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FROM SILYLPHOSPHANES AND OXAZOLONES TO NEW PHOSPHORUS AMIDO-ACIDS

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Silylphosphanes **3** and **4** gave 1,4-additions with the O=C-C=C moiety of oxazolones **1a-e** and **2a-f** to afford the adducts **5–8**. Oxidation or sulfuration of **5–8** followed by hydrolysis led to oxyphosphorus (or thiophosphorus) amido-acids **9–11** and **15, 19, 20** respectively. A great difference was observed in the behaviour of thiophosphane oxides **16** (R = Me) and **17**(R = Ph) toward hydrolysis: **16** led directly to the amido-acid **19** by opening of the lactonic ring whereas, from **17**, the heterocyclic intermediate **18** could be isolated.

Keywords: Silylphosphanes; oxazolones; phosphane oxides; thiophosphane oxides; phosphorus amido-acids; 1,4-additions

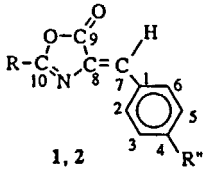
INTRODUCTION

The use of chemical fertilizers, to increase the yields of crops, and of pesticides, to eliminate all kinds of parasites able to attack the cultivations, will be in the future more and more important because one of the great problems facing the world will be to provide food to an increasing number of men. Such fertilizers and pesticides should become more active and selective but also less toxic toward humans and the environment. Thus,

* Corresponding Author.

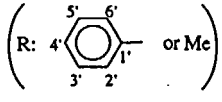
new types of compounds have to be synthesized. Most of the pesticides commercially available are phosphorus derivatives, particularly phosphates or phosphonates, and many of them include a nitrogen cyclic structure [1–3].

The purpose of this work was to obtain new families of potentially biologically active phosphorus compounds such as phosphorylated amido-acids, with three carbon atoms on phosphorus. For the introduction of a phosphorus group on various substrates we have used, following our first experiments[4], the silylphosphanes $Me_3Si\text{-}PR'_2$ (R': Et, iPr) which react generally easily with α,β-ethylenic ketones. Then, the removal of the silicon moiety can be obtained by simple hydrolysis. In order to make comparisons about the influence of various substituents on the biological activity of the compounds synthesized, we have used the same oxazolone skeleton **1, 2** with a methyl or a phenyl group on carbon 10 and six different groups on carbon 4:



1, 2

R = Me, R" =		R = Ph, R" =	
H	**1a**	H	**2a**
Me	**1b**	Me	**2b**
OMe	**1c**	OMe	**2c**
F	**1d**	F	**2d**
CF_3	**1e**	CF_3	**2e**
		NO_2	**2f**

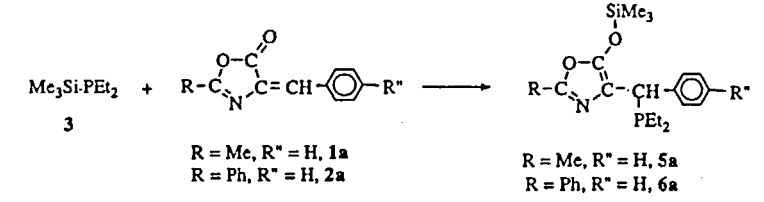


We describe in this paper the reactivity of the diethyl(trimethylsilyl)phosphane **3** (Me_3SiPEt_2)[5] and of the diisopropyl(trimethylsilyl)phosphane **4** ($Me_3SiPiPr_2$)[6] with oxazolones **1** [7] and **2** [7] and the reactivity of the adducts toward hydrolysis, oxydation and sulfuration.

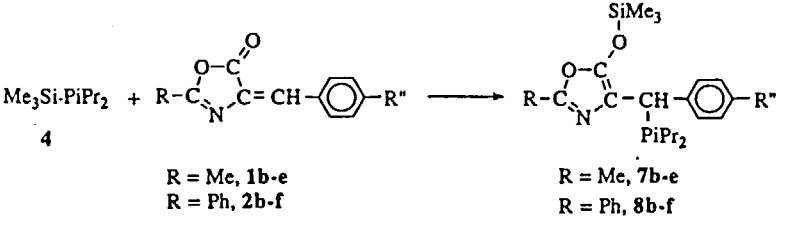
RESULTS AND DISCUSSION

1) Synthesis of adducts 5 – 8

The silylphosphane **3** reacts at room temperature with oxazolones **1a** and **2a** to give almost quantitatively the adducts **5a** and **6a**:



A similar reaction was observed between the more crowded silylphosphane **4** and oxazolones **1b-e** and **2b-f:**



Despite the larger steric hindrance due to two iPr groups on phosphorus, **4** reacts also almost quantitatively at room temperature with oxazolones **1b-e** and **2b-f**. In all cases only the 1,4-adducts have been obtained; the formation of the 1,2-adducts involving the sole carbonyl group has not been observed, neither the addition on the C=C double bond which was of course very unlikely. These results are in agreement with those previously reported in the reaction between silylphosphanes and α,β-ethylenic ketones [4,8]. 1,4-additions also occur in the reactions between the silylphosphanes Ph(R)P-$SiMe_3$ and some acrylic esters $H_2C{=}C(R')COOMe$ (R': H, Me) [9], but, when the steric hindrance around phosphorus is high, 1,2-additions on the C=C double bond were also observed in minor ratio.

The 1,4-addition was easily proved by a ^1H and ^{13}C NMR study. In ^1H NMR spectra, the hydrogen on carbon 7 gave a doublet, due to coupling with phosphorus, at about 4 ppm. In the case of a 1,2-addition on the CO group, this signal, corresponding to an ethylenic hydrogen, should be a singlet at lower field.

In ^{13}C NMR spectra, the carbon 9 gave around 150 ppm a singlet or a doublet with a small P-C coupling constant ($^3J_{P\text{-}C}$ = 3 to 4 Hz), corresponding to an ethylenic carbon bonded to two oxygens whereas in the case of the 1,2-addition on the CO group, this carbon should resonate at higher field (80–100 ppm) in the form of a doublet with a large $^1J_{PC}$ coupling.

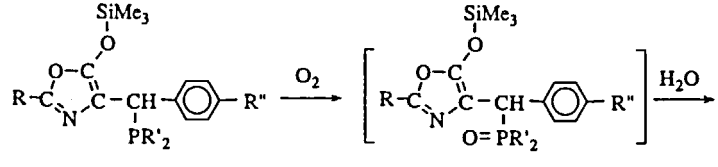
In mass spectrometry the molecular peak was generally observed.

All these adducts are air-and-moisture sensitive and must be handled under inert atmosphere to avoid the cleavage of the silicon-oxygen bond.

2) Oxidation and hydrolysis

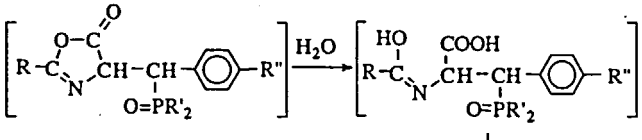
The adducts **5a, 6a, 7b-e** and **8b-f** slowly oxidized and hydrolyzed when left in solution in air or when treated with wet oxygen. The final products were the phosphorus amido-acids **9–11.**

The first step of these reactions was probably the formation of the phosphane oxides **12** followed immediately by the cleavage of the Si-O bond leading to **13**; this cleavage was in this case very easy since the formation of the hexamethyldisiloxane $(Me_3Si)_2O$ is extremely favourable. The next step is the opening of the five membered-ring due to the cleavage of the lactonic ring leading to **14** and finally the formation of the phosphorus amido-acids **9a, 10** and **11.** Intermediates **12, 13** and **14** could not be evidenced by NMR but the proof of this reaction process is given by the study of the sulfuration (see further).

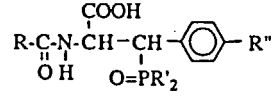


R = Me; R' = H, **5a**
R = Ph; R' = Et, **6a** , R' = iPr, **8b-f**
R = Me; R' = iPr, **7b-e**

12



13 **14**



R = Ph; R' = Et, **9a**, R' = iPr, **11b-f**
R = Me; R' = iPr, **10bde**

The amido-acids **9a, 10bde** and **11b-f** are poorly soluble in solvents such as Et_2O, THF or chloroform, and the NMR study could only be made in DMSO-d_6.

The NMR analysis performed immediately after reaction showed surprisingly only one diasteroisomer instead of the two expected due to chiral C_7 and C_8.

Physicochemical data for 9, 10 and 11

^{31}P NMR spectra display signals between 55 and 59 ppm, in the expected range for phosphane oxides.

In ^1H NMR, the methyls of the iPr groups appear generally as a complex multiplet which could be fully resolved only for **11e**; in this case we observed the four expected doublets of doublets (the two methyl groups of every iPr and the two iPr are diastereotopic) due to a ^3J coupling with proton and phosphorus. The larger $^3J_{P\text{-}H}$ coupling of 15.8 Hz (instead of 11–12 Hz in trivalent phosphorus compounds) proves the formation of a P(IV) derivative.

The proton on C_8 gives a ^3J coupling with phosphorus, proton on C_7 and proton on nitrogen and could be analyzed only in some cases (**10d, 11b, 11e**).

The NH chemical shifts for compounds **10** and **11** are different: they were observed respectively in the range 7.75–7.95 ppm (**10b, 10d, 10e**) and generally about 1 ppm at lower field for **11c-f** (8.89–9.00 ppm) with smaller $^3J_{HH}$ coupling constants for **11c-f** (3.0 to 5.3 Hz) than for **10b, 10d, 10e** and **11b** (5.7 to 8.3 Hz). Similar differences appeared for the acidic proton, in the range 9.35–9.40 ppm for **10b** and **10d** and 12.50–12.87 ppm for **11b-f**.

In $^{13}C\{^1H\}$ NMR, the methyls of iPr groups give only two doublets (instead of the four expected like in ^1H NMR) with a large ^2J coupling with phosphorus of 20–30 Hz characteristic of a P(IV) (generally 9–11 Hz in compounds **6, 7**and **8** with a P(III)). Since the two iPr groups are different, as proved by the presence of a doublet for every CH (excepted in **10b** and **10e**), we can suppose that the two methyls of every iPr are isochrone.

In IR, two absorptions are observed round 1650–1660 cm^{-1} and 1695–1720 cm^{-1} attributed to the CO amide and acid respectively.

In mass spectrometry, the molecular peaks are observed, whereas one of the most important fragment generally corresponds to the loss of both $P(O)iPr_2$ and COOH.

3) Sulfuration and hydrolysis

The proof of the process of oxidation and hydrolysis of **6–8** was given by the reaction of **5a, 7b-e** and **8b-f** with sulfur, followed by hydrolysis: the thiophosphane oxides **16b-e** and **17b-f**, analogues of the intermediate phosphane oxides **12**, have been isolated when the sulfuration is carried out under nitrogen. Hydrolysis with excess of water gives the corresponding thiophosphorus amido-acids **19b-e** and **20b-f.**

However, the hydrolysis reaction is quite different for the compounds substituted on C_{10} by a methyl (**16b-e**) or by a phenyl group (**17b-f**). Whereas **16bde** in wet benzene give directly the phosphorus amido-acids **19bde** by opening of the five-membered ring, **17b-f** give first the hydrolysis compounds **18b-f** due to the cleavage of the Si-O bond, with formation of a carbonyl group, but without opening of the ring. ^{1}H and ^{31}P NMR analyses show that **18b-f** are obtained in the form of two diastereoisomers **18′b-f** and **18″b-f**. A slow thermodynamic equilibrium occurred in all cases (see table I); the final ratio was observed after about 2 days in solution at room temperature.

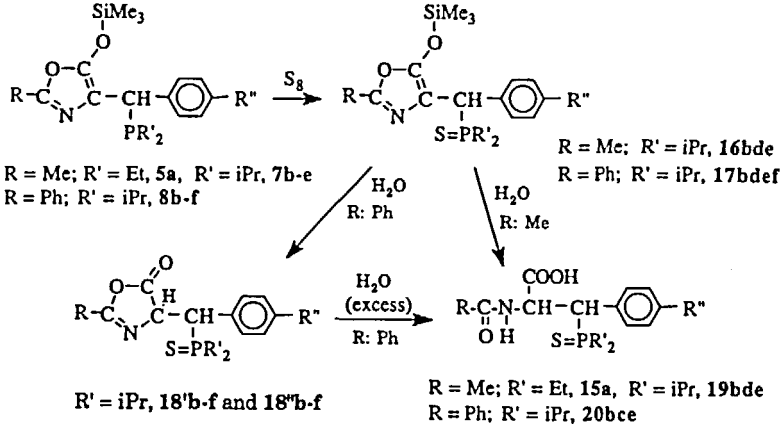
TABLE I ^{1}H NMR data for C7 and C8 in derivatives **18** and ratio **18′/18″**

	ratio	HC_7 *(ppm)*	HC_8 *(ppm)*	$^{3}J_{HH}$ *(Hz)*	$^{2}J_{HP}$ *(Hz)*	$^{3}J_{HP}$ *(Hz)*
18′b	75	3.81	5.90	2.6	17.2	9.8
18″b	25	4.01	4.96	3.7	13.3	20.7
18′c	70	3.98	5.87	2.5	17.2	9.6
18″c	30	4.02	4.97	4.0	12.8	20.4
18′d	62	3.66	5.88	2.5	16.9	9.8
18″d	38	4.03	4.95	4.3	13.3	19.7
18′e	70	3.94	5.95	2.5	16.5	9.9
18″e	30	4.01	5.00	4.4	12.7	19.6
18′f	45	3.97	5.87	2.5	16.0	10.0
18″f	55	4.10	5.06	5.4	11.7	18.6

As their isomerisation is slow, it has been possible by fractional crystallization to isolate the almost pure diastereoisomers **18′b-e** and **18″f** and to

perform their dynamic NMR study immediately after their dissolution. By contrast the minor diastereoisomers could not be isolated in completely pure form.

When excess of water was added to **18b-f**, the amido-acids **20b-f** were obtained, generally after heating at 50°C, in the form of only one diastereoisomer:



Physicochemical data for 16–20

In ^{31}P NMR spectra, signals were observed in the expected range for thiophosphorus derivatives, between 73–75 ppm for **16** and **17**, and between 63–70 ppm for **18, 19** and **20**.

In ^{13}C NMR spectra, generally 4 doublets with a very small $^{2}J_{PC}$ coupling constant (between 2 and 3 Hz) were observed for the methyls of iPr groups in **16**. Surprisingly, for compounds **19**, there is only one doublet for these groups which thus appear isochrone whereas two doublets are as expected observed for the CH of the iPr.

By contrast, in compounds with R = Ph (**17, 18** and **20**), the signals of the methyls of iPr could not be analyzed, except in the case of **17b**.

In ^{1}H NMR, the two diastereoisomers **18'** and **18"** present great differences (see table I). In each case two doublets of doublets are observed, as expected, for the H on C_7 and C_8; but, if the chemical shifts are similar in **18'** and **18"** for (H)C_7, they are extremely different for (H)C_8: about 1 ppm at lower field in **18'** than in **18"**. Similar huge differences are observed for coupling constants, particularly for $^{3}J_{HP}$ which changes from 9.6 to 9.8 Hz

in **18′** to 18.6 to 20.7 Hz in **18″**. The explanation of such a phenomenon is not clear and may be due to a great difference of conformations of the diastereoisomers.

Preliminary experiments show that amido-acids **10–11** and **19–20** seem good precursors of new types of oxo (or thio)phosphorus amino-acids by acidic cleavage of the C(O)-N(H) bond. Such reactions are now in progress as well as the pesticide screening of the various amido-acids synthesized in this study.

EXPERIMENTAL SECTION

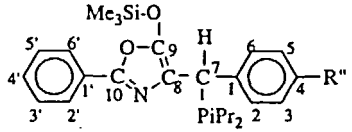
As the starting silylphosphanes **3** and **4** and adducts **5–8** and **16–17** are highly air- and moisture-sensitive, their synthesis and handling require high-vacuum techniques and the use of carefully deoxygenated solvents which must be freshly distilled from sodium benzophenone.

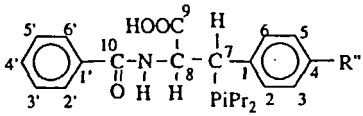
^{1}H NMR spectra were recorded on Bruker AC 80, AC 200 and AC 250 instruments at 80.1, 200.1 and 250.1 MHz (reference: TMS) respectively ; $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AC 200 and AC 250 instruments at 50.3 and 62.9 MHz (reference TMS), respectively. ^{31}P NMR spectra were recorded on a Bruker AC 80 and AC 200 at 32.4 and at 81.0 MHz (reference H_3PO_4), respectively. The NMR solvent was $CDCl_3$ except when another solvent is reported. Chemical shifts are reported in ppm.

IR spectra were recorded on a Perkin-Elmer 1600 FT instrument. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz microscope heating stage 350. Elemental analyses, performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse, France" gave satisfactory results within 0.4% error and are not reported.

The starting oxazolones **1** and **2** have been prepared according to known procedures, by reaction of the acids $RCONHCH_2COOH$ with the aldehydes $R''C_6H_4$-C(H)O in the presence of sodium acetate and acetic anhydride[7]. The diethyl(trimethylsilyl)phosphane **3**[5] was prepared from chlorotrimethylsilane and the corresponding lithium phosphide.

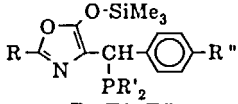
The numbering of the atoms is as follows:



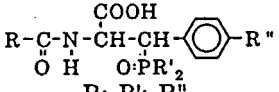


Yield, color, melting points and $\delta^{31}P$ NMR for all the isolated compounds are reported in table II. As $\delta^{1}H$ and $\delta^{13}C$ NMR, IR and MS data are similar in every series of compounds, we give in this experimental section such data for only one compound in every series. The full experimental section with all the physicochemical data (yield, color, melting points, ^{1}H, ^{13}C, ^{31}P NMR, IR and MS) for all the isolated compounds (16 pages) will be sent upon request from the French authors in Toulouse.

TABLE II Yields, color, melting points and $\delta\ ^{31}P$ NMR for the isolated compounds

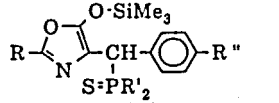
 R; R'; R"		*Yield (%)*	*color*	*m.p. (°C)*	*$\delta\ ^{31}P$ NMR ($CDCl_3$)*
Me; Et; H	**5a**	73	yellow	90–93	-3.7
Ph; Et; H	**6a**	69	yellow	120–123	-1.8
Me; iPr; Me	**7b**	80	white	122–124	19.6
Me; iPr; OMe	**7c**	70	white	*	19.6
Me; iPr; F	**7d**	85	yellow	150–152	21.0
Me; iPr; CF_3	**7e**	80	white	160–162	22.5
Ph; iPr; Me	**8b**	81	yellow	127–128	21.8
Ph; iPr; OMe	**8c**	75	yellow	148	19.2
Ph; iPr; F	**8d**	85	yellow	162	22.5
Ph; iPr; CF_3	**8e**	82	yellow	197–199	25.0
Ph; iPr; NO_2	**8f**	73	yellow	139–140	28.1

* isolated in not completely pure form (~ 90 %).



R; R'; R"

		yield (%)	*color*	*m.p. (°C)*	$\delta^{31}P$ *NMR (DMSO-d_6)*
Ph; Et; H	**9a**	57	white	202–205	53.9
Me; iPr; Me	**10b**	75	white	174–175	56.1
Me; iPr; F	**10d**	80	white	178–180	55.0
Me; iPr; CF_3	**10e**	77	white	226–227	55.8
Ph; iPr; Me	**11b**	78	yellow	264	58.6
Ph; iPr; OMe	**11c**	70	yellow	220	59.1
Ph; iPr; F	**11d**	80	white	203–205	59.0
Ph; iPr; CF_3	**11e**	78	white	210–212	58.6
Ph; iPr; NO_2	**11f**	76	white	215–216	58.7

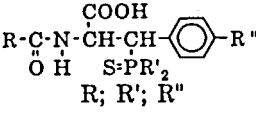


R; R'; R"

		yield (%)	*color*	*m.p. (°C)*	$\delta^{31}P$ *NMR (CDCl$_3$)*
Me; iPr; Me	**16b**	76	yellow	113	73.1
Me; iPr; F	**16d**	81	yellow	204–206	73.4
Me; iPr; CF_3	**16e**	85	yellow	128	73.8
Ph; iPr; Me	**17b**	82	yellow	130	73.7
Ph; iPr; F	**17d**	79	yellow	170–172	74.0
Ph; iPr; CF_3	**17e**	85	yellow	115	74.4
Ph; iPr; NO_2	**17f**	78	yellow	139–140	75.0

		*yield (%)*	*color*	*m.p. (°C)*	$\delta^{31}P$ *NMR (CDCl₃)*
Me	**18′b**	75	yellow	140	74.1
Me	**18″b**	**			69.3
OMe	**18′c**	83	yellow	178	74.1
OMe	**18″c**	**			69.3
F	**18′d**	85	white	134	73.9
F	**18″d**	**			70.1
CF_3	**18′e**	81	white	224	74.4
CF_3	**18″e**	**			70.5
NO_2	**18′f**	**			71.1
NO_2	**18″f**	79	yellow	148–150	74.6

** minor isomer not isolated.

		*yield (%)*	*color*	*m.p. (°C)*	$\delta^{31}P$ *NMR (DMSO-d_6)*
Me; iPr; Me	**19b**	77	white	273–275	66.1
Me; iPr; F	**19d**	68	white	197–198	66.3
Me; iPr; CF_3	**19e**	84	white	270–275	68.7
Ph; iPr; Me	**20b**	88	yellow	268	63.4
Ph; iPr; OMe	**20c**	83	white	233	68.3
Ph; iPr; CF_3	**20e**	85	white	115	70.0

Synthesis of diisopropyl(trimethylsilyl)phosphane 4

(**4** has been reported in reference 6 as K. Brandt, Diplomarbeit, Universität Munster, 1997, but without any physicochemical data).

One equivalent of nBuLi 1.6 M in hexane (71.5 ml) was added at room temperature to a solution of iPr_2PH (13.50 g, 114.41 mmol) in Et_2O (50 ml). The yellow solution obtained was refluxed for 1h then cooled again at room temperature. Me_3SiCl (12.41 g, 114.41 mmol) was added dropwise. After 1h at 35°C, the lithium salts were removed by filtration and 15.43 g (71%) of **4** were obtained by distillation; bp: 90/15 mmHg.

NMR: ^{1}**H** : 0.15 (d, $^3J_{HP}$: 3.8 Hz, Me_3Si), 1.04 and 1.12 (2dd, $^3J_{HH}$: 7.1 Hz, $^3J_{HP}$: 12.7 Hz, $C\underline{H}_3CHP$), 1.99 (sept d, $^3J_{HH}$: 7.1 Hz, $^2J_{HP}$: 3.8 Hz, PCH).

^{13}**C** : 0.69 (d, $^2J_{CP}$: 10.6 Hz, Me_3Si), 20.84 (d, $^1J_{CP}$: 13.8 Hz, PCH), 22.60 (d, $^2J_{CP}$: 12.2 Hz, PCH$\underline{Me}$), 22.83 (d, $^2J_{CP}$: 11.1 Hz, PCH$\underline{Me}$)

^{31}**P**: – 42.7.

Synthesis of 5a and 6a

To a solution of **1a** (0.63 g, 3.90 mmol) or **2a** (0.98 g, 3.90 mmol) in Et_2O (20 ml) was added one equivalent of **3** (0.73 g) in solution in Et_2O (5 ml). After stirring for 1h at room temperature and removal of Et_2O, crude **5a** and **6a** were crystallized from pentane (yellow crystals).

5a: 0.99 g (73%), mp: 90–93°C

NMR: ^{1}**H** : 0.26 (s, $SiMe_3$), 0.78–1.45 (m, CH_3CH_2P), 2.36 (s, MeC), 3.74 (d, $^2J_{HP}$: 4.6 Hz, CHP), 7.12–7.46 (m, Ph).

^{31}**P**: – 3.7.

6a: 1.10 g (69%), mp: 120–123°C

NMR: ^{1}**H** : 0.32 (s, $SiMe_3$), 0.86–1.46 (m, CH_3CH_2P), 4.85 (d, $^2J_{HP}$: 8.0 Hz, CHP), 7.21–7.91 (m, Ph).

^{31}**P**: – 1.8.

General procedure for the synthesis of 7b-e and 8b-f

To a solution of **1b-e** or **2b-f** (4.0 mmol) in C_6H_6 (20 ml) was added one equivalent of **4** (0.76 g). The reaction mixture was stirred for one hour at room temperature. In the case of **2f**, half an hour at 50°C was necessary to

complete the reaction. Then benzene was removed *in vacuo*. Recrystallization from Et_2O gave pure **7b-e** and **8b-f.**

7b: 0.91 g (80 %), white crystals, mp: 122–124°C

NMR: ^{1}**H** : 0.23 (s, $SiMe_3$), 0.83, 0.88, 0.96 and 1.03 (4dd, $^3J_{HH}$: 7.0 Hz, $^3J_{HP}$: 11.9 Hz, $C\underline{H}_3CHP$), 1.24–2.01 (m, $CH_3C\underline{H}P$), 2.21 and 2.23 (2s, $\underline{Me}Ph$ and $\underline{Me}CO$), 3.94 (d, $^2J_{HP}$: 4.7 Hz, HC_7), 7.02 (d, $^3J_{HH}$: 8.0 Hz, $HC_{3,5}$), 7.39 (d, $^3J_{HH}$: 8.0 Hz, $HC_{2,6}$).

^{13}**C** : 1.07 ($SiMe_3$), 14.34 ($\underline{Me}CO$), 4 d for $\underline{C}H_3CHP$ at 19.79 ($^2J_{CP}$: 9.0 Hz), 20.20 (11.6 Hz), 20.33 (13.2 Hz) and 20.73 (15.6 Hz), 21.07 ($\underline{Me}Ph$), 2 d for $CH_3\underline{C}HP$ at 23.08 ($^1J_{CP}$: 19.0 Hz) and 23.30 (19.5 Hz), 37.40 (d, $^1J_{CP}$: 20.4 Hz, C_7), 114.54 (d, $^2J_{CP}$: 9.6 Hz, C_8), 128.89 (C_3C_5), 128.98 (d, $^3J_{CP}$: 9.0 Hz, C_2C_6), 135.43 (C_4), 139.30 (d, $^2J_{CP}$: 9.8 Hz, C_1), 149.50 (C_9), 150.28 (C_{10}).

^{31}**P**: 19.6

MS: 392 (M + 1, 1), 274 (M – $PiPr_2$, 40), 201 (M – $PiPr_2$ - $SiMe_3$, 40), 131 ($CHPiPr_2$ + 1, 100), 73 ($SiMe_3$, 60).

8c: 1.32 g (75 %), yellow crystals, mp: 148 °C

NMR: ^{1}**H** : 0.34 (s, $SiMe_3$), 0.92, 0.97, 1.06 and 1.10 (4dd, $^3J_{HH}$: 7.1 Hz, $^3J_{HP}$: 11.3 Hz, $C\underline{H}_3CHP$), 1.74 and 1.87 (2 × d.sept, $^2J_{HP}$: 1.5 Hz, $^3J_{HH}$: 7.5 Hz, $CH_3C\underline{H}P$), 3.74 (s, OMe), 4.11 (d, $^2J_{HP}$: 4.4 Hz, HC_7), 6.82 (d, $^3J_{HH}$: 8.2 Hz, $HC_{3,5}$), 7.55 (d, $^3J_{HH}$: 8.2 Hz, $HC_{2,6}$), 7.30–7.45 and 7.86–7.99 (m, Ph).

^{13}**C** : 0.26 ($SiMe_3$), 4 d for $\underline{C}H_3CHP$ at 19.88 ($^2J_{CP}$: 9.2 Hz), 20.31 (10.4 Hz), 20.50 (12.8 Hz) and 20.73 (16.8 Hz), 23.20 (d, $^1J_{CP}$: 18.8 Hz, $CH_3\underline{C}HP$), 37.02 (d, $^1J_{CP}$: 20.3 Hz, C_7), 55.10 (OMe), 113.65 (C_3C_5), 116.80 (d, $^2J_{CP}$: 8.7 Hz, C_8), 125.27 ($C_{2'}C_{6'}$), 128.25 ($C_{1'}$), 128.80 ($C_{3'}C_{5'}$), 129.03 ($C_{4'}$), 130.17 (d, $^3J_{CP}$: 6.4 Hz, C_2C_6), 134.23 (d, $^2J_{CP}$: 9.9 Hz, C_1), 150.30 (d, $^3J_{CP}$: 3.8 Hz, C_9), 150.58 (C_{10}), 158.05 (C_4).

^{31}**P:** 19.2

MS: 469 (M, 1), 454 (M-Me, 2), 426 (M – iPr, 20), 352 (M – $PiPr_2$, 100).

Synthesis of 9a

Wet oxygen was bubbled through a solution of 1.41 g (3.43 mmol) of **6a** in Et_2O (20 ml). After 1h stirring, recrystallization of crude **9a** in a 50/50 mixture Et_2O/pentane gave 0.66 g (57 %) of white crystals (mp : 202 – 205°C).

NMR: ^{1}**H** (DMSO-d_6): 0.57–2.08 (m, CH_3CH_2P), 3.84 (dd, $^{3}J_{HH}$: 7.5, $^{2}J_{HP}$: 9.6 Hz, HC_7), 5.15 (dt, $^{3}J_{HH}$= $^{3}J_{HP}$: 6.3, $^{3}J_{HNH}$: 7.5 Hz, HC_8), 7.23–7.76 (m, arom. H), 8.67 (d, $^{3}J_{HH}$: 7.5 Hz, NH), 12.76 (s, COOH).

^{13}**C** (DMSO-d_6): 5.10 (d, $^{2}J_{CP}$: 4.7 Hz, $\underline{C}H_3CH_2P$), 5.89 (d, $^{2}J_{CP}$: 4.5 Hz, $\underline{C}H_3CH_2P$), 18.96 (d, $^{1}J_{CP}$: 67.4 Hz, CH_2P), 19.22 (d, $^{1}J_{CP}$: 63.2 Hz, CH_2P), 43.90 (d, $^{1}J_{CP}$: 56.6 Hz, C_7), 52.60 (C_8), 127.02–131.38 (arom. CH), 133.70 (C_1'), 134.7 (d, $^{2}J_{CP}$: 4.4 Hz, C_1), 166.80 (C_{10}), 170.87 (d, $^{3}J_{CP}$: 6.9 Hz, C_9)

^{31}**P**((DMSO-d_6) : 53.9.

MS: 373 (M, 2), 329 (M – CO_2, 5), 105 (PhCO, 100).

General procedure for the synthesis of 10bde and 11b-f

Solutions of **7bde** or **8b-f** (3.5 mmol) in C_6H_6 (20 ml) were both oxidized and hydrolyzed by oxygen containing water. After two hours under stirring the reaction was complete. The same result was obtained when solutions of **7bde** or **8b-f** were left for a few days at room temperature in air; the oxydation and hydrolysis products slowly precipitate. Benzene was removed *in vacuo* and the crude material was washed with Et_2O to afford pure **10bde** and **11b-f**.

10d: 0.99 g (80 %), white crystals, mp: 178 – 180 °C

^{1}**H** (DMSO-d_6): 0.60–1.34 (m, $C\underline{H}_3CHP$), 1.45–2.30 (m, $CH_3C\underline{H}P$), 1.82 (s, $\underline{Me}CO$), 3.84 (dd, $^{3}J_{HH}$: 5.4, $^{2}J_{HP}$: 9.3 Hz, HC_7), 5.04 (ddd, $^{3}J_{HH}$: 5.4, $^{3}J_{HP}$: 8.0, $^{3}J_{HNH}$: 5.7 Hz, HC_8), 7.03–7.76 (m, arom. H), 7.85 (d, $^{3}J_{HNH}$: 5.7 Hz, NH), 9.40 (s, COOH).

^{13}**C** (DMSO-d_6): 2 d for $\underline{C}H_3CHP$ at 16.03 ($^{2}J_{CP}$: 23.8 Hz) and 16.29 (17.6 Hz), 22.39 ($\underline{Me}CO$), 25.72 (d, $^{1}J_{CP}$: 62.5 Hz, $CH_3\underline{C}HP$), 25.87 (d, $^{1}J_{CP}$: 60.4 Hz, $CH_3\underline{C}HP$), 51.82 (C_8), 114.90 ($^{2}J_{CF}$: 21.3 Hz, C_3C_5), 127.00 (C_1), 131.89 (d, $^{3}J_{CF}$ or C_P: 8.3 Hz, C_2C_6), 161.62 (d, $^{1}J_{CF}$: 244.0 Hz, C_4), 169.33 (C_{10}), 170.99 ($^{3}J_{CP}$: 9.6 Hz, C_9).

^{31}**P** (DMSO-d_6): 55.0.

IR: 1650 (CONH) and 1702 (COOH) cm^{-1}.

MS: 358 (M + 1, 9), 181 (M – P(O)iPr_2 -MeCO, 16), 179 (M – P(O)iPr_2 – COOH, 13), 134 (P(O)iPr_2 + 1, 42), 43 (iPr or MeCO, 100).

11e: 1.26 g (78 %), white crystals, mp: 210-212 °C

^{1}**H** (DMSO-d_6): 0.83, 0.91, 1.23 and 1.27 (4dd, $^{3}J_{HH}$: 7.2 Hz, $^{3}J_{HP}$: 15.8 Hz, $C\underline{H}_3CHP$), 1.90–1.99 and 2.43–2.52 (m, $CH_3C\underline{H}P$), 4.16 (dd, $^{3}J_{HH}$: 6.1, $^{2}J_{HP}$: 8.1 Hz, HC_7), 5.04 (ddd, $^{3}J_{HH}$: 6.1, $^{3}J_{HP}$: 9.1, $^{3}J_{HNH}$:

5.3 Hz, HC_8), 7.35–7.83 (m, arom. H), 8.97 (d, $^3J_{HNH}$: 5.3 Hz, NH), 12.40 (broad s, COOH).

^{13}C (DMSO-d_6): 2 d for $\underline{C}H_3CHP$ at 15.78 ($^2J_{CP}$: 21.0Hz) and 16.26 (27.9 Hz), 2 d for $CH_3\underline{C}HP$ at 25.83 ($^1J_{CP}$: 59.8 Hz) and 26.30 (63.1 Hz), 54.01 (C_8), 124.59 ($^1J_{CF}$: 318.6 Hz, CF_3), 124.96 (C_3C_5), 126.90, 128.22 and 128.46 ($C_{2'} - C_{6'}$), 129.28 (C'_1), 131.54 ($^3J_{CP}$: 8.0 Hz, C_2C_6), 133.40 ($C_{1'}$), 138.98 (C_1), 166.24 (C_{10}), 169.64 ($^3J_{CP}$: 9.3 Hz, C_9).

^{31}P (DMSO-d_6): 58.6.

IR(cm^{-1}) : 1662 (CONH), 1720 (COOH), 1121 (CF_3).

MS: 470 (M + 1, 22), 425 (M – COOH + 1, 12), 336 (M – P(O)iPr_2, 10), 292 (M - P(O)iPr_2 – COOH + 1, 74), 134 (P(O)iPr_2 + 1, 100), 105 (PhCO, 75).

Sulfuration and hydrolysis of 5a

To a solution of 1.35 g (3.87 mmol) of **5a** was added one equivalent of sulfur. The reaction mixture was refluxed for 1 h and then hydrolyzed. After extraction with Et_2O and drying over Na_2SO_4, recrystallization of the crude compound from Et_2O gave pure **15a** (1.02 g, 81%), white crystals, mp: 74 – 77°C.

^1H : 0.82–2.19 (m, CH_3CH_2P), 1.92 (s, Me), 3.00 (dd, $^3J_{HH}$: 6.7 Hz, $^2J_{HP}$: 11.4 Hz, C_7), 5.24 (ddd, $^3J_{HH}$: 6.7 Hz, $^3J_{HP}$: 13.3 Hz, $^3J_{HNH}$: 8.1 Hz, CHN), 6.84 (d, $^3J_{HH}$: 8.1 Hz, NH), 7.24–7.73 (m, arom. H), 9.91 (s, COOH).

IR(cm^{-1}) : 1650 (CONH), 1703 (COOH).

MS: 328 (M + 1, 2), 327 (M, 1), 206 (M – P(S)Et_2, 43), 121 (P(S)Et_2, 18), 43 (iPr or MeCO, 100).

General procedure for the sulfuration of 7b-e and 8bdef: synthesis of 16bde and 17bdef

One equivalent of sulfur was added to solutions of **7b-e** or **8b-f** (3.0 mmol) in benzene (20 ml) under nitrogen. After an hour under stirring, a NMR analysis showed the complete disappearance of the starting material and the formation of new compounds; then the solvent was removed *in vacuo*. Recrystallization from Et_2O, under nitrogen, gave pure **16bde** or **17bde**. **17f** was not recrystallized due to its poor solubility; the crude product,

after removal of benzene, was washed with dry acetone; **17c** could not be obtained in pure form.

16e: 1.20 g (85 %), yellow crystals, mp: 128°C

NMR: ^{1}**H** : 0.18 (s, $SiMe_3$), 0.75–1.30 (m, $C\underline{H}_3CHP$), 1.90–2.78 (m, $CH_3C\underline{H}P$), 2.33 (s, $\underline{Me}CO$), 4.37 (d, $^{2}J_{HP}$: 18.1 Hz, HC_7), 7.49 (d, $^{3}J_{HH}$: 8.3 Hz, $HC_{3,5}$), 7.85 (d, $^{3}J_{HH}$: 8.3 Hz, $HC_{2,6}$).

^{13}**C** : 0.02 ($SiMe_3$), 14.44 ($\underline{Me}CO$), 4 d for $\underline{C}H_3CHP$ at 16.82 ($^{2}J_{CP}$: 2.7 Hz), 16.92 (1.9 Hz), 17.15 (1.8 Hz) and 18.01 (1.9 Hz), 2 d for $CH_3\underline{C}HP$ at 27.32 ($^{1}J_{CP}$: 43.2 Hz) and 28.20 (45.2 Hz), 43.50 (d, $^{1}J_{CP}$: 37.9 Hz, C_7), 108.77 (d, $^{2}J_{CP}$: 5.1 Hz, C_8), 124.28 (q, $^{1}J_{CF}$: 272.2 Hz, CF_3), 124.57 (q, $^{2}J_{CF}$: 21.3 Hz, C_3C_5), 129.04 (q, $^{2}J_{CF}$: 20.9 Hz, C_4), 130.36 (d, $^{3}J_{CP}$: 3.5 Hz, C_2C_6), 140.37 (C_1), 150.82 (C_{10}), 151.77 (d, $^{3}J_{CP}$: 9.6 Hz, C_9), .

^{31}**P**: 73.8

MS: 478 (M + 1, 2), 458 (M – F, 1), 405 (M + 1 – $SiMe_3$, 2), 328 (M – P(S)iPr_2, 100), 256 (M + 1 – $SiMe_3$ – P(S)iPr_2, 14).

17b: 1.19 g (82 %), yellow crystals, mp: 130°C

NMR: ^{1}**H** : 0.29 (s, $SiMe_3$), 0.96–1.41 (m, $C\underline{H}_3CHP$), 2.05–2.80 (m, $CH_3C\underline{H}P$), 2.32 (s, $\underline{Me}Ph$), 4.50 (d, $^{2}J_{HP}$: 18.5 Hz, HC_7), 7.04–7.95 (arom. H).

^{13}**C** : 0.19 ($SiMe_3$), 4 d for $\underline{C}H_3CHP$ at 16.93 ($^{2}J_{CP}$: 2.8 Hz), 17.11 (1.9 Hz), 17.24 (1.5 Hz) and 18.43 (1.4 Hz), 21.20 ($\underline{Me}Ph$), 2 d for $CH_3\underline{C}HP$ at 27.32 ($^{1}J_{CP}$: 43.2 Hz) and 27.50 (44.6 Hz), 44.35 (d, $^{1}J_{CP}$: 38.9 Hz, C_7), 111.93 (d, $^{2}J_{CP}$: 4.6 Hz, C_8), 127.84 ($C_{1'}$), 132.69 (C_4), 125.24–130.32 (other arom. CH), 136.83 (d, $^{2}J_{CP}$: 2.9 Hz, C_1), 150.79 (C_{10}), 152.14 (d, $^{3}J_{CP}$: 9.9 Hz, C_9).

^{31}**P**: 73.7

MS: 486 (M + 1, 2), 336 (M – P(S)iPr_2, 100), 263 (M – $SiMe_3$ – P(S)iPr_2, 26), 105 (PhCO, 33).

General procedure for the synthesis of 18′b-f and 18″b-f

To solutions of **17b-f** (2.5 mmol) in benzene (20 ml) were added by syringe one equivalent of water. The reaction mixture was stirred overnight: the ^{1}H NMR analysis showed a mixture of the two diastereoisomers **18′b-f** and **18″b-f. 18′b-f** is the diastereoisomer which presents for HC_8 the signal the most deshielded. After removal of benzene *in vacuo,* recrystallization from Et_2O/pentane (50/50) afforded pure compounds **18′b-e.**

18″b-e could not be obtained in pure form. In the case of the compound with R″ being NO_2, it is the contrary: only **18″f**, poorly soluble, was obtained in pure form by washing with acetone. The physicochemical data could be obtained only for **18′b-e** or **18″f** which were obtained in pure form; for the minor isomers **18″b-e** and **18′f** only some signals could be determined in NMR, the others overlapped the signals of the major isomer.

18′b: 0.77 g (75 %), yellow crystals, mp: 140°C

NMR: ^{1}**H** : 4 dd for $C\underline{H}_3CHP$ at 0.99, 1.14, 1.20, 1.55 ($^3J_{HP}$: 17.9 Hz, $^3J_{HH}$: 7.0 Hz), 2.16 (s, Me Ph), 1.95–2.95 (m, $CH_3C\underline{H}P$), 3.81 (dd, $^2J_{HP}$: 17.2 Hz, $^3J_{HH}$: 2.6 Hz, HC_7), 5.90 (dd, $^3J_{HH}$: 2.6 Hz, $^3J_{HP}$: 9.8 Hz, HC_8), 6.89–7.93 (arom. H).

^{13}**C** : 16.75 to 18.38 (m, $\underline{C}H_3CHP$), 2 d for $CH_3\underline{C}HP$ at 25.56 ($^1J_{CP}$: 44.0 Hz) and 28.55 (48.3 Hz), 48.46 (d, $^1J_{CP}$: 38.5 Hz, C_7), 66.15 (C_8), 125.73 ($C_{1'}$), 128.01, 128.81 and 129.62 ($C_3C_5C_{2'}C_{3'}C_{5'}C_{6'}$), 130.24 (d, $^3J_{CP}$: 4.7 Hz, C_2C_6), 138.51 (C_1), 161.55 (C_{10}), 177.09 (d, $^3J_{CP}$: 17.6 Hz, C_9).

^{31}**P** : 74.1

IR(cm^{-1}) : 1654 (C=N) and 1812 (CO).

MS: 414 (M + 1, 8), 370 (M − iPr, 1), 264 (M − $iPr_2P(S)$, 100), 105 (PhCO, 72).

18″b: NMR: ^{1}**H** : 1 dd for $C\underline{H}_3CHP$ at 0.65 ($^3J_{HP}$: 17.5 Hz, $^3J_{HH}$: 7.0 Hz), 2.35 (s, Me Ph), 4.01 (dd, $^2J_{HP}$: 13.3 Hz, $^3J_{HH}$: 3.7 Hz, HC_7), 4.96 (dd, $^3J_{HH}$: 3.7 Hz, $^3J_{HP}$: 20.7 Hz, HC_8).

^{13}**C** : 45.57 (d, $^1J_{CP}$: 40.1 Hz, C_7), 68.03 (C_8), 125.95 ($C_{1'}$), 138.40 (C_1), 164.05 (C_{10}), 176.50 (C_9).

^{31}**P** : 69.3

18′f: NMR: ^{1}**H** : 3.97 (dd, $^2J_{HP}$: 16.0 Hz, $^3J_{HH}$: 2.5 Hz, HC_7), 5.87 (dd, $^3J_{HH}$: 2.5 Hz, $^3J_{HP}$: 10.0 Hz, HC_8).

^{13}**C** : 2 d for $CH_3\underline{C}HP$ at 26.14 ($^1J_{CP}$: 44.3 Hz) and 28.87 (46.7 Hz), 48.44 (d, $^1J_{CP}$: 35.3 Hz, C_7), 65.81 ($^2J_{CP}$: 7.3 Hz, C_8), 124.10 ($C_{1'}$), 162.17 (C_{10}), 175.92 (d, $^3J_{CP}$: 6.1 Hz, C_9).

^{31}**P**: 71.1

18″f: 0.87 g (79 %), yellow crystals, mp: 148 − 150°C

NMR: ^{1}**H** : 4 dd for $C\underline{H}_3CHP$ at 0.70, 1.06, 1.23, 1.41 ($^3J_{HP}$: 16.4 Hz, $^3J_{HH}$: 7.1 Hz), 2.05–2.95 (m, $CH_3C\underline{H}P$), 4.10 (dd, $^2J_{HP}$: 11.7 Hz, $^3J_{HH}$: 5.4 Hz, HC_7), 5.06 (dd, $^3J_{HH}$: 5.4 Hz, $^3J_{HP}$: 18.6 Hz, HC_8), 7.24–8.30 (arom. H).

^{13}C : 16.83 to 18.30 (m, $\underline{C}H_3CHP$), 2 d for $CH_3\underline{C}HP$ at 27.18 ($^1J_{CP}$: 44.7 Hz) and 28.40 (44.7 Hz), 45.56 (d, $^1J_{CP}$: 36.7 Hz, C_7), 66.98 (d, $^2J_{CP}$: 1.2 Hz, C_8), 123.83 to 133.43 (arom CH), 125.01 ($C_{1'}$), 163.50 (C_{10}), 177.46 (d, $^3J_{CP}$: 16.2 Hz, C_9).

^{31}P : 74.6

MS: 444 (M, 3), 412 (M – S, 35), 294 (M – $iPr_2P(S)$-1, 20), 105 (PhCO, 100), 43 (iPr, 60).

General procedure for the synthesis of 19bde

To solutions of **16b-e** (2.5 mmol) in C_6H_6 (20 ml) was added an excess of water. After stirring overnight, benzene was removed *in vacuo* to afford crude **19b-e**. Recrystallization in Et_2O gave pure **19bde, 19c** was not obtained in completely pure form after several recrystallizations.

19d: 0.73 g (68 %), white crystals, mp: 197–198 °C

NMR ^{1}H (DMSO-d_6): 4 dd for $C\underline{H}_3CHP$ at 0.85, 0.88, 1.22, 1.30 ($^3J_{HP}$: 16.0 Hz, $^3J_{HH}$: 7.1 Hz), 1.80–2.60 (m, $CH_3C\underline{H}P$), 1.76 (s, MeCO), 4.17 (dd, $^3J_{HH}$: 5.3, $^2J_{HP}$: 11.3 Hz, HC_7), 5.19 (ddd, $^3J_{HH}$: 5.3 and 9.2 Hz, $^3J_{HP}$: 8.0 Hz, HC_8), 7.16 (t, $^3J_{HH} = {}^3J_{HF}$: 8.8 Hz, $HC_{3,5}$), 7.62 (dd, $^3J_{HH}$: 8.8 Hz, $^4J_{HF}$: 5.7 Hz, $HC_{2,6}$), 7.92 (d, $^3J_{HH}$: 9.2 Hz, NH), 10.49 (s, COOH).

^{13}C : 16.86 (d, $^2J_{CP}$: 6.5 Hz, $\underline{C}H_3CHP$), 22.36 ($\underline{Me}CO$), 2 d for $CH_3\underline{C}HP$ at 28.08 ($^1J_{CP}$: 58.6 Hz) and 28.99 (57.4 Hz), 41.28 (d, $^1J_{CP}$: 40.4 Hz, C_7), 51.88 (C_8), 129.73 (C_1), 114.71 (d, $^2J_{CF}$: 21.3 Hz, C_3C_5), 132.81 (C_2C_6), 161.78 (d, $^1J_{CF}$: 244.8 Hz, C_4), 169.26 (C_{10}), 171.39 (d, $^2J_{CP}$: 9.0 Hz, C_9).

^{31}P (DMSO-d_6): 66.3.

IR (cm^{-1}) : 1625 (CONH) and 1712 (COOH),

MS: 374 (M + 1, 18), 298 (M – S – iPr (or MeCO), 8), 224 (M – $P(S)iPr_2$, 100), 108 (CHC_6H_4F, 12), 43 (iPr or MeCO, 37).

General procedure for the synthesis of 20bce

20bce can be obtained from **17** or from **18**. In both cases, starting from 2.5 mmol of pure **17be**, crude **17c** or **18bce** in C_6H_6 an excess of water was added and the reaction mixture was heated for lh at reflux. After removal of benzene *in vacuo,* recrystallization in Et_2O/pentane (50/50) afforded pure **20 bce.**

20c: 1.19 g (83 %), white crystals, mp: 233 °C

^{1}H (DMSO-d_6): 4 dd for $C\underline{H}_3CHP$ at 0.87, 0.90, 1.25, 1.27 ($^3J_{HP}$: 16.0 Hz, $^3J_{HH}$: 7.7 Hz), 1.80–2.10 and 2.45–2.65 (m, $CH_3C\underline{H}P$), 3.72 (OMe), 4.28 (dd, $^3J_{HH}$: 5.8, $^2J_{HP}$: 11.0 Hz, HC_7), 5.14 (ddd, $^3J_{HH}$: 5.8 and 6.7 Hz, $^3J_{HP}$: 6.0 Hz, HC_8), 6.91 (d, $^3J_{HH}$: 8.7 Hz, C_3C_5), 7.43–7.61 (m, Ph), 7.78 (d, $^3J_{HH}$: 8.7 Hz, C_2C_6), 8.58 (d, $^3J_{HH}$: 6.7 Hz, NH), 12.85 (s, COOH).

^{13}C (DMSO-d_6): 16.05–17.00 (m, $\underline{C}H_3CHP$), 2 d for $CH_3\underline{C}HP$ at 28.09 ($^1J_{CP}$: 46.5 Hz) and 28.96 (41.8 Hz), 40.35 (d, $^1J_{CP}$: 39.5 Hz, C_7), 54.05 (C_8), 54.94 (OMe), 113.45 (C_3C_5), 125.30 ($^2J_{CP}$: 3.9 Hz, C_1), 127.09 ($C_{2'}C_{6'}$), 128.37 ($C_{3'}C_{5'}$), 131.51 ($C_{4'}$), 131.84 ($^3J_{CP}$: 4.8 Hz, C_2C_6), 133.60 ($C_{1'}$), 158.87 (C_4), 167.09 (C_{10}), 170.45 (d, $^2J_{CP}$: 9.4 Hz, C_9).

^{31}P (DMSO-d_6): 68.3.

IR(cm^{-1}) : 1614 (CONH) and 1739 (COOH),

MS: 448 (M + 1, 2), 298 (M − P(S)iPr_2, 24), 253 (M − P(S)iPr_2 − COOH, 15), 105 (PhCO, 100), 43 (iPr, 69).

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