ax}–C(5)); 4.27 (*B* of *ABX–P*, $^2J = 11.4$, $^3J(5eq,P) = 24.8$, $^3J(5eq,6) = 1.2$, H_{eq}–C(5)); 3.58, 3.55 (*AB*, $^2J = 13.5$, PhCH_2); 3.18 (*dt*, $^2J = 13.0$, $^3J(10eq,1) = {}^4J(10eq,8eq) = 2.1$, H_{eq}–C(10)); 3.00 (*dquint.*-like, $^2J = 12$, $^3J(8eq,7ax) \approx {}^3J(8eq,7eq) \approx 4.5$, $^4J(8eq,10eq) = 2.1$, H_{eq}–C(8)); 2.29 (*qd*, $^2J = {}^3J(7ax,8ax) = 12.0$, $^3J(7ax,8eq) = 4.3$, H_{ax}–C(7)); 2.26 (*ddd*, $^2J = 13.0$, $^3J(10ax,1) = 1.8$, $^4J(10ax,P) = 5.9$, H_{ax}–C(10)); 2.12 (*td*, $^2J = {}^3J(8ax,7ax) = 11.7$, $^3J(8ax,7eq) = 2.4$, H_{ax}–C(8)); 1.77 (*X* of *ABX–P*, *dquint.*-like, $w_{1/2} \approx 25$, H–C(6)); 1.56 (*m*, *dq*-like, $w_{1/2} \approx 25$, H_{eq}–C(7)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.5 (C(1')); 128.7 (C(3'), C(5')); 128.2 (C(2'), C(6')); 127.1

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[15]) The formation of the minor, equatorially substituted *P*-epimer is evidenced by TLC. Due to epimerization during workup, it was characterized only in the mixture by ^{31}P-NMR and its amount estimated from the relative intensities of the signals.

(C(4′)); 78.5 (*d*, ^2J(1,P) = 7.2, C(1)); 73.1 (*d*, ^2J(5,P) = 7.1, C(5)); 61.9 (Ph*C*H$_2$); 56.4 (*d*, ^3J(9,P) = 9.1, C(10)); 51.7 (C(8)); 34.3 (*d*, ^3J(6,P) = 5.6, C(6)); 22.8 (C(7)). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −16.5 (*ddd*, ^1J(P,F) = 1006, ^3J(P,H$_{eq}$−C(5)) = 24.8, ^4J(P,H$_{ax}$−C(10)) = 5.9). EI-MS: 285 (14, $M^{+\bullet}$), 194 (4, $[M-PhCH_2]^+$), 160 (65), 147 (22), 118 (22), 91 (100, $PhCH_2^+$), 80 (22). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.98, H 6.32, N 5.24.

*(1*RS*,3*RS*,6*SR*)-9-Benzyl-3-fluoro-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**23b**). Colorless plates (55%). M.p. 95–98°. R_f (Et_2O) 0.07. IR ($CHCl_3$): 2953*s*, 2930*s*, 2813*s*, 2787*s*, 2768*s*, 1954*w*, 1876*w*, 1816*w*, 1737*w*, 1602*w*, 1586*w*, 1495*m*, 1454*s*, 1443*s*, 1370*s*, 1329*s*, 1093*s*, 1076*s*, 1012*s*, 984*s*, 949*s*, 886*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.36–7.24 (*m*, H−C(2′) to H−C(6′)); 4.80 (*m*, $w_{1/2}\approx30$, H−C(1)); 4.53 (*A* of *ABX*−*P*, ^2J = 11.4, ^3J(5ax,P) = 16.4, ^3J(5ax,6) = 3.5, H$_{ax}$−C(5)); 4.39 (*B* of *ABX*−*P*, ^2J = 11.4, ^3J(5eq,P) = 16.4, ^3J(5eq,6) = 4.8, H$_{eq}$−C(5)); 3.58 (*s*, Ph*C*H$_2$); 2.84 (*m*, *dt*-like, ^2J = 11.8, H$_{eq}$−C(8)); 2.70 (*m*, *td*-like, ^2J = 11.8, H$_{eq}$−C(8)); 2.44 (*m*, $w_{1/2}\approx20$, CH$_2$(10)); 2.30 (*X* of A*BX*−*P*, *m*, $w_{1/2}\approx30$, H−C(6)); 1.82 (*m*, *q*-like, $w_{1/2}\approx15$, CH$_2$(7)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.2 (C(1′)); 128.7 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.3 (C(4′)); 79.2 (^2J(1,P) = 7.7, C(1)); 69.7 (*d*, ^2J(5,P) = 6.4, C(5)); 62.2 (Ph*C*H$_2$); 53.6 (C(10)); 49.3 (C(8)); 32.8 (*d*, ^3J(6,P) = 8.1, C(6)); 24.3 (C(7)). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −16.9 (*dtd*, ^1J(P,F) = 997, ^3J(P,H$_{eq}$−C(5)) = ^3J(P,H$_{ax}$−C(5) = 16.4, ^3J(P,1) = 7.5). EI-MS: 285 (7, $M^{+\bullet}$); 194 (8, $[M-PhCH_2]^+$), 171 (13), 160 (25), 91 (100, $PhCH_2^+$), 65 (14). EI-MS: 285 (16, $M^{+\bullet}$), 194 (24, $[M-PhCH_2]^+$), 160 (48), 147 (19), 118 (25), 91 (100, $PhCH_2^+$), 80 (29). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.52, H 5.81, N 4.69.

*(1*RS*,3*SR*,6*SR*)-9-Benzyl-3-chloro-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**24a**)[14]. Colorless oil (80%). IR ($CHCl_3$): 3420*w* (br.), 2991*m*, 2901*m*, 2501*m*, 1496*w*, 1449*m*, 1412*s*, 1304*s*, 1250*m*, 1229*m*, 1205*m*, 1103*s*, 1069*s*, 994*s*, 968*s*, 932*w*, 814*m*, 777*s*, 742*m*, 725*m*, 700*s*, 669*s*, 571*s*, 540*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.26–7.17 (*m*, H−C(2′) to H−C(6′)); 4.64 (*q*-like, $w_{1/2}\approx6$, H−C(1)); 4.52 (*A* of *ABX*−*P*, ^2J = 11.0, ^3J(5ax,6) = 2.5, ^3J(5ax,P) ≈ 3, H$_{ax}$−C(5)); 4.18 (*B* of *ABX*−*P*, ^2J = 11.0, ^3J(5eq,P) = 29.8, ^3J(5eq,6) = 1.5, H$_{eq}$−C(5)); 3.52, 3.44 (*AB*, ^2J = 13.5, Ph*C*H$_2$); 3.09 (*dt*-like, ^2J = 13.1, ^3J(10eq,1) ≈ ^4J(10eq,8eq) ≈ 2, H$_{eq}$−C(10)); 2.92 (*dquint.*-like, ^2J = 11.0, ^3J(8eq,7ax) ≈ ^3J(8eq,7eq) ≈ 3.5, ^4J(8eq,10eq) ≈ 2, H$_{eq}$−C(8)); 2.28–2.15 (*m*, H$_{ax}$−C(7), H$_{ax}$−C(10)); 2.04 (*td*, ^2J = ^3J(8ax,7ax) = 11.0, ^3J(8ax,7eq) = 2.5, H$_{ax}$−C(8)); 1.71 (*X* of *ABX*−*P*, *d*-like, $w_{1/2}\approx20$, H−C(6)); 1.49 (*m*, *dsext.*-like, $w_{1/2}\approx20$, H$_{eq}$−C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 137.5 (C(1′)); 128.6 (C(3′), C(5′)); 128.1 (C(2′), C(6′)); 127.0 (C(4′)); 78.7 (*d*, ^2J(1,P) = 8.3, C(1)); 73.2 (*d*, ^2J(4,P) = 7.6, C(5)); 61.8 (Ph*C*H$_2$); 56.3 (*d*, ^3J(10,P) = 9.9, C(10)); 51.8 (C(8)); 34.3 (*d*, ^3J(6,P) = 5.8, C(6)); 23.1 (C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −2.6 (*d*, ^3J(P,H$_{eq}$−C(5)) = 29.8). CI-MS: 304 (34, $[M(^{37}Cl)+H]^+$); 302 (100, $[M(^{35}Cl)+H]^+$).

*(1*RS*,3*SR*,6*SR*)-9-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-9-aza-3-phospha-bicyclo[4.4.0]decane 3-Oxide* (**25a**). Yellow foam (41%). IR ($CHCl_3$): 2952*w*, 2916*w*, 2811*w*, 2765*w*, 1615*w*, 1594*m*, 1525*s*, 1493*s*, 1348*s*, 1311*s*, 1110*s*, 1093*m*, 1075*m*, 1043*m*, 1026*m*, 1005*s*, 988*s*, 926*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.23 (*AA′* of *AA′BB′*, *J* = 9.1, H−C(3′), H−C(5′)); 7.40 (*BB′* of *AA′BB′*, *J* = 9.1, H−C(2′), H−C(6′)); 7.42–7.22 (*m*, H−C(2″) to H−C(6″)); 4.75 (*s*, $w_{1/2}\approx6$, H−C(1)); 4.59 (*A* of *ABX*−*P*, ^2J = 11.4, ^3J(5ax,6) = 2.5, ^3J(5ax,P) = 1.5, H$_{ax}$−C(5)); 4.28 (*B* of *ABX*−*P*, ^2J = 11.4, ^3J(5eq,P) = 24.5, ^3J(5eq,6) = 1.2, H$_{eq}$−C(5)); 3.60, 3.56 (*AB*, ^2J = 13.5, Ph*C*H$_2$); 3.18 (*dt*-like, ^2J = 13.0, ^3J(10eq,1) ≈ ^4J(10eq,8eq) ≈ 2, H$_{eq}$−C(10)); 3.01 (*dquint.*-like, ^2J = 11.5, ^3J(8eq,7ax) ≈ ^3J(8eq,7eq) ≈ 3.5, ^4J(8eq,10eq) ≈ 2, H$_{eq}$−C(8)); 2.36 (*qd*, ^2J = ^3J(7ax,6) = ^3J(7ax,8ax) = 11.8, ^3J(7ax,8eq) = 4.0, H$_{ax}$−C(7)); 2.27 (*ddd*, ^2J = 13.0, ^3J(10ax,1) = 1.8, ^4J(10ax,P) = 7.0, H$_{ax}$−C(10)); 2.12 (*td*, ^2J = ^3J(8ax,7ax) = 11.8, ^3J(8ax,7eq) = 2.4, H$_{ax}$−C(8)); 1.79 (*X* of *ABX*−*P*, *m*, $w_{1/2}\approx20$, H−C(6)); 1.58 (*m*, *d*-like, $w_{1/2}\approx20$, H$_{eq}$−C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 155.5 (*d*, ^2J(1′,P) = 6.0, C(1′)); 144.3 (C(4′)); 137.4 (C(1″)); 128.7 (C(3″), C(5″)); 128.2 (C(2″), C(6″)); 127.0 (C(4″)); 125.6 (C(3′), C(5′)); 120.0 (*d*, ^3J(2′ and 6′,P) = 5.5, C(2′), C(6′)); 78.1 (*d*, ^2J(1,P) = 7.6, C(1)); 72.7 (*d*, ^2J(5,P) = 7.2, C(5)); 61.9 (Ph*C*H$_2$); 56.5 (*d*, ^3J(10,P) = 8.9, C(10)); 51.7 (C(8)); 34.3 (*d*, ^3J(6,P) = 5.7, C(6)); 22.9 (C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −14.5 (*dd*, ^3J(P,H$_{eq}$−C(5)) = 24.5, ^3J(P,H$_{ax}$−C(10)) = 7.0). CI-MS: 405 (100, $[M+H]^+$).

*(1*RS*,3*RS*,6*SR*)-9-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**25b**). Slightly brown viscous oil (31%). IR ($CHCl_3$): 3080*w*, 2953*w*, 2919*w*, 2813*w*, 1613*s*, 1526*s*, 1493*s*, 1349*s*, 1286*s*, 1248*m*, 1165*m*, 1110*m*, 1092*m*, 1072*s*, 1051*m*, 1027*m*, 1003*s*, 984*s*, 951*s*, 930*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.24 (*AA′* of *AA′BB′*, *J* = 9.0, H−C(3′), H−C(5′)); 7.47 (*BB′* of *AA′BB′*, *J* = 9.0, H−C(2′), H−C(6′)); 7.37–7.25 (*m*, H−C(2″) to H−C(6″)); 4,87 (*sept.*-like, ^3J(1,6) ≈ ^3J(1,10ax) ≈ ^3J(1,10eq) ≈ 3, ^3J(1,P) ≈ 2.5, H−C(1)); 4.60 (*A* of *ABX*−*P*, ^2J = 11.6, ^3J(5ax,P) = 8.6, ^3J(5ax,6) = 3.5, H$_{ax}$−C(5)); 4.31 (*B of ABX*−*P*, ^2J = 11.6, ^3J(5eq,P) = 16.7, ^3J(5eq,6) = 4.7, H$_{eq}$−C(5)); 3.57, 3.51 (*AB*, ^2J = 13.2, Ph*C*H$_2$); 3.03 (*dd*, ^2J = 12.3, ^3J(10eq,1) = 5.3, H$_{eq}$−C(10)); 2.61 (*m*, $w_{1/2}\approx20$, H$_{ax}$−C(10)); 2.51 (*ddd*, ^2J = 12.4, ^3J(8eq,7ax) = 4.6, ^3J(8eq,7eq) = 3.0, H$_{eq}$−C(8)); 2.19 (*ddd*, ^2J = 12.0, ^3J(8ax,7ax) = 9.5, ^3J(8ax,7eq) = 3.5, H$_{ax}$−C(8)); 2.05 (*X* of *ABX*−*P*, *m*, $w_{1/2}\approx25$, H−C(6)); 1.76 (*dddd*, ^2J = 13.5, ^3J(7ax,6) ≈ ^3J(7ax,8ax) = 9.5, ^3J(7ax,8eq) = 4.0, H$_{ax}$−C(7)); 1.61–1.88

(*m*, H_{eq}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 156.1 (*d*, ^2J(1′,P) = 5.8, C(1′)); 143.2 (C(4′)); 137.4 (C(1″)); 128.6 (C(3″), C(5″)); 128.2 (C(2″), C(6″)); 127.3 (C(4″)); 125.4 (C(3′), C(5′)); 120.1 (*d*, ^3J(2′ and 6′,P) = 5.3, C(2′), C(6′)); 77.6 (*d*, ^2J(1,P) = 6.6, C(1)); 70.6 (*d*, ^2J(5,P) = 5.8, C(5)); 62.1 (Ph*C*H_2); 55.7 (*d*, ^3J(10,P) = 5.8, C(10)); 50.5 (C(8)); 33.7 (*d*, ^3J(6,P) = 6.2, C(6)); 23.7 (C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −12.5 (*m*, $w_{1/2}$ = 32). CI-MS: 405 (100, $[M+H]^+$).

*(1*RS,*3*SR,*6*SR*)-9-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**26a**). Slightly yellow powder (35%). IR ($CHCl_3$): 2927*w*, 2854*w*, 2812*w*, 1609*s*, 1541*s*, 1485*m*, 1455*m*, 1347*s*, 1316*s*, 1270*m*, 1091*m*, 1069*m*, 1007*s*, 983*m*, 935*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.75 (*dd*, ^4J(3′,5′) = 2.8, ^5J(3′,6′) = 1.2, H–C(3′)); 8.39 (*dd*, ^3J(5′,6′) = 9.2, ^4J(5′,3′) = 2.8, H–C(5′)); 8.10 (*dd*, ^3J(6′,5′) = 9.2, ^5J(6′,3′) = 1.2, H–C(6′)); 7.28–7.18 (*m*, H–C(2″) to H–C(6″)); 4.80 (*s*, $w_{1/2} \approx 6$, H–C(1)); 4.68 (*A* of *ABX*–*P*, ^2J = 11.3, ^3J(5ax,6) = 2.4, ^3J(5ax,P) ≈ 1, H_{ax}–C(5)); 4.21 (*B* of *ABX*–*P*, ^2J = 11.3, ^3J(5eq,P) = 25, ^3J(5eq,6) ≈ 1, H_{eq}–C(5)); 3.53, 3.47 (*AB*, ^2J = 13.4, Ph*C*H_2); 3.08 (*dt*-like, ^2J = 13.0, ^3J(10eq,1) ≈ ^4J(10eq,8eq) ≈ 2, H_{eq}–C(10)); 2.96 (*dquint.*-like, ^2J = 11.5, ^3J(8eq,7ax) ≈ ^3J(8eq,7eq) ≈ 3.5, ^4J(8eq,10eq) ≈ 2, H_{eq}–C(8)); 2.27 (*qd*, ^2J = ^3J(7ax,6) = ^3J(7ax,8ax) = 12.8, ^3J(7ax,8eq) = 4.0, H_{ax}–C(7)); 2.27 (*ddd*, ^2J = 13.0, ^3J(10ax,1) = 1.8, ^4J(10ax,P) = 7, H_{ax}–C(10)); 2.06 (*td*, ^2J = ^3J(8ax,7ax) = 11.5, ^3J(8ax,7eq) = 2.5, H_{ax}–C(8)); 1.77 (*X* of *ABX*–*P*, *d*-like, $w_{1/2} \approx 20$, H–C(6)); 1.52 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{eq}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 148.2 (*d*, ^2J(1′,P) = 5.1, C(1′)); 144.8 (C(4′)), 141.9 (br., C(2′)); 137.4 (C(1″)); 129.0 (C(5′)); 128.7 (C(2″), C(6″)); 128.2 (C(3″), C(5″)); 127.1 (C(4″)); 122.7 (*d*, ^3J(6′,P) = 2.3, C(6′)); 121.5 (C(3′)); 78.7 (*d*, ^2J(1,P) = 7.7, C(1)); 73.3 (*d*, ^2J(5,P) = 7.2, C(5)); 61.8 (Ph*C*H_2); 56.3 (*d*, ^3J(10,P) = 9.0, C(10)); 51.6 (C(8)); 34.3 (*d*, ^3J(6,P) = 5.7, C(6)); 22.8 (C(7)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −15.5 (*dd*, ^3J(P,H_{eq}–C(5)) = 25, ^3J(P,H_{ax}–C(10)) = 7). CI-MS: 450 (100, $[M+H]^+$), 289 (93), 243 (15), 222 (27), 204 (47), 186 (40).

*(1*RS,*3*RS,*6*SR*)-9-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-9-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**26b**)[15]. Yellow viscous oil (*ca.* 15%). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −15.0 (*m*, $w_{1/2} \approx 35$).

*(*1RS,*3*SR,*6*RS,*9*RS*)-9-Benzyl-3-chloro-9-methyl-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**27a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 2:1). White powder (40%). ^{1}H-NMR (300 MHz, $(CD_3)_2SO$)[16]): 7.73–7.58 (*m*, H–C(2′) to H–C(6′)); 5.27–5.15 (*m*, not resolved, H–C(1)); 4.96 (br. *s*, Ph*C*H_2); 4.72–4,62 (*AB of ABX*–*P*, not resolved, CH_2(5)); 3.90–3.86 (*m*, CH_2(8), CH_2(10)); 3.44 (*s*, Me_{ax}–N); 3.37 (*s*, Me_{eq}–N); 2.80–1.83 (*m*, H–C(6), CH_2(7)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2SO$): −3.3 (*d*, ^3J(P,H_{eq}–C(5)) = 30). ESI-MS: 318 (33, $[M(^{37}Cl) - CF_3SO_3]^+$), 316 (100, $[M(^{35}Cl) - CF_3SO_3]^+$).

*(1*RS,*3*SR,*6*RS,*9*RS*)-9-Benzyl-9-methyl-3-(4-nitrophenoxy)-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**28a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 5:1). White foam (56%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$)[16]): 8.27 (*AA′* of *AA′BB′*, *J* = 9.2, H–C(3′), H–C(5′)); 7.72 (*BB′* of *AA′BB′*, *J* = 9.2, H–C(2′), H–C(6′)); 7.58–7.46 (*m*, H–C(2″) to H–C(6″)); 5.32 (*td*, ^3J(1,6) = ^3J(1,10eq) = 10.9, ^3J(1,10eq) = 4.6, H–C(1)); 4.98 (*s*, Ph*C*H_2, (B)); 4.93 (*s*, Ph*C*H_2, (A)); 4.74–4.55 (*AB* of *ABX*–*P*, not resolved, CH_2(5)); 3.99–3.78 (*m*, CH_2(8), CH_2(10)); 3.39 (*s*, Me_{ax}–N); 3.33 (*s*, Me_{eq}–N); 2.62 (*X* of *ABX*–*P*, *oct.*-like, $w_{1/2} \approx 20$, H–C(6)); 2.25–2.17 (*m*, CH_2(7)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −14.3 (*d*, ^3J(P,H_{eq}–C(5)) = 22.5). ESI-MS: 419 (100, $[M - CF_3SO_3]^+$).

*(1*RS,*3*RS,*6*RS,*9*RS*)-9-Benzyl-9-methyl-3-(4-nitrophenoxy)-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**28b**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 4:1). Yellow viscous oil (27%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$)[16]): 8.32 (*AA′* of *AA′BB′*, *J* = 8.8, H–C(3′), H–C(5′)); 7.73 (*BB′* of *AA′BB′*, *J* = 8.8, H–C(2′), H–C(6′)); 7.60–7.54 (*m*, H–C(2″) to H–C(6″)); 5.27 (*td*, ^3J(1,6) = ^3J(1,10eq) = 11.0, ^3J(1,10eq) = 4.7, H–C(1)); 5.01 (*s*, Ph*C*H_2 (B)); 4.95 (*s*, Ph*C*H_2 (A)); 4.85–4.53 (*AB* of *ABX*–*P*, CH_2(5)); 4.05–3.92 (*m*, CH_2(8), CH_2(10)); 3.42 (*s*, Me_{ax}–N); 3.34 (*s*, Me_{eq}–N); 2.87 (*X* of *ABX*–*P*, *oct.*-like, $w_{1/2} \approx 30$, H–C(6)); 2.31–2.09 (*m*, CH_2(7)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −12.9 (A), −13.0 (B) (each *t*-like, ^3J(P,H_{eq}–C(5)) ≈ ^3J(P,H_{ax}–C(5)) ≈ 10). ESI-MS: 419 (100, $[M - CF_3SO_3]^+$).

*(1*RS,*3*SR,*6*RS,*9*RS*)-9-Benzyl-3-(2,4-dinitrophenoxy)-9-methyl-2,4-dioxa-9-azonia-3-phosphabicyclo-[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**29a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 3:1). White foam (92%). IR (KBr): 3500*w*, 1725*w*, 1710*w*, 1691*w*, 1658*w*, 1641*w*, 1611*m*, 1546*m*, 1536*m*, 1483*m*, 1441*m*, 1350*m*, 1262*s*, 1165*m*, 1053*m*, 1030*s*, 939*m*, 906*m*, 835*m*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$)[16]): 8.88 (*dd*, ^4J(3′,5′) = 2.9, ^5J(3′,6′) = 1.0, H–C(3′)); 8.62 (*dd*, ^3J(5′,6′) = 9.2, ^4J(5′,3′) = 2.9, H–C(5′)); 7.97 (*dd*, ^3J(6′,5′) = 9.2,

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[16]) For reasons of simplicity, the chemical shifts are given for the predominant epimer A, and only the MeN groups are specified. The epimer B exhibits paramagnetic shifts of the respective H-atoms (*ca.* 0.1–0.3 ppm)).

^5J(6′,3′) = 1.0, H–C(6′)); 7.77–7.54 (*m*, H–C(2″) to H–C(6″)); 5.37 (*td*, ^3J(1,6) = ^3J(1,10ax) = 10.8, ^3J(1,10eq) = 4.8, H–C(1)); 4.98 (*s*, PhCH_2)); 4.80–4.71 (*AB* of *ABX–P*, not resolved, CH_2(5)); 4.05–3.81 (*m*, CH_2(8), CH_2(10)); 3.39 (*s*, Me_{ax}–N); 3.37 (*s*, Me_{eq}–N); 2.73 (*X* of *ABX–P*, *oct.*-like, $w_{1/2} \approx 30$, H–C(6)); 2.31–2.06 (*m*, CH_2(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): epimer A: 148.3 (*d*, ^2J(1′,P) = 5.6, C(1′)); 145.1 (C(4′); 141.9 (*d*, ^3J(2′,P) = 7.5, C(2′)); 134.5 (C(2″), C(6″)); 131.9 (C(4″)); 130.4 (C(5′)); 130.2 (C(3″), C(5″)); 127.7 (C(1″)); 124.6 (*d*, ^3J(6′,P) = 2.5, C(6′)); 122.8 (C(3′)); 122.1 (*q*, ^1J(C,F) = 320, CF_3SO_3); 75.7 (*d*, ^2J(1,P) = 6.4, C(1)); 74.0 (*d*, ^2J(5,P) = 7.5, C(5)); 73.1 (Ph*C*H_2); 61.0 (C(8)); 60.6 (*d*, ^3J(10,P) = 8.9, C(10)); 46.7 (MeN); 38.9 (*d,* ^3J(6,P) = 6.4, C(6)); 20.1 (C(7)); epimer B: 148.3 (*d*, ^2J(1′,P) = 5.6, C(1′)); 145.1 (C(4′)); 141.9 (*d*, ^3J(2′,P) = 7.5, C(2′)); 134.0 (C(2″), C(6″)); 132.0 (C(4″)); 130.5 (C(3″), C(5″)); 130.4 (C(5′)); 128.0 (C(1″)); 124.6 (*d*, ^3J(6′,P) = 2.5, C(6′)); 122.9 (C(3′)); 122.1 (*q*, ^1J(C,F) = 320, CF_3SO_3); 75.0 (*d*, ^2J(1,P) = 6.7, C(1)); 74.1 (*d*, ^2J(5,P) = 7.1, C(5)); 73.1 (Ph*C*H_2); 63.6 (C(8)); 60.7 (*d*, ^3J(10,P) = 9.5, C(10)); 53.7 (MeN); 38.8 (*d,* ^3J(6,P) = 6.8, C(6)); 20.3 (C(7)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −15.0 (A), −15.1 (B) (each *d*, ^3J(P,H_{eq}–C(5)) = 27.0). ESI-MS: 464 (100, $[M - CF_3SO_3]^+$). Anal. calc. for $C_{15}H_{19}F_3N_3O_{11}PS \cdot 2\,H_2O$ (573.36): C 31.40, H 4.04, N 7.33; found: C 31.28, H 4.35, N 7.68.

*(1*RS*,3*SR*,6*RS*)-3-(2,4-Dinitrophenoxy)-9,9-dimethyl-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**30a**). White foam (90%). IR ($CHCl_3$): ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 8.90 (*d*, ^4J(3′,5′) = 3.0, H–C(3′)); 8.67 (*dd*, ^3J(5′,6′) = 9.2, ^4J(5′,3′) = 3.0, H–C(5′)); 7.99 (*d*, ^3J(6′,5′) = 9.2, H–C(6′)); 5.37 (*td*, ^3J(1,6) = ^3J(1,10ax) = 11.1, ^3J(1,10eq) = 4.5, H–C(1)); 4.82–4.64 (*AB* of *ABX–P*, not resolved, CH_2(5)); 3.95–3.75 (*m*, CH_2(8), CH_2(10)); 3.58 (*s*, Me_{ax}–N); 3.51 (*s*, Me_{eq}–N); 2.69 (*X* of *ABX–P*, *oct.*-like, $w_{1/2} \approx 30$, H–C(6)); 2.29–2.17 (*m*, CH_2(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 147.2 (*d*, ^2J(1′,P) = 5.9, C(1′)); 144.1 (C(4′)); 140.9 (*m*, $w_{1/2} \approx 6$, C(2′)); 129.4 (C(5′)); 123.6 (*d*, ^3J(6′,P) = 2.5, C(6′)); 121.8 (C(3′)); 121.0 (*q*, ^1J(C,F) = 321, CF_3SO_3); 74.4 (*d*, ^2J(1,P) = 5.9, C(1)); 73.0 (*d*, ^2J(5,P) = 7.9, C(5)); 61.8 (br. *d*, ^3J(10,P) ≈ 10, C(10)); 61.7 (C(8)); 56.6 (Me_{ax}–N); 48.0 (Me_{eq}–N); 37.6 (*d,* ^3J(6,P) = 6.4, C(6)); 19.3 (C(7)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −15.0 (br. *d*, ^3J(P,H_{eq}–C(5)) ≈ 25). ESI-MS: 388 (100, $[M - CF_3SO_3]^+$). Anal. calc. for $C_{21}H_{23}F_3N_3O_{11}PS \cdot H_2O$ (631.44): C 39.94, H 3.39, N 6.65; found: C 40.12, H 3.65, N 6.53.

*(1*RS*,3*RS*,6*RS*)-3-(2,4-Dinitrophenoxy)-9,9-dimethyl-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**30b**)[17]). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −14.0 (*t*-like, ^3J(P,H) ≈ 11).

*(1*RS*,3*SR*,6*SR*,9*SR*)-9-Benzyl-3-chloro-9-methyl-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**31a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 3:1). White powder (50%). ^{1}H-NMR (300 MHz, $(CD_3)_2SO$[16]): 7.61–7.48 (*m*, H–C(2′) to H–C(6′)); 4.91 (*s*, $w_{1/2} \approx 8$, H–C(1)); 4.65, 4.64 (*AB*, ^2J = 12.6, PhCH_2); 4.40, 4.12 (*AB* of *ABX–P*, CH_2(5)); 3.77–3.33 (*m*, CH_2(8), CH_2(10)); 3.08 (*s*, Me_{ax}–N); 2.91 (*s*, Me_{eq}–N); 2.23–1.82 (*m*, H–C(6), CH_2(7). ^{13}C-NMR (75.4 MHz, $(CD_3)_2SO$): epimer A: 133.7 (C(3′), C(5′)); 130.8 (C(4′)); 129.3 (C(2′), C(6′)); 127.4 (C(1′)); 120.0 (*q*, ^1J(C,F) = 322, CF_3SO_3); 73.5 (*d*, ^2J(1,P) = 5.5 C(1)); 71.0 (PhCH_2); 70.0 (*d*, ^2J(5,P) = 6.1, C(5)); 62.0 (*d*, ^3J(10,P) = 8.8, C(10)); 58.6 (C(8)); 47.3 (MeN); 31.5 (*d*, ^3J(6,P) = 4.2, C(6)); 18.1 (C(7)); epimer B: 133.7 (C(3′), C(5′)); 130.8 (C(4′)); 129.3 (C(2′), C(6′)); 127.4 (C(1′)); 120.0 (*q*, ^1J(C,F) = 322, CF_3SO_3); 73.2 (*d*, ^2J(1,P) = 6.2, C(1)); 70.3 (*d*, ^2J(5,P) = 6.2, C(5)); 63.4 (PhCH_2); 60.7 (*d*, ^3J(10,P) = 8.2, C(10)); 59.6 (C(8)); 52.3 (MeN); 31.7 (*d*, ^3J(6,P) = 4.3, C(6)); 20.3 (C(7)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2SO$): −7.5 (A), −7.2 (B) (each *d*, ^3J(P,H_{eq}–C(5)) ≈ 24). ESI-MS: 318 (29, $[M(^{37}Cl) - CF_3SO_3]^+$), 316 (100, $[M(^{35}Cl) - CF_3SO_3]^+$).

*(1*RS*,3*SR*,6*SR*,9*SR*)-9-Benzyl-9-methyl-3-(4-nitrophenoxy)-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]-decane 3-Oxide Trifluoromethanesulfonate* (**32a**). *N*-Epimer B (Me_{eq}) not detectable. Slightly yellow pasty foam (53%). IR (KBr): 2961*w*, 1614*m*, 1589*s*, 1531*s*, 1487*s*, 1462*m*, 1348*s*, 1315*s*, 1280*s*, 1226*s*, 1192*m*, 1151*s*, 1116*m*, 1070*m*, 1031*s*, 1007*s*, 982*s*, 970*s*, 934*s*, 866*m*, 840*m*, 812*m*, 787*m*, 771*m*, 758*m*, 743*m*, 727*m*, 706*m*, 671*w*, 639*s*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 8.30 (*AA′* of *AA′BB′*, *J* = 9.3, H–C(3′), H–C(5′)); 7.60 (*BB′* of *AA′BB′*, *J* = 9.3, H–C(2′), H–C(6′)); 7.61–7.50 (*m*, H–C(2″) to H–C(6″)); 5.52 (*s*, $w_{1/2} \approx 6$, H–C(1)); 4.96 (*A* of *ABX–P*, ^2J = 12.0, ^3J(5ax,6) ≈ ^3J(5ax,P) ≈ 1, H_{ax}–C(5)); 4.87, 4.86 (*AB*, ^2J = 13.0, PhCH_2); 4.56 (*B* of *ABX–P*, ^2J = 12.0, ^3J(5ax,P) = 25.5, H_{eq}–C(5)); 4.16 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{eq}–C(10)); 4.03–3.92 (*m*, H_{eq}–C(8), H_{ax}–C(10)); 3.82 (br. *d*, ^2J = 12.8, $w_{1/2} \approx 15$, H_{ax}–C(8)); 3.39 (*s*, MeN); 2.70–2.55 (*m*, H–C(6), H_{eq}–C(7)); 2.22 (*m*, *d*-like, $w_{1/2} \approx$ 20, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 155.6 (*d*, ^2J(1′,P) = 6.2, C(1′)); 145.6 (C(4′)); 134.1 (C(3″), C(5″)); 131.4 (C(4″)); 129.7 (C(2″), C(6″)); 127.4 (C(1″)); 126.3 (C(3′), C(5′)); 126.9 (*q*, ^1J(C,F) = 322, CF_3SO_3); 121.3 (*d*, ^3J(2′ and 6′,P) = 5.5, C(2′), C(6′)); 77.0 (*d*, ^2J(1,P) = 6.8, C(1)); 72.95 (*d*, ^2J(5,P) = 7.2, C(5)); 72.9

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17) The formation of the minor, equatorially substituted *P*-epimer is evidenced by ^{31}P-NMR of the crude reaction mixture and its amount estimated from the relative intensity of the signals (*ca.* 1:2). Due to fast epimerization, it could not be isolated.

(Ph*C*H$_2$); 62.3 (br. *d*, ^3J(10,P) ≈ 10, C(10)); 60.0 (C(8)); 48.0 (MeN); 32.1 (*d*, ^3J(6,P) = 5.2, C(6)); 18.6 (C(7)). ^{31}P-NMR (121.4 MHz, (CD$_3$)$_2$CO): −15.2 (*d*, ^3J(P,H$_{eq}$−C(5)) = 25.5). ESI-MS: 419 (100, [*M* − CF$_3$SO$_3$]$^+$).

*(1*RS*,3*RS*,6*SR*,9*SR*)-9-Benzyl-9-methyl-3-(4-nitrophenoxy)-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**32b**). *N*-Epimer B (Me$_{eq}$) not detectable. Yellow viscous oil (28%). ^{1}H-NMR (300 MHz, (CD$_3$)$_2$CO)[18]: 8.30 (*AA′* of *AA′BB′*, *J* = 9.1 H−C(3′), H−C(5′)); 7.67–7.48 (*m*, H−C(2′), H−C(6′), H−C(2″) to H−C(6″)); 5.48 (*s*, $w_{1/2}$ ≈ 6, H−C(1)); 4.96 (*A* of *ABX*−*P*, not resolved, H$_{ax}$−C(5)); 4.82, 4.81 (*AB*, ^2J = 12.8, Ph*C*H$_2$); 4.60 (*B* of *ABX*−*P*, ^2J = 12.0, ^3J(5eq,P) = 20.5, H$_{eq}$−C(5)); 4.13 (*m*, *d*-like, $w_{1/2}$ ≈ 20, H$_{eq}$−C(10)); 3.98–3.82 (*m*, H$_{eq}$−C(8), H$_{ax}$−C(10)); 3.82 (br. *d*, ^2J = 12.8, $w_{1/2}$ ≈ 20, H$_{ax}$−C(8)); 3.18 (*s*, MeN); 2.61 (*m*, *d*-like, $w_{1/2}$ ≈ 20, H$_{eq}$−C(7)); 2.34 (*X* of *ABX*−*P*, *m*, $w_{1/2}$ ≈ 30, H−C(6)); 2.23 (*m*, *t-like*, $w_{1/2}$ ≈ 30, H$_{ax}$−C(7)). ^{13}C-NMR (75.4 MHz, CDCl$_3$): 154.7 (*d*, ^2J(1′,P) = 6.2, C(1′)); 145.3 (C(4′)); 133.3 (C(3″), C(5″)); 130.7 (C(4″)); 129.0 (C(2″), C(6″)); 126.6 (C(1″)); 125.7 (C(3′), C(5′)); 126.4 (*q*, ^1J(C,F) = 320, CF$_3$SO$_3$); 121.5 (*d*, ^3J(2′ and 6′,P) = 5.5, C(2′), C(6′)); 75.0 (*d*, ^2J(1,P) = 4.2, C(1)); 71.4 (Ph*C*H$_2$); 70.9 (*d*, ^2J(5,P) = 5.5, C(5)); 61.2 (br. *d*, ^3J(10,P) ≈ 10, C(10)); 58.8 (C(8)); 47.3 (MeN); 31.6 (*d*, ^3J(6,P) = 4.5, C(6)); 18.4 (C(7)). ^{31}P-NMR (121.4 MHz, (CD$_3$)$_2$CO)[18]: −10.9 (*d*, ^3J(P,H$_{eq}$−C(5)) = 20.5). ESI-MS: 419 (100, [*M* − CF$_3$SO$_3$]$^+$).

*(1*RS*,3*SR*,6*SR*,9*SR*)-9-Benzyl-3-(2,4-dinitrophenoxy)-9-methyl-2,4-dioxa-9-azonia-3-phosphabicyclo-[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**33a**). Mixture of *N*-epimers (A = Me$_{ax}$, B = Me$_{eq}$, A/B *ca.* 1.5 : 1). Colorless fine needles (73%). M.p. 110–113°. IR (KBr): *ca.* 3750–3400*m*, 3113*m*, 2362*w*, 1610*m*, 1540*w*, 1482*m*, 1349*s*, 1321*m*, 1263*s*, 1225*m*, 1160*m*, 1069*m*, 1031*s*, 1009*m*, 975*m*, 939*m*, 904*m*, 835*m*, 788*m*, 741*m*, 727*m*, 705*m*, 638*s*, 574*m*, 518*m*, 471*m*. ^{1}H-NMR (300 MHz, (CD$_3$)$_2$CO)[16]: 8.89 (*dd*, ^4J(3′,5′) = 2.8, ^5J(3′,6′) = 1.0, H−C(3′)); 8.64 (*dd*, ^3J(5′,6′) = 9.2, ^4J(5′,3′) = 2.8, H−C(5′)); 8.02 (*dd*, ^3J(6′,5′) = 9.2, ^5J(6′,3′) = 1.0, H−C(6′)); 7.79–7.45 (*m*, H−C(2″) to H−C(6″)); 5.48 (*s*, $w_{1/2}$ ≈ 6, H−C(1)); 5.05–4.75 (*m*, not resolved, H$_{ax}$−C(5), Ph*C*H$_2$); 4.66 (*B* of *ABX*−*P*, ^2J = 11.9, ^3J(5ax,P) = 25.5, H$_{eq}$−C(5)); 4.25–4.19 (*m*, H$_{eq}$−C(10)); 4.05–3.85 (*m*, CH$_2$(8), H$_{ax}$−C(10)); 3.42 (*s*, Me$_{ax}$−N); 3.37 (*s*, Me$_{eq}$−N); 2.80–2.48 (*m*, H$_{eq}$−C(7)); 2.37–2.22 (*m*, H−C(6), H$_{ax}$−C(7)). ^{13}C-NMR (75.4 MHz, CDCl$_3$): epimer A: 148.2 (*d*, ^2J(1′,P) = 5.1, C(1′)); 144.9 (C(4′)); 141.2 (*d*, ^3J(2′,P) = 6.6, C(2′)); 134.2 (C(2″), C(6″)); 131.9 (C(4″)); 130.1 (C(5′)); 129.9 (C(3″), C(5″)); 127.7 (C(1″)); 124.6 (*d*, ^3J(6′,P) = 2.2, C(6′)); 122.7 (C(3′)); 121.7 (*q*, ^1J(C,F) = 321, CF$_3$SO$_3$); 77.8 (*d*, ^2J(1,P) = 5.8, C(1)); 73.7 (*d*, ^2J(5,P) = 7.4, C(5)); 73.2 (Ph*C*H$_2$); 62.4 (*d*, ^3J(10,P) = 8.6, C(10)); 60.1 (C(8)); 48.3 (MeN); 32.2 (*d*, ^3J(6,P) = 5.3, C(6)); 18.8 (C(7)); epimer B: 148.2 (*d*, ^2J(1′,P) = 5.1, C(1′)); 144.9 (C(4′); 141.2 (*d*, ^3J(2′,P) = 6.6, C(2′)); 134.2 (C(2″), C(6″)); 131.9 (C(4″)); 130.1 (C(5′)); 129.9 (C(3″), C(5″)); 127.7 (C(1″)); 124.6 (*d*, ^3J(6′,P) = 2.2, C(6′)); 122.7 (C(3′)); 121.7 (*q*, ^1J(C,F) = 321, CF$_3$SO$_3$); 77.3 (*d*, ^2J(1,P) = 6.2, C(1)); 72.6 (*d*, ^2J(5,P) = 6.8, C(5)); 69.9 (Ph*C*H$_2$); 60.6 (br. *d*, ^3J(10,P) ≈ 10, C(10)); 63.8 (C(8)); 52.2 (MeN); 32.1 (*d*, ^3J(6,P) = 5.1, C(6)); 19.1 (C(7)). ^{31}P-NMR (121.4 MHz, (CD$_3$)$_2$CO): −15.8 (B), −16.0 (A) (each *d*, ^3J(P,H$_{eq}$−C(5)) = 25.5). ESI-MS: 464 (100, [*M* − CF$_3$SO$_3$]$^+$), 450 (20, [*M* − CF$_3$SO$_3$ − Me]$^+$). Anal. calc. for C$_{21}$H$_{23}$F$_3$N$_3$O$_{11}$PS · H$_2$O (631.44): C 39.94, H 3.99, N 6.65; found: C 39.94, H 3.85, N 6.60.

*(1*RS*,3*SR*,6*SR*)-3-(2,4-Dinitrophenoxy)-9,9-dimethyl-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**34a**). Colorless resin (23%). ^{1}H-NMR (300 MHz, (CD$_3$)$_2$CO): 8.90 (*dd*, ^4J(3′,5′) = 2.4, ^5J(3′,6′) = 1.0, H−C(3′)); 8.66 (*dd*, ^3J(5′,6′) = 9.1, ^4J(5′,3′) = 2.7, H−C(5′)); 8.05 (*dd*, ^3J(6′,5′) = 9.1, ^5J(6′,3′) = 1.0, H−C(6′)); 5.50 (*s*, $w_{1/2}$ ≈ 6, H−C(1)); 4.99 (*A* of *ABX*−*P*, ^2J = 11.8, H$_{ax}$−C(5)); 4.66 (*B* of *ABX*−*P*, ^2J = 11.8, ^3J(5eq,P) = 25.8, H$_{eq}$−C(5)); 4.18–3.83 (*m*, CH$_2$(8), CH$_2$(10)); 3.52 (*s*, Me$_{ax}$−N)); 3.48 (*s*, Me$_{eq}$−N)); 2.71–2.46 (*m*, H−C(6), H$_{eq}$−C(7)); 2.24 (*m*, *t*-like, $w_{1/2}$ ≈ 30, H$_{ax}$−C(7)). ^{13}C-NMR (75.4 MHz, CDCl$_3$): 148.2 (*d*, ^2J(1′,P) = 5.0, C(1′)); 144.9 (C(4′)); 141.1 (br. *d*, $w_{1/2}$ ≈ 5, C(2′)); 130.3 (C(5′)); 123.8 (*d*, ^3J(6′,P) = 2.4, C(6′)); 122.6 (C(3′)); 122.0 (*q*, ^1J(C,F) = 321, CF$_3$SO$_3$); 77.9 (*d*, ^2J(1,P) = 5.9, C(1)); 73.7 (*d*, ^2J(5,P) = 7.5, C(5)); 64.1 (*d*, ^3J(10,P) = 8.9, C(10)); 62.2 (C(8)); 58.0 (Me$_{eq}$−N); 51.6 (Me$_{ax}$−N); 31.9 (*d*, ^3J(6,P) = 5.2 C(6)); 19.0 (C(7)). ^{31}P-NMR (121.4 MHz, (CD$_3$)$_2$CO): −15.9 (*d*, ^3J(P,H$_{eq}$−C(5)) = 25.8). ESI-MS: 388 (100, [*M* − CF$_3$SO$_3$]$^+$), 374 (10). Anal. calc. for C$_{15}$H$_{19}$F$_3$N$_3$O$_{11}$PS · 2 H$_2$O (573.36): C 31.40, H 4.04, N 7.33; found: C 31.75, H 4.31, N 7.69.

*(1*RS*,3*RS*,6*SR*)-3-(2,4-Dinitrophenoxy)-9,9-dimethyl-2,4-dioxa-9-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**34b**)[17]). ^{31}P-NMR (121.4 MHz, CDCl$_3$): −15.4 (*dd*, ^3J(P,H) ≈ 26, 7)[18]).

6. *2,4-Dioxa-8-aza-3-phosphadecalins* **35**–**50** *of Type* **II**. *(1*RS*,3*RS*,6*SR*)-8-Benzyl-3-fluoro-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**35a**). Colorless prisms (25%). M.p. 173.5°. R_f (Et$_2$O) 0.36. IR (KBr): 3062*w*, 3027*m*, 3006*w*, 2958*m*, 2936*m* 2867*w*, 2818*m*, 2802*m*, 2775*m*, 2726*w*, 1495*m*, 1484*w*, 1471*w*, 1446*m*, 1391*w*, 1368*w*, 1320*s*, 1262*w*, 1220*m*, 1185*m*, 1142*m*, 1130*w*, 1100*m*, 1079*w*, 1069*m*, 1042*s*, 994*s*, 975*m*, 963*m*, 915*m*,

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[18]) According to ^{1}H- and ^{31}P-NMR spectra, the conformation of the P-heterocycle is rather chair-like than a twist-boat.

894*s*, 876*m*, 846*w*, 797*m*, 783*m*, 741*m*, 694*m*, 659*m*, 626*w*, 570*m*, 532*m*, 504*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.36–7.24 (*m*, H–C(2′) to H–C(6′)); 4.28 (*A* of *ABX–P*, ^2J = 11.0, ^3J(5eq,P) = 24.5, ^3J(5eq,6) = 4.5, H_{eq}–C(5)); 4.18 (*td*, ^3J(1,6) = ^3J(1,10ax) = 12.1, ^3J(1,10eq) = 4.7, H–C(1)); 4.10 (*B* of *ABX–P*, ^2J = ^3J(5ax,6) = 11.0, ^3J(5ax,P) = 1.0, H_{ax}–C(5)); 3.58, 3.46 (*AB*, ^2J = 13.2, PhCH_2); 3.01 (*dsext.*-like, ^2J = 12.1, ^3J(9eq,10ax) = 4.5, ^3J(9eq,10eq) = 2.5, ^4J(9eq,7eq) = 2.2, H_{eq}–C(9)); 2.81 (*ddd*, ^2J = 11.2, ^3J(7eq,6) = 3.7, ^4J(7eq,9eq) = 2.2, H_{eq}–C(7)); 2.34 (*X* of *ABX–P*, ^3J(6,1) = 12.1, ^3J(6,5ax) = 11.0, ^3J(6,5eq) = 4.5, ^3J(6,7ax) = 11.2, ^3J(6,7eq) = 3.7, H–C(6)); 2.12 (*td*, ^2J = ^3J(9ax,10ax) = 12.1, ^3J(9ax,10eq) = 2.5, H_{ax}–C(9)); 2.08 (*ddt*, ^2J = 12.1, ^3J(10eq,1) = 4.7, ^3J(10eq,9ax) = ^3J(10eq,9eq) = 2.5, H_{eq}–C(10)); 1.94 (*qd*, ^2J = ^3J(10ax,1) = ^3J(10ax,9ax) = 12.1, ^3J(10ax,9eq) = 4.5, H_{ax}–C(10)); 1.70 (*t*, ^2J = ^3J(7ax,6) = 11.2, H_{ax}–C(7)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.4 (C(1′)); 128.7 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.4 (C(4′)); 83.0 (*d*, ^2J(1,P) = 6.5, C(1)); 71.8 (*d*, ^2J(5,P) = 7.6, C(5)); 62.9 (PhCH_2); 51.1 (C(9)); 51.0 (C(7)); 39.6 (*d*, ^3J(6,P) = 6.2, C(6)); 31.6 (*d*, ^3J(10,P) = 9.2, C(10)). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −19.9 (*dd*, ^1J(P,F) = 1010, ^3J(P,H_{eq}–C(5)) = 24.5. EI-MS: 285 (20, $M^{+\cdot}$), 208 (10), 194 (8, $[M-PhCH_2]^+$), 186 (14), 185 (13), 172 (12), 126 (15), 94 (21), 92 (26), 91 (100, $PhCH_2^+$), 65 (17). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.45, H 5.88, N 4.83.

*(1*RS*,3*SR*,6*SR*)-8-Benzyl-3-fluoro-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**35b**). Colorless prisms (20%). M.p. 113–114°. R_f (Et_2O) 0.28. IR (KBr): 3062*w*, 3025*w*, 2976*w*, 2941*w*, 2917*w*, 2873*w*, 2825*m*, 2777*w*, 1602*w*, 1495m, 1477*w*, 1452*m*, 1392*m*, 1368*m*, 1342*s*, 1324*s*, 1278*w*, 1220*w*, 1200*w*, 1185*w*, 1175*w*, 1144*w*, 1128*w*, 1105*m*, 1080*m*, 1065*m*, 1045*s*, 1002*m*, 973*m*, 956m, 912*m*, 894*s*, 871*m*, 846*m*, 794*w*, 769*m*, 747*m*, 702*w*, 675*m*, 630*w*, 570*m*, 532*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.36–7.24 (*m*, H–C(2′) to H–C(6′)); 4.37 (*A* of *ABX–P*, ^2J = ^3J(5eq,P) = 10.5, ^3J(5eq,6) = 5.7, H_{eq}–C(5)); 4.31 (*dddd*, ^3J(1,10ax) = ^3J(1,6) = 11.5, ^3J(1,10eq) = 4.5, ^4J(1,F) = 2.0, H–C(1)); 4.13 (*B* of *ABX–P*, ^2J = ^3J(5ax,P) = ^3J(5ax,6) = 10.5, ^4J(5ax,F) = 3.7, H_{ax}–C(5)); 3.58, 3.46 (*AB*, ^2J = 13.2, CH_2); 3.01 (*dsext.*-like, ^2J = 11.5, ^3J(9eq,10ax) = 4.2, ^3J(9eq,10eq) = 2.5, ^4J(9eq,7eq) = 2.3, H_{eq}–C(9)); 2.84 (*ddd*, ^2J = 11.0, ^3J(7eq,6) = 3.8, ^4J(7eq,9eq) = 2.3, H_{eq}–C(7)); 2.48 (*X* of *ABX–P*, ^3J(6,1) = 11.5, ^3J(6,5ax) = 10.5, ^3J(6,5eq) = 5.7, ^3J(6,7ax) = 11.0, ^3J(6,7eq) = 3.8, H–C(6)); 2.15 (*m*, not resolved, H_{eq}–C(10)); 2.12 (*td*, ^2J = ^3J(9ax,10ax) = 11.5, ^3J(9ax,10eq) = 2.5, H_{ax}–C(9)); 1.90 (*qd*, ^2J = ^3J(10ax,1) = ^3J(10ax,9ax) = 11.5, ^3J(10ax,9eq) = 4.2, H_{ax}–C(10)); 1.72 (*t*, ^2J = ^3J(7ax,6) = 11.0, H_{ax}–C(7)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.4 (C(1′)); 128.7 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.4 (C(4′)); 82.3 (*d*, ^2J(1,P) = 6.6, C(1)); 71.4 (*d*, ^2J(5,P) = 7.1, C(5)); 62.0 (PhCH_2; 52.0 (C(7)); 51.0 (C(9)); 38.5 (*d*, ^3J(6,P) = 12.6, C(6)); 32.0, ^3J(10,P) = 7.1 (C(10)). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −15.6 (*dt*, ^1J(P,F) = 998, ^3J(P,H_{ax}–C(5) = ^3J(P,H_{eq}–C(5)) = 10.5). EI-MS: 285 (19, $M^{+\cdot}$), 208 (12), 194 (34, $[M-PhCH_2]^+$), 186 (3), 172 (3), 160 (3), 132 (7), 126 (14); 112 (15), 94 (10), 92 (26), 91 (100, $PhCH_2^+$), 67 (8), 65 (17), 55 (5). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.59, H 5.72, N 4.79.

*(1*RS*,3*RS*,6*SR*)-8-Benzyl-3-chloro-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**36a**)[14]. Colorless viscous oil (55%). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.30–7.19 (*m*, H–C(2′) to H–C(6′)); 4.22 (*A* of *ABX–P*, ^2J = 11.1, ^3J(5eq,P) = 28.5, ^3J(5eq,6) = 4.5, H_{eq}–C(5)); 4.19–4.08 (*m*, not resolved, H–C(1)); 4.08 (*B* of *ABX–P*, ^2J = ^3J(5ax,6) = 11.1, ^3J(5ax,P) = 2.5, H_{ax}–C(5)); 3.52, 3.42 (*AB*, ^2J = 13.1, PhCH_2); 2.99 (*dsext.*-like, ^2J = 12, ^3J(9eq,10ax) ≈ ^3J(9eq,10eq) ≈ ^4J(9eq,7eq) ≈ 2, H_{eq}–C(9)); 2.75 (*ddd*, ^2J = 11.4, ^3J(7eq,6) = 3.7, ^4J(7eq,9eq) = 2.2, H_{eq}–C(7)); 2.29 (*X* of *ABX–P*, ^3J(6,1) = ^3J(6,5ax) = ^3J(6,7ax) = 11.1, ^3J(6,5eq) = 4.5, ^3J(6,7eq) = 3.5, H–C(6)); 2.11–1.86 (*m*, H_{ax}–C(7), H_{ax}–C(9), CH_2(10)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 137.7 (C(1′)); 128.7 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.3 (C(4′)); 83.0 (*d*, ^2J(1,P) = 7.8, C(1)); 71.7 (*d*, ^2J(5,P) = 8.6, C(5)); 61.9 (PhCH_2); 51.1, 51.0 (C(7), C(9)); 39.6 (*d*, ^3J(6,P) = 6.6, C(6)); 31.3 (*d*, ^3J(10,P) = 9.8, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −2.3 (*d*, ^3J(P,H_{eq}–C(5)) = 28.5). CI-MS: 304 (31, $[M(^{37}Cl)+H]^+$), 302 (100, $[M(^{35}Cl)+H]^+$).

*(1*RS*,3*RS*,6*SR*)-8-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-8-aza-3-phospha-bicyclo[4.4.0]decane 3-Oxide* (**37a**). Slightly yellow powder (31%). IR ($CHCl_3$): 2952*w*, 2809*w*, 2766*w*, 1615*m*, 1594*m*, 1525*s*, 1493*s*, 1348*s*, 1311*s*, 1040*s*, 1012*m*, 968*m*, 931*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.26 (*AA′* of *AA′BB′*, *J* = 9.1, H–C(3′), H–C(5′)); 7.42 (*BB′* of *AA′BB′*, *J* = 9.1, H–C(2′), H–C(6′)); 7.39–7.26 (*m*, H–C(2″) to H–C(6″)); 4.30 (*A* of *ABX–P*, ^2J = 10.9, ^3J(5eq,P) = 24.5, ^3J(5eq,6) = 4.5, H_{eq}–C(5)); 4.12 (*sext.*-like, ^3J(1,10ax) ≈ ^3J(1,6) ≈ 11, ^3J(1,10eq) ≈ 5, H–C(1)); 4.13 (*B* of *ABX–P*, ^2J = ^3J(5ax,6) = 10.9, ^3J(5ax,P) = 1.0, H_{ax}–C(5)); 3.59, 3.49 (*AB*, ^2J = 13.2, PhCH_2); 3.04 (*m*, *dq*-like, $w_{1/2}$ ≈ 18, H_{eq}–C(9)); 2.84 (*ddd*, ^2J = 11.3, ^3J(7eq,6) = 3.5, ^4J(7eq,9eq) = 2.2, H_{eq}–C(7)); 2.41 (*X* of *ABX–P*, ^3J(6,1) ≈ 11, ^3J(6,5ax) = 10.9, ^3J(6,5eq) = 4.5, ^3J(6,7ax) = 11.2, ^3J(6,7eq) = 3.5, H–C(6)); 2.17–1.99 (*m*, H_{ax}–C(9), H_{eq}–C(10)); 1.97 (*qd*-like, ^2J ≈ ^3J(10ax,9ax) ≈ ^3J(10ax,1) ≈ 11, ^3J(10ax,9eq) = 4.0, H_{ax}–C(10)); 1.73 (*t*, ^2J = ^3J(7ax,6) = 11.2, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 155.6 (*d*, ^2J(1′,P) = 6, C(1′)); 144.7 (C(4″)); 137.3 (C(1″); 128.7 (C(3″), C(5″)); 128.3 (C(2″), C(6″)); 127.3 (C(4″)); 125.7 (C(3′), C(5′)); 120.0 (*d*, ^3J(2′ and 6′,P) = 5.6, C(2′), C(6′)); 82.6 (*d*, ^2J(1,P) = 7.3, C(1)); 71.5 (*d*, ^2J(5,P) = 8.0, C(5)); 62.1 (PhCH_2); 51.1 (C(7)); 51.0 (C(9)); 39.7 (*d*, ^3J(6,P) = 6.4, C(6)); 31.7 (*d*, ^3J(10,P) = 6.1, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −14.2 (*d*, ^3J(P,H_{eq}–C(5)) = 24). CI-MS: 405 (100, $[M+H]^+$).

*(1*RS,*3*SR,*6*SR*)-8-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**37b**). Yellow viscous oil (32%). IR ($CHCl_3$): 3008*w*, 2962*w*, 2810*w*, 2766*w*, 1615*m*, 1593*s*; 1526*s*; 1493*s*; 1454*m*, 1365*m*, 1348*s*, 1294*s*, 1248*m*, 1171*m*, 1104*s*, 1079*m*, 1086*s*, 1044*s*, 1012*s*, 970*s*, 933*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.23 (*AA′* of *AA′BB′*, $J = 9.0$, H–C(3′), H–C(5′)); 7.38 (*BB′* of *AA′BB′*, $J = 9.0$, H–C(2′), H–C(6′)); 7.34–7.24 (*m*, H–C(2″) to H–C(6″)); 4.17–4.42 (*AB* of *ABX–P* and *m*, not resolved, H–C(1), CH_2(5)); 3.57, 3.46 (*AB*, $^2J = 13.1$, PhCH_2); 3.01 (*m*, *dquint.*-like, $w_{1/2} \approx 20$, H_{eq}–C(9)); 2.82 (*ddd*, $^2J = 11.3$, ^3J(7eq,6) = 3.7, ^4J(7eq,9eq) = 2.2, H_{eq}–C(7)); 2.40 (*X* of *ABX*, *ttq*-like, $w_{1/2} \approx 22$, H–C(6)); 2.16–2.08 (*m*, H_{ax}–C(9), H_{eq}–C(10)); 1.86 (*qd*-like, $^2J \approx {}^3J$(10ax,1) $\approx {}^3J$(10ax,9ax) ≈ 13, ^3J(10ax,9eq) ≈ 4, H_{ax}–C(10)); 1.73 (*t*, $^2J = {}^3J$(7ax,6) = 11.2, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 155.7 (*d*, ^2J(1′,P) = 6, C(1′)); 144.9 (C(4′)); 137.4 (C(1″)); 128.7 (C(3″), C(5″)); 128.3 (C(2″), C(6″)); 127.3 (C(4″)); 125.5 (C(3′), C(5′)); 120.6 (*d*, ^3J(2′ and 6′,P) = 5.3, C(2′), C(6′)); 81.5 (*d*, ^2J(1,P) = 5.7, C(1)); 70.8 (*d*, ^2J(5,P) = 7.0, C(5)); 62.0 (PhCH_2); 51.8 (*d*, ^4J(7,P) = 0.8, C(7)); 51.1 (*d*, ^4J(9,P) = 2.1, C(9)); 39.0 (*d*, ^3J(6,P) = 9.0, C(6)); 31.9 (*d*, ^3J(10,P) = 7.8, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −12.0 (*dd*, ^3J(P,H_{eq}–C(5)) = 15, ^3J(P,H_{ax}–C(5)) = 8). CI-MS: 405 (100, $[M+H]^+$).

*(1*RS,*3*RS,*6*SR*)-8-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**38a**). Slightly yellow powder (48%). IR ($CHCl_3$): 3030*w*, 2962*w*, 2811*w*, 2766*w*, 1609*s*, 1541*s*, 1485*w*, 1454*m*, 1347*s*, 1317*s*, 1266*s*, 1131*m*, 1094*m*, 1069*s*, 1037*s*, 995*s*, 935*s*, 901*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.83 (*d*, ^4J(3′,5′) = 2.9, H–C(3′)); 8.47 (*dd*, ^3J(5′,6′) = 9.2, ^4J(5′,3′) = 2.9, H–C(5′)); 8.13 (*d*, ^3J(6′,5′) = 9.2, H–C(6′)); 7.38–7.27 (*m*, H–C(2″) to H–C(6″)); 4.45 (*td*, ^3J(1,6) = ^3J(1,10ax) = 10.2, ^3J(1,10eq) = 5.8, H–C(1)); 4.36–4.25 (*AB* of *ABX–P*, not resolved, CH_2(5)); 3.67, 3.58 (*AB*, $^2J = 13.0$, PhCH_2); 3.11 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{eq}–C(9)); 2.92 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{eq}–C(7)); 2.51 (*X* of *ABX–P*, *m*, $w_{1/2} \approx 30$, H–C(6)); 2.25 (br. *t*, $^2J \approx {}^3J$(9ax,10ax) $\approx$ 12, H_{ax}–C(9)); 2.07 (*m*, $w_{1/2} \approx 20$, CH_2(10)), 1.89 (*t*, $^2J = {}^3J$(7ax,6) = 11.5, H_{ax}–C(7)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 148.3 (*d*, ^2J(1′,P) = 5.5, C(1′)); 145.0 (C(4′)); 141.9 (*d*, ^3J(2′,P) = 7.2, C(2′)); 137.5 (C(1″)); 129.3 (C(5′)); 129.0 (C(2″), C(6″)); 128.6 (C(3″), C(5″)); 127.6 (C(4″)); 123.1 (*d*, ^3J(6′,P) = 2, C(6′)); 121.8 (C(3′)); 83.3 (*d*, ^2J(1,P) = 7.3, C(1)); 72.2 (*d*, ^2J(5,P) = 8.0, C(5)); 62.2 (PhCH_2); 51.4 (C(7)); 51.3 (C(9)); 39.9 (*d*, ^3J(6,P) = 6.4, C(6)); 31.7 (*d*, ^3J(10,P) = 9.2, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −15.2 (br. *d* ^3J(P,H_{eq}–C(5)) = 26). CI-MS: 450 (100, $[M+H]^+$).

*(1*RS,*3*SR,*6*SR*)-8-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**38b**)[15]). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −14.0 (*t* ^3J(P,H_{ax}–C(5)) $\approx {}^3J$(P,H_{eq}–C(5)) $\approx$ 11).

*(1*RS,*3*RS,*6*RS*)-8-Benzyl-3-fluoro-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**39a**). Colorless prisms (30%). M.p. 112–112.5°. R_f (AcOEt/MeOH 98:2) 0.20. IR (KBr): 3086*w*, 3062*w*, 3026*w*, 2964*m*, 2923*m*, 2905*m*, 2829*w*, 2800*m*, 2779*m*, 1496*w*, 1480*w*, 1451*w*, 1420*w*, 1384*w*, 1370*w*, 1360*w*, 1352*w*, 1340*m*, 1309*s*, 1276*w*, 1215*m*, 1158*w*, 1129*w*, 1096*m*, 1073*s*, 1051*m*, 1023*s*, 992*s*, 970*m*, 948*m*, 909*m*, 891*s*, 852*w*, 832*m*, 786*w*, 770*m*, 742*m*, 722*m*, 697*m*, 641*m*, 546*w*, 512*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.34–7.25 (*m*, H–C(2′) to H–C(6′)); 4.87 (*q*, ^3J(1,6) = ^3J(1,10ax) = ^3J(1,10eq) = 2.6, H–C(1)); 4.53 (*A* of *ABX–P*, $^2J = 11.7$, ^3J(5ax,6) = 2.9, H_{ax}–C(5)); 4.21 (*B* of *ABX–P*, $^2J = 11.7$, ^3J(5eq,6) < 1, ^3J(5eq,P) = 24.8, H_{eq}–C(5)); 3.60, 3.50 (*AB*, $^2J = 13.0$, PhCH_2); 2.72 (*dquint.*-like, $^2J = 11.8$, ^3J(9eq,10ax) $\approx {}^3J$(9eq,10eq) = 2.4, ^4J(9eq,7eq) ≈ 1, H_{eq}–C(9)); 2.69 (br. *dd*, $^2J = 11.8$, ^3J(7eq,6) = 4.6, ^4J(7eq,9eq) ≈ 1, H_{eq}–C(7)); 2.54 (*t*, $^2J = {}^3J$(7ax,6) = 11.8, H_{ax}–C(7)); 2.39 (*td*, $^2J = {}^3J$(9ax,10ax) = 11.8, ^3J(9ax,10eq) = 2.9, H_{ax}–C(9)); 2.06 (*X* of *ABX–P*, ^3J(6,1) = 2.6, ^3J(6,5ax) = 2.9, ^3J(6,5eq) < 1, ^3J(6,7ax) = 11.8, ^3J(6,7eq) = 4.6, H–C(6)); 2.01 (br. *dddd*, $^2J = 14.5$, ^3J(10eq,1) = 2.6, ^3J(10eq,9ax) = 2.9, ^3J(10eq,9eq) = 2.4, ^4J(10eq,P) ≈ 1, H_{eq}–C(10)); 1.96 (*qdd*-like, $^2J = 14.5$, ^3J(10ax,1) = 2.6, ^3J(10ax,9ax) = 11.9, ^3J(10ax,9eq) = 2.4, ^4J(10ax,P) = 6.0, H_{ax}–C(10)[19]). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.9 (C(1′)); 129.0 (C(2′), C(6′)); 128.3 (C(4′)); 127.3 (C(2′), C(6′)); 127.3 (C(4′)); 78.5 (*d*, ^2J(1,P) = 6.6, C(1)); 72.3 (*d*, ^2J(5,P) = 6.9, C(5)); 62.9 (PhCH_2); 49.5 (C(7)); 46.7 (C(9)); 35.5 (*d*, ^3J(6,P) = 5.9, C(6)); 31.0 (*d*, ^3J(10,P) = 8.9, C(10)). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −16.6 (*ddd*, ^1J(P,F) = 1009, ^3J(P,H_{eq}–C(5)) = 24.8, ^4J(P,H_{ax}–C(10)) = 6.0[19]). EI-MS: 285 (9, $M^{+\cdot}$), 208 (3), 194 (7, $[M - PhCH_2]^+$), 185 (15), 172 (18), 144 (5), 132 (7), 118 (7), 94 (18), 92 (10), 91 (100, $PhCH_2^+$), 67 (10), 65 (17). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.96, H 5.84, N 4.77.

*(1*RS,*3*SR,*6*RS*)-8-Benzyl-3-fluoro-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**39b**). Colorless viscous oil (30%). R_f (AcOEt/MeOH 98:2) 0.32. IR (KBr): 3026*w*, 2962*m*, 2815*m*, 1492*m*, 1474*w*, 1451*m*, 1400*w*, 1327*s*, 1236*w*, 1203*w*, 1170*m*, 1131*m*, 1055*s*, 1031*s*, 1002*m*, 970*m*, 939*m*, 910*w*, 878*m*, 867*m*, 848*m*, 797*w*,

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[19]) This ^4J(10,P) had been assigned to H_{eq}–C(10) in the *cis*-decalin series [5]. However, the ^{1}H{^{31}P}-NMR spectra at 600 MHz clearly showed that it originates from H_{ax}–C(10). H_{eq}–C(10) exhibits a small ^4J (*ca.* 1 Hz).

779w, 737*m*, 700*m*, 671*w*, 628*w*, 568*w*, 516*m*. ^{1}H-NMR (600 MHz, $CDCl_3$)[20]: 7.33–7.30 (2 H), 7.29–7.24 (3 H) (each *m*, H–C(2′) to H–C(6′)); 4.83 (*X* of *ABX–P*, br. *t*-like, $w_{1/2} \approx 30$, H_{ax}–C(5)); 4.71 (*quint.d*-like, $^3J(1,P) = 18$, $^3J(1,6) \approx {}^3J(1,10ax) \approx 5$, $^3J(1,10eq) \approx 3$, H–C(1)); 4.36 (*ddd*, $^3J(5eq,P) = 18$, $^2J = 11.5$, $^3J(5eq,6) = 4.5$, Heq–C(5)); 3.50, 3.40 (*AB*, $^2J = 13.0$, PhCH_2); 2.85 (*m*, br. *d*-like, $w_{1/2} \approx 25$, $^2J = 11$, H_{eq}–C(9)); 2.71 (*ddd*, $^2J = 12.5$, $^3J(7eq,6) = 3.8$, $^4J(7eq,9eq) = 1.6$, H_{eq}–C(7)); 2.51 (*X* of *ABX–P*, *quint.*-like, $w_{1/2} \approx 20$, H–C(6)); 2.31 (*dd*, $^2J = 12.5$, $^3J(7ax,6) = 3.5$, H_{ax}–C(7)); 2.25 (*qt*-like, $^2J \approx {}^3J(10ax,9ax) \approx 11$, $^3J(10ax,1) \approx {}^3J(10ax,9eq) \approx 5$, H_{ax}–C(10)); 2.17 (br. *t*-like, $^2J \approx {}^3J(9ax,10ax) \approx 11$, H_{ax}–C(9)); 2.08 (*m*, $w_{1/2} \approx 25$, H_{eq}–C(10)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.8 (C(1′)); 128.6 (C(3′), C(5′)); 128.4 (C(2′), C(6′)); 127.4 (C(4′)); 80.7 (*dd*, $^2J(1,P) = 6.5$, $^3J(1,F) = 2$, C(1)); 70.1 (*d*, $^2J(5,P) = 6.9$, C(5)); 62.1 (Ph*C*H_2); 51.7 (C(7)); 50.9 (C(9)); 35.1 (*d*, $^3J(6,P) = 8.1$, C(6)); 28.5 (C(10)). ^{31}P-NMR (121.4 MHz, $CDCl_3$)[20]: −17.0 (*dt*, $^1J(P,F) = 1002$, $^3J(P,H_{ax}$–C(5)) = $^3J(P,H_{eq}$–C(5)) = 18). EI-MS: 285 (19, $M^{+\bullet}$), 208 (15), 194 (26, $[M - PhCH_2]^+$), 172 (5), 133 (6), 132 (10), 94 (17), 92 (22), 91 (100, $PhCH_2^+$), 67 (10), 65 (18). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.65, H 6.22, N 5.14.

*(1*RS*,3*RS*,6*RS*)-8-Benzyl-3-chloro-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**40a**)[14]). Colorless viscous oil (68%). IR ($CHCl_3$): 3429*w* (br.), 3039*w*, 2941*m*, 2482*s*, 1498*m*, 1457*s*, 1412*m*, 1357*m*, 1356*m*, 1307*s*, 1264*m*, 1244*m*, 1202*m*, 1137*m*, 1086*m*, 1067*s*, 1013*s*, 968*s*, 925*m*, 823*s*, 790*s*, 751*s*, 726*s*, 700*s*, 643*m*, 603*s*, 554*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.26–7.19 (*m*, H–C(2′) to H–C(6′)); 4.81 (*quint.*, $^3J(1,6) \approx {}^3J(1,10ax) \approx {}^3J(1,10eq) \approx {}^4J(1,9eq) \approx 2$, H–C(1)); 4.48 (*A* of *ABX–P*, $^2J = 12.0$, $^3J(5ax,6) = {}^3J(5ax,P) = 2.7$, H_{ax}–C(5)); 4.11 (*B* of *ABX–P*, $^2J = 12.0$, $^3J(5eq,6) = 1.2$, $^3J(5eq,P) = 29.7$, H_{eq}–C(5)); 3.52, 3.40 (*AB*, $^2J = 13.0$, PhCH_2); 2.66 (*m*, *dquint.*-like, not resolved, H_{eq}–C(9)); 2.63 (br. *dd*, $^2J = 11.8$, $^3J(7eq,6) \approx 4.5$, $^4J(7eq,9eq) \approx 1$, H_{eq}–C(7)); 2.45 (*t*, $^2J = {}^3J(7ax,6) = 11.8$, H_{ax}–C(7)); 2.39 (*td*-like, $^2J \approx {}^3J(9ax,10ax) \approx 11$, $^3J(9ax,10eq) \approx 4$, H_{ax}–C(9)); 1.98 (*X* of *ABX–P*, br. *d*-like, $w_{1/2} \approx 22$, H–C(6)); 1.91 (*m*, *oct.*-like, $w_{1/2} \approx 10$, CH_2(10)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 137.7 (C(1′)); 128.9 (C(3′), C(5′)); 128.2 (C(2′), C(6′)); 127.1 (C(4′)); 78.5 (*d*, $^2J(1,P) = 8.2$, C(1)); 72.2 (*d*, $^2J(5,P) = 7.8$, C(5)); 62.8 (Ph*C*H_2); 49.7 (C(7)); 46.7 (C(9)); 35.5 (*d*, $^3J(6,P) = 5.9$, C(6)); 30.8 (*d*, $^3J(10,P) = 9.5$, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −2.5 (*d*, $^3J(P,H_{eq}$–C(5)) = 29.7). CI-MS: 304 (29, $[M(^{37}Cl) + H]^+$), 302 (100, $[M(^{35}Cl) + H]^+$).

*(1*RS*,3*RS*,6*RS*)-8-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**41a**). Slightly yellow powder (29%). IR ($CHCl_3$): 3086*w*, 3007*w*, 2954*w*, 2827*w*, 1615*m*, 1594*s*, 1526*s*, 1493*s*, 1470*m*, 1348*s*, 1310*s*, 1248*m*, 1165*m*, 1112*m*, 1096*m*, 1072*s*, 1050*m*, 1020*s*, 982*s*, 928*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.24 (*AA′* of *AA′BB′*, *J* = 9.3 H–C(3′), H–C(5′)); 7.42 (*BB′* of *AA′BB′*, *J* = 9.3, H–C(2′), H–C(6′)); 7.35–7.31 (4 H), 7.29–7.26 (1 H) (each *m*, H–C(2″) to H–C(6″)); 4.91 (*q*, $^3J(1,6) = {}^3J(1,10ax) = {}^3J(1,10eq) = 2.6$, H–C(1)); 4.57 (*A* of *ABX–P*, $^2J = 11.7$, $^3J(5ax,6) = 2.8$, $^3J(5ax,P) = 1.0$, H_{ax}–C(5)); 4.22 (*B* of *ABX–P*, $^2J = 11.7$, $^3J(5eq,6) = 1.2$, $^3J(5eq,P) = 24.5$, H_{eq}–C(5)); 3.62, 3.52 (*AB*, $^2J = 13.0$, PhCH_2); 2.76–2.70 (*m*, H_{eq}–C(7), H_{eq}–C(9)); 2.65 (*t*, $^2J = {}^3J(7ax,6) = 11.9$, H_{ax}–C(7)); 2.43 (*td*, $^2J = {}^3J(9ax,10ax) = 11.5$, $^3J(9ax,10eq) = 4.3$, H_{ax}–C(9)); 2.11 (*X* of *ABX–P*, *m*, $w_{1/2} \approx 25$, H–C(6)); 2.05–1.96 (*m*, CH_2(10)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 155.4 (*d*, $^2J(1′,P) = 6$, C(1′)); 144.6 (C(4′)); 137.8 (C(1″)); 128.9 (C(3″), C(5″)); 128.2 (C(2″), C(6″)); 127.2 (C(4″)); 125.7 (C(3′), C(5′)); 120.0 (*d*, $^3J(2′$ and $6′,P) = 5.8$, C(2′), C(6′)); 77.8 (*d*, $^2J(1,P) = 7.4$, C(1)); 71.9 (*d*, $^2J(5,P) = 7.4$, C(5)); 62.8 (Ph*C*H_2); 49.6 (C(7)); 46.7 (C(9)); 35.6 (*d*, $^3J(6,P) = 5.6$, C(6)); 31.0 (*d*, $^3J(10,P) = 8.6$, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −14.5 (*d*br. *d*, $^3J(P,H_{eq}$–C(5)) = 24.5, $^3J(P,H_{ax}$–C(5)) = 3.5, $^4J(P,H_{ax}$–C(10)) ≈ 1). CI-MS: 405 (100, $[M + H]^+$).

*(1*RS*,3*SR*,6*RS*)-8-Benzyl-3-(4-nitrophenoxy)-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**41b**). Yellow viscous oil (26%). IR ($CHCl_3$): 3030*w*, 2951*w*, 2816*w*, 1615*m*, 1594*s*, 1525*s*, 1493*s*, 1469*w*, 1374*m*,1348*s*, 1292*s*, 1248*s*, 1167*m*, 1112*m*, 1058*s*, 1020*m*, 974*m*, 933*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.26 (*AA′* of *AA′BB′*, *J* = 9.0, H–C(3′), H–C(5′)); 7.41 (*BB′* of *AA′BB′*, *J* = 9.0, H–C(2′), H–C(6′)); 7.35–7.23 (*m*, H–C(2″) to H–C(6″)); 4.71 (*m*, *oct.*-like, $w_{1/2} \approx 20$, H–C(1)); 4.62, 4.49 (*AB* of *ABX–P*, not resolved, CH_2(5)); 3.48, 3.44 (*AB*, $^2J = 13.2$, PhCH_2); 2.59–2.18 (*m*, H–C(6), CH_2(7), CH_2(9), H_{eq}–C(10)); 2.02 (*m*, $w_{1/2} \approx 20$, H_{ax}–C(10)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 155.6 (*d*, $^2J(1′,P) = 6$, C(1′)); 144.6 (C(4′)); 137.1 (C(1″)); 128.7 (C(3″), C(5″)); 128.3 (C(2″), C(6″)); 127.4 (C(4″)); 125.9 (C(3′), C(5′)); 120.8 (*d*, $^3J(2′$ and $6′,P) = 5.2$, C(2′), C(6′)); 78.9 (*d*, $^2J(1,P) = 6.9$, C(1)); 70.2 (*d*, $^2J(5,P) = 6.2$, C(5)); 62.3 (PhCH_2); 50.9 (C(7)); 49.2 (C(9)); 35.2 (*d*, $^3J(6,P) = 7.1$, C(6)); 29.2 (*d*, $^3J(10,P) = 4.1$, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −13.4 (*m*, $w_{1/2} \approx 35$). CI-MS: 405 (100, $[M + H]^+$).

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[20]) According to ^{1}H- and ^{31}P-NMR spectra, the conformation of the P-heterocycle is neither a chair nor a common twist-boat, see [23].

*(1*RS,*3*RS,*6*RS*)-8-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**42a**). Slightly yellow powder (14%). IR ($CHCl_3$): 2952*w*, 2826*w*, 1609*s*, 1541*s*, 1486*m*, 1455*m*, 1348*s*, 1316*s*, 1266*m*, 1165*m*, 1068*s*, 1020*s*, 985*s*, 936*s*, 924*s*, 918*s*, 894*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.83 (*d*, $^4J(3',5')=2.7$, H–C(3′)); 8.47 (*dd*, $^3J(5',6')=9.3$, $^4J(5',3')=2.7$, H–C(5′)); 8.13 (*d*, $^3J(6',5')=9.3$, H–C(6′)); 7.36–7.26 (*m*, H–C(2″) to H–C(6″)); 5.06 (*q*, $^3J(1,6)=^3J(1,10ax)=^3J(1,10eq)=2.3$, H–C(1)); 4.71 (*A* of *ABX*–*P*, $^2J=11.6$, $^3J(5ax,6)=2.6$, $^3J(5ax,P)<1$, H_{ax}–C(5)); 4.22 (*B* of *ABX*–*P*, $^2J=11.6$, $^3J(5eq,6)\approx1$, $^3J(5eq,P)=25.0$, H_{eq}–C(5)); 3.62, 3.53 (*AB*, $^2J=13.0$, PhCH_2); 2.72–2.77 (*m*, H_{eq}–C(7), H_{eq}–C(9)); 2.60 (*t*, $^2J=^3J(7ax,6)=11.8$, H_{ax}–C(7)); 2.40 (*td*, $^2J=^3J(9ax,10ax)=11.5$, $^3J(9ax,10eq)=4.5$, H_{ax}–C(9)); 1.99 (*X* of *ABX*–*P*, *m*, $w_{1/2}\approx22$, H–C(6)); 2.01–1.98 (*m*, CH_2(10)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 148.1 (*d*, $^2J(1',P)=5.7$, C(1′)); 144.8 (C(4′)); 142.0 (*d*, $^3J(2',P)=7.5$, C(2′)); 137.4 (C(1″)); 129.1 (C(5′)); 128.9 (C(2″), C(6″)); 128.3 (C(3″), C(5″)); 127.3 (C(4″)); 122.9 (*d*, $^3J(6',P)=2.2$, C(6′)); 121.6 (C(3′)); 78.7 (*d*, $^2J(1,P)=7.3$, C(1)); 72.5 (*d*, $^2J(5,P)=7.3$, C(5)); 62.8 (Ph*C*H_2); 49.6 (C(7)); 46.7 (C(9)); 35.5 (*d*, $^3J(6,P)=5.9$, C(6)); 31.0 (*d*, $^3J(10,P)=8.7$, C(10)). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −15.7 (*dd*, $^3J(P,H_{eq}-C(5))=25.0$, $^3J(P,H_{ax}-C(5))=4.2$). CI-MS: 450 (100, $[M+H]^+$).

*(1*RS,*3*SR,*6*RS*)-8-Benzyl-3-(2,4-dinitrophenoxy)-2,4-dioxa-8-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**42b**)[15]. Yellow viscous oil (*ca.* 5%). ^{31}P-NMR (161.9 MHz, $CDCl_3$): −14.8 (*t*-like, not resolved, $^3J(P,H_{ax}-C(5))\approx{}^3J(P,H_{eq}-C(5))\approx10$).

*(1*RS,*3*RS,*6*SR,*8*SR*)-8-Benzyl-3-chloro-8-methyl-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**43a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 2:1). White powder (25%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$[16]): 7.79–7.50 (*m*, H–C(2′) to H–C(6′)); 5.1–4.4 (*m*, not resolved, H–C(1), CH_2(5), PhCH_2); 4.0–3.5 (*m*, CH_2(7), CH_2(9)); 3.43 (*s*, Me_{ax}–N); 3.39 (*s*, Me_{eq}–N); 3.5–2.4 (*m*, H–C(6), CH_2(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −2.8 (*d*, $^3J(P,H_{eq}-C(5))=30$). ESI-MS: 318 (28, $[M(^{37}Cl)-CF_3SO_3]^+$), 316 (100, $[M(^{35}Cl)-CF_3SO_3]^+$).

*(1*RS,*3*RS,*6*SR,*8*SR*)-8-Benzyl-8-methyl-3-(4-nitrophenoxy)-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**44a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 2:1). Slightly yellow powder (52%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$[16])[21]: 8.31 (*AA′* of *AA′BB′*, *J* = 8.8, H–C(3′), H–C(5′)); 7.78–7.45 (*m*, H–C(2′), H–C(6′), H–C(2″) to H–C(6″)); 5.23–5.03 (*m*, H–C(1)); 4.92, 4.88 (*AB*, $^2J=13$, PhCH_2)); 4.73–4.48 (*AB* of *ABX*–*P*, not resolved, CH_2(5)); 4.08–3.37 (*m*, CH_2(7), CH_2(9)); 3.44 (*s*, Me_{ax}–N); 3.23 (*s*, Me_{eq}–N); 3.11, 2.89 (each *m*, $w_{1/2}\approx30$, H–C(6)); 2.69–2.27 (*m*, CH_2(10)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): epimer A: 156.2 (*d*, $^2J(1',P)=6$, C(1′)); 146.2 (C(4′)); 132.7 (C(3″), C(5″)); 130.4 (C(4″)); 130.3 (C(2″), C(6″)); 128.2 (C(1″)); 126.9 (C(3′), C(5′)); 122.1 (*q*, $^1J(C,F)=320$, CF_3SO_3); 121.9 (*d*, $^3J(2'$ and $6',P)=4.2$, C(2′), C(6′)); 77.8 (*d*, $^2J(1,P)=6.9$, C(1)); 71.5 (Ph*C*H_2); 70.1 (*d*, $^3J(5,P)=7.9$, C(5)); 58.5 (C(7)); 57.5 (C(9)); 44.8 (MeN); 34.5 (*d*, $^3J(6,P)=5.9$, C(6)); 26.1 (*d*, $^3J(10,P)=10.2$, C(10)); epimer B: 156.2 (*d*, $^2J(1',P)=6$, C(1′)); 146.2 (C(4′)); 132.7, (C(3″), C(5″)); 130.4 (C(4″)); 130.3 (C(2″), C(6″)); 128.2 (C(1″)); 126.9 (C(3′), C(5′)); 121.9 (*d*, $^3J(2'$ and $6',P)=4.2$, C(2′), C(6′)); 77.9 (*d*, $^2J(1,P)=7$, C(1)); 71.5 (Ph*C*H_2); 70.1 (*d*, $^3J(5,P)=7.9$, C(5)); 61.7 (C(7)); 60.6 (C(9)); 52.2 (MeN); 37.5 (*d*, $^3J(6,P)=5.9$, C(6)); 28.9 (*d*, $^3J(10,P)=9.9$, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −14.2 (*d*, $^3J(P,H_{eq}-C(5))=22.5$). ESI-MS: 419 (100, $[M-CF_3SO_3]^+$), 405 (60, $[M+H-Me]^+$).

*(1*RS,*3*SR,*6*SR,*8*SR*)-8-Benzyl-8-methyl-3-(4-nitrophenoxy)-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**44b**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 3:1). Yellow viscous oil (47%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$[16]): 8.31 (*AA′* of *AA′BB′*, *J* = 9.1, H–C(3′), H–C(5′)); 7.70 (*BB′* of *AA′BB′*, *J* = 9.1, H–C(2′), H–C(6′)); 7.65–7.48 (*m*, H–C(2′), H–C(6′), H–C(2″) to H–C(6″)); 5.02–4.92 (*m*, H–C(1)); 4.88 (*s*, PhCH_2)); 4.69–4.43 (*AB* of *ABX*–*P*, not resolved, CH_2(5)); 4.03–3.71 (*m*, H_{eq}–C(7), H_{eq}–C(9)); 3.41 (*s*, Me_{ax}–N); 3.24 (*s*, Me_{eq}–N); 3.56–3.14 (*m*, H–C(6), H_{ax}–C(7), H_{ax}–C(9)); 2.57–2.51 (*m*, CH_2(10)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): epimer A: 155.0 (*d*, $^2J(1',P)=6.8$, C(1′)); 145.0 (C(4′)); 133.3 (C(3″), C(5″)); 130.7 (C(4″)); 129.0 (C(2″), C(6″)); 126.8 (C(1″)); 125.6 (C(3′), C(5′)); 122.2 (*q*, $^1J(C,F)=320$, CF_3SO_3); 121.1 (*d*, $^3J(2'$ and $6',P)=5.0$, C(2′), C(6′)); 77.0 (*d*, $^2J(1,P)=5.3$, C(1)); 71.5 (Ph*C*H_2); 69.6 (*d*, $^3J(5,P)=7.2$, C(5)); 58.8 (C(7)); 57.9 (C(9)); 44.9 (MeN); 33.7 (*d*, $^3J(6,P)=8.9$, C(6)); 26.4 (*d*, $^3J(10,P)=9.4$, C(10)); epimer B: 155.0 (*d*, $^2J(1',P)=6.8$, C(1′)); 145.0 (C(4′)); 133.3 (C(3″), C(5″)); 130.7 (C(4″)); 129.0 (C(2″), C(6″)); 126.8 (C(1″)); 125.6 (C(3′), C(5′)); 122.2 (*q*, $^1J(C,F)=320$, CF_3SO_3); 121.1 (*d*, $^3J(2'$ and $6',P)=5.0$, C(2′), C(6′)); 77.2 (*d*, $^2J(1,P)=5.7$, C(1)); 68.6 (*d*, $^3J(5,P)=6.5$, C(5)); 65.1 (Ph*C*H_2); 61.7 (C(7)); 60.5 (C(9)); 52.2 (MeN); 36.3 (*d*, $^3J(6,P)=10.0$, C(6)); 28.9 (*d*, $^3J(10,P)=7.5$, C(10)). ^{31}P-NMR

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[21]) Due to partial overlapping and marginal resolution of the signals, only tentative assignments.

(121.4 MHz, $(CD_3)_2CO$): −11.3 (B), −11.8 (A) (each br. *dd*, ^3J(P,H_{eq}−C(5)) ≈ 15, ^3J(P,H_{ax}−C(5)) ≈ 10). ESI-MS: 419 (100, $[M-CF_3SO_3]^+$) 405 (35, $[M+H-Me]^+$).

*(1*RS*,3*RS*,6*SR*,8*SR*)-8-Benzyl-3-(2,4-dinitrophenoxy)-8-methyl-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**45a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 3:1). White foam (92%). M.p. 97–98°. IR (KBr): 3550–3200*m*, 1816*w*, 1765*w*, 1726*w*, 1710*w*, 1692*w*, 1658*w*, 1611*m*, 1546*m*, 1483*m*, 1350*s*, 1260*s*, 1159*m*, 1096*m*, 1050*m*, 1030*s*, 938*m*, 907*m*, 834*m*, 754*m*, 704*w*, 638*m*, 574*w*, 518*m*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$)[16]: 8.93 (*dd*, $^4J(3',5')=2.8$, $^5J(3',6')\approx 1$, H−C(3′)); 8.67 (*dd*, $^3J(5',6')=9.2$, $^4J(5',3')=2.8$, H−C(5′)); 8.13 (*dd*, $^3J(6',5')=9.2$, $^5J(6',3')\approx 1$, H−C(6′)); 7.68–7.49 (*m*, H−C(2″) to H−C(6″)); 5.04 (*td*, $^3J(1,6)=^3J(1,10ax)=11.0$, $^3J(1,10eq)=5.5$, H−C(1)); 4.895, 4.89 (*AB*, $^2J=13.0$, PhCH_2); 4.69–4.60 (*AB* of *ABX*−*P*, not resolved, CH_2(5)); 4.09–3.76 (*m*, CH_2(7), CH_2(9)); 3.52 (*s*, Me_{ax}−N); 3.30 (*s*, Me_{eq}−N); 3.18 (*X* of *ABX*−*P*, *oct.*-like, $w_{1/2}\approx 30$, H−C(6)); 2.69–2.50 (*m*, CH_2(10)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): epimer A: 147.4 (*d*, $^2J(1',P)=5.5$, C(1′)); 144.0 (C(4′)); 140.7 (br. *d*, $^3J(2',P)\approx 7$, C(2′)); 133.4 (C(3″), C(5″)); 130.7 (C(4″)); 129.4 (C(5′)); 129.0 (C(2″), C(6″)); 126.9 (C(1″)); 123.2 (*d*, $^3J(6',P)\approx 2$, C(6′)); 120.9 (*q*, ^1J(C,F) = 309, CF_3SO_3); 121.8 (C(3′)); 78.6 (*d*, $^2J(1,P)=7.1$, C(1)); 71.5 (PhCH_2); 70.6 (*d*, $^2J(5,P)=8.4$, C(5)); 58.9 (C(7)); 57.5 (C(9)); 45.0 (MeN); 34.3 (*d*, $^3J(6,P)=5.3$, C(6)); 26.1 (*d*, $^3J(10,P)=10$, C(10)); epimer B: 147.4 (*d*, $^2J(1',P)=5.5$, C(1′)); 144.0 (C(4′)); 140.7 (br. *d*, $^3J(2',P)\approx 7$, C(2′)); 133.4 (C(3″), C(5″)); 130.7 (C(4″)); 129.4 (C(5′)); 129.0 (C(2″)), C(6″)); 126.9 (C(1″)); 123.2 (*d*, $^3J(6',P)\approx 2$, C(6′)); 120.9 (*q*, ^1J(C,F) = 309, CF_3SO_3); 121.8 (C(3′)); 78.6 (*d*, $^2J(1,P)=7.1$, C(1)); 71.5 (PhCH_2); 70.6 (*d*, $^2J(5,P)=8.0$, C(5)); 61.7 (C(7)); 60.5 (C(9)); 52.2 (MeN); 37.4 (*d*, $^3J(6,P)=6.3$, C(6)); 29.0 (*d*, $^3J(10,P)=11$, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −14.7 (A), −14.8 (B) (each br. *d*, ^3J(P,H_{eq}−C(5) = 26). ESI-MS: 464 (100, $[M-CF_3SO_3]^+$), 450 (5, $([M+H-CF_3SO_3-Me]^+$). Anal. calc. for $C_{21}H_{23}F_3N_3O_{11}PS\cdot H_2O$ (631.44): C 39.94, H 3.39, N 6.65; found: C 39.36, H 3.72, N 6.70.

*(1*RS*,3*RS*,6*SR*)-3-(2,4-Dinitrophenoxy)-8,8-dimethyl-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**46a**). White foam (30%). IR (KBr): 3550–3200*m*, 1820*w*, 1765*w*, 1723*w*, 1708*w*, 1695*w*, 1660*w*, 1610*m*, 1545*m*, 1480*m*, 1350*s*, 1260*s*, 1162*m*, 1098*m*, 1050*m*, 1032*s*, 940*m*, 905*m*, 830*m*, 758*m*, 707*w*, 640*m*, 570*w*, 525*m*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 8.90 (*dd*, $^4J(3',5')=2.7$, $^5J(3',6')=1.2$, H−C(3′)); 8.65 (*dd*, $^3J(5',6')=9.2$, $^4J(5',3')=2.7$, H−C(5′)); 8.02 (*dd*, $^3J(6',5')=9.2$, $^5J(6',3')=1.2$, H−C(6′)); 5.02 (*td*, $^3J(1,6)=^3J(1,10ax)=10.9$, $^3J(1,10eq)=5.2$, H−C(1)); 4.62 (*A* of *ABX*−*P*, $^2J=11.0$, $^3J(5eq,P)=23$, $^3J(5eq,6)=4.6$, H_{eq}−C(5)); 4.56 (*B* of *ABX*−*P*, $^2J=11.0$, $^3J(5ax,6)=11.8$, H_{ax}−C(5)); 3.97–3.77 (*m*, H_{eq}−C(7), CH_2(9)); 3.70 (*t*, $^2J=^3J(7ax,6)=12.8$, H_{ax}−C(7)); 3.60 (*s*, Me_{ax}−N); 3.51 (*s*, Me_{eq}−N); 3.29 (*X* of *ABX*−*P*, *m*, $w_{1/2}\approx 30$, H−C(6)); 2.68–2.36 (*m*, CH_2(10)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 147.1 (*d*, $^2J(1',P)=4.8$, C(1′)); 141.7 (C(4′)); 138.5 (*m*, $w_{1/2}\approx 15$, C(2′)); 127.2 (C(5′)); 121.0 (*d*, $^3J(6',P)=2.2$, C(6′)); 119.6 (C(3′)); 118.7 (*q*, ^1J(C,F) = 320, CF_3SO_3); 76.3 (*d*, $^2J(1,P)=7.2$, C(1)); 68.4 (*d*, $^2J(5,P)=8.1$, C(5)); 58.5 (C(7)); 57.6 (C(9)); 54.0 (Me_{eq}−N); 46.1 (Me_{ax}−N); 32.4 (*d*, $^3J(6,P)=5.9$, C(6)); 24.2 (*d*, $^3J(10,P)=10.0$, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −14.7 (*d*, ^3J(P,H_{eq}−C(5)) = 23). ESI-MS: 388 (100, $[M-CF_3SO_3]^+$), 374 (18, $[M+H-CF_3SO_3-Me]^+$), 250 (15). Anal. calc. for $C_{15}H_{19}F_3N_3O_{11}PS\cdot 2H_2O$ (573.36): C 31.40, H 4.04, N 7.33; found: C 31.60, H 4.20, N 7.47.

*(1*RS*,3*SR*,6*RS*)-3-(2,4-Dinitrophenoxy)-8,8-dimethyl-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**46b**)[17]). ^{31}P-NMR (121.4 MHz, $CDCl_3$): −13.7 (*t*-like, ^3J(P,H) ≈ 15).

*(1*RS*,3*RS*,6*RS*,8*RS*)-8-Benzyl-3-chloro-8-methyl-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**47a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 5:1). White powder (58%). M.p. 146–148°. IR (KBr): 3700–3300*m*, 2923*w*, 2360*m*, 2341*m*, 1734*w*, 1636*w*, 1558*w*, 1458*m*, 1311*s*, 1255*s*, 1226*s*, 1167*m*, 1083*m*, 1064*m*, 1033*s*, 995*m*, 968*m*, 946m, 873*w*, 830*w*, 794*m*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$)[16]): 7.81–7.77 (2 H), 7.61–7.53 (3 H) (each *m*, H−C(2′) to H−C(6′)); 5.24 (*s*, $w_{1/2}\approx 8$, H−C(1)); 5.05 (*s*, PhCH_2); 4.85 (*A* of *ABX*−*P*, $^2J=12.6$, $^3J(5ax,6)=^3J(5ax,P)\approx 2.7$, H_{ax}−C(5)); 4.19 (*B* of *ABX*−*P*, $^2J=12.6$, $^3J(5eq,P)=30.2$, $^3J(5eq,6)\approx 1$, H_{eq}−C(5)); 4.05 (*t*, $^2J=^3J(7ax,6)=13$, H_{ax}−C(7)); 3.93 (*td*, $^2J=^3J(9ax,10ax)=13.5$, $^3J(9ax,10eq)=3.0$, H_{ax}−C(9)); 3.84, 3.71 (each *m*, *d-quint.*-like, $w_{1/2}\approx 20$, H_{eq}−C(7), H_{eq}−C(9)); 3.33 (*s*, MeN); (3.07 (*m*, *d*-like, $w_{1/2}\approx 20$, H_{eq}−C(10)); 2.78 (*X* of *ABX*−*P*, *m*, $w_{1/2}\approx 30$, H−C(6)); 2.37 (*m*, *d*-like, $w_{1/2}\approx 20$, H_{ax}−C(10)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): epimer A: 131.3 (C(3′), C(5′)); 128.3 (C(4′)); 126.8 (C(2′), C(6′)); 125.2 (C(1′)); 118.6 (*q*, ^1J(C,F) = 322, CF_3SO_3); 69.1 (*d*, $^2J(1,P)=5.6$ C(1)); 68.1 (PhCH_2); 65.8 (*d*, $^2J(5,P)=6.2$, C(5)); 53.5 (C(7)); 53.1 (C(9)); 41.4 (MeN); 27.5 (*d*, $^3J(6,P)=4.1$, C(6)); 23.1 (*d*, $^3J(10,P)=8.7$, C(10)); epimer B: 131.3 (C(3′), C(5′)); 128.3 (C(4′)); 126.8 (C(2′), C(6′)); 125.2 (C(1′)); 118.6 (*q*, ^1J(C,F) = 322, CF_3SO_3); 69.7 (*d*, $^2J(1,P)=6$, C(1)); 68.1 (PhCH_2); 65.9 (*d*, $^2J(5,P)=6$, C(5)); 57.5 (C(7)); 57.0 (C(9)); 49.8 (MeN); 30.1 (*d*, $^3J(6,P)=4$, C(6)); 25.6 (*d*, $^3J(10,P)=9$, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −3.4 (*d*, ^3J(P,H_{eq}−C(5) = 30.2). ESI-MS: 318 (28, $[M(^{37}Cl)-CF_3SO_3]^+$), 316 (100, $[M(^{35}Cl)-CF_3SO_3]^+$).

*(1*RS,*3*RS,*6*RS,*8*RS*)-8-Benzyl-8-methyl-3-(4-nitrophenoxy)-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**48a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 6:1). White powder (87%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$[16]): 8.27 (*AA′* of *AA′BB′*, *J* = 9.1, H–C(3′), H–C(5′)); 7.73 (*BB′* of *AA′BB′*, *J* = 9.1, H–C(2′), H–C(6′)); 7.58–7.45 (*m*, H–C(2″) to H–C(6″)); 5.29 (*q*, $^3J(1,6) \approx {}^3J(1,10ax) \approx {}^3J(1,10eq) \approx 2$, H–C(1)); 4.99 (*s*, PhCH_2); 4.91 (*A* of *ABX–P*, ^2J = 12.2, ^3J(5ax,6) = 2.5, H_{ax}–C(5)); 4.42 (*B* of *ABX–P*, ^2J = 12.2, ^3J(5eq,P) = 25, H_{eq}–C(5)); 4.02 (*t*, $^2J = {}^3J$(7ax,6) = 13.1, H_{ax}–C(7)); 3.93–3.59 (*m*, H_{eq}–C(7), CH_2(9)); 3.34 (*s*, Me_{ax}–N); 3.26 (*s*, Me_{eq}–N); 2.96 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{eq}–C(10)); 2.66 (*X* of *ABX–P*, *m*, $w_{1/2} \approx 30$, H–C(6)); 2.27 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{ax}–C(10)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): 155.0 (*d*, ^2J(1′,P) = 6, C(1′)); 144.9 (C(4′)); 133.4 (C(3″), C(5″)); 131.3 (C(4″)); 129.0 (C(2″), C(6″)); 126.9 (C(1″)); 125.7 (C(3′), C(5′)); 121.2 (*q*, ^1J(C,F) = 321, CF_3SO_3); 120.6 (*d*, ^3J(2′ and 6′,P) = 5.5, C(2′), C(6′)); 74.5 (*d*, ^2J(1,P) = 7.0, C(1)); 71.5 (PhCH_2); 70.5 (*d*, ^3J(5,P) = 7.9, C(5)); 55.5 (C(7)); 54.2 (C(9)); 52.4 (Me_{eq}–N); 43.6 (Me_{ax}–N); 30.1 (*d*, ^3J(6,P) = 5.0, C(6)); 25.4 (*d*, ^3J(10,P) = 9.0, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −14.3 (A), −14.4 (B) (each *d*, ^3J(P,H_{eq}–C(5) = 25). ESI-MS: 419 (100, $[M - CF_3SO_3]^+$), 405 (15, $[M + H - CF_3SO_3 - Me]^+$).

*(1*RS,*3*SR,*6*RS,*8*RS*)-8-Benzyl-8-methyl-3-(4-nitrophenoxy)-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**48b**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 6:1). Slightly yellow oil (64%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$[16])[18]): 8.37 (*AA′* of *AA′BB′*, *J* = 9.1, H–C(3′), H–C(5′)); 7.69 (*BB′* of *AA′BB′*, *J* = 9.1, H–C(2′), H–C(6′)); 7.60–7.46 (*m*, H–C(2″) to H–C(6″)); 5.25 (*q*, $^3J(1,6) \approx {}^3J(1,10ax) \approx {}^3J(1,10eq) \approx 2.5$, H–C(1)); 4.93, 4.50 (*AB* of *ABX–P*, not resolved, CH_2(5)); 4.80 (*s*, PhCH_2); 3.80–3.58 (*m*, CH_2(7), CH_2(9)); 3.34 (*s*, Me_{ax}–N); 3.14 (*s*, Me_{eq}–N); 3.04 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{eq}–C(10)); 2.73 (*X* of *ABX–P*, *m*, $w_{1/2} \approx 30$, H–C(6)); 2.38 (*m*, *t*-like, $w_{1/2} \approx 30$, H_{ax}–C(10)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): 154.7 (*d*, ^2J(1′,P) = 5.8, C(1′)); 145.3 (C(4′)); 133.4 (C(3″), C(5″)); 130.7 (C(4″)); 129.0 (C(2″), C(6″)); 126.6 (C(1″)); 125.7 (C(3′), C(5′)); 121.1 (*q*, ^1J(C,F) = 322, CF_3SO_3); 121.5 (*d*, ^3J(2′ and 6′,P) = 4.5, C(2′), C(6′)); 72.9 (*d*, ^2J(1,P) = 4.5, C(1)); 71.9 (PhCH_2); 69.1 (*d*, ^3J(5,P) = 5.7, C(5)); 55.5 (C(7)); 53.7 (C(9)); 52.7 (Me_{eq}–N); 44.4 (Me_{ax}–N); 30.4 (*d*, ^3J(6,P) = 5.1, C(6)); 25.4 (*d*, ^3J(10,P) = 9.4, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$)[18]): −9.8 (B), −10.0 (A) (each br. *d*, ^3J(P,H_{eq}–C(5)) ≈ 20). ESI-MS: 419 (100, $[M - CF_3SO_3]^+$), 405 (18, $[M + H - CF_3SO_3 - Me]^+$).

*(1*RS,*3*RS,*6*RS,*8*RS*)-8-Benzyl-3-(2,4-dinitrophenoxy)-8-methyl-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**49a**). Mixture of *N*-epimers (A = Me_{ax}, B = Me_{eq}, A/B *ca.* 2:1). White powder (57%). M.p. 88–90°. IR (KBr): 3700–3300*m*, 1736*w*, 1611*m*, 1543*m*, 1483*m*, 1351*s*, 1261*s*, 1164*m*, 1085*m*, 1066*m*, 1030*s*, 972*m*, 939*m*, 904*m*, 873*w*, 803*w*, 756*m*, 741*m*, 710*w*, 638*m*, 574*w*, 554*w*, 518*w*, 476*w*. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$[16]): 8.95 (*d*, ^4J(3′,5′) = 2.5, H–C(3′)); 8.71 (*dd*, ^3J(5′,6′) = 9.2, ^4J(5′,3′) = 2.5, H–C(5′)); 8.11 (*d*, ^3J(6′,5′) = 9.2, H–C(6′)); 7.85–7.63 (*m*, H–C(2″) to H–C(6″)); 5.41 (*q*, $^3J(1,6) \approx {}^3J(1,10ax) \approx {}^3J(1,10eq) \approx 2$, H–C(1)); 5.12 (*s*, PhCH_2); 5.04 (*A* of *ABX–P*, ^2J = 12.3, ^3J(5ax,P) = 7, ^3J(5ax,6) ≈ 2, H_{ax}–C(5)); 4.73 (*B* of *ABX–P*, ^2J = 12.3, ^3J(5eq,P) = 25.5, H_{eq}–C(5)); 4.20 (*t*, $^2J = {}^3J$(7ax,6) = 13.0, H_{ax}–C(7)); 3.96 (*td*-like, $^2J \approx 12$, ^3J(9eq,10ax) ≈ ^{3}J(9eq,10eq ≈ 3, H_{eq}–C(9)); 3.91–3.61 (*m*, H_{eq}–C(7), H_{ax}–C(9)); 3.41 (*s*, Me_{ax}–N); 3.29 (*s*, Me_{eq}–N); 3.18 (*m*, *d*-like, $w_{1/2} \approx 20$, H_{eq}–C(10)); 2.81 (*X* of *ABX–P*, *m*, $w_{1/2} \approx 30$, H–C(6)); 2.31 (*m*, *d*-like, $w_{1/2} \approx 25$, H_{ax}–C(10)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): epimer A: 148.3 (*d*, ^2J(1′,P) = 5.8, C(1′)); 144.8 (C(4′)); 141.4 (*d*, ^3J(2′,P) = 6.8, C(2′)); 133.3 (C(3″), C(5″)); 130.8 (C(4″)); 129.4 (C(5′)); 129.1 (C(2″), C(6″)); 126.8 (C(1″)); 123.1 (*d*, ^3J(6′,P) ≈ 2, C(6′)); 119.9 (*q*, ^1J(C,F) = 322, CF_3SO_3); 121.9 (C(3′)); 76.2 (*d*, ^2J(1,P) = 7.3, C(1)); 71.8 (*d*, ^2J(5,P) = 8.2, C(5)); 71.7 (PhCH_2); 55.4 (C(7)); 54.1 (C(9)); 44.5 (MeN); 31.0 (d, ^3J(6,P) = 6.3, C(6)); 26.3 (*d*, ^3J(10,P) = 9.0, C(10)); epimer B: 148.3 (*d*, ^2J(1′,P) = 5.8, C(1′)); 144.8 (C(4′)); 141.4 (*d*, ^3J(2′,P) = 6.8, C(2′)); 133.3 (C(3″), C(5″)); 130.8 (C(4″)); 129.4 (C(5′)); 129.1 (C(2″), C(6″)); 126.8 (C(1″)); 123.1 (*d*, ^3J(6′,P) ≈ 2, C(6′)); 119.9 (*q*, ^1J(C,F) = 322, CF_3SO_3); 121.9 (C(3′)); 76.4 (*d*, ^2J(1,P) = 7.6, C(1)); 72.5 (*d*, ^2J(5,P) ≈ 8, C(5)); 71.7 (PhCH_2); 56.3 (C(7)); 55.8 (C(9)); 52.5 (MeN); 33.6 (*d*, ^3J(6,P) = 5.5, C(6)); 28.8 (*d*, ^3J(10,P) = 5.5, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): −15.0 (B), −15.2 (A) (each *dd*, ^3J(P,H_{eq}–C(5)) = 25.5, ^3J(P,H_{ax}–C(5)) = 7). ESI-MS: 464 (100, $[M - CF_3SO_3]^+$), 450 (18, $[M + H - CF_3SO_3 - Me]^+$). Anal. calc. for $C_{21}H_{23}F_3N_3O_{11}PS \cdot 3\,H_2O$ (667.47): C 37.78, H 4.38, N 6.29; found: C 38.04, H 4.01, N 6.10.

*(1*RS,*3*RS,*6*RS*)-3-(2,4-Dinitrophenoxy)-8,8-dimethyl-2,4-dioxa-8-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**50a**)[22]). White foam (95%). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 8.90 (*d*, ^4J(3′,5′) = 2.7, H–C(3′)); 8.65 (*dd*, ^3J(5′,6′) = 9.1, ^4J(5′,3′) = 2.7, H–C(5′)); 8.11 (*d*, ^3J(6′,5′) = 9.1, H–C(6′)); 5.35 (*q*, $^3J(1,6) = {}^3J(1,10ax) = {}^3J(1,10eq) = 2.3$, H–C(1)); 4.99 (*A* of *ABX–P*, ^2J = 12.3, ^3J(5ax,6) = 2.5, H_{ax}–C(5));

[22]) The equatorially substituted *P*-epimer was not detected in the reaction mixture.

4.55 (*B* of *ABX*–*P*, ^2J = 12.3, ^3J(5eq,P) = 26.5, H_{eq}–C(5)); 4.01–3.02 (*m*, CH_2(7), CH_2(9)); 3.61 (*s*, Me_{ax}–N); 3.46 (*s*, Me_{eq}–N); 3.18 (*m*, *dd*-like, $w_{1/2} \approx 20$, H_{eq}–C(10)); 2.79 (*X* of *ABX*–*P*, *m*, $w_{1/2} \approx 30$, H–C(6)); 2.36 (*m*, *d*-like, $w_{1/2} \approx 25$, H_{ax}–C(10)). ^{13}C-NMR (75.4 MHz, $(CD_3)_2CO$): 148.4 (*d*, ^2J(1′,P) = 6.0, C(1′)); 144.8 (C(4′)); 141.4 (*d*, ^3J(2′,P) ≈ 7, C(2′)); 130.3 (C(5′)); 123.7 (*d*, ^3J(6′,P) ≈ 2, C(6′)); 122.7 (C(3′)); 121.5 (*q*, ^1J(C,F) = 320, CF_3SO_3); 75.7 (*d*, ^2J(1,P) = 7.5, C(1)); 71.8 (*d*, ^2J(5,P) = 7.9, C(5)); 58.3 (C(7)); 57.2 (Me_{eq}–N); 56.8 (C(9)); 48.2 (Me_{ax}–N); 31.2 (*d*, ^3J(6,P) = 5.5, C(6)); 26.5 (*d*, ^3J(10,P) = 9.0, C(10)). ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$): –15.2 (*d*, ^3J(P,H_{eq}–C(5)) = 26). ESI-MS: 388 (100, $[M - CF_3SO_3]^+$), 374 (20, $[M + H - CF_3SO_3 - Me]^+$), 349 (42), 248 (40), 174 (58). Anal. calc. for $C_{15}H_{19}F_3N_3O_{11}PS \cdot 2\,H_2O$ (573.36): C 31.40, H 4.04, N 7.33; found: C 31.36, H 4.18, N 6.92.

7. *2,4-Dioxa-7-aza-3-phosphadecalins* **59**–**66** *of Type* **III**. *(1*RS,*3*RS,*6*SR*)-7-Benzyl-3-fluoro-2,4-dioxa-7-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**59a**). Colorless prisms (22%). M.p. 116.5–118.5°. R_f (hexane/Et_2O 1:2) 0.26. IR (KBr): 3027*w*, 2961*m*, 2918*m*, 2815*m*, 2723*w*, 1495*w*, 1455*m*, 1402*w*, 1335*s*, 1285*m*, 1146*m*, 1123*m*, 1103*w*, 1071*m*, 1051*s*, 1006*s*, 988*m*, 955*w*, 928*w*, 887*s*, 848*w*, 824*w*, 788*m*, 756*s*, 705*m*, 646*w*, 593*m*, 564*m*, 526*m*, 516*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.34–7.23 (*m*, H–C(2′) to H–C(6′)); 4.69 (*A* of *ABX*–*P*, ^2J = 10.9, ^3J(5eq,P) = 25.2, ^3J(5eq,6) = 4.2, H_{eq}–C(5)); 4.33 (*ddd*, ^3J(1,6) = 10.5, ^3J(1,10ax) = 9.0, ^3J(1,10eq) = 4.8, H–C(1)); 4.21 (*B* of *ABX*–*P*, $^2J = {}^3J$(5ax,6) = 10.8, ^3J(5ax,P) ≈ 1, H_{ax}–C(5)); 3.78, 3.36 (*AB*, ^2J = 13.8, PhCH_2); 2.83 (*m*, *d*-like, $w_{1/2} \approx 15$, $^2J \approx 12$, H_{eq}–C(8)); 2.66 (*X* of *ABX*–*P*, ^3J(6,1) = 10.5, ^3J(6,5ax) = 10.8, ^3J(6,5eq) = 4.2, ^5J(6,F) = 1.2, H–C(6)); 2.17 (*m*, $w_{1/2} \approx 15$, H_{eq}–C(10)); 2.12 (*td*, $^2J = {}^3J$(8ax,9ax) = 11.8, ^3J(8ax,9eq) = 3.0, H_{ax}–C(8)); 1.73 (*m*, *d*-like, $w_{1/2} \approx 15$, $^2J \approx 11$, ^5J(9eq,P) ≈ 2, H_{eq}–C(9)); 1.64–1.56 (*m*, H_{ax}–C(9), H_{ax}–C(10)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.7 (C(1′)); 128.5 (C(3′), C(5′)); 128.2 (C(2′), C(6′)); 127.5 (C(4′)); 81.0 (*dd*, ^2J(1,P) = 7.2, ^3J(1,F) = 1.9, C(1)); 72.2 (*d*, ^2J(5,P) = 7.8, C(5)); 61.4 (*d*, ^3J(6,P) = 4.8, C(6)); 58.0 (PhCH_2); 52.9 (C(8)); 30.9 (*d*, ^3J(10,P) = 9.6, C(10)); 22.9 (*d*, ^4J(9,P) = 2.5, C(9)). ^{31}P-NMR (242.9 MHz, $CDCl_3$): –16.3 (*d*br. *d*, ^1J(P,F) = 1013, ^3J(P,H_{eq}–C(5)) = 25.2, ^5J(9eq,P) ≈ 2). ^{19}F{^{1}H}-NMR (564.5 MHz, $CDCl_3$): –86.7 (*d*, ^1J(F,P) = 1013). EI-MS: 285 (4, $M^{+\bullet}$), 194 (4, $[M - PhCH_2]^+$), 171 (12), 160 (17), 91 (100, $PhCH_2^+$), 65 (14). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.45 H 5.58, N 4.83.

*(1*RS,*3*SR,*6*SR*)-7-Benzyl-3-fluoro-2,4-dioxa-7-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**59b**). Colorless plates (23%). M.p. 86–90.5°. R_f (hexane/Et_2O 1:2) 0.19. IR (KBr): 3062*w*, 3028*w*, 2961*m*, 2859*m*, 2723*w*, 1604*w*, 1494*m*, 1480*m*, 1455*m*, 1439*m*, 1398*m*, 1325*s*, 1292*s*, 1262*m*, 1228*w*, 1126*m*, 1080*s*, 1008*s*, 953*m*, 924*m*, 878*s*, 847*m*, 806*w*, 777*m*, 741*s*, 699*s*, 653*m*, 597*m*, 566*m*, 524*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.34–7.23 (*m*, H–C(2′) to H–C(6′)); 4.74 (*A* of *ABX*–*P*, ^2J = 10.2, ^3J(5eq,P) = 9.2, ^3J(5eq,6) = 5.5, H_{eq}–C(5)); 4.45 (*sept.*-like, ^3J(1,10ax) ≈ ^3J(1,6) ≈ 10, ^3J(1,10eq) = 4.5, ^4J(1,F) = 3.5, ^3J(1,P) ≈ 1, H-C(1)); 4.38 (*B* of *ABX*–*P*, ^3J(5ax,P) = 14.0, $^2J = {}^3J$(5ax,6) = 10.0, ^4J(5ax,F) = 2.8, H_{ax}–C(5)); 3.71, 3.25 (*AB*, ^2J = 13.6, PhCH_2); 2.80 (*m*, *d*-like, $^2J \approx 12$, H_{eq}–C(8)); 2.77 (*X* of *ABX*, ^3J(6,1) ≈ 10, ^3J(6,5ax) = 10.0, ^3J(6,5eq) = 5.5, ^5J(6,F) = 2.6, H–C(6)); 2.24 (*m*, $w_{1/2} \approx 18$, H_{eq}–C(10)); 2.12 (*td*, $^2J = {}^3J$(8ax,9ax) = 11.8, ^3J(8ax,9eq) = 2.7, H_{ax}–C(8)); 1.72 (*m*, *d*-like, $w_{1/2} \approx 15$, $^2J \approx 11$, ^5J(9eq,P) ≈ 2, H_{eq}–C(9)); 1.63–1.50 (*m*, H_{ax}–C(9), H_{ax}–C(10)). ^{13}C-NMR (105.9 MHz, $CDCl_3$): 137.4 (C(1′)); 128.6 (C(3′), C(5′)); 128.4 (C(2′), C(6′)); 127.6 (C(4′)); 80.9 (*dd*, ^2J(1,)P = 6.2, ^3J(1,F) = 1.6, C(1)); 72.7 (*d*, ^2J(5,P) = 7.6, C(5)); 60.5 (*d*, ^3J(6,P) = 9.8, C(6)); 58.1 (PhCH_2); 52.4 (C(8)); 31.1 (*d*, ^3J(10,P) = 7.8, C(10)); 22.7 (*d*, ^4J(9,P) = 2.3, C(9)). ^{31}P-NMR (124.9 MHz, $CDCl_3$): –15.1 (*d*br. *dd*, ^1J(P,F) = 997, ^3J(P,H_{ax}–C(5) = 14.0, ^3J(P,H_{eq}–C(5)) = 9.2, ^5J(9eq,P) ≈ 2). ^{19}F{^{1}H}-NMR (564.5 MHz, $CDCl_3$): –72.8 (*d*, ^1J(F,P) = 997). ^{19}F-NMR (564.5 MHz, $CDCl_3$): –72.8 (*dq*, ^1J(F,P) = 997, ^4J(F,H–C(1)) ≈ ^4J(F,H_{ax}–C(5)) ≈ ^5J(F,H–C(6)) ≈ 3 (see ^{1}H-NMR). CI-MS: 571 (99, $[2M + H]^+$), 303 (16, $[M + NH_4]^+$); 286 (100, $[M + H]^+$). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.18, H 5.56, N 4.82.

*(1*RS,*3*RS,*6*RS*)-7-Benzyl-3-fluoro-2,4-dioxa-7-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**60a**). Colorless prisms (23%). M.p. 107–110.5°. R_f (hexane/AcOEt 1:1) 0.24. IR (KBr): 3082*w*, 3030*w*, 2969*m*, 2950*m*, 2807*m*, 2785*m*, 1606*w*, 1493*m*, 1450*m*, 1431*w*, 1381*m*, 1360*m*, 1343*s*, 1325*s*, 1252*m*, 1229*m*, 1203*w*, 1151*s*, 1121*m*, 1111*m*, 1085*s*, 1073*m*, 1058*s*, 1046*s*, 1033*s*, 988*s*, 968*m*, 930*w*, 904*s*, 884*s*, 869*m*, 848*w*, 827*s*, 760*s*, 730*s*, 700*m*, 649*m*, 538*w*, 524*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.35–7.24 (*m*, H–C(2′) to H–C(6′)); 4.86 (*A* of *ABX*–*P*, ^2J = 12.7, ^3J(5eq,P) = 25.5, ^3J(5eq,6) = 1.5, H_{eq}–C(5)); 4.79 (*m*, $w_{1/2} \approx 6$, H–C(1)); 4.34 (*B* of *ABX*–*P*, ^2J = 12.7, ^3J(5ax,6) = ^3J(5ax,P) = 1.5, H_{ax}–C(5)); 4.13, 3.29 (*AB*, ^2J = 13.6, PhCH_2); 2.93 (*m*, *dt*-like, $w_{1/2} \approx 15$, ^2J = 12.5, H_{eq}–C(8)); 2.48 (*X* of *ABX*–*P*, ^3J(6,1) = ^3J(6,5ax) = ^3J(6,5eq) = ^4J(6,P) = 1.5, H–C(6)); 2.12 (*td*, $^2J = {}^3J$(8ax,9ax) = 12.5, ^3J(8ax,9eq) = 2.5, H_{ax}–C(8)); 2.09 (*m*, *d*-like, $w_{1/2} \approx 18$, H_{eq}–C(10)); 1.97 (*qt*, $^2J = {}^3J$(9ax,8ax) = ^3J(9ax,10ax) = 12.5, ^3J(9ax,8eq) = ^3J(9ax,10eq) = 3.8, H_{ax}–C(9)); 1.63 (*m*, $w_{1/2} \approx 30$, ^4J(10ax,P) = 7.5, H_{ax}–C(10)); 1.47 (*m*, *dq*-like, $w_{1/2} \approx 18$, ^2J = 12.5, H_{eq}–C(9)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.7 (C(1′)); 128.6 (C(3′), C(5′)); 128.4 (C(2′), C(6′)); 127.2 (C(4′)); 80.2 (*d*, ^2J(1,P) = 7.9, C(1)); 69.1 (*dd*, ^2J(5,P) = 6.9, ^3J(5,F) = 0.8, C(5)); 58.1 (*d*, ^3J(6,P) = 5.4, C(6)); 57.1 (PhCH_2); 51.8 (C(8)); 30.0 (*d*, ^3J(10,P) = 8.8, C(10)); 19.5 (*d*, ^4J(9,P) = 2.5, C(9)). ^{31}P-NMR (242.9 MHz, $CDCl_3$): –16.7 (*ddd*, ^1J(P,F) = 997,

^3J(P,H$_{eq}$–C(5)) = 25.5, ^4J(P,H$_{ax}$–C(10) = 7.5). ^{19}F{^{1}H}-NMR (564.5 MHz, $CDCl_3$): −84.2 (*d*, ^1J(F,P) = 997). EI-MS: 285 (14, $M^{+\bullet}$), 194 (4, $[M - PhCH_2]^+$), 160 (65), 147 (22), 118 (22), 91 (100, $PhCH_2^+$); 80 (22). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.88, H 5.41, N 4.90.

*(1*RS,*3*SR,*6*RS*)-7-Benzyl-3-fluoro-2,4-dioxa-7-aza-3-phosphabicyclo[4.4.0]decane 3-Oxide* (**60b**). Colorless plates (28%). M.p. 93–94.5°. R_f (hexane/Et_2O 1:2) 0.26. IR (KBr): 3086*w*, 3063*w*, 3028*w*, 2962*m*, 2948*m*, 2934*w*, 1495*w*, 1486*w*, 1463*w*, 1450*w*, 1385*w*, 1364*w*, 1329*m*, 1299*s*, 1245*w*, 1225*w*, 1200*w*, 1447*m*, 1121*m*, 1106*m*, 1088*s*, 1054*s*, 997*s*, 910*m*, 878*m*, 849*m*, 838*w*, 821*m*, 766*w*, 722*m*, 697*m*, 652*w*, 600*w*, 582*w*, 543*w*, 532*w*. ^{1}H-NMR (600 MHz, $CDCl_3$)[20])[23]) 7.35–7.27 (*m*, H–C(2′) to H–C(6′)); 4.82–4.76 (*A* of *ABX*–*P* and *m*, not resolved, ^3J(5eq,P) = 10, ^3J(5eq,6) = 7.6, ^3J(1,P) = 15, ^4J(1,F) = 2.5, H$_{eq}$–C(5), H–C(1)); 4.46 (*B* of *ABX*–*P*, $^2J = {}^3J$(5ax,P) = 15, ^3J(5ax,6) = 3.2, ^4J(5ax,F) = 1.5, H$_{ax}$–C(5)); 3.92, 3.54 (*AB*, ^2J = 13.5, Ph*C*H$_2$); 3.14 (*X* of *ABX*–*P*, ^3J(6,5eq) = 7.6, ^3J(6,5ax) = 3.2, ^3J(6,1) = 3.7, ^4J(6,P) = 2.0, H–C(6)); 2.66 (*m*, *ddd*-like, $w_{1/2} \approx 18$, ^2J = 12.0, H$_{eq}$–C(8)); 2.35 (*m*, *ddd*-like, $w_{1/2} \approx 25$, ^2J = 12.0, H$_{ax}$–C(8)); 2.17 (*m*, br. *d*-like, $w_{1/2} \approx 18$, H$_{eq}$–C(10)); 1.96 (*m*, $w_{1/2} \approx 25$, H$_{ax}$–C(10)); 1.81, 1.57 (each *m*, $w_{1/2} \approx 25$, CH$_2$(9)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.6 (C(1′)); 128.5 (C(3′), C(5′)); 128.3 (C(2′), C(6′)); 127.5 (C(4′)); 80.3 (*dd*, ^2J(1,P) = 8.2, ^3J(1,F) = 1.2, C(1)); 65.9 (*d*, ^2J(5,P) = 6.5, C(5)); 58.1 (Ph*C*H$_2$); 55.6 (*d*, ^3J(6,P) = 8.6, C(6)); 48.1 (C(8)); 27.8 (*d*, ^3J(10,P) = 2.3, C(10)); 21.6 (C(9)). ^{31}P-NMR (242.9 MHz, $CDCl_3$)[20]): −16.7 (*d*br. *dd*, ^1J(P,F) = 1003, ^3J(P,H$_{ax}$–C(5)) = ^3J(P,H–C(1)) = 15, ^3J(P,H$_{eq}$–C(5)) = 10, ^4J(P,Hax–C(10)) ≈ 2). ^{19}F{^{1}H}-NMR (564.5 MHz, $CDCl_3$): −75.3 (*d*, ^1J(F,P) = 1003). ^{19}F-NMR (564.5 MHz, $CDCl_3$): −75.3 (*m*, *d*-like, ^1J(F,P) = 1003, ^4J(F,H–C(1)) ≈ ^4J(F,H$_{ax}$–C(5)) ≈ ^4J(F,H$_{eq}$–C(5)) ≈ ^5J(F,H$_{eq}$–C(10)) ≈ 2. EI-MS: 285 (6, $M^{+\bullet}$), 194 (4, $[M - PhCH_2]^+$), 171 (9), 160 (20), 91 (100, $PhCH_2^+$), 65 (16). Anal. calc. for $C_{13}H_{17}FNO_3P$ (285.24): C 54.75, H 6.01, N 4.91; found: C 54.66, H 5.80, N 4.84.

*(1*RS,*3*RS,*6*SR,*7*RS*)-7-Benzyl-3-fluoro-7-methyl-2,4-dioxa-7-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**61**). The mixture of **59a** (33 mg) and methyl trifluoromethanesulfonate (33 µl) was heated at 100° in a dry flask under dry N_2 (30 min), then evaporated, and dried at 50°/0.05 Torr to afford a colorless viscous oil (35 mg, 100%). According to ^{31}P-NMR (121.4 MHz, CD_3CN), the oil consisted of **60** (80%) as a mixture of *N*-epimers (A = Me$_{ax}$, B = Me$_{eq}$, A/B *ca.* 10:1), its hydrolysis product (15%; δ −7.0 (*d*, ^3J(P,H$_{eq}$–C(5)) = 21.0), and starting **59a** (5%).

Data of **61**: ^{1}H-NMR (300 MHz, CD_3CN): 7.54–7.48 (*m*, H–C(2′) to H–C(6′)); 5.18 (*A* of *ABX*–*P*, ^2J = 11.2, ^3J(5eq,P) = 24.5, ^3J(5eq,6) = 4.5, H$_{eq}$–C(5)); 4.92 (*tdd*, ^3J(1,6) = ^3J(1,10ax) = 10.7, ^3J(1,10eq) = 4.8, ^3J(1,P) = 1.0, H–C(1)); 4.88 (*B* of *ABX*–*P*, $^2J = {}^3J$(5ax,6) = 11.2, ^3J(5ax,P) = 1.5, H$_{ax}$–C(5)); 4.63, 4.18 (*AB*, ^2J = 13.0, Ph*C*H$_2$); 3.84 (*X* of *ABX*–*P*, ^3J(6,5ax) = 11.2, ^3J(6,1) = 10.7, ^3J(6,5eq) = 4.5, H–C(6)); 3.25 (*m*, *dquint.*-like, $w_{1/2} \approx 15$, $^2J \approx 11$, H$_{eq}$–C(8)); 3.00 (*m*, *qt*-like, $w_{1/2} \approx 25$, H$_{ax}$–C(8)); 2.39 (*s*, MeN); 2.26 (*m*, *dt*-like, $w_{1/2} \approx 15$, H$_{eq}$–C(10)); 2.04 (*m*, *d*-like, $w_{1/2} \approx 15$, $^2J \approx 12$, H$_{eq}$–C(9)); 1.93–1.78 (*m*, *qt*-like, H$_{ax}$–C(9), H$_{ax}$–C(10)). ^{13}C-NMR (75.4 MHz, CD_3CN): 132.4 (C(3′), C(5′)); 131.6 (C(4′)); 130.5 (C(2′), C(6′)); 128.7 (C(1′)); 121.3 (*q*, ^1J(C,F) = 318, CF_3SO_3); 78.4 (*dd*, ^2J(1,P) = 7.8, ^3J(1,F) = 1.6, C(1)); 68.3 (*d*, ^2J(5,P) = 8.9, C(5)); 60.4 (*d*, ^3J(6,P) = 5.2, C(6)); 59.3 (Ph*C*H$_2$); 53.8 (C(8)); 29.4 (*d*, ^3J(10,P) = 9.5, C(10)); 20.5 (*d*, ^4J(9,P) = 2.3, C(9)); 20.0 (MeN). ^{31}P-NMR (121.4 MHz, CD_3CN): epimer A: −17.4 (*dd*, ^1J(P,F) = 1020, ^3J(P,H$_{eq}$–C(5)) = 24.5); epimer B: −15.2 (*dd*, ^1J(P,F) = 1039, ^3J(P,H$_{eq}$–C(5)) ≈ 25). ESI-MS: 300 (100, $[M - CF_3SO_3]^+$].

*(1*RS,*3*RS,*6*SR*)-3-Fluoro-7,7-dimethyl-2,4-dioxa-7-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**62**)[8]). *a*) A soln. of **59a** (53 mg) and trifluoromethanesulfonic acid (16 µl) in abs. MeOH (4 ml) was hydrogenolyzed with 10% Pd/C (60 mg) by vigorous stirring under a slight pressure of H_2 (rubber balloon, 15 min). The catalyst was removed by filtration over *Celite*, the residue washed with MeOH, the filtrate evaporated, and the resulting viscous oil dried at 50°/0.05 Torr. Then, methyl trifluoromethanesulfonate (205 µl) and Li_2CO_3 (26 mg) in abs. MeCN (5 ml) were added to the crude product, and the mixture was sonicated until it became clear (r.t., 1 h.). After removal of the volatile components at 50°/0.05 Torr, the residue was washed twice with $CHCl_3$ and dried at 50°/0.05 Torr to afford crude **62** as a clear viscous oil (40 mg, 100%). According to ^{13}C- and ^{31}P-NMR spectra, the anticipated signals for **62** are present but the product is quite impure. ^{1}H-NMR (300 MHz, CD_3CN): not interpretable mixture, no arom. H. ^{13}C-NMR (75.4 MHz, CD_3CN)[24]): 121.4 (*q*, ^1J(C,F) = 320, CF_3SO_3); 78.4 (*d*, ^2J(1,P) = 7.6, C(1)); 68.9 (*d*, ^2J(5,P) = 8.1, C(5)); 53.9 (*d*, ^3J(6,P) = 6.0, C(6)); 46.4 (C(8)); 42.6 (Me$_{eq}$–N); 32.2 (Me$_{ax}$–N); 29.3 (*d*, ^3J(10,P) = 9.0, C(10)); 20.7 (C(9)). ^{31}P-NMR (121.4 MHz, CD_3CN)[19]): −16.8 (*dd*, ^1J(P,F) = 1016, ^3J(P,H$_{eq}$–C(5)) = 24.5). *b*) To the soln. of **64** (68 mg) in anh. THF

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[23]) Coupling constants from ^{1}H,^{1}H–COSY and heteronuclear decoupling experiments; H$_{eq}$–C(5) resonates 8 Hz downfield from H–C(1).

[24]) Only the signals relevant for the supposed structure **62** are indicated.

(0.5 ml), $POCl_2F$ (21 µl) was added (r.t.). After 1 min, the volatile components were removed and the residue dried at 30°/0.05 Torr to yield a viscous oil (82 mg, 100%). According to ^{31}P-NMR (121.4 MHz, $(CD_3)_2CO$), the mixture contained **62** (δ −18.1 (*dd*, ^1J(P,F) = 1030, ^3J(P,H_{eq}−C(5)) ≈ 25) and probably also the respective equatorial epimer (δ −8.7 (*dt*-like, ^1J(P,F) = 950, ^3J(P,H_{ax}−C(5)) ≈ ^3J(P,H_{eq}−C(5) ≈ 8)), besides $POF(OH)_2$ (δ −6.9 (*d*, ^1J(P,F) = 925)) and several other minor components.

*(*1RS,*3*RS,*6*SR*)-3-Fluoro-2,4-dioxa-7-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**65**). A soln. of **59a** (28 mg) and trifluoromethanesulfonic acid (8.6 µl) in abs. EtOH (1 ml) was hydrogenolysed over 10% Pd/C (40 mg) by vigorous stirring under a slight pressure of H_2 (rubber balloon). After complete debenzylation (15 min; TLC control), the catalyst was removed by filtration through a glass-fiber filter and the clear soln. evaporated and dried at 30°/0.05 Torr: **65** as a colorless, hygroscopic oil (34 mg, 100%).

Applying the analogous conditions to **59b** afforded **65** (100%).

Data of **65**: IR (Film): 3482*w* (br.), 3032*m* (br.), 2851*m*, 2364*w*, 2340*w*, 2261*w*, 1472*m*, 1457*m*, 1437*w*, 1440*m*, 1224*s*, 1165*s*, 1107*s*, 1080*s*, 1027*s*, 1046*s*, 985*m*, 930*w*, 947*m*, 926*m*, 904*m*, 887*m*, 871*m*, 841*w*, 807*w*, 700*m*, 787*w*, 760*w*, 639*s*, 578*w*, 556*m*, 522*m*, 512*w*. ^{1}H-NMR (300 MHz, CD_3CN): 7.67 (br. *s*, NH_2); 4.79 (*td*, ^3J(1,6) = ^3J(1,10ax) = 10.6, ^3J(1,10eq) = 4.6, H−C(1)); 4.66 (*A* of *ABX*−*P*, ^2J = 11.1, ^3J(5eq,P) = 24.5, ^3J(5eq,6) = 4.7, H_{eq}−C(5)); 4.58 (*B* of *ABX*−*P*, ^2J = ^3J(5ax,6) = 11.1, ^3J(5ax,P) = 1.2, H_{ax}−C(5)); 3.66 (*X* of *ABX*−*P*, ^3J(6,5ax) = 11.1, ^3J(6,1) = 10.7, ^3J(6,5eq) = 4.5, H−C(6)); 3.50 (*m*, *dquint.*-like, $w_{1/2}$ ≈ 15, ^2J ≈ 12, H_{eq}−C(8)); 3.04 (*m*, *qt*-like, $w_{1/2}$ ≈ 25, H_{ax}−C(8)); 2.29 (*m*, *dt*-like, $w_{1/2}$ ≈ 15, ^2J ≈ 11, H_{eq}−C(10)); 2.06 (*m*, *d*-like, $w_{1/2}$ ≈ 15, H_{eq}−C(9)); 1.90–1.80 (*m*, *qt*-like, H_{ax}−C(9), H_{ax}−C(10)). ^{13}C-NMR (75.4 MHz, CD_3CN): 121.9 (*q*, ^1J(C,F) = 320, CF_3SO_3); 76.5 (*dd*, ^2J(1,P) = 7.9, ^3J(1,F) = 1.9, C(1)); 67.2 (*d*, ^2J(5,P) = 8.6, C(5)); 52.6 (*d*, ^3J(6,P) = 6.0, C(6)); 44.9 (C(8)); 28.1 (*d*, ^3J(10,P) = 9.3, C(10)); 19.3 (*d*, ^4J(9,P) = 2.4, C(9)). ^{31}P-NMR (121.4 MHz, CD_3CN): −17.1 (*dd*, ^1J(P,F) = 1020, ^3J(P,H_{eq}−C(5)) = 24.5). CI-MS: 213 (46, $[M+NH_4]^+$), 197 (15, $[M+H]^+$), 196 (100, M^+), 164 (20).

*(*1RS,*3*RS,*6*RS*)-3-Fluoro-2,4-dioxa-7-azonia-3-phosphabicyclo[4.4.0]decane 3-Oxide Trifluoromethanesulfonate* (**66**). As described above, **60a** (47 mg) in EtOH (1 ml) was hydrogenolyzed over 10% Pd/C (59 mg) in the presence of trifluoromethanesulfonic acid (14.5 µl): **66** (57 mg, 100%). Colorless, hygroscopic foam.

Applying the analogous conditions to **60b** afforded **66** (100%).

Data of **66**: IR (Film): 3488*w* (br.), 3024*m* (br.), 2846*m*, 2360*w*, 2262*w*, 1610*w*, 1449*m*, 1376*w*, 1343*m*, 1322*m*, 1288*s*, 1239*s*, 1224*s*, 1168*m*, 1130*m*, 1095*m*, 1029*s*, 1016*s*, 986*m*, 937*m*, 947*m*, 915*m*, 881*m*, 831*m*, 761*m*, 739*w*, 638*s*, 579*w*, 542*w*, 521*m*, 507*w*. ^{1}H-NMR (300 MHz, CD_3CN): 6.56 (br. *s*, NH_2); 5.15 (*m*, $w_{1/2}$ ≈ 6, H−C(1)); 4.81 (*A* of *ABX*−*P*, ^2J = 12.5, ^3J(5ax,6) = ^3J(5ax,P) = 1.7, H_{ax}−C(5)); 4.65 (*B* of *ABX*−*P*, ^2J = 12.5, ^3J(5eq,P) = 25.0, ^3J(5eq,6) = 1.7, H_{eq}−C(5)); 3.66 (*X* of *ABX*−*P*, ^3J(6,1) = ^3J(6,5ax) = ^3J(6,5eq) = 1.7, H−C(6)); 3.84 (*m*, *d*-like, $w_{1/2}$ ≈ 15, ^2J ≈ 13, H_{eq}−C(8)); 3.16 (*td*, ^2J = ^3J(8ax,9ax) = 12.8, ^3J(8ax,9eq) = 3.4, H_{ax}−C(8)); 2.18 (*m*, *dt*-like, $w_{1/2}$ ≈ 15, ^2J ≈ 12, H_{eq}−C(10)); 2.02–1.77 (*m*, CH_2(9), H_{ax}−C(10)). ^{13}C-NMR (75.4 MHz, CD_3CN): 120.5 (*q*, ^1J(C,F) = 320, CF_3SO_3); 76.5 (*d*, ^2J(1,P) = 7.1, C(1)); 70.1 (*d*, ^2J(5,P) = 7.2, C(5)); 50.8 (*d*, ^3J(6,P) = 4.8, C(6)); 44.3 (C(8)); 26.5 (*d*, ^3J(10,P) = 8.7, C(10)); 15.1 (*d*, ^4J(9,P) = 2.4, C(9)). ^{31}P-NMR (121.4 MHz, CD_3CN): −17.0 (*ddd*, ^1J(P,F) = 1016, ^3J(P,H_{eq}−C(5)) = 25.0, ^4J(P,H_{ax}−C(10)) = 4.6). CI-MS: 213 (32, $[M+NH_4]^+$), 197 (10, $[M+H]^+$), 196 (100, M^+), 164 (15).

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