MILD PREPARATION OF 1-BENZYLOXYIMINOALKYLPHOSPHONIC DICHLORIDES: APPLICATION TO THE SYNTHESIS OF CYCLIC PHOSPHONIC DIESTERS AND CYCLIC MONOESTER AMIDES

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Abstract - *1-Benzyloxyiminophosphonates (**3**) were converted under very mild conditions to the corresponding phosphonyl dichlorides (**5**). The application toward the synthesis of diastereomeric 1,3,2-oxazaphospholidines (**6/7**), and diastereomeric 1,3,2-dioxaphosphorinanes (**8/9**) is reported. The structure of **9a** was confirmed by X-ray analysis.*

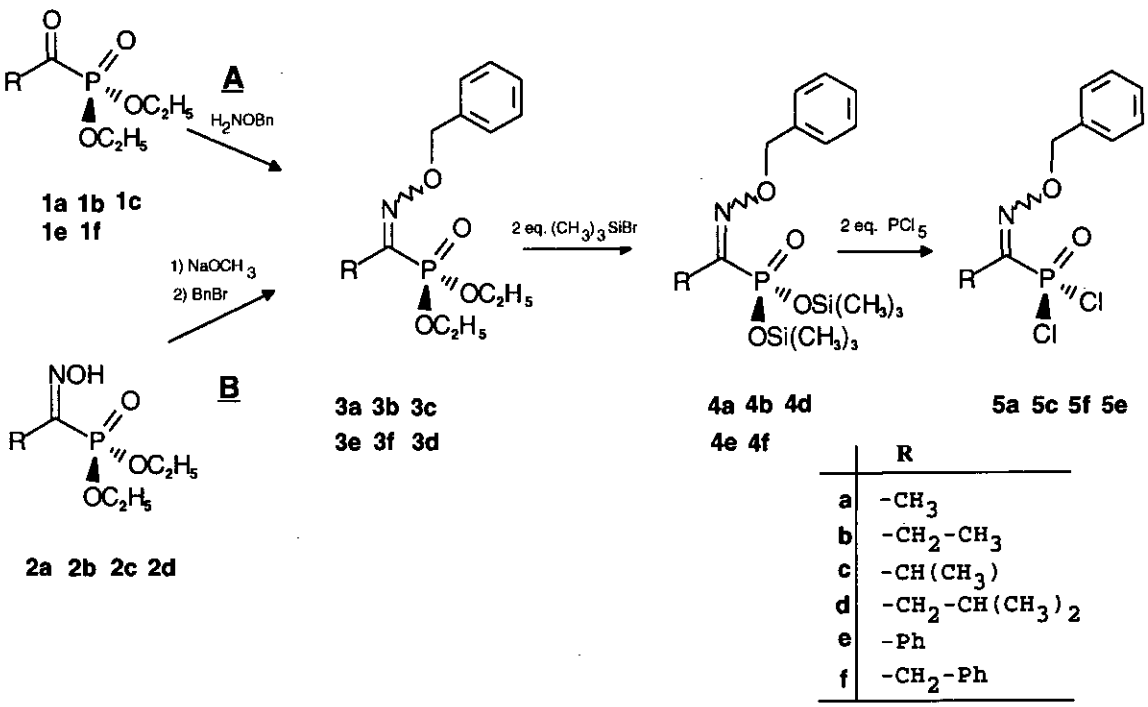
Introduction

While dialkyl α-oxyiminophosphonates are readily available from acylphosphonates, the chemistry of the *O*-alkyl ethers is, apart from their use as synthons for the synthesis of α-aminophosphonic acids [2], poorly explored.[1] We consider this group of compounds worthy of interest, because of their potential use as chiral starting materials for the asymmetric synthesis of enantiomeric pure 1-hydroxyaminophosphonates.

The present paper describes the results of our studies concerning the preparation and reactions of 1-benzyloxyiminophosphonoyl dichlorides (**5**) with (-) ephedrine and chloramphenicol.

Results and Discussion

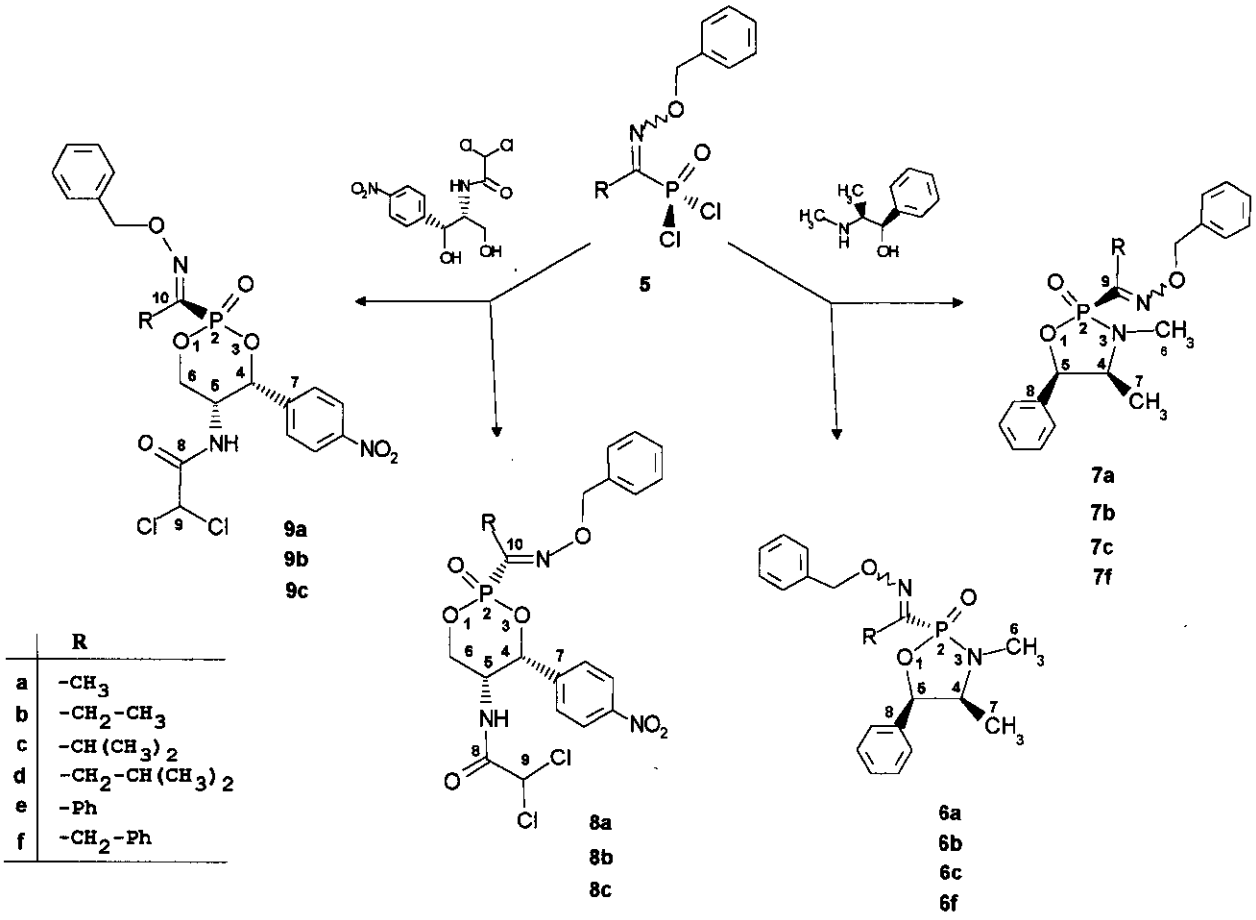
Dialkyl α-hydroxyiminophosphonates were first obtained by reaction of dialkyl-acylphosphonates [2] with hydroxylamine [3]. Application of this method using *O*-benzylhydroxylamine for preparation of α-benzyloxyiminophosphonates (**3**) also proved to be a reliable procedure, which yielded the desired compounds in high yields (method **A**). Examination of the products obtained by ^{31}P-nmr spectroscopy revealed that in most cases **3** was composed of two isomeric oximes [$\Delta\delta$ ^{31}P 4-6 ppm in $CDCl_3$].[4]



Scheme 1

A second way for the preparation of **3** in good yields is the alkylation of deprotonated oximes (**2**) with benzyl bromide in boiling methanol. Compounds (**3 a-f**) are colourless oils, which are poorly soluble in unpolar solvents like pentane, but very good soluble in dichloromethane, chloroform and diethylether. ^{31}P nmr studies indicated, that in contrast to method **A** products prepared this way were composed except **3c** exclusively of the *E*-isomer.[5] Beside ^{31}P-nmr measurements ^{13}C-nmr spectroscopy was found to be a useful diagnostic tool for indicating

Scheme 2: Preparation of 1,3,2-oxazaphospholidines (**6**/**7**) and 1,3,2-dioxaphosphorinanes (**8**/**9**)



	R
a	$-CH_3$
b	$-CH_2-CH_3$
c	$-CH(CH_3)_2$
d	$-CH_2-CH(CH_3)_2$
e	$-Ph$
f	$-CH_2-Ph$

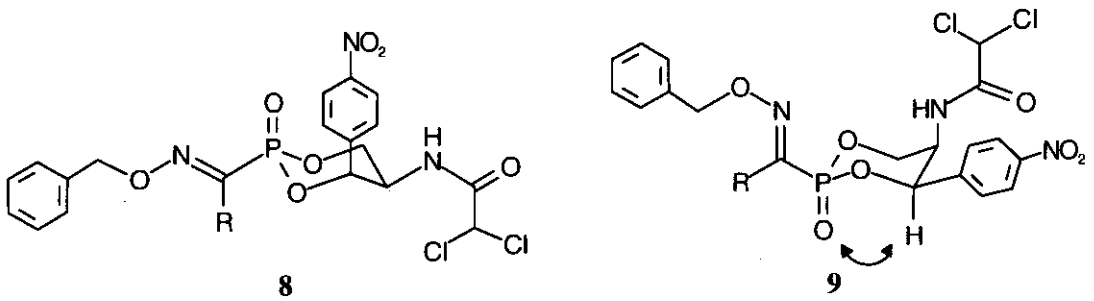
structural assignments. While (*Z*)-1-benzyloxyiminophosphonates showed in ^{13}C-nmr measurements ^{1}J (P,C) coupling constants of 160 ± 5 Hz, ^{1}J (P,C) values of *E*-configurated oximes ranged between 200 and 220 Hz.

Attempts to synthesize the phosphonoyl dichlorides (**5**) using established methods were unsuccesful and resulted in loss of starting material without formation of the desired phosphonoyl dichlorides (**5**). This was not wholly unexpected since these methods require conditions which can alter various functional groups and can even cause phosphorus-carbon bond rupture[6]. Consequently we sought a more mild and convenient way for the preparation of **5**. We found, that reaction of the phosphonates (**3**) with bromotrimethylsilane in dichloromethane [7] for 6 h at room temperature resulted in complete dealkylation, whereas at reaction temperatures above 40°C cleavage of the nitrogen-oxygen bond was observed. Evaporation of all volatiles at 40°C/ 10^{-3}torr resulted quantitative the very clean, moist sensitive bis(trimethylsilyl)phosphonates (**4**) as colorless oils, which are very good soluble in dichloromethane and ether and not distillable without decomposition. Treatment of **4** with 2 equivalents of PCl_5 in dichloromethane [7] at 40°C, followed by removal of the resulting phosphoryl chloride and chlorotrimethylsilane in vacuo (30°C, 10^{-3} torr) yielded the phosphonoyl dichlorides (**5**) as viscous, yellow brown liquids, which could be seperated by very careful bulb-to-bulb destillation; in some cases, however, distillation resulted in a rather violent decomposition. Alternatively it was also possible to use crude **5** by estimating formed **5** at 80%, thereby avoiding a dangerous destillation step.

Reaction of **5** in dry ether or in dry tetrahydrofuran with (-)-ephedrine and two equivalents of triethylamine led to the diastereomeric cyclic phosphonic monoester amides (**6**) and (**7**), which could easily separated on silica gel, using ether/acetone. Compounds (**6**) and (**7**) are with the exception of **6a** highly viscous, pale yellow oils, which decomposed upon standing for several days. Formed diastereomers (**6**) and (**7**) could be differentiated by ^{1}H-nmr experiments. Compared to **6** the ^{1}H-nmr spectra of **7** showed a downfield shift of 0.45 ppm for the cyclic H-5 proton and 0.1 ppm for the cyclic H-4 proton , attributed to the anisotropic effect of the adjacent P=O group.[8]

Reaction of **5** in dry tetrahydrofuran with chloramphenicol and three equivalents of triethylamine gave the diastereomeric 1,3,2-dioxaphosphorinanes (**8**) and (**9**), which also were easily separable on silica gel, using chloroform/acetonitrile as eluent. **8a-c** and **9a-c** are pale yellow, crystalline solids, poorly soluble in ether and very good soluble in tetrahydrofuran and chloroform.

Whereas yields of **9** ranged from 30% - 38%, only small amounts of **8** were obtained, due to the fact of the axial positioned 4-nitrophenyl group in compounds (**8**) as shown in Scheme 3.



Scheme 3

Compared to **8**, the ^{1}H-nmr spectra of **9a - c** show a downfield shift of 0.5 ppm for the benzylic cyclic H-4 proton, explained by the anisotropic effect of the adjacent P=O group as depicted in Scheme 3. This assumption was verified by X-ray crystallographic analysis of compound (**9a**) (Figure 1).

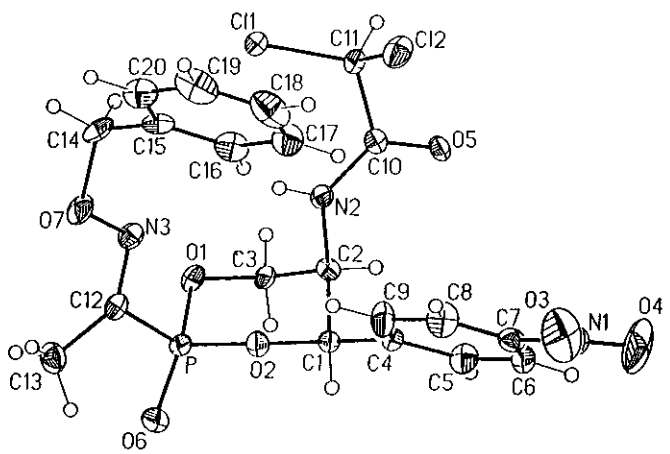


Figure 1: X-Ray crystallographic structure of **9a**

EXPERIMENTAL

Melting points were determined on an electrothermal digital melting point apparatus and are uncorrected. Ir spectra were recorded on a Carl Zeiss DMR4 spectrophotometer. ^{1}H- and ^{13}C-Nmr spectra were obtained with a Bruker WM-250 instrument using $CDCl_3$ as solvent unless otherwise indicated. All chemical shifts are reported in ppm downfield from internal tetramethylsilane; coupling constants J are given in Hz. ^{31}P-Nmr spectra were recorded on a Bruker AC 200 at 81.0 MHz (internal standard 85% H_3PO_4). EI mass spectra were recorded on a Varian MAT 311A spectrometer (70eV).- Numbering of atoms in 1,3,2-oxazaphospholidines and 1,3,2-oxazaphosphinanes was labelled as depicted in Scheme 2.

General procedure for preparation of 1-benzyloxyiminophosphonates 3:

Method A: To a solution of 10 mmol of acylphosphonate [9] (**1**) (**1a**: 1.8g, **1b**: 1.95g, **1c**: 2.1g, **1d**: 2.55g) in 20 ml of dry ethanol was added 1.6 g (10 mmol) of *O*-benzylhydroxylamine hydrochloride,[10] dissolved in 10 ml of dry pyridine. The solution was stirred at 45°C for 12 h. After evaporation of the solvent under reduced pressure, the residue was suspended in 60 ml of ether. The organic phase was washed with 30 ml of 1M HCl, H_2O (50 ml x3) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the oily residue was chromatographed on silica gel with ether: n-hexane (9:1) to give **3** as colorless oils.

Method B: To a solution of 0.54 g (10 mmol) of NaOMe in 50 ml of dry methanol was added dropwise a solution of 10 mmol of 1-hydroxyiminophosphonate **2** (**2a:** 1.95 g, **2b:** 2.1 g, **2c:** 2.25 g). After stirring 30 min at 50°C, 1.71 g (10 mmol) of benzyl bromide was added and refluxed for 5 h. Evaporation of the solvent under reduced pressure afforded a pulpy residue, which was suspended in 60 ml of ether. The organic phase was washed with H_2O (50 ml x3) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the oily residue was chromatographed on silica gel with n-hexan:ether (1:9) to give **3** as colorless oils.

(E)-Diethyl 1-benzyloxyiminoethylphosphonate (3a) 2.55g (89%) (method A) resp. 2.0 g (70%) (method B) were obtained as colorless oil. ^{1}H-Nmr ($CDCl_3$) δ :1.29 (6H, m, O-CH_2-$C\underline{H}_3$), 2.05 (d, 3H, **CH_3**, J= 12.2), 4.12 (m, 4H, O-$C\underline{H}_2$-CH_3), 5.25 (s, 2H, O-$C\underline{H}_2$-Ph), 7.28-7.37 (m, 5H, **H_{Ar}**).- ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ : 12.7 (d, **C-2**, $^{3}J(P,C)$= 16.2), 16.2 (d, O-CH_2-CH_3, $^{3}J(P,C)$= 6.1), 63.0 (d, O-CH_2-CH_3, $^{2}J(P,C)$= 6.1), 77.0 (s, O-CH_2-Ph), 128.1, 128.3, 128.6, 129 (s, **C_{Ar}**), 137.2 (s, C_i), 151.4 (d, **C-1**, $^{1}J(P,C)$= 213). ^{31}P-Nmr δ: 7.90. Ir (NaCl, film) ν = 3100(w), 3070(w), 3040(m), 3000(s), 2940(s), 2910(m), 2880(m), 1605(m) **C=N**, 1500(m), 1480(m), 1455(m), 1445(m), 1395(m), 1370(s), 1275(s,b) **P=O**, 1200(m), 1165(m), 1100(m), 1025(s,b) **P-O-C**,

985(s,b) **P-O-C**, 885(m,b), 795(s), 755(s), 730(s), 700(s), 610(s), 595(m) cm^{-1}. Anal. Calcd for $C_{13}H_{20}NO_4P$: C,54.73; H,7.06; N,4.91; P,10.86. Found: C,54.67; H,7.21; N,5.02; P,10.64.

(E)-Diethyl 1-benzyloxyiminopropylphosphonate (3b) 2.55 g (85%) (method A), 1.85 g (61.9%) (method B), colorless oil. ^{1}H-Nmr ($CDCl_3$) δ = 1.12 (t, 3H, **CH$_3$**, ^{3}J(P,H)= 8.0), 1.30 (virt. t, 6H, O-CH_2-C**H$_3$**), 2.52 (dq, 2H, **CH$_2$**, ^{3}J(P,H)= 12.8), 4.10 (m, 4H, O-C**H$_2$**-CH_3), 5.22 (s, 2H, O-C**H$_2$**-Ph), 7.2-7.4 (m, 5H, Ar-**H**). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ =10.4 (s, **C-3**), 16.2 (d , O-CH_2-**C**H_3, ^{3}J(P,C)= 6.2), 20.8 (d, **C-2**, ^{2}J(P,C)= 15.2), 62.9 (d, O-**C**H_2-CH_3, ^{2}J(P,C)= 6.1), 76.9 (s, O-**C**H_2-Ph), 128.0, 128.2, 128.4, (s, **C$_{Ar}$**), 137.3 (s, **C$_i$**), 156.4 (d, **C-1**, ^{1}J(P,C)= 206.2). ^{31}P-Nmr ({^{1}H}, $CDCl_3$) δ= 7.8. Ir (NaCl, film) ν = 3090(w), 3070(w), 3040(w), 2080(s), 2940(m), 1600(w) **C=N**, 1500(w), 1480(w), 1455(m), 1440(m), 1390(m), 1370(m), 1250(s) **P=O**, 1210(w), 1185(w), 1160(m), 1100(m), 1050(s), 1025(vs,b) **P-O-C**, 980(s), 950(s), 880(w), 800(m), 760(s), 730(m), 700(s), 600(s), 590(s) cm^{-1}. Anal. Calcd for $C_{14}H_{22}NO_4P$: C,56.18; H;7.40; N,4.68; P,10.35. Found: C, 56.25; H,7.36; N,4.62; P,10.17.

Diethyl 1-benzyloxyimino-2-methylpropylphosphonate (3c) yield 2.45 g (78%) (method A:), 2.1 g (70.0%) (method B), colourless oil. ^{1}H-Nmr ($CDCl_3$) δ = 1.22 (m, 12H, O-CH_2-C**H$_3$** ,**H-3** , **H-4**), 2.88 (m, 1H, **H-2**, Z-isomer), 3.30 (m, 1H, **H-2**, E-isomer), 4.10 (m, 4H, O-C**H$_2$**-CH_3), 5.22 (s, 2H, O-C**H$_2$**-Ph), 7.22-7.40 (m, 5H, **H$_{Ar}$**). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) E-isomer: δ = 16.3 (d, O-CH_2-**C**H_3,^{3}J(P,C)= 6.1), 18.8 (virt. d, **C-3 + C-4**), 28.1 (d, **C-2**, ^{2}J(PC)= 15.4), 62.8 (d, O-**C**H_2-CH_3, ^{2}J(P,C)= 6.2), 77.1 (s, O-**C**H_2-Ph), Z-isomer: 16.3 (d, O-CH_2-**C**H_3,^{3}J(P,C)= 6.1), 20.72(virt. d, **C-3 + C-4**), 32.8 (d, **C-2**, ^{2}J(P,C)= 16.8), 62.2 (d, O-**C**H_2-CH_3, ^{2}J(P,C)= 6.2),77.1 (s, O-**C**H_2-Ph,), 127.9, 128.0, 128.1, 128.3, 128.4 (s, **C$_{Ar}$**), 137.2(s,**C$_i$**), 157.2 (d, **C-1**, ^{1}J(P,C)= 148.2).^{31}P-Nmr ($CDCl_3$, {^{1}H}) δ = 2.9 (Z-isomer), 7.6 (E-isomer). Ir (NaCl, film) ν = 3080(w), 3060(w), 3020(w), 2970(s), 2920(m), 2860(m), 1580(m,b) **C=N**, 1495(w), 1465(m), 1450(m), 1390(m), 1360(m), 1250(s) **P=O**, 1205(m), 1160(m), 1120(m), 1080(m), 1050(s) **P-O-C**, 1020(s) **P-O-C**, 965(s), 850(w,b), 795(m), 750(s), 690(s), 600(s), 590(s) cm^{-1}. Anal. Calcd for $C_{15}H_{24}NO_4P$: C,57.50; H,7.72; N,4.47; P,9.89. Found: C,57.24; H,7.61; N,4.75; P,9.74.

(E) Diethyl 1-benzyloxyimino-3-methylbutylphosphonate (3d) yield 1.75 g (53%) (method B); colorless oil. ^{1}H-Nmr ($CDCl_3$) δ = 0.95 (virt. d, 6H, **H-4, H-4´**, ^{3}J(H,H)= 6.8), 1.30 (virt. t, 6H, O-CH_2-CH_3), 2.09 - 2.21 (m, 1H, **H-3**), 2.43 (dd, 2H, **H-2,** ^{3}J(H,H)= 7.5, ^{3}J(P,H) = 14.9), 4.08 (m, 4H, O-C**H$_2$**-CH_3), 5.21 (s, 2H, O-C**H$_2$**-Ph), 7.3 (m, 5H, **H$_{Ar}$**). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 16.0 (d, O-CH_2-**C**H_3, ^{3}J(P,C)= 6.2), 22.5 (s, **C-4**, **C-5**), 26.2 (s, **C-3**), 35.8 (d, **C-2**, ^{3}J(P,C) 15), 62.6 (d, O-**C**H_2CH$_3$, ^{2}J(P,C)= 6.2), 76.7 (s, O-**C**H_2-Ph), 127.7, 127.8, 128.1 (s, **C$_{Ar}$**), 137.0 (s, **C$_i$**), 154.8 (d, **C-1**, ^{1}J(P,C)= 207). Ir(NaCl, film) ν= 3100(w), 3080(m),

3040(m), 2980(s), 2940(s), 2920(s), 2880(s), 1595(m), 1500(m), 1470(s), 1460(s), 1390(s), 1370(s), 1265(s,b), 1215(m), 1170(s), 1100(s), 1025(s), 970(s,b), 880(m), 790(s,b), 755(s,b), 740(s), 700(s), 605(s), 595(s) cm^{-1}. HRms: 327.1608 calcd for $C_{16}H_{26}NO_4P$: 327.1600.

(E)/(Z) Diethyl 1-benzyloxyiminobenzylphosphonate (3e) yield: 2.95g (85%) (method A), colorless oil. ^{1}H-Nmr ($CDCl_3$) δ = 1.20 (m, 6H, O-CH_2-C**H**$_3$), 3.9-4.2 (m, 4H, O-C**H**$_2$-CH_3), 5.22 (s, ½ v. 2H, O-CH_2-Ph), 5.35 (s, ½ v. 2H, O-C**H**$_2$-Ph), 7.21-7.6 (m, 10H, **H**$_{Ar}$). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 16.0 (d, O-CH_2-**C**H_3, ^{3}J(P,C)= 6.7), 62.7(d, O-**C**H_2-CH_3, ^{2}J(P,C)= 6.2), 63.3 (d, ^{2}J(P,C)= 6.4), 77.2 (s, O-CH_2-Ph), 77.7 (s, O-C**H**$_2$-Ph), 127.8, 127.9, 128.0, 128.2, 128.2, 128.2, 128.5, 128.5, 129.1, 129.3 (**C**$_{Ar}$), 130.0 (s, **C**$_i$), 133.8 (d, **C-2**), 136.6 (s, **C**$_i$), 137.0 (s, **C**$_i$), 151.7 (d, **C-1**, ^{1}J(P,C)= 212, E-Isomer), 152.0 (d, **C-1**, ^{1}J(P,C)= 155, Z-Isomer). ^{31}P-Nmr ({^{1}H}, $CDCl_3$) δ= 1.3 (Z-isomer), 6.1 (E-isomer). Ir (NaCl,film) ν= 3100(m), 3070(m), 3040(m), 2990(s), 2940(s), 2920(s), 2880(m), 1585(m), 1500(s), 1480(m), 1460(s), 1450(s), 1395(s), 1370(s), 1260(vs), 1215(m), 1170(s), 1100(s,sh), 1030(vs,b), 960(vs,b), 795(s), 770(s,b), 695(s), 650(m), 600(s,sh) cm^{-1}. Anal. Calcd for $C_{18}H_{22}NO_4P$: C,62.24; H,6.38; N,4.03. Found: C,61.89; H,6.27; N,4.12.

Diethyl 1-benzyloxyimino-2-phenylethylphosphonate (3f) yield 2.00 g (55%) (method A), colorless oil. ^{1}H-Nmr ($CDCl_3$) δ= 1.08-1.21 (m, 6H, O-CH_2-C**H**$_3$), 3.73 (d, H-2, ^{3}J(P,H)= 12.7), 3.88 (d, H-2, ^{3}J(P,H)= 13.7, Z-isomer), 5.36 (s, 2H, O-C**H**$_2$-Ph), 7.2-7.6 (m, 10H, H$_{Ar}$). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 16.0 (d, O-CH_2-**C**H_3, ^{3}J(P,C)= 6.2), 33.1 (d, C-2, ^{2}J(P,C)= 15.8, E-isomer), 38.9 (d, C-2, ^{2}J(P,C)= 17.4, Z-isomer), 62.9 (d, O-**C**H_2-CH_3, ^{2}J(P,C)= 5.8), 77.2 (s, O-**C**H_2-Ph), 126.5, 126.6, 128.0,128.3, 129.2, 129.3, (s, C$_{Ar}$), 135.5 (s, C$_2$), 137.0 (s, C$_i$), 153.4 (d, C-1, ^{1}J$_{PC}$= 208). ^{31}P-Nmr ({^{1}H}, $CDCl_3$) δ= 2.0(Z), 7.3(E). Ir (NaCl, film) ν= 3100(w), 3080(w), 3040(m), 2995(s), 2940(m), 2920(m), 2880(w,sh), 1610(w), 1590(w), 1500(s), 1460(s), 1395(m), 1370(m), 1265(s,b), 1170(m), 1100(m), 1030(s,b), 980(s,b), 890(w), 800(s), 735(s,sh), 700(s), 650(w), 610(s), 600(s) cm^{-1}. Anal. Calcd for $C_{19}H_{24}NO_4P$: C,63.15; H,6.69; N,3.88; P,8.57. Found: C,62.94; H,6.86; N,4.15; P,8.39.

General procedure for preparation of bis(trimethylsilyl)phosphonates 4:

To a solution of 3.5 mmol of **3** (**3a:** 1.0 g, **3b:** 1.1 g, **3d:** 1.15 g, **3e:** 1.25 g, **3f:** 1.3 g) in 30 ml of dry dichloromethane was added 0.9 ml (7.0 mmol) of bromotrimethylsilane. The pale yellow solution was stirred for 5 h at room temperature. Evaporation of all volatile compounds under reduced pressure (40°C/0.01 torr) afforded **4** as clean, colorless oils in quantitative yield.

Bis(trimethylsilyl) 1-benzyloxyiminoethylphosphonate 4a . colorless oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.21 (s, 18H, -O-Si-C**H**$_3$), 1.98 (d, ^{3}J(P,H)= 12.0, 3H, H-2), 5.15 (s, 2H, O-C**H**$_2$-Ph), 7.2 - 7.35 (m, 5H, H$_{Ar}$). ^{13}C-Nmr

($CDCl_3$, {^1H}) δ= 0.8 (s, O-Si-CH_3), 12.4 (d, ^2J(P,C)= 17.0, C-2), 76.5 (s, O-CH_2-Ph), 127.9, 128.0, 128.3 (s, C_{Ar}), 137.5 (s, C_i), 153.1 (d, ^1J(P,C)= 222.6, C-1). Ir (NaCl, film) ν =3100(w), 3080(w), 3040(m), 2970(s), 2950(w,sh), 1610(m) C=N, 1500(m), 1460(m), 1370(m), 1260(vs), 1210(s, sh), 1050(s,sh), 930(vs, sh), 855(vs), 760(s), 740(s, sh), 700(s), 665(m), 610(s) cm^{-1}. HRms: 373.1295 calcd for $C_{15}H_{28}NO_4PSi_2$: 373.1297.

Bis(trimethylsilyl) 1-benzyloxyiminopropylphosphonate 4b. colorless oil. ^1H-Nmr ($CDCl_3$) δ= 0.33 (s, 18H, O-Si-CH_3), 1.17 (t, ^3J(H,H)= 8.0, 3H, H-3), 2.58 (dq, ^3J(P,H)= 20.2, ^3J(H,H)= 10.1, H-2), 5.25 (s, 2H, O-CH_2-Ph), 7.30 - 7.50 (m, 5H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^1H}) δ= 0.6 (s, Si-CH_3), 10.4 (d, J(^{3}P,C)= 5.5, **C-3**), 20.4 (d, ^2J(P,C)= 16.3, **C-2**), 76.6 (s, O-CH_2-Ph), 127.8, 127.9, 128.3, (s, C_{Ar}), 137.3 (s, C_i). Ir (NaCl, film) ν= 3090(w), 3060(w), 3040(w), 2960(m), 2940(m), 2880(m), 1600(w) **C=N**, 1455(m), 1365(m), 1260(vs) **Si-CH_3**, 1230(s,b), 1060 - 1020 (s,b) **P-O-C**, **O-Si**, 950(s, sh), 840(s) **Si-CH_3**, 750(m) **Si-CH_3**, 730(m), 700(m) cm^{-1}. HRms: 387.1452 calcd for $C_{15}H_{28}NO_4PSi_2$: 387.1451.

Bis(trimethylsilyl) 1-benzyloxyimino-3-methylbutylphosphonate 4d . colorless oil. ^1H-Nmr ($CDCl_3$) δ= 0.31 (s, 18H, O-SiC<u>H</u>$_3$), 0.98 (d, ^3J(H,H)= 8.1 , 6H, **H-4**, **H-4'**), 2.31 (m, 1H, **H-3**), 2.54 (dd, ^3J(P,H)= 15.8, ^3J(H,H)= 7.8), 5.28 (s, 2H,O-C<u>H</u>$_2$-Ph), 7.31 - 7.45 (m, 5H, H_{Ar}). Ir (NaCl, film) ν= 3100(w), 3075(w), 3040(m), 2970(s), 2940(m), 2880(m), 1600(w) **C=N**, 1560(w), 1540(w), 1500(w), 1470(m), 1455(m), 1380(m), 1260(s) **Si-CH_3**, 1230(s,b), 1080 - 1010 (s,b), 855(s) **Si-CH_3**, 760(s) **SiCH_3**, 740(m), 700(s) cm^{-1}. HRms: 415.1766 calcd for $C_{19}H_{34}NO_4PSi_2$: 415.1764.

Bis(trimethylsilyl) 1-benzyloxyiminobenzylphosphonate 4e. colorless oil. ^1H-Nmr ($CDCl_3$) δ= 0.19 (s, 18H, O-SiC<u>H</u>$_3$), 5.22 (s, 2H, O-CH_2-Ph), 7.28 - 7.58 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^1H}) δ= 0.65 (s, O-Si-<u>C</u>H_3), 77.1 (s, O-CH_2-Ph), 128.0, 128.3, 128.7, 129.2, 130.0, 132.0, 137.2, 137.7 (s, C_{Ar}), 153.2 (d, ^1J(P,C)= 224.4, **C-1**). HRms: 435.1451 calcd for $C_{20}H_{30}NO_4PSi_2$: 435.1451.

Bis(trimethylsilyl) 1-benzyloxyimino-2-phenylethylphosphonate 4f . colorless oil; ^1H-Nmr ($CDCl_3$) δ= 0.15 (s, 18H, O-Si-C<u>H</u>$_3$), 3.87 (d, ^3J(P,H)= 14.4, 2H, H-2), 5.23 (s, 2H, O-C<u>H</u>$_2$-Ph), 6.98 - 7.25 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^1H}) δ= 0.5 (s, O-Si-CH_3), 32.6 (d, ^2J(PC)= 16.9, C-2), 76.6 (s, O-CH_2-Ph), 126.1, 127.7, 127.8, 128.0, 129.0 (s, C_{Ar}), 135.5 (s, C-3), 136.9 (s, C_i), 154.3 (d, $^1J_{P,C}$= 230 , C-1). HRms: 449.1600 calcd for $C_{21}H_{32}NO_4PSi_2$: 449.1608.

<u>General procedure for preparation of phosphonyl dichlorides 5</u>

To a solution of 3.5 mmol of **3** (**3a:** 1.0 g, **3c:**, **3e:**,**3f:** 1.3 g) in 35 ml of dry dichloromethane was added 0.9 ml of (7.0 mmol) bromotrimethylsilane. The pale yellow solution was stirred for 5 h at room temperature. 1.4 g

(7.0 mmol) of PCl_5 were added and the yellow solution was stirred for 1 h at 40°C. Evaporation of all volatile compounds at 40°C / 0.01 torr afforded a viscous brown residue, which was careful distilled in a Kugelrohr apparatus. As in some cases violent decompositions were observed, it is recommended to distillate small amounts (<1 g) of **5** or to use the crude product, estimating formed **5** at 80%.

1-Benzyloxyiminoethylphosphonoyl dichloride 5a. bp 120°-140°C/ 0.01 torr (Kugelrohr apparatus); yield: 0.6g (65%), pale yellow viscous oil. ^{1}H-Nmr ($CDCl_3$) δ=2.20 (d, $^3J(P,H)$= 16.2, 3H, **H-2**), 5.43 (s, 2H, O-C**H**$_2$-Ph), 7.30 - 7.41 (m, 5H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 12.0 (d, $^2J(P,C)$= 22.5, **C-2**), 78.5 (s, O-CH_2-Ph), 128.4, 128.5, 128.6 (s, C_{Ar}), 135.7 (s, C_i), 154.0 (d, $^1J(P,C)$= 190.9, **C-1**). Ms (70eV, 95°C) m/z(%)= 265(2), 230(0.9), 117(3.2), 105(1.6), 91(100), 77(9), 65(7), 50(4), 46(2). HRms: 264.9826 calcd for $C_8H_{10}Cl_2NO_2P$: 264.9826.

1-Benzyloxyimino-2-methylpropylphosphonoyl dichloride 5c. bp 120°-145°C/ 0.01 torr (Kugelrohr apparatus), yield 0.8g (78%). ^{1}H-Nmr ($CDCl_3$) δ=1.32 (d, $^3J(H,H)$= 6.5, 6H, **H-3, H-3'**), 3.34 (m, 1H, **H-2**), 5.30 (s, 2H, O-CH_2-Ph), 7.30 - 7.45 (m, 5H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 18.6 (d,$^3J(P,C)$= 3.5, **C-3**, **C-3'**), 29.8 (-, d, $^2J(P,C)$= 21.3, **C-2**), 78.7 (s, O-CH_2-Ph), 127.5, 128.6, 128.8 (s, C_{Ar}), 136.0 (s, C_i), 161.0 (d, $^1J(P,C)$= 175.3, **C-1**). Ms (70eV, 30°C) m/z(%)= 293(6), 258(1), 166(1), 144(1), 117(2), 105(3), 91(100); 77(20), 65(15), 43(13). HRms: 293.0138 calcd for $C_{10}H_{14}Cl_2NO_2P$: 293.0139.

1-Benzyloxyiminobenzylphosphonoyl dichloride 5e. bp 120°-145°C/ 0.01torr (Kugelrohr apparatus), yield 0.63 g (55.3%). ^{1}H-Nmr ($CDCl_3$) δ= 5.28 (s, 2H, O-C**H**$_2$-Ph), 7.21-7.72(m, 10H, H_{AR}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 78.4 (s, O-CH_2-Ph), 126.3 (d, $^2J(P,C)$= 24.1, C_{AR}-**2**), 128.0, 128.2, 128.5, 128.6, 130.2, 130.3 (s, C_{AR}), 135.2 (s, O-CH_2-C_{AR}), 153.8(d, $^2J(P,C)$= 193, **C-1**). Ms(70ev, 65°C) m/z(%)= 327(0.6), 310(0.1), 215(4), 211(0.6), 163(0.8), 152(0.4), 117(5), 91(100), 77(8), 65(0.4). HRms: 326.9984 calcd for $C_{14}H_{12}Cl_2NO_2P$:326.9983.

1-Benzyloxyimino-2-phenylethylphosphonoyl dichloride 5f. bp 140° - 165°C/ 0.01torr (Kugelrohr apparatus), yield 0.3g (25%). yellow highly viscous oil. ^{1}H-Nmr ($CDCl_3$) δ= 4.03 (d, $^3J(P,H)$= 19.3, 2H, **H-2**), 5.33 (s, 2H, O-C**H**$_2$-Ph), 7.15 - 7.40 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 32.5 (d, $^3J(P,C)$= 21.4, **C-2**), 78.7(s, O-CH_2-Ph), 127.1, 128.2, 128.3, 128.5, 128.6, 129.0 (s, C_{Ar}), 133.6 (s, **C-3**), 135.5 (s, C_i), 156.0 (d,

^{1}J(P,C)= 188, **C-1**). Ms(70eV, 134°C) 341(0.3), 224(2), 206(2), 192(1), 167(1), 116(3), 91(100), 77(7), 65(7), 51(3). HRms: 341.0139 calcd for $C_{15}H_{14}Cl_2NO_2P$: 341.0139.

General procedure for preparation of 1,3,2 oxazaphospholidines 6 and 7:

A solution of (-)-ephedrine (0.58 g, 3.5 mmol) dissolved in 40 ml of tetrahydrofuran and 1.0 ml (7.7 mmol) of dry triethylamine was added slowly to a stirred solution of 3.5 mmol of **5** (**5a:** 0.95 g, **5c**: 1.0 g, **5f:** 1.2 g) in 100 ml of dry tetrahydrofuran. After 3 h the precipitated ammonium salt was filtered off and washed with tetrahydrofuran (20 ml, 3x). Evaporation of all volatile compounds under reduced pressure (40°C/ 0.01torr) left a brown syrupy residue, which was subjected to column chromatography (silica gel, CH_2Cl_2/acetone (11:1, v/v)).

(2S,4S,5R)-2-(1-Benzyloxyiminoethyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 6a

372 mg (29.7%) were obtained after chromatographic separation; white crystals, mp 85°C (hexane). ^{1}H-Nmr ($CDCl_3$) δ= 0.76 (d, ^{3}J(H,H)= 6.9, 3H, **H-7**), 2.15 (d, ^{3}J(P,H)= 11.5, 3H, **H-10**), 2.59 (d, ^{3}J(P,H)= 10.4, 3H, **H-6**), 3.59 (m, 1H; **H-4**), 5.25 (s, 2H, O-CH_2-Ph), 5.33 (dd, ^{3}J(P,H)= 6.3, ^{3}J(H,H)= 6.3, 1H, **H-5**), 7.30 - 7.41 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 13.4 (d, ^{2}J(P,C)= 15.0, **C-10**), 15.1 (d, ^{3}J(P,C)= 4.1, **C-7**), 28.8 (d, ^{2}J(P,C)= 6.1, **C-6**), 58.5 (d, ^{2}J(P,C)= 10.9, **C-4**), 76.7(s, O-CH_2-Ph), 81.4 (s, **C-5**), 126.4, 128.0, 128.3, 128.3 (s, C_{Ar}), 136.0 (d, ^{3}J(P,C)= 5.9, **C-8**), 137.4 (s, C_i), 153.7 (d, ^{1}J(P,C)= 188, **C-9**). Ir (KBr) ν= 3100(w), 3080(w), 3040(m), 2995(m), 2970(m), 2940(m), 2880(m), 2830(w), 1610(m) **C=N**, 1500(m), 1460(m), 1450(m), 1435(m), 1390(m), 1385(m), 1370(m), 1365(m), 1335(m), 1300(s), 1270(s) **P=O**, 1230(s) **P=O**, 1210(s), 1190(s), 1165(m, sh), 1130(w), 1125(w), 1090(m), 1050(s), 1010-970 (s, b) **P-O-C**, 930(s), 880(m), 855(s), 810(m), 780(m), 750(s), 715(s), 700(s), 610(m), 570(m), 540(s), 520(m), 510(w), 495(m), 480(s) cm^{-1}. Anal. Calcd for $C_{19}H_{23}N_2O_3P$: C, 63.68; H,6.47; N,7.82; P, 8.64. Found: C, 63.70; H,6.38; N,7.84; P,8.60.

(2R,4S,5R)-2-(1-Benzyloxyiminoethyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 7a

420 mg (33.5%) were obtained after chromatographic separation; viscous, pale yellow oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.60 (d, ^{3}J(H,H)= 6.9, 3H, **H-7**), 2.21 (d, ^{3}J(P,H)= 11.2, 3H, **H-10**), 2.71 (d, ^{3}J(P,H)= 9.4, 3H, **H-6**), 3.69 (m, 1H, **H-4**), 5.21 (s, 2H, O-CH_2-Ph), 5.79 (d, ^{3}J(H,H)= 7, 1H, **H-5**), 7.15-7.41 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 13.4 (d, ^{2}J(P,C)= 15.0, **C-10**), 12.9 (s, **C-7**), 29.3 (d, ^{2}J(P,C)= 7.0, **C-6**), 60.7 (d, ^{2}J(P,C)= 10.5, **C-4**), 76.7(s, O-CH_2-Ph), 80.8 (s, **C-5**), 125.6, 127.7, 127.9, 127.9, 128.1 (s, C_{Ar}), 135.6 (d, ^{3}J(P,C)=

9.1, **C-8**), 137.4 (s, C_i), 153.7 (d, $^1J(P,C)$= 196.2, **C-9**). Ir (NaCl, film) ν= 3100(w), 3070(w), 3040(w), 3000(m), 2940(m), 2920(m), 2830(w), 1600(m) **C=N**, 1560(w), 1500(m), 1455(s), 1385(w), 1285(m), 1260(s), **P=O**, 1220(s,sh), 1190(s), 1115(w,sh), 1085(s), 1065(s), 1010(s) **P-O-C**, 975(s), 880(m), 860(m), 810(w), 755(s), 705(s), 665(w) cm^{-1}. Anal. Calcd for $C_{19}H_{23}N_2O_3P$: C, 63.68; H,6.47; N,7.82; P, 8.64. Found: C, 63.66; H,6.52; N,7.87; P,8.83.

(2S,4S,5R)-2-(1-Benzyloxyiminopropyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 6b

400 mg (30.7%) were obtained after chromatographic separation as viscous, pale yellow oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.72 (d, $^3J(H,H)$= 6.9, 3H, H-7), 1.18 (t, $^3J(H,H)$= 7.8, 3H, H-11), 2.55 (d, $^3J(P,H)$= 10.0, 3H, H-6), 2.60 (m, 2H, H-10), 3.59 (m, $^3J(P,H)$= 8.6, H-4), 5.21 (s, 2H, O-CH_2-Ph), 5.33 (t, $^3J(P,H)$= 6.3, $^3J(H,H)$= 6.3, 1H, H-5), 7.24 - 7.50 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 10.4 (s, C-11), 15.0 (d, $^3J(P,C)$= 4.0, C-7), 21.0 (d, $^2J(P,C)$=14.5, C-10), 28.8 (d, $^2J(P,C)$= 6.0, C-6), 58.3 (d, $^2J(P,C)$= 11.3, C-4), 76.6(s, O-CH_2-Ph), 81.3 (s, C-5), 126.4, 127.8, 128.0, 128.1, 128.1, 128.2 (s, C_{Ar}), 136.0 (d, $^3J(P,C)$= 5.5, C-8), 137.4 (s, C_i), 158.7 (d, $^1J(P,C)$= 183.5, C-9). Ir (NaCl, film) ν= 3070(m), 3040(m), 2980(s), 2940(s), 2880(m), 2830(w), 1600(m) C=N, 1500(m), 1455(s), 1385(m,sh), 1370(s), 1340(s), 1300(s), 1260(vs) P=O, 1220(s), 1190(s), 1115(w, sh), 1080(m), 1065(s), 1040(s,sh), 980(vs), 950(vs), P-O-C, 920(m), 880(s), 850(s), 810(m), 755(vs,sh), 740(vs,sh), 700(s), 665(w), 600(m), 590(m) cm^{-1}. Anal. Calcd for $C_{20}H_{25}N_2O_3P$: C, 64.51; H,6.76; N,7.52. Found: C,64.64; H,6.85; N,7.84.

(2R,4S,5R)-2-(1-Benzyloxyiminopropyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 7b

460 mg (35.3%) were obtained after chromatographic separation; viscous, pale yellow oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.60 (d, $^3J(H,H)$= 6.9, 3H, **H-7**), 1.25 (t, $^3J(H,H)$= 7.7, 3H, **H-11**), 2.70 (d, $^3J(P,H)$= 8.6, 3H, **H-6**), 2.70 (m, 2H, **H-10**), 3.69 (m, $^3J(P,H)$= 14.9, **H-4**), 5.20 (s, 2H, O-CH_2-Ph), 5.78 (d, $^3J(H,H)$= 7.2, 1H, **H-5**), 7.15 - 7.38 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 10.6 (s, **C-11**), 13.0 (s, **C-7**), 21.2 (d, $^2J(P,C)$= 15.3, **C-10**), 29.3 (d, $^2J(P,C)$= 7.2, **C-6**), 60.8 (d, $^2J(P,C)$= 11.3, **C-4**), 76.5(s, O-CH_2-Ph), 80.9 (s, **C-5**), 125.7, 127.8, 127.9, 128.0, 128.3 (s, C_{Ar}), 135.8 (d, $^3J(P,C)$= 9.2, **C-8**), 137.7 (s, C_i), 159.6 (d, $^1J(P,C)$= 191.3, **C-9**). Ir(NaCl, film) ν= 3100(w), 3070(w), 3040(m), 2980(s), 2940(s), 2880(m, sh), 2830(w,sh), 1600(m) **C=N**, 1500(m), 1460(s), 1385(m), 1370(m), 1335(s), 1260(vs) **P=O**, 1220(s), 1190(s), 1120(m), 1085(m), 1065(s), 1010(vs), 980-950(vs, b), **P-O-C**, 880(s), 855(s), 810(m), 760(vs), 740(vs), 700(vs), 625(w) cm^{-1}. Anal. Calcd for $C_{20}H_{25}N_2O_3P$: C,64.51; H,6.76; N,7.52. Found: C,64.74; H,6.82; N,7.78.

(2S,4S,5R)-2-(1-Benzyloxyimino-2-methylpropyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 6c 350 mg (25.8%) were obtained after chromatographic separation as viscous, pale yellow oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.71 (d, ^{3}J(H,H)= 7.0, 3H, **H-7**), 1.28 (d, ^{3}J(H,H)= 7.5, 3H, **H-11**), 1.30 (d, ^{3}J(H,H)= 7.5, 3H, **H-11'**), 2.54 (d, ^{3}J(H,H)= 8.8, 3H, **H-6**), 3.33 - 3.68 (m, 2H, **H-10** + **H-4**), 5.20 (s, 2H, O-C$\underline{H}_2$-Ph), 5.22 (virt. t, ^{3}J(H,H) = 6.7, ^{3}J(P,H)= 6.7, **H-5**), 7.25 - 7.40 (m, 10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 15.1 (d, ^{3}J(P,C)= 4.5, **C-7**), 18.5 (s, **C-11**), 19.1 (s, **C-12**), 27.8 (d, ^{2}J(P,C)= 13.8, **C-10**), 28.9 (d, ^{2}J(P,C)= 6.0, **C-6**), 57.9 (d, ^{2}J(P,C)= 11.5, **C-4**), 76.5 (s, O-CH_2-Ph), 81.1 (s, **C-5**), 126.5, 127.8, 128.0, 128.1, 128.2, (s, C_{Ar}), 136.2 (d, ^{3}J(P,C)= 6.1, **C-8**), 137.6 (s, C_i), 162.2 (d, ^{1}J(P,C)= 176.7, **C-9**). Ir (NaCl, film) ν= 3100(w), 3070(m), 3040(m), 2980(s), 2940(m), 2880(m), 1610(m) **C=N**, 1500(m), 1475(m), 1455(s), 1385(m), 1370(m), 1340(m), 1300(m), 1260(s,b) **P=O**, 1105(s,sh), 1080(s), 980(s) **P-O-C**, 900(s), 880(s, sh), 855(s), 810(m), 750(s), 720(s), 700(s), 605(m), 595(m) cm^{-1}. HRms: 386.1760 calcd for $C_{21}H_{27}N_2O_3P$: 386.1759.

(2R,4S,5R)-2-(1-Benzyloxyimino-2-methylpropyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 7c 525 mg (38.8%) were obtained after chromatographic separation as viscous, pale yellow oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.54 (d, ^{3}J(H,H)= 7.0, 3H, **H-7**), 1.32 (d, ^{3}J(H,H)= 7.2, 3H, **H-11**), 1.34 (d, ^{3}J(H,H)= 7.2, 3H, **H-12**), 2.70 (d, ^{3}J(H,H)= 8.6, 3H, **H-6**), 3.37 - 3.72 (m, 2H, **H-10** + **H-4**), 5.15 (s, 2H, O-C$\underline{H}_2$-Ph), 5.22 (virt. d, ^{3}J(H,H) = 6.5, **H-5**), 7.12 - 7.40 (m,10H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ=12.5 (s, **C-7**), 18.7 (s, **C-11**), 19.2 (s, **C-11'**), 28.0 (d, ^{2}J(P,C)= 13.7, **C-10**), 29.7 (d, ^{2}J(P,C)= 3.6, **C-6**), 60.4 (d, ^{2}J(P,C)= 10.6, **C-4**), 76.3 (s, O-CH_2-Ph), 80.8 (s, **C-5**), 125.4, 127.6, 127.8, 128.1, (s, C_{Ar}), 135.7 (d, ^{3}J(P,C)= 9.1, **C-8**), 137.6 (s, C_i), 163.1 (d, ^{1}J(P,C)= 186.1, **C-9**). Ir (NaCl, film) ν= 3100(w), 3070(m), 3040(m), 2980(m), 2940(m), 2880(m), 2840(m), 1610(w) **C=N**, 1500(m), 1470(m), 1455(s), 1385(m), 1365(m), 1350(w), 1330(m), 1260(s,b) **P=O**, 1190(s), 1110(m,sh), 1085(m), 11060(m), 975(s) **P-O-C**, 890(m), 850(m), 815(w), 755(m), 700(s), 625(m) cm^{-1}. HRms: 386.1760 calcd for $C_{21}H_{27}N_2O_3P$: 386.1759.

(2S,4S,5R)-2-(1-Benzyloxyimino-2-phenylethyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 6f 180 mg (11.8%) were obtained after chromatographic separation, using acetone/dichloromethane (1:25) as viscous, pale yellow oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.70 (d, ^{3}J(H,H)= 6.3, 3H, **H-7**), 2.32 (d, ^{3}J(H,H)= 9.7, 3H, **H-6**), 3.50 (m, 1H, **H-4**), 3.98 (d, ^{3}J(P,H)= 12.8, 2H, **H-10**), 5.25 (s, 2H, O-C$\underline{H}_2$-Ph), 5.26 (virt. t, ^{3}J(H,H) = 6.25, ^{3}J(P,H)= 6.25, **H-5**), 7.12 - 7.40 (m, 15H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 15.0 (d, ^{3}J(P,C)= 3.5, **C-7**), 28.4 (d, ^{2}J(P,C)= 6.1, **C-6**), 33.5 (d, ^{2}JP,C)= 15.1, **C-10**), 58.2 (d, ^{2}J(P,C)= 12.0, **C-4**), 76.9 (s, O-

CH_2-Ph), 81.6 (s, **C-5**), 126.4, 126.5, 128.0, 128.2, 128.2, 128.3, 129.4 (s, C_{Ar}), 135.6 (s, **C-11**), 136.1 (d, $^3J(P,C)$= 4.6, **C-8**), 137.7 (s, C_i), 155.7 (d, $^1J(P,C)$= 186.1, **C-9**). Ir (NaCl, film) ν= 3100(w), 3080(m), 3040(m), 3980(m), 3940(m), 3880(m,sh), 3840(w), 1720(w), 1605(m), 1590(m), 1500(s), 1460(s), 1390(m), 1370(m), 1340(m), 1300(m), 1270(vs) **P=O**, 1190(s), 1160(w, sh), 115(w), 1085(m), 1065(m), 990(vs,b) **P-O-C**, 920(m), 880(s), 855(s), 810(m), 790(m), 755(s), 740(s), 705(s), 610(m), 600m,sh) cm^{-1}. Anal. Calcd for $C_{25}H_{27}N_2O_3P$: C,69.11; H,6.26; N,6.54; P,7.13 . Found: C,69.06; H,6.34; N,6.54; P,7.14.

(2R,4S,5R)-2-(1-Benzyloxyimino-2-phenyl-ethyl)-3,4-dimethyl-2-oxo-5-phenyl-2λ^5-1,3,2-oxazaphospholidine 7f 195 mg (12.6%) were obtained after chromatographic separation, using acetone/dichloromethane (1:25, v/v) as viscous, pale yellow oil. ^{1}H-Nmr ($CDCl_3$) δ= 0.50 (d, $^3J(H,H)$= 7.0, 3H, **H-7**), 2.51 (d, $^3J(H,H)$= 9.2, 3H, **H-6**), 3.60 (m, 1H, **H-4**), 4.09 (m, 2H, **H-10**), 5.21 (s, 2H, O-C**H**$_2$-Ph), 5.70 (virt. d, $^3J(P,H)$ ≈ 6.8, **H-5**), 6.90 - 7.40 (m, 15H, H_{Ar}). ^{13}C-Nmr ($CDCl_3$, {^{1}H}) δ= 12.8 (s, **C-7**), 29.1 (d, $^2J(P,C)$= 6.4, **C-6**), 33.4 (d, $^2J(P,C)$= 15.3, **C-10**), 60.9 (d, $^2J(P,C)$= 10.7, **C-4**), 76.7 (s, O-CH_2-Ph), 80.8 (s, **C-5**), 125.6, 126.5, 127.8, 127.9, 128.0 128.1, 128.3, 128.4, 129.4 (s, C_{Ar}), 135.6 (s, **C-11**), 135.7 (d, $^3J(P,C)$= 9.5, **C-8**), 137.3 (s, C_i), 156.0 (d, $^1J(P,C)$= 193.2, **C-9**). Ir (NaCl, film) ν= 3100(w), 3080(m), 3040(m), 3980(m), 3940(m), 3880(m,sh), 3840(w), 1720(w), 1605(m), 1590(m), 1500(s), 1460(s), 1390(m), 1370(m), 1340(m), 1300(m), 1270(vs) **P=O**, 1190(s), 1160(w, sh), 115(w), 1085(m), 1065(m), 990(vs,b) **P-O-C**, 920(m), 880(s), 855(s), 810(m), 790(m), 755(s), 740(s), 705(s), 610(m), 600m,sh) cm^{-1}. Anal. Calcd for $C_{25}H_{27}N_2O_3P$: C,69.11; H,6.26; N,6.54; P,7.13 . Found: C,69.08; H,6.42; N,6.50; P,7.00.

General procedure for preparation of 1,3,2 dioxaphosphorinanes 8 and 9:

A solution of chloramphenicol (1.13 g, 3.5 mmol) dissolved in 40 ml of dry tetrahydrofuran and 1.4 ml (10.5 mmol) of dry triethylamine was added slowly to a stirred solution of 3.5 mmol of **5** (**5a:** 0.9g, **5b:** 0.95g **5c**: 1.0g) in 100 ml of dry tetrahydrofuran. After 3 h the precipitated ammonium salt was filtered off and washed with tetrahydrofuran (20 ml, 3x). Evaporation of the solvent under reduced pressure (40°C/ 0.01 torr) afforded a brown syrupy residue, which was subjected to column chromatography (silica gel, $CHCl_3$/MeCN (12:1, v/v)).

N-[(2S,4R,5R)-2-(1-Benzyloxyiminoethyl)-4-(4-nitrophenyl)-2-oxo-[1,3,2]dioxaphosphinan-5-yl]-2,2'-dichloroacetamide 8a. yield 215 mg (12%), white crystals, mp 137°C (benzene). ^{1}H-Nmr ($CDCl_3$) δ= 2.18 (d, $^3J(P,H)$= 11.9, 3H, **H-11**), 4.25-4.43 (m, 2H, **H-6^e**, **H-5**), 4.52 (m, 1H, **H-6^a**), 5.30 (s, 2H, O-CH_2-Ph), 5.62

(bs, 1H, **H-4**), 5.98(s, 1H, **H-9**), 7.35-7.52 (m, 7H, H_{AR}), 8.15 (d, 2H, H_{AR}), 8.58 (d, $^3J(H,H)$= 9.8, 1H, **N-H**). ^{13}C-Nmr ($CDCl_3$) δ= 12.9 (d, $^3J(P,C)$= 16.6, **C-11**), 48.3 (d, $^3J(P,C)$= 6.1, **C-5**), 65.3 (s, **C-9**), 72.0 (d, $^2J(P,C)$= 6.5, **C-6**), 77.1 (s, O-CH_2-Ph), 81.6 (d, $^2J(P,C)$= 6.6, **C-4**), 123.6, 126.5, 128.4, 128.6, 128.7 (s, C_{AR}), 137.3 (s, O-CH_2-C_{Ar}), 141.7 (d, $^3J(P,C)$= 8.7, **C-7**), 147.9 (s, C_{AR}-NO_2), 151.4 (d, $^1J(P,C)$= 213, **C-10**), 164.5 (s, **C-8**). Ir (KBr) ν= 3230(m), 3060(w), 2920(w), 1710(s), 1605(m), 1550(m), 1520(s),1500(w), 1345(s), 1275(s), 1200(m), 1050(s), 975(s), 940(m), 910(w), 870(w), 860(w), 810(s), 780(m) cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_3O_7Cl_2P$: C,46.53; H,3.90; N,8.14; P,6.00. Found: C,46.22; H,4.10; N,8.01; P,6.06. .

N-[(2S,4R,5R)-2-(1-Benzyloxyimino-propyl)-4-(4-nitrophenyl)-2-oxo-[1,3,2]dioxaphosphinan-5-yl]-2,2'-dichloroacetamide 8b. yield 275 mg (14.7%), white crystals, mp 140°C (benzene). ^{1}H-Nmr ($CDCl_3$) δ= 1.19 (t, $^3J(H,H)$= 7.8, **H-12**), 2.63 (m, 2H, **H-11**), 4.20-4.41 (m, 2H, **H-6^e**, **H-5**), 4.50 (m, 1H, **H-6^a**) , 5.30 (s, 2H, O-CH_2-Ph), 5.68 (bs, 1H, **H-4**), 5.98(s, 1H, **H-9**), 7.30-7.48 (m, 7H, H_{AR}), 8.15 (d, 2H, H_{AR}), 8.43 (d, $^3J(H,H)$= 9.9, 1H, **N-H**). ^{13}C-Nmr ($CDCl_3$) δ= 10.3 (s, **C-12**), 20.9 (d, $^3J(P,C)$= 16.3, **C-11**), 48.2 (d, $^3J(P,C)$= 6.0, **C-5**), 65.2 (s, **C-9**), 72.0 (d, $^2J(P,C)$= 6.8, **C-6**), 77.0 (s, O-CH_2-Ph), 81.4 (d, $^2J(P,C)$= 6.7, **C-4**), 123.5, 126.4, 128.2, 128.5, 128.7 (s, C_{AR}), 137.4 (s, O-CH_2-C_{Ar}), 141.7 (d, $^3J(P,C)$= 8.6, **C-7**), 147.9 (s, C_{AR}-NO_2), 156.4 (d, $^1J(P,C)$= 202, **C-10**), 164.5 (s, **C-8**). Ir (KBr) ν= 3250(m), 3080(m), 2960(m), 1720((vs)), 1615(m), 1560(m), 1530(s), 1460(m), 1355(s), 1270((vs)), 1210(m), 1140(w), 1120(w), 1060(vs), 980(s), 950(s), 815(s) cm^{-1}. Anal. Calcd for $C_{21}H_{22}N_3O_7Cl_2P$: C,47.56; H,4.18; N,7.92. Found: C,47.53; H,4.13; N,7.88.

N-[(2S,4R,5R)-2-(1-Benzyloxyimino-2-methyl-propyl)-4-(4-nitrophenyl)-2-oxo-[1,3,2]dioxaphosphinan-5-yl]-2,2'-dichloroacetamide 8c. yield 170 mg (9%), white crystals, mp 73°C (benzene). ^{1}H-Nmr ($CDCl_3$) δ= 1.30 (d, $^3J(H,H)$= 7.8, **H-12**), 1.32 (d, $^3J(H,H)$= 7.8, **H-12'**), 3.39 (m, 1H, **H-11**), 4.21-4.53 (m, 2H, **H-6^e**, **H-5**, **H-6^a**), 5.30 (s, 2H, O-CH_2-Ph), 5.55 (bs, 1H, **H-4**), 6.05 (s, 1H, **H-9**), 7.31-7.49 (m, 7H, H_{AR}), 8.13 (d, 2H, H_{AR}), 8.48 (d, $^3J(H,H)$= 9.9, 1H, **N-H**). ^{13}C-Nmr ($CDCl_3$) δ= 18.5 (s,**C-12**), 18.8 (s, **C-12'**), 28.1 (d, $^3J(P,C)$= 17.1, **C-11**), 48.8 (d, $^3J(P,C)$= 5.3, **C-5**), 65.7 (s, **C-9**), 69.3 (d, $^2J(P,C)$= 7.0, **C-6**), 77.5 (s, O-CH_2-Ph), 77.9 (d, $^2J(P,C)$= 6.5, **C-4**), 123.6, 126.3, 128.3, 127.6, 128.6, (s, C_{AR}), 136.4 (s, O-CH_2-C_{Ar}), 141.9 (d, $^3J(P,C)$= 8.7, **C-7**), 147.9 (s, C_{AR}-NO_2), 159.5 (d, $^1J(P,C)$= 209, **C-10**), 164.6 (s, **C-8**). Ir (KBr, tablet) ν= 3330(m), 3070(w), 2980(w), 2940(w), 1690(vs), 1615(m), 1525(s), 1460(m), 1350(s), 1270(s), 1210(m), 1060(s), 980(s). Anal. Calcd for $C_{22}H_{24}N_3O_7Cl_2P$: C,48.55; H,4.44; N,7.72; P,5.69; Cl,13.03. Found: C,48.67; H,4.47; N,7.71; P,5.78; Cl, 13.09.

N-[(2R,4R,5R)-2-(1-Benzyloxyiminoethyl)-4-(4-nitrophenyl)-2-oxo-[1,3,2]dioxaphosphinan-5-yl]-2,2'-dichloroacetamide 9a. yield 540 mg (30.2%), white crystals, mp 148°C (benzene). ^{1}H-Nmr ($CDCl_3$) δ= 2.28 (d, ^{3}J(P,H)= 12.8, 3H, **H-11**), 4.38 (m, 1H, **H-6^e**), 4.68(m, 1H, **H-5**), 5.03 (m, 1H, **H-6^a**) [11], 5.43 (s, 2H, O-CH_2-Ph), 5.62 (s, 1H, **H-9**), 6.09 (bs, 1H, **H-4**), 7.23 (d, 1H, ^{3}J(H,H)= 6.0, **NH**), 7.32-7.59 (m, 7H, H_{AR}), 8.18 (d, 2H, H_{AR}). ^{13}C-Nmr ($CDCl_3$) δ= 13.4 (d, ^{3}J(P,C)= 18.1, **C-11**), 48.6 (d, ^{3}J(P,C)= 4.7, **C-5**), 65.7 (s, **C-9**), 69.5 (d, ^{2}J(P,C)= 7.3, **C-6**), 77.7 (s, O-CH_2-Ph), 78.3 (d, ^{2}J(P,C)= 6.6, **C-4**), 123.7, 126.4, 127.7 128.4, 128.6, (s, C_{AR}), 136.3 (s, O-CH_2-C_{Ar}), 141.7 (d, ^{3}J(P,C)= 8.7, **C-7**), 148.0 (s, C_{AR}-NO_2), 151.2 (d, ^{1}J(P,C)= 223, **C-10**), 163.9 (s, **C-8**). Ir (KBr, tablet) ν= 3280(m), 3230(m), 3050(w), 3000(w),1705(vs), 1605(m), 1590(m), 1550(m), 1520(vs), 1460(m), 1350(vs), 1260(vs), 1195(s), 1135(m), 1055(vs), 960Km, 950(s), 875(m) cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_3O_7Cl_2P$: C,46.53; H,3.90; N,8.14; P,6.00. Found: C,46.36; H,3.99; N,7.96; P,5.91.

N-[(2R,4R,5R)-2-(1-Benzyloxyiminopropyl)-4-(4-nitrophenyl)-2-oxo-[1,3,2]dioxaphosphinan-5-yl]-2,2'-dichloroacetamide 9b. yield 660 mg (35.4%), white crystals, mp 114°C (benzene). ^{1}H-Nmr ($CDCl_3$) δ= 1.23 (t, ^{3}J(H,H)= 8.0, **H-12**), 2.73 (m, 2H, **H-11**), 4.38(m, 1H, **H-6^e**), 4.65(m, 1H, **H-5**) 5.02(m, 1H, **H-6^a**) , 5.41 (s, 2H, O-CH_2-Ph), 5.61 (s, 1H, **H-9**), 6.10 (bs, 1H, **H-4**), 7.22 (d, ^{3}J(H,H)= 9.9, 1H, **N-H**),.7.30-7.55 (m, 7H, H_{AR}), 8.15 (d, 2H, H_{AR}). ^{13}C-Nmr ($CDCl_3$) δ= 10.5 (s, **C-12**), 21.1 (d, ^{3}J(P,C)= 17.0, **C-11**), 48.6 (d, ^{3}J(P,C)= 5.5, **C-5**), 65.7 (s, **C-9**), 69.4 (d, ^{2}J(P,C)= 7.4, **C-6**), 77.5 (s, O-CH_2-Ph), 78.1 (d, ^{2}J(P,C)= 6.2, **C-4**), 123.7, 126.4, 127.6, 128.3, 128.6 (s, C_{AR}), 136.4 (s, O-CH_2-C_{Ar}), 141.8 (d, ^{3}J(P,C)= 7.9, **C-7**), 147.9 (s, C_{AR}-NO_2), 156.3 (d, ^{1}J(P,C)= 215, **C-10**), 163.8 (s, **C-8**). Ir (KBr, tablet) ν= 3400(s), 3000(m), 1700(vs), 1615(m), 1580(m), 1535(vs), 1460(m), 1440kw, 1350(vs), 1270(vs), 1240km, 1220(w), 1190(w), 1140(w), 1110kw, 1060(vs), 1060(vs), 1020(s), 995(s) cm^{-1}. Anal. Calcd for $C_{21}H_{22}N_3O_7Cl_2P$: C,47.56; H,4.18; N,7.92. Found: C,47.53; H,4.23; N,7.98.

N-[(2R,4R,5R)-2-(1-Benzyloxyimino-2-methylpropyl)-4-(4-nitrophenyl)-2-oxo-[1,3,2]dioxaphosphinan-5-yl]-2,2'-dichloroacetamide 9c. yield 482 mg (25.3%), white crystals, m.p. 112°C (benzene). ^{1}H-Nmr ($CDCl_3$) δ= 1.32 (d, ^{3}J(H,H)= 7.4, **H-12, H-12'**), 3.60 (m, 1H, **H-11**), 4.38 (m, 2H, **H-6^e**), 4.62 (m, 1H, **H-5**), 5.02 (m, 1H, **H-6^a**), 5.38 (s, 2H, O-CH_2-Ph), 5.62 (s, 1H, **H-9**), 6.09 (bs, 1H, **H-4**), 7.18 (d, ^{3}J(H,H)= 9.4, 1H, **N-H**), 7.30-7.52 (m, 7H, H_{AR}), 8.20 (d, 2H, H_{AR}). ^{13}C-Nmr ($CDCl_3$) δ= 18.6 (s,**C-12**), 18.7 (s, **C-12'**), 28.1 (d, ^{3}J(P,C)= 17.1, **C-11**), 48.7 (d, ^{3}J(P,C)= 5.4, **C-5**), 65.7 (s, **C-9**), 69.2 (d, ^{2}J(P,C)= 7.4, **C-6**), 77.0 (s, O-CH_2-Ph), 77.8 (d, ^{2}J(P,C)= 6.2, **C-4**), 123.7, 126.3, 127.6, 128.3, (s, C_{AR}), 136.4 (s, O-CH_2-C_{Ar}), 141.8 (d,

$^3J(P,C)$= 8.7, **C-7**), 148.0 (s, C_{AR}-NO_2), 159.6 (d, $^1J(P,C)$= 208, **C-10**), 163.8 (s, **C-8**). Ir (KBr) ν= 3400(w), 2980(w), 1715(vs), 1615(m), 1520(vs), 1350(s), 1265(vs), 1220(m), 1190(w), 1090(vs), 1070(m), 980(s), 910(m), 860(m), 840(m), 810(m) cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_3O_7Cl_2P$: C,48.55; H,4.44; N,7.72; P,5.69; Cl,13.03. Found: C,48.69; H,4.51; N,7.67; P,5.82; Cl, 13.00.

X-Ray Crystal Structure Analysis of 9a. Suitable crystals were obtained by crystallization from n-hexane-ethyl acetate. $C_{21}H_{19}N_3O_7Cl_2P$, mol. weight = 527.28, ρ_{cald}= 1.585 g/cm^3, space group P $2_12_12_1$ (#19), a=8.845(3) Å b= 10.029(3) Å c=24.903(7) Å α= 90°, β= 90°, γ= 90°, Vol.= 2210(1) $Å^3$, no absorption correction was applied. A total of 2982 reflections were collected, of which 2743 were observed [$F_o \leqq 4\sigma$ (F)] on a Nicolet R3m diffractometer using graphit monchromated K_α (λ= 0.71069 Å) radiation. The structure was solved by direct phase determination methods and refined by 'cascading blocked diagonal least square ' algorithm [SHELXTL-PLUS by G.M. Sheldrick] on a Micro VAX II to a final R= 4.58%.

Table 1: Positional Parameters of **9a** for Non-Hydrogen Atoms with Their Standard Deviations in Parentheses.

Atom	x	y	z	Ueq	Atom	x	y	z	Ueq
P	8682(1)	9167(1)	6747(1)	164(3)	C(4)	9614(5)	5614(4)	6212(2)	177(12)
Cl(1)	4004(1)	6107(1)	7287(1)	227(3)	C(5)	10639(5)	4585(5)	6274(2)	249(14)
Cl(2)	4483(1)	3754(1)	6615(1)	292(4)	C(6)	10700(5)	3552(5)	5916(2)	262(14)
N(1)	9753(5)	2488(1)	5094(2)	350(15)	C(7)	9699(5)	3571(5)	5483(2)	238(14)
N(2)	7293(4)	5981(4)	7086(1)	174(11)	C(8)	8664(6)	4574(5)	5416(2)	303(15)
Hn(2)	6645	6608	6969	150(119)	C(9)	8625(5)	5588(5)	5783(2)	282(15)
N(3)	5836(4)	9266(4)	6499(1)	206(11)	C(10)	6761(5)	4765(4)	7199(2)	157(13)
O(1)	(153(3)	8635(3)	7317(1)	203(9)	C(11)	5037(5)	4597(4)	7207(2)	192(13)
O(2)	8856(3)	7855(3)	6398(1)	177(8)	C(12)	7057(5)	9944(4)	6450(2)	170(13)
O(3)	9049(6)	2599(4)	4677(1)	577(16)	C(13)	7245(6)	11262(5)	6184(2)	271(14)
O(4)	10515(6)	1499(4)	5208(2)	674(17)	C(14)	3258(5)	9101(5)	6313(2)	260(14)
O(5)	7523(3)	3796(3)	7294(1)	242(10)	C(15)	3122(3)	8016(3)	5897(1)	232(14
O(6)	9987(3)	10041(3)	6757(1)	235(9)	C(16)	4153	6964	5887	296(15)
O(7)	4616(3)	9898(3)	6258(1)	268(10)	C(17)	4001	5951	5507	355(17)
C(1)	9640(5)	6714(4)	6622(2)	170(13)	C(18)	2818	5989	5137	408(18)
C(2)	8856(5)	6347(4)	7156(2)	148(12)	C(19)	1786	7041	5147	396(19)
C(3)	8974(5)	7488(4)	7544(2)	188(13)	C(20)	1938	8054	5527	300(15)

Table 2: Distances [Å] and angles [°] in **9a**

P-O(1)	1.587(3)	P-O(2)	1.584(3)
P-O(6)	1.448(3)	P-C(12)	1.794(4)
Cl(1)-C(11)	1.780(4)	Cl(2)-C(11)	1.769(4)
N(1)-O(3)	1.215(6)	N(1)-O(4)	1.232(6)
N(1)-C(7)	1.457(6)	N2-Hn(2)	0.899
N(2)-C(2)	1.441(6)	N(2)-C(10)	1.338(6)
N(3)-O(7)	1.387(5)	N(3)-C(12)	1.283(6)
O(1)-C(3)	1.474(5)	O(2)-C(1)	1.450(5)
O(5)-C(10)	1.206(5)	O(7)-C(14)	1.449(6)
C(1)-C(2)	1.543(6)	C(1)-C(4)	1.503(6)
C(2)-C(3)	1.501(6)	C(4)-C(5)	1.382(6)
C(4)-C(9)	1.380(6)	C(5)-C(6)	1.369(6)
C(6)-C(7)	1.394(6)	C(7)-C(8)	1.370(7)
C(8)-C(9)	1.369(7)	C(10)-C(11)	1.534(6)
C(12)-C(13)	1.487(6)	C(14)-C(15)	1.508(6)

O(1)-P-O(2)	103.9(2)	O(1)-P-O(6)	115.0(2)
O(2)-P-O(6)	115.8(2)	O(1)-P-C(12)	106.1(2)
O(2)-P-C(12)	102.3(2)	O(6)-P-C(12)	112.5(2)
O(3)-N(1)-O(4)	123.5(5)	O(3)-N(1)-C(7)	118.8(4)
O(4)-N(1)-C(7)	117.6(4)	Hn(2)-N(2)-C(2)	118.2(2)
Hn(2)-N(2)-C(10)	118.8(2)	C(2)-N(2)-C(10)	123.0(4)
O(7)-N(3)-C(12)	111.8(3)	P-O(1)-C(3)	117.4(2)
P-O(2)-C(1)	119.4(2)	N(3)-O(7)-C(14)	110.6(3)
O(2)-C(1)-C(2)	107.8(3)	O(2)-C(1)-C(4)	108.1(3)
C(2)-C(1)-C(4)	113.8(3)	N(2)-C(2)-C(1)	112.8(3)
N(2)-C(2)-C(3)	109.8(3)	C(1)-C(2)-C(3)	110.0(3)
O(1)-C(3)-C(2)	108.3(3)	C(1)-C(4)-C(5)	117.5(4)
C(1)-C(4)-C(9)	123.3(4)	C(5)-C(4)-C(9)	119.2(4)
C(4)-C(5)-C(6)	121.2(4)	C(5)-C(6)-C(7)	118.7(4)
N(1)-C(7)-C(6)	118.9(4)	N(1)-C(7)-C(8)	119.2(4)
C(6)-C(7)-C(8)	121.9(4)	C(7)-C(8)-C(9)	118.7(4)
C(4)-C(9)-C(8)	121.0(5)	N(2)-C(10)-O(5)	125.4(4)
N(2)-C(10)-C(11)	116.9(4)	O(5)-C(10)-C(11)	117.7(4)
Cl(1)-C(11)-Cl(2)	111.0(2)	Cl(1)-C(11)-C(10)	114.7(7)
Cl(2)-C(11)-C(10)	108.5(3)	P-C(12)-N(3)	113.9(3)
P-C(12)-C(13)	118.7(3)	N(3)-C(12)-C(13)	127.4(4)
O(7)-C(14)-C(15)	113.5(3)	C(14)-C(15)-C(16)	120.4(2)
C(14)-C(15)-C(20)	119.6(2)		

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Dedicated on 70th birthday of Edward C. Taylor, Princeton, with best wishes.

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