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Reactions of lithiated *P*-diphenyl(alkyl)(*N*-methoxycarbonyl)-phosphazenes with Michael acceptors and aldehydes. Synthesis of 1*H*-1,2-azaphosphinin-6-ones, β-hydroxy(*N*-methoxycarbonyl)-phosphazenes and 5,6-dihydro-1,3,4-oxazaphosphinin-2-ones

Julia M. Álvarez-Gutiérrez,[†] Emma Peralta-Pérez, Isidro Pérez-Álvarez and Fernando López-Ortiz[*]

Área de Química Orgánica, Universidad de Almería, Carretera de Sacramento s/n, 04120 Almería, Spain

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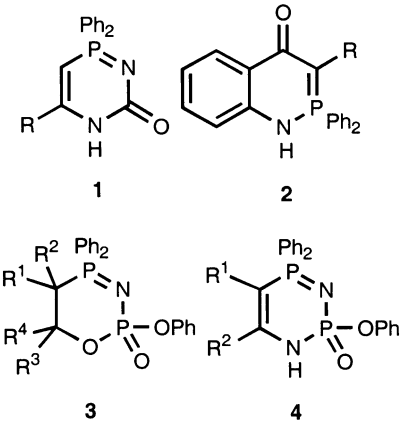
Abstract—Lithium (*N*-methoxycarbonyl)phosphazenes add *C*-regioselectively to DMAD, dimethyl malonate, fumarate, and butylidenmalonate in a [1,4] manner. Only one diastereoisomer is observed with the olefinic electrophiles. With DMAD the initial adduct evolves through cyclocondensation with the CO_2Me group of the phosphazene and 1*H*-1,2-azaphosphinin-6-ones are obtained. Exceptionally, methyl phenylpropiolate reacted exclusively through the carbonyl yielding a mixture of *C*- and *N*-acylated compounds. The addition to aldehydes at −80°C affords β-hydroxyphosphazenes diastereoselectively. For lithium α,α-dimethyl(*N*-methoxycarbonyl)phosphazenes, the intermediate alkoxides cyclocondense at room temperature to 5,6-dihydro-1,3,4-oxazaphosphinin-2-ones.

1. Introduction

Phosphorus-stabilised carbanions are very important synthetic tools for the formation of carbon–carbon[1] and carbon–heteroatom[2] bonds. Numerous examples are known where these anions have been applied to the synthesis of phosphorus substituted nitrogen heterocycles.[3] In the particular case of phosphazenes, the activation of the α position to the phosphorus towards the metalation may be combined with the appropriate functionalisation in the nitrogen of the PN linkage in order to achieve cyclocondensation reactions yielding phosphorus–nitrogen heterocycles where the phosphazene contributed as a CPNX [X=CO, C=CCO, P(O)OR)] building block to the formation of six-membered rings. This strategy has been successfully applied to the synthesis of 1,3,4-diazaphosphinin-2-ones **1**,[4] 1*H*-benzo[*e*]-1,2-azaphosphinin-4-ones **2**,[5] 1,3-oxaza-2,4-diphosphinine 2-oxides **3**,[6] and 1,3-diaza-2,4-diphosphinine 2-oxides **4**.[7]



In principle, phosphazene-stabilised carbanions could react with electrophiles either through carbon or nitrogen. In fact, some examples of phosphazene–aminoylide tautomer equilibria have been reported showing that the position of the equilibrium is determined by the substituents on the carbon and nitrogen atoms of the CPN moiety (Scheme 1).[8]

According to quantum mechanic calculations on the model compound $[Li(CH_2PH_2NH)]\cdot(Me_2O)_2$ the HOMO exhibits a much higher coefficient for the carbon than for the nitrogen,[9] which supports the *C*-regioselectivity exclusively observed in the reactions of lithium (*N*-substituted)phosphazenes with electrophiles reported to date.[10] Even though, the

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* Corresponding author. Tel.: +34-950-015478; fax: +34-950-015481; e-mail: flortiz@ual.es

† Present address: The Scripps Research Institute, BCC-104, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA

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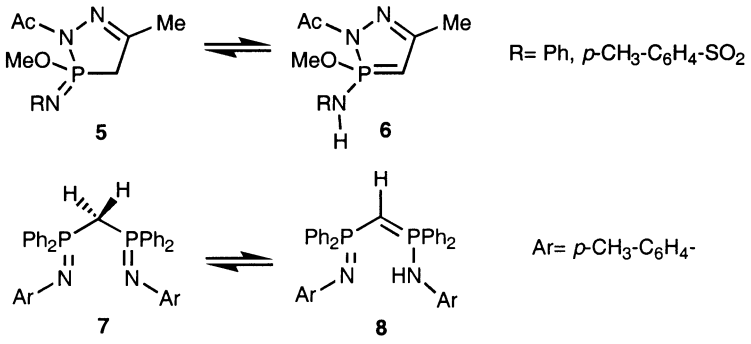


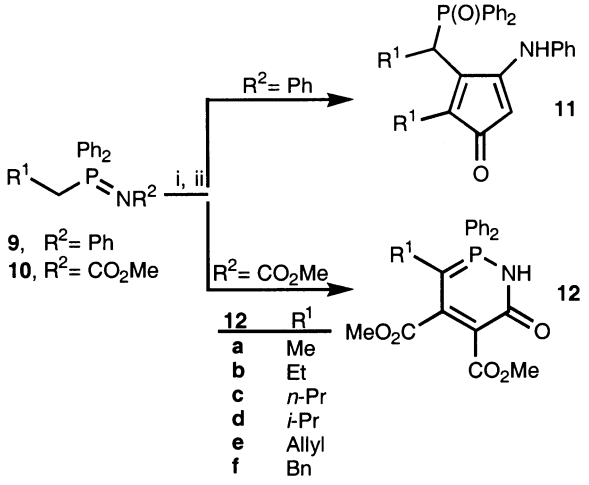
Scheme 1.

reactivity of these anions (and obviously the neutral species[10d]) strongly depends on the substituent in the nitrogen of the phosphazene. Thus, the addition of dimethyl acetylenedicarboxylate (DMAD) to metalated *P*-diphenyl(alkyl)(*N*-phenyl)phosphazenes **9** afforded cyclopentenones[11] **11** in a process initiated by the addition of the carbanion to one methoxycarbonyl group of the DMAD.[12] Instead, we have recently reported[13] that the use of the corresponding (*N*-methoxycarbonyl)phosphazenes **10** under the same reaction conditions leads to the formation of 1*H*-1,2-azaphosphinin-6-ones **12** due to the *C*-regioselective addition of the metalated phosphazene to the triple bond of the DMAD (Scheme 2).

Here we will give the full details of the synthesis and structural characterisation of heterocycles **12** and will present the results of extending the study of the reactivity of lithium *P*-diphenyl(alkyl)(*N*-methoxycarbonyl)phosphazenes to other Michael acceptors as well as to aldehydes. With this last electrophiles it has been possible to obtain 5,6-dihydro-1,3,4-oxazaphosphinin-2-ones **21**.

2. Results and discussion

The phosphazenes **10** used in this study are given in Table 1 and were easily prepared in high yield by one of the following routes (Scheme 3): (A) Staudinger reaction[14] of a commercial phosphine (R^1 H, Me) and methoxycarbonyl azide, (B) alkylation of a simpler phosphazene by treating **10a**,**b** with ^{n}BuLi followed by addition of the appropriate alkyl halide,10b,d and (C) *one pot* process consisting of the synthesis of the required phosphine by alkylation of lithium diphenylphosphide[15] (obtained through reductive lithiation of triphenylphosphine in THF) and subsequent in situ Staudinger reaction with N_3CO_2Me.



Scheme 2. (i) ^{n}BuLi, −20°C, THF, 30 min; (ii) DMAD, −70–25°C, 12 h.

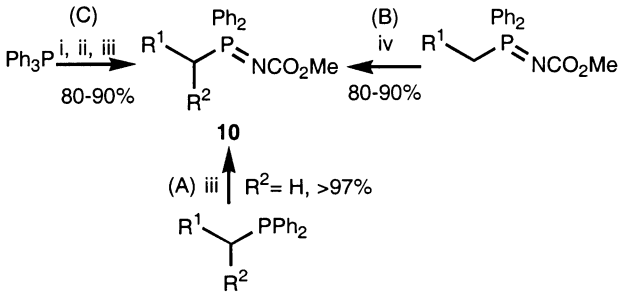
As mentioned above, the reaction of lithium phosphazenes **10**, metalated by treating the neutral compounds with ^{n}BuLi in THF at −30°C during 30 min, with DMAD at −78°C led to 1*H*-1,2λ^5-azaphosphinin-6-ones **12**.[13] In the first essays stoichiometric quantities of phosphazene, base and electrophile were used and systematically a 50% of the starting phosphazene was recovered. We reasoned that through the reaction the lithiated phosphazenes were acting both as nucleophile and as base. Therefore, an excess of ^{n}BuLi would be necessary to improve the reaction yield. We found that by using a phosphazene/^{n}BuLi/DMAD 1:2:2 ratio the heterocycles **12** were obtained practically in quantitative yields.

The structure of **12** was assigned based on their spectral data.[16,17] The formation of **12** can be explained by a Michael addition of the lithium phosphazene to the DMAD and subsequent cyclocondensation promoted by the intramolecular attack of the new carbanion to the methoxycarbonyl bonded to the nitrogen. The 3*H*-1,2-azaphosphinine obtained tautomerised to the final 2*H*-isomer (Scheme 4). The NH of compounds **12** justifies the need for using two

Table 1. δ^{31}P (ppm) and melting points (°C) of phosphazenes **10**

Product	R^1	R^2	δ^{31}P	Mp
10a[a]	H	H	23.54	65–66
10b[a]	H	CH_3	28.95	86–87
10c[b]	H	CH_3CH_2	25.79	92–93
10d[b]	H	CH_2=$CHCH_2$	25.64	81–82
10e[c]	H	$CH_3CH_2CH_2$	26.20	70–71
10f[c]	H	$(CH_3)_2CH$	24.10	94–95
10g[c]	H	$PhCH_2$	25.91	126–127
10h[b]	CH_3	CH_3	34.05	112–113
10i[b]	CH_3	$CH_3(CH_2)_3$	33.64	122–133
10j[b]	CH_3	$PhCH_2$	32.77	115–116
10k[b]	CH_3	CH_2=$CHCH_2$	32.94	77–78
10l[b]	$CH_3(CH_2)_3$	$PhCH_2$	33.35	oil

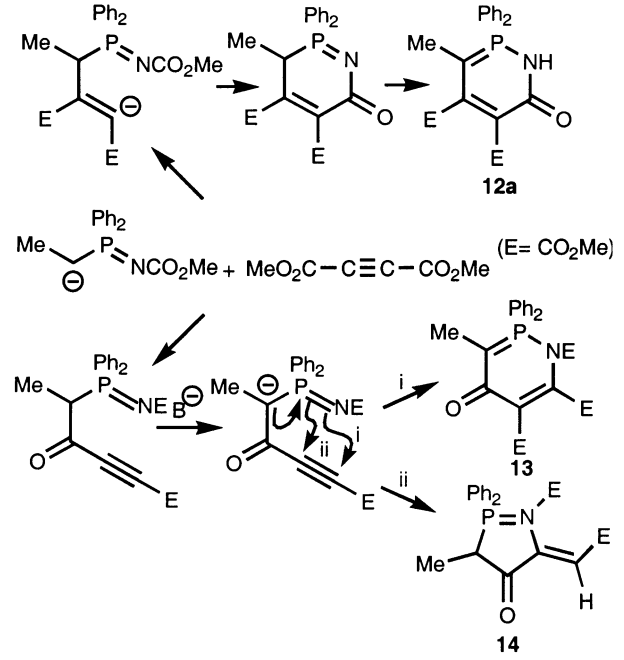
[a] Method A.
[b] Method B.
[c] Method C.



Scheme 3. (i) Li (2.2 equiv.), THF, 25°C, 2 h; (ii) (a) NH_4Cl, (b) R^1R^2CHX; (iii) N_3CO_2Me; (iv) (a) ^{n}BuLi, −30°C, THF, 30 min; (b) R^2X, −70–25°C, 3 h.

equivalents of ^{n}BuLi, otherwise up to 50% of the lithium phosphazene could be quenched assuming the quantitative formation of heterocycles **12**. Taking into account the reaction mechanism proposed for the synthesis of cyclopentenones **11** one could argue about the feasibility of compounds **13** and **14** as alternative structures for **12**. The reaction leading to **13**–**14** would involve the following steps: (i) addition of the carbanion to one carbonyl group of the DMAD, (ii) metalation of the resulting α-acylphosphazene, and (iii) intramolecular attack of the nitrogen to the triple bond. Depending on the regioselectivity, this attack could produce either **13** or **14** (Scheme 4). They can be easily ruled out by considering that both structures lack any exchangeable proton and, on the contrary, exhibit a conjugated ketone carbonyl carbon that should appear close to 200 ppm in the ^{13}C spectrum (and should show a correlation with the methyl protons in the 2D HMBC spectrum), which is not observed.

Surprisingly, in spite of the reaction conditions, the simplest phosphazene **10a** failed to give any heterocycle. By contrast, lithiated **10a** do react with other electrophiles (see below). λ^5-Azaphosphinines are compounds of

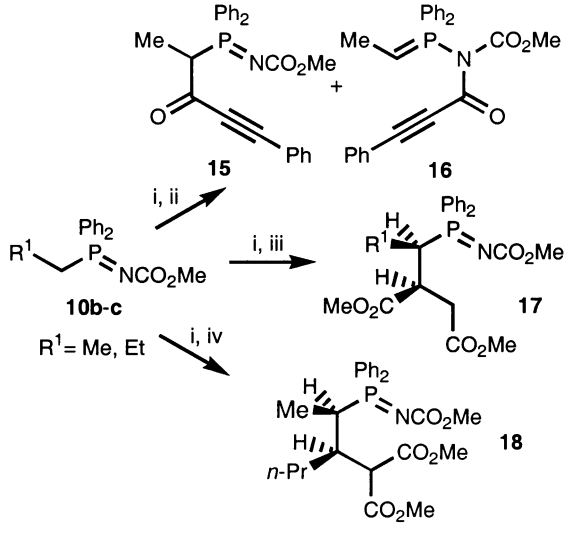


Scheme 4.

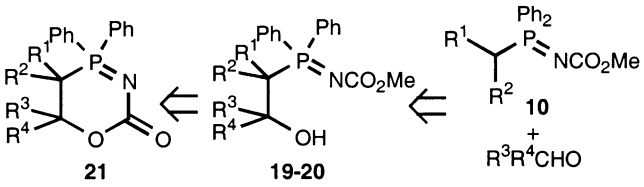
renewed interest in the last years.[18] Nevertheless, there are only a few reports on the synthesis of 1,2-λ^5-azaphosphinine derivatives.[19] The method we present here represents an efficient synthesis of this type of compound using readily available starting materials.

In order to extend the scope of the reaction and to have an insight into the mechanism we studied the behaviour of lithium phosphazenes **10** with other Michael acceptors related to DMAD. The reaction with ethyl phenylpropiolate afforded a 55:45 mixture of two compounds **15** (δ_P 35.65) and **16** (δ_P 26.55) in 70% yield (Scheme 5), which could not be separated. The NMR spectra of the mixture allowed to identify these compounds as the *C*- and *N*-acylation products, respectively. Thus, the ^{1}H spectrum of **15** showed a doublet for the methyl protons (δ 1.70, $^3J_{PH}$=14.5 Hz), whereas the ylide fragment of **16** is characterised by a double doublet at δ 1.54 ($^3J_{HH}$=7.0, $^3J_{PH}$=10.1 Hz) and a double quartet at δ 4.49 ($^3J_{HH}$=7.0, $^2J_{PH}$=27.3 Hz). Accordingly, the conjugated carbonyl carbon of **15** and **16** appeared, respectively, at δ 182.12 and 159.45 as expected for a ketone and an amide. To the best of our knowledge, this is the first time that a competition between *C*- vs *N*-regioselective attack of lithium *P*-diphenyl(alkyl)phosphazenes has been experimentally observed. Also, worthy of note is the [1,2] addition of lithiated **10a** to ethyl phenylpropiolate in contrast with the [1,4] addition leading to heterocycles **12**.

Dimethyl maleate and dimethyl butylidenmalonate reacted with lithium phosphazenes **10b**,**c** in the same way as DMAD. The reaction yielded the [1,4] adducts **17a**,**b** and **18**. The stereoselectivity of the addition was excellent. Only one diastereoisomer was detected in the ^{31}P NMR spectra of the crude products (Scheme 5). Their structures were easily assigned from the conventional analysis of the ^{1}H, ^{13}C and DEPT spectra.[20] The relative stereochemistry of the stereogenic centres was assigned based on the magnitude of the vicinal coupling constants of the methine protons of these centres. The small $^3J_H{}^{\alpha}{}_H{}^{\beta}$ values measured, 2.5 Hz for



Scheme 5. (i) ^{n}BuLi, −20°C, THF, 30 min; (ii) PhC≡CCO_2Et, −700–25°C, 12 h; (iii) MeO_2CCH=$CHCO_2Me$, −700–25°C, 12 h; (iv) ^{n}PrCH=$C(CO_2Me)CO_2Me$, −700–25°C, 12 h.

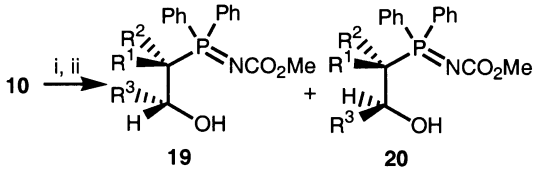


Scheme 6.

17a and 1.7 Hz for **18**, are in the expected range[21] for an *erythro* configuration. No heterocyclic compounds could be detected, which suggests that the anion arising from the initial Michael addition to both electrophiles is now less reactive than in the case of DMAD due to the delocalisation through the adjacent carbonyl group(s). The formation of **17**–**18** supports the mechanism proposed for the analogous reaction with DMAD and evidences again the different chemical behaviour of lithium (*N*-methoxycarbonyl)-phosphazenes vs. their *N*-phenyl derivatives. These last compounds led to cyclopentenones by reaction with dimethyl maleate or fumarate.

So far, all synthesis of phosphorus heterocycles from (*N*-methoxycarbonyl)phosphazenes involve a cyclo-condensation step promoted by either a nucleophilic carbon or nitrogen.[10b,13] In principle, cyclisations based on a trans-esterification reaction, i.e. promoted by an oxygen atom, could be formally carried out in the two steps process represented retrosynthetically in Scheme 6, consisting in the formation of a carbon–carbon bond by addition of a lithiated (*N*-methoxycarbonyl)phosphazene to an aldehyde or ketone followed by cyclocondensation of the intermediate β-hydroxyphosphazene **19**–**20** to yield 5,6-dihydro-1,3,4λ^5-oxazaphosphinin-2-ones **21**.

The reaction of lithiated phosphazenes **10** (prepared by addition of ^{n}BuLi to a solution of **10** in THF at −30°C during 30 min) with aldehydes at −80°C during 2 h afforded the expected β-hydroxy(*N*-methoxycarbonyl)phosphazenes **19**–**20** in high yield with good to excellent diastereo-selectivity[22] (Scheme 7, Table 2). The assignment of the



Scheme 7. (i) ^{n}BuLi, −35°C, THF, 30 min; (ii) R^{3}CHO, −80°C, 2 h.

Table 2. β-Hydroxyphosphazenes **19**–**20** obtained

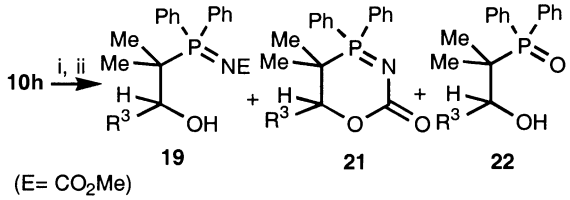
Product	R^1	R^2	R^3	Rdto.(%)	19/20 (%)
19a/20a	H	CH_3	C_6H_5	80	83:17
19b[a]	H	$CH_2C_6H_5$	C_6H_5	95	>97
19c/20c	H	CH_3	C_6H_{11}	90	86:14
19d/20d	H	CH_3	*p*-ClC_6H_4	87	86:14
19e[a]	H	$CH_2C_6H_5$	*p*-ClC_6H_4	>97	>97
19f	CH_3	CH_3	C_6H_5	90	
19g	CH_3	CH_3	*p*-ClC_6H_4	95	
19h	CH_3	CH_3	CH_3CH_2	75	
19i	CH_3	CH_3	$C_6H_4CH_2CH_2$	70	

[a] The isomer *threo* is not detectable by NMR.

relative stereochemistry of each isomer was achieved as previously discussed for **17**–**18,** by associating a small/large $H^{\alpha}H^{\beta}$ vicinal coupling with an *erythro*/*threo* configuration, respectively. The $^3J_H{}^{\alpha}{}_H{}^{\beta}$ for the major isomer **19** were in all cases cero corresponding to the *erythro* diastereoisomer, in agreement with the values measured in β-hydroxy(*N*-phenyl)phosphazenes.[20b,23] On the other hand, the *threo* stereoisomer **20** exhibited an average $^3J_H{}^{\alpha}{}_H{}^{\beta}$ coupling of 16.5 Hz. The ^{31}P chemical shifts of **19**–**20** also followed a general trend, with **19** being shielded by ca. 2 ppm related to **20**. Hence, δ_P can be used as an alternative tool for structural assignment on account of the ^{31}P chemical shifts of both diastereoisomers were known.

We reasoned that an increase in the temperature and reaction time could favour the cyclisation of the adduct derived from the reaction between the metalated phosphazenes **10** and aldehydes. To simplify the stereochemical course of the reaction we focused on phosphazene **10h** having two methyl groups on the carbon α to the phosphorus. Thus, **10h** was metalated in THF as mentioned above and then benzaldehyde was added at −25°C. The reaction was allowed to reach room temperature and stirred during 10 h. Aqueous work-up afforded a reaction crude containing a small amount of the starting phosphazene **10h** (δ_P 34.05, 13%) and the β-hydroxy derivative **19f** (δ_P 39.54, 10%), plus two new compounds **21a** (δ_P 26.20, 52%) and 22a (δ_P 45.49, 27%) (Scheme 8).[24]

Increasing the reaction time to 22 h produced a decrease of the yield of **21a** (45%) in favour of the acyclic compounds for an overall conversion of **10h** of 91%. This result suggested the existence of an equilibrium between the heterocycle and the alkoxide precursor. Therefore, the yield of heterocycle obtained could be increased through its selective precipitation from the medium using relatively short reaction times (Table 3). In diethyl ether **21a** proved to be more soluble than the open chain compounds **19f** and **22a**. Consequently, the reaction mixture was dominated by the acyclic derivatives (4% of **21a** entry 3 and 7% of **21b** entry 6 in Table 3). The best results were obtained by performing the reaction in a mixture THF/diethyl ether 1:1 during 14 h (entry 4, Table 3). In these conditions **21a** was isolated in 89% yield and only a 11% of **22a** remained in solution. The reaction with *p*-chlorobenzaldehyde afforded the highest yield of **21b** when pure THF was used as solvent (43%, entry 5, Table 3) implying that the cyclization step is sensitive to the solvent as well as to the substituent R^3 of the electrophile. Significantly, the reaction works also well with aliphatic aldehydes in THF or mixtures THF/Et_2O 1:1 (Table 4).



Scheme 8. (i) ^{n}BuLi −35°C, THF (or THF/Et_2O 1:1), 1 h; (ii) R^{3}CHO, −80–25°C, 14 h.

Table 3. Optimization of the synthesis of heterocycles **21** and distribution of compounds obtained

Entry	Solvent	R^3	Metalation time (min)	Reaction time (h)	21 (%)	22 (%)	19 (%)	Yield (%)
1	THF	Ph	20	14	60	9	31	87
2	THF	Ph	20	22	45	22	33	91
3	Et_2O	Ph	60	14	4	90	6	91
4	THF/Et_2O[a]	Ph	60	14	89	11		87
5	THF	*p*-ClC_6H_4	30	14	43	43	14	97
6	Et_2O	*p*-ClC_6H_4	60	13	7	93		89
7	THF/Et_2O[b]	*p*-ClC_6H_4	30	26	34	66		91

[a] THF/Et_2O 1:1, the aldehyde was added at −80°C.
[b] THF/Et_2O 1:1.7.

Table 4. 1,3,4-Oxazaphosphin-2-ones **21** obtained

Product	R^3	Yield[a] (%)	δ ^{31}P (ppm)
21a	C_6H_5	77[b]	26.20
21b	*p*-ClC_6H_4	43[c]	25.90
21c	CH_3CH_2	65[c]	25.37
21d	$PhCH_2CH_2$	64[b]	25.94

[a] Isolated yield.
[b] Solvent THF/Et_2O 1:1.
[c] Solvent THF.

All attempts to obtain oxazaphosphinin-2-ones from β-hydroxyphosphazenes **19** bearing only one alkyl substituent in the α position to the phosphorus failed. They included: (i) standard conditions above mentioned, (ii) heating of neutral **19** at 140°C during 5 h under vacuum, (iii) refluxing in THF the alkoxide of **19** formed in situ during 10 h. It is worth of mention that in the last case the ratio of diastereoisomers **19/20** was the same obtained when the reaction was carried out at room temperature, i.e., no isomerisation took place.

3. Conclusions

Lithium (*N*-alkoxycarbonyl)phosphazenes add preferentially in a [1,4] manner to Michael acceptors with an almost exclusive *C*-regioselectivity, a behaviour which contrasts with the exclusive [1,2] addition observed for the analogous reactions of (*N*-phenyl)phosphazenes. Thus, 1*H*-1,2-azaphosphinin-6-ones were obtained in high yields with DMAD. The reactions with dimethyl maleate, fumarate and butylidenmalonate afforded the corresponding *C*-alkylated acyclic compounds with excellent diastereoselectivity. Most probably, the stabilisation of the anion resulting from the addition step to these electrophiles prevented their participation in a further cyclocondensation reaction. The results with methyl phenylpropiolate were exceptional: it is the single case were a lithium (*N*-methoxycarbonyl)-phosphazene added to the carbonyl carbon ([1,2] mode), not to the triple bond and for the first time a metalated phosphazene reacted through both extremes of the stabilised carbanion giving a mixture of *C*- and *N*-acylated compounds. This reaction can be considered the bordeline example linking the behaviour of lithium (*N*-alkoxycarbonyl)- and (*N*-phenyl)-phosphazenes.

The addition to aldehydes at −80°C afforded β-hydroxy(*N*-alkoxycarbonyl)phosphazenes in high yield and good to excellent diastereoselectivities. When the reaction was carried out at room temperature with phosphazenes having two methyl groups in the carbon α to the phosphorus then 5,6-dihydro-1,3,4-oxazaphosphinin-2-ones were obtained through cyclocondensation of the intermediate alcoholate formed in the addition step to the carbonyl group of the aldehyde.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of nitrogen using dried glassware. Solvents were distilled before use. THF and TMEDA were dried with sodium and potassium respectively, and distilled under nitrogen. All starting materials were purchased from ALDRICH. Liquids, except ^{n}BuLi, were distilled prior to use. Methyldiphenyl- and ethyldiphenylphosphine were commercially available. All other phosphines were prepared by reacting the appropriate alkyl halide with lithium diphenylphosphide[15,25] and transformed in situ in the corresponding phosphazene. TLC was performed on Merck plates with aluminum backing and silica gel 60 F_{254}. For column chromatography silica gel 60 (40–63 μm) from Scharlau was used.

Melting points were recorded on a Büchi–Tottoli apparatus and were uncorrected. Infrared spectra were obtained in KBr pellets using a UNICAM Mattson 3020 FT spectrometer. Mass spectra were determined by electron impact on a Hewlett Packard 5987A or 1100. Microanalysis was performed on a Perkin–Elmer 2400. NMR spectra were measured on a Bruker Avance 300 DPX or a Bruker 400 AMX spectrometer. Chemical shifts are referred to internal tetramethylsilane for ^1H and ^{13}C, and to external 85% H_3PO_4 for ^{31}P. 2D NMR Correlation spectra (COSY, NOESY, HMQC and HMBC) were acquired using standard Bruker software and processing routines.

4.2. Synthesis of phosphazenes 10

Method A. To a solution of phosphine (35 mmol) in diethyl ether (50 mL) was added dropwise a solution of methoxycarbonyl azide (35 mmol) in diethyl ether (30 mL). Once the nitrogen evolution ceased the reaction mixture was concentrated under vacuum to a third of its volume. Phosphazenes precipitated as white solids. They were filtrated, dried, and used without further purification. Phosphazenes **10a**,**b** were obtained through this method.

Method B. To a Schlenk with the appropriated phosphazene (20 mmol) dissolved in 40 mL of dry THF was added a solution of ^{n}BuLi (13.8 mL of a 1.6 M solution in hexane, 22 mmol) at −30°C. After 30 min of metallation the temperature was lowered at −70°C and was added the desired alkyl halide (20 mmol). The reaction mixture was stirred for 6 h and allowed to reach room temperature. Addition of water (25 mL) followed by extraction with CH_2Cl_2 (3×15 mL) and solvent evaporation under vacuum afforded one colorless oil. Digestion of this oil in diethyl ether yielded phosphazenes **10e–g** as white solids. They were filtrated, dried, and used without further purification.

Method C. To a Schlenk with triphenylphosphine (5.3 g, 20 mmol) dissolved in THF (40 mL) was added an excess of freshly cut small pieces of lithium metal (0.27 g, 40 mmol). The mixture was stirred at room temperature for 2 h. The unreacted lithium metal was filtered off and ammonium chloride (1.06 g, 20 mmol) was added slowly over a period of 30 min. Then, the appropriated alkyl halide (20 mmol) was added and the color of the solution changed from red to yellow. The mixture was stirred for 2 h and after this time a solution of methoxycarbonyl azide (20 mmol) in THF (10 mL) was added. Aqueous work-up as described in method B afforded phosphazenes **10c**,**d** and **h–l**.

4.2.1. *P,P*-Diphenyl-*P*-(methyl)(*N*-methoxycarbonyl)phosphazene (10a). White solid. Yield 98%. Mp (°C): 65–66. IR (KBr), ν (cm^{-1}): 1630, 1290. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 2.17 (d, $^2J_{PH}$=13.4 Hz, 3H), 3.55 (s, 3H), 7.35–7.42 (m, 6H^{ar}), 7.65–7.70 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 12.69 (d, $^1J_{PC}$=66.1 Hz), 52.49 (d, $^4J_{PC}$=3.6 Hz), 128.63 (d, $^3J_{PC}$=12.0 Hz), 128.94 (d, $^1J_{PC}$=102.7 Hz), 131.31 (d, $^2J_{PC}$=9.6 Hz), 132.24 (d, $^4J_{PC}$=2.4 Hz), 163.0 (d, $^2J_{PC}$=1.2 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 23.54. Anal. Calcd for $C_{15}H_{16}NO_2P$: C, 65.93; H, 5.86; N, 5.13. Found. C, 65.90; H, 5.87; N, 5.15. MS (API-ES) *m/z*: 296 (M^++23, 18%), 274 (M^++1, 100%), 217 (95%).

4.2.2. *P,P*-Diphenyl-*P*-(ethyl)(*N*-methoxycarbonyl)phosphazene (10b). White solid. Yield 98%. Mp (°C): 86–87. IR (KBr), ν (cm^{-1}): 1629, 1295. H NMR. (300.13 MHz, $CDCl_3$), δ (ppm): 1.08 (dt, $^3J_{HH}$=7.6 Hz, $^3J_{PH}$=18.0 Hz, 3H), 2.63 (dc, $^3J_{HH}$=7.6 Hz, $^3J_{PH}$=12.2 Hz, 2H), 3.58 (s, 3H), 7.40–7.52 (m, 6H^{ar}), 7.70–7.77 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 5.62 (d, $^2J_{PC}$=4.8 Hz), 18.75 (d, $^1J_{PC}$=64.3 Hz), 52.53 (d, $^4J_{PC}$=3.6 Hz), 127.65 (d, $^1J_{PC}$=99.7 Hz), 128.68 (d, $^3J_{PC}$=12.0 Hz), 131.46 (d, $^2J_{PC}$=9.6 Hz), 132.21 (d, $^4J_{PC}$=2.4 Hz), 162.87 (d, $^2J_{PC}$=2.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 28.95. Anal. Calcd for $C_{16}H_{18}NO_2P$: C, 66.90; H, 6.27; N, 4.88. Found. C, 66.92; H, 6.28; N, 4.85. MS (API-ES) *m/z*: 310 (M^++23, 16%), 288 (M^++1, 100%), 231 (52%).

4.2.3. *P,P*-Diphenyl-*P*-(propyl)(*N*-methoxycarbonyl)phosphazene (10c). White solid. Yield 72%. Mp (°C): 92–93. IR (KBr), ν (cm^{-1}): 1626, 1591, 1279. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.10 (t, $^3J_{HH}$=7.1 Hz, 3H), 1.50 (m, 2H), 2.62 (m, 2H), 3.65 (s, 3H), 7.41–7.54 (m, 6H^{ar}), 7.80 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.07, 15.20 (d, $^2J_{PC}$=20.7 Hz), 22.28 (d, $^1J_{PC}$=62.8 Hz), 52.31 (d, $^4J_{PC}$=3.6 Hz), 127.51 (d, $^1J_{PC}$=103.6 Hz), 128.40 (d, $^3J_{PC}$=11.9 Hz), 131.52 (d, $^2J_{PC}$=9.2 Hz), 131.97, 162.68. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.79. Anal. Calcd for $C_{17}H_{20}NO_2P$: C, 67.76; H, 6.69; N, 4.65. Found. C, 67.74; H, 6.72; N, 4.60. MS (EI) *m/z*: 301 (M^+, 5%), 259 (100%), 202 (70%).

4.2.4. *P,P*-Diphenyl-*P*-(3-butenyl)(*N*-methoxycarbonyl)-phosphazene (10d). White solid. Yield 69%. Mp (°C): 81–82. IR (KBr), ν (cm^{-1}): 1625, 1589, 1293. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 2.23 (m, 2H), 2.71 (m, $^3J_{PH}$=16.0 Hz, 1H), 3.62 (s, 3H), 4.97 (dq, $^3J_{HH}$=16.8 Hz, $^2J_{HH}$=$^4J_{HH}$=1.3 Hz, 1H), 4.99 (dq, $^3J_{HH}$=10.3 Hz, $^2J_{HH}$=$^4J_{HH}$=1.3 Hz, 1H), 5.78 (ddd, $^3J_{HH}$=16.8 Hz, $^3J_{HH}$=10.3 Hz, $^3J_{HH}$=6.5 Hz) 1H), 7.45–7.60 (m, 6H^{ar}), 7.72–7.75 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 24.68 (d, $^1J_{PC}$=71.7 Hz), 25.30, 52.43 (d, $^4J_{PC}$=3.5 Hz), 115.37, 127.61 (d, $^1J_{PC}$=103.6 Hz), 128.57 (d, $^3J_{PC}$=13.6 Hz), 131.59 (d, $^2J_{PC}$=11.9 Hz), 132.13, 136.45 (d, $^3J_{PC}$=16.2 Hz), 162.67. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.64. Anal. Calcd for $C_{18}H_{20}NO_2P$: C, 69.00; H, 6.43; N, 4.47. Found. C, 69.05; H, 6.40; N, 4.49. MS (EI) *m/z*: 313 (M^+, 20%), 312 (40%), 282 (100%).

4.2.5. *P,P*-Diphenyl-*P*-(butyl)(*N*-methoxycarbonyl)phosphazene (10e). White solid. Yield 70%. Mp (°C): 70–71. IR (KBr), ν (cm^{-1}): 1638, 1589, 1298. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.85 (t, $^3J_{HH}$=6.1 Hz, 3H), 1.45 (m, 4H), 2.67 (m, 2H), 3.60 (s, 3H), 7.40–7.59 (m, 6H^{ar}), 7.70 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 13.35, 23.32, 23.65 (d, $^2J_{PC}$=15.4 Hz), 25.11 (d, $^1J_{PC}$=63.40 Hz), 52.42, 128.47 (d, $^1J_{PC}$=119.5 Hz), 128.52 (d, $^3J_{PC}$=11.9 Hz), 131.61 (d, $^2J_{PC}$=9.1 Hz), 132.03, 162.89. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.20. Anal. Calcd for $C_{18}H_{22}NO_2P$: C, 68.56; H, 7.03; N, 4.44. Found. C, 68.52; H, 7.08; N, 4.46. MS (EI) *m/z*: 315 (M^+, 5%), 284 (100%), 272 (60%).

4.2.6. *P,P*-Diphenyl-*P*-(2-methylpropyl)(*N*-methoxycarbonyl)phosphazene (10f). White solid. Yield 69%. Mp (°C): 94–95. IR (KBr), ν (cm^{-1}): 1652, 1530, 1298. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.87 (d, $^3J_{HH}$= 6.5 Hz, 6H), 1.97 (m, 1H), 2.71 (dd, $^2J_{PH}$=12.0, $^3J_{HH}$=6.9 Hz, 2H), 3.60 (s, 3H), 7.35–7.50 (m, 6H^{ar}), 7.75 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 23.36 (d, $^2J_{PC}$=33.1 Hz), 24.16 (d, $^3J_{PC}$=8.8 Hz), 33.12 (d, $^1J_{PC}$= 63.5 Hz), 52.42 (d, $^4J_{PC}$=3.5 Hz), 128.64 (d, $^1J_{PC}$=99.8 Hz), 128.46 (d, $^3J_{PC}$=11.9 Hz), 131.51(d, $^2J_{PC}$=9.3 Hz), 131.89, 162.79. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 24.10. Anal. Calcd for $C_{18}H_{22}NO_2P$: C, 68.56; H, 7.03; N, 4.44. Found. C, 68.54; H, 7.06; N, 4.47. MS (EI) *m/z*: 315 (M^+, 20%), 284 (100%), 215 (75%).

4.2.7. *P,P*-Diphenyl-*P*-(2-phenylethyl)(*N*-methoxycarbonyl)phosphazene (10g). White solid. Yield 85%. Mp (°C): 126–127. IR (KBr), ν (cm^{-1}): 1625, 1291. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 2.78–2.86 (m, 2H), 2.91–3.01 (m, 2H), 3.67 (s, 3H), 7.13–7.28 (m, 5H^{ar}), 7.46–7.57(m, 6H^{ar}), 7.77–7.84 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 27.42 (d, $^2J_{PC}$=12.6 Hz), 27.84 (d, $^1J_{PC}$=46.3 Hz), 52.69 (d, $^4J_{PC}$=3.6 Hz), 126.40, 127.77 (d, $^1J_{PC}$=99.7 Hz), 128.06, 128.43, 128.81 (d, $^3J_{PC}$=12.0 Hz), 131.80 (d, $^2J_{PC}$=9.0 Hz), 132.37 (d, $^4J_{PC}$=3.0 Hz), 140.52 (d, $^3J_{PC}$=15.6 Hz), 162.68 (d,

$^{2}J_{PC}$=2.0 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.91. Anal. Calcd for $C_{22}H_{22}NO_2P$: C, 72.71; H, 6.10; N, 3.85. Found. C, 72.75; H, 6.13; N, 3.89. MS (API-ES) *m/z*: 364 (M^++1, 100%), 307 (8%).

4.2.8. *P,P*-Diphenyl-*P*-(1-methylethyl)(*N*-methoxycarbonyl)phosphazene (10h). White solid. Yield 95%. Mp (°C): 112–113. IR (KBr), ν (cm^{-1}): 1622, 1299. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.17 (dd, $^{3}J_{PH}$=16.9, $^{3}J_{HH}$=7.1 Hz, 6H), 2.67 (dsep, $^{2}J_{PH}$=12.3, $^{3}J_{HH}$=7.1 Hz, 1H), 3.59 (s, 3H), 7.48–7.61 (m, 6H^{ar}), 7.78–8.50 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.01 (d, $^{2}J_{PC}$=1.7 Hz), 24.31 (d, $^{1}J_{PC}$=66.9 Hz), 55.53 (d, $^{4}J_{PC}$= 3.9 Hz), 125.48 (d, $^{1}J_{PC}$=93.4 Hz), 128.48 (d, $^{3}J_{PC}$= 11.6 Hz), 132.23 (d, $^{4}J_{PC}$=2.2 Hz), 132.92 (d, $^{2}J_{PC}$= 8.8 Hz), 162.76 (d, $^{2}J_{PC}$=1.7 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 34.05. Anal. Calcd for $C_{17}H_{20}NO_2P$: C, 67.77; H, 6.64; N, 4.66. Found. C, 67.75; H, 6.63; N, 4.69. MS (API-ES) *m/z*: 302 (M^++1, 100%), 245 (35%).

4.2.9. *P,P*-Diphenyl-*P*-(1-methylpenthyl)(*N*-methoxycarbonyl)phosphazene (10i). White solid. Yield 92%. Mp (°C): 122–123. IR (KBr), ν (cm^{-1}): 1629, 1292. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.83 (t, $^{3}J_{HH}$=6.6 Hz, 3H), 1.2 (m, 4H), 1.14 (dd, $^{3}J_{PH}$=18.0, $^{3}J_{HH}$=7.0 Hz, 3H), 1.43 (m, 1H), 1.82 (m, 1H), 3.04 (m 1H), 3.57 (s, 3H), 7.44–7.56 (m, 6H^{ar}), 7.73–7.81 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 12.68 (d, $^{3}J_{PC}$=1.8 Hz), 13.86, 22.28, 28.98 (d, $^{1}J_{PC}$=64.9 Hz), 29.03 (d, $^{2}J_{PC}$=1.5 Hz), 29.59 (d, $^{3}J_{PC}$=13.2 Hz), 52.46 (d, $^{4}J_{PC}$=3.6 Hz), 125.68 (d, $^{1}J_{PC}$= 93.4 Hz), 125.79 (d, $^{1}J_{PC}$=93.4 Hz), 128.43 (d, $^{3}J_{PC}$= 12.0 Hz), 132.14 (d, $^{4}J_{PC}$=1.8 Hz), 132.81 (d, $^{2}J_{PC}$= 8.4 Hz), 132.88 (d, $^{2}J_{PC}$=9.0 Hz), 162.64 (d, $^{2}J_{PC}$=1.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.64. Anal. Calcd for $C_{20}H_{26}NO_2P$: C, 76.92; H, 8.33; N, 4.49. Found. C, 76.90; H, 8.34; N, 4.50. MS (API-ES) *m/z*: 344 (M^++1, 100%), 287 (13%).

4.2.10. *P,P*-Diphenyl-*P*-(1-methylbenzyl)(*N*-methoxycarbonyl)phosphazene (10j). White solid. Yield 75%. Mp (°C): 115–116. IR (KBr), ν (cm^{-1}): 1630, 1292. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.03 (dd, $^{3}J_{PH}$=15.5 Hz, $^{3}J_{HH}$=7.0 Hz, 3H), 2.21 (ddd, $^{3}J_{PH}$=15.9 Hz, $^{3}J_{HH}$=13.6 Hz, $^{3}J_{HH}$=11.9 Hz, 1H), 3.28–3.42 (m, 2H), 3.61 (s, 3H), 7.14–7.30 (m, 5H^{ar}), 7.48–7.58 (m, 6H^{ar}), 7.81–7.88 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 12.53, 31.61 (d, $^{1}J_{PC}$=63.7 Hz), 35.57, 52.64 (d, $^{4}J_{PC}$=3.6 Hz), 125.36 (d, $^{1}J_{PC}$=95.5 Hz), 125.75(d, $^{1}J_{PC}$=93.1 Hz), 126.48, 128.46, 128.60 (d, $^{3}J_{PC}$=11.4 Hz), 128.66 (d, $^{3}J_{PC}$=11.4 Hz), 128.99, 132.38 (d, $^{4}J_{PC}$=2.4 Hz), 132.78 (d, $^{2}J_{PC}$=9.0 Hz), 132–96 (d, $^{2}J_{PC}$=9.6 Hz), 138.85 (d, $^{3}J_{PC}$ 15.0 Hz), 162.72 (d, $^{2}J_{PC}$=2.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 32.77. Anal. Calcd for $C_{23}H_{24}NO_2P$: C, 73.19; H, 6.41; N, 3.71. Found. C, 73.20; H, 6.43; N, 3.70. MS (API-ES) *m/z*: 378 (M^++1, 100%), 321 (70%).

4.2.11. *P,P*-Diphenyl-*P*-(1-methylbut-3-enyl)(*N*-methoxycarbonyl)phosphazene (10k). White solid. Yield 90%. Mp (°C): 77–78. IR (KBr), ν (cm^{-1}): 1616, 1285. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.14 (dd, $^{3}J_{PH}$=17.5, $^{3}J_{HH}$=7.3 Hz, 3H), 1.78 (m, 1H), 2.68 (m, 1H), 3.13 (m, 1H), 3.61 (s, 3H), 5.02 (dd, $^{2}J_{HH}$=1.6, $^{3}J_{HH}$=17.0 Hz, 1H), 5.07 (dd, $^{2}J_{HH}$=1.6, $^{3}J_{HH}$=10.5 Hz, 1H), 5.73 (ddd, $^{3}J_{HH}$=10.5, $^{3}J_{HH}$ 17.0, $^{3}J_{HH}$=5.7 Hz, 1H), 7.48–7.75 (m, 6H^{ar}), 7.78–7.82 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 12.51, 29.04 (d, $^{1}J_{PC}$=66.1 Hz), 34.03, 52.55 (d, $^{4}J_{PC}$=4.2 Hz), 117.59, 125.52 (d, $^{1}J_{PC}$=93.7 Hz), 125.62 (d, $^{1}J_{PC}$=94.3 Hz), 128.55 (d, $^{3}J_{PC}$=12.0 Hz), 132.30 (d, $^{4}J_{PC}$=2.4 Hz), 132.84 (d, $^{2}J_{PC}$=9.0 Hz), 135.04 (d, $^{3}J_{PC}$=15.6 Hz), 162.67 (d, $^{2}J_{PC}$=2.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 32.94. Anal. Calcd for $C_{19}H_{22}NO_2P$: C, 69.72; H, 6.73; N, 4.28. Found. C, 69.75; H, 6.72; N, 4.26. MS (API-ES) *m/z*: 328 (M^++1, 100%), 271 (27%).

4.2.12. *P,P*-Diphenyl-*P*-(1-benzylpenthyl)(*N*-methoxycarbonyl)phosphazene (10l). Oil. Yield 95%. IR (neat), ν (cm^{-1}): 1692, 1293. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.56 (t, $^{3}J_{HH}$=7.1 Hz, 3H), 0.93–1.80 (m, 6H), 2.80 (m, 1H), 2.99 (m, 1H), 3.28 (m, 1H), 3.55 (s, 3H,), 7.1–7.41 (m, 11H^{ar}), 7.77–7.80 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 13.51, 22.33, 28.49, 29.74 (d, $^{3}J_{PC}$=9.0 Hz), 33.66, 39.20 (d, $^{1}J_{PC}$=69.7 Hz), 52.62 (d, $^{4}J_{PC}$=3.7 Hz), 126.12 (d, $^{1}J_{PC}$=96.1 Hz), 126.25 (d, $^{1}J_{PC}$= 93.1 Hz), 127.02–132.26 (11C^{ar}), 132.57 (d, $^{2}J_{PC}$=9.0 Hz), 132.65 (d, $^{2}J_{PC}$=8.4 Hz), 139.77 (d, $^{3}J_{PC}$=12.6 Hz), 162.62 (d, $^{2}J_{PC}$=1.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.35. Anal. Calcd for $C_{26}H_{30}NO_2P$: C, 74.46; H, 7.16; N, 3.34. Found. C, 74.44; H, 7.17; N, 3.35. MS (API-ES) *m/z*: 420 (M^++1, 100%), 362 (23%).

4.3. General procedure for the reaction of lithium phosphazenes with Michael acceptors

Synthesis of **12**, **15**, **16**, **17** and **18**. To a solution of 3.1 mmol of ^{n}BuLi in 10 ml of dry THF at −20°C was added dropwise a solution of 3 mmol of the appropriated phosphazene in 20 ml of THF. After 30 minutes of metalation the reaction was cooled to −70°C. Then 1.5 mmol of electrophile dissolved in 20 ml of THF were added. The solution was allowed to reach room temperature overnight, quenched with water and extracted 3 times with dichloromethane. The combined organic layers were dried with $MgSO_4$ and solvents were evaporated under reduced pressure. Purification was achieved through column chromatography using ether as eluent. Solid compounds were then recrystallyzed from hexane/dichloromethane. The electrophiles used were: DMAD, ethyl phenylpropiolate, dimethyl maleate, and dimethyl butylidenmalonate.

4.3.1. 1*H*-2,2-Diphenyl-4,5-dimethoxycarbonyl-3-methyl-1,2-azaphosphinin-6-one (12a). White solid. Yield 90%. Mp (°C): 172–173. IR (KBr), ν (cm^{-1}): 1724, 1624, 1498. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.74 (d, $^{3}J_{PH}$=13.2 Hz, 3H), 3.74 (s, 3H), 3.84 (s, 3H), 7.49–7.67 (m, 10H^{ar}), 14.03 (s, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 14.17 (d, $^{2}J_{PC}$=9.2 Hz), 51.78, 52.13, 81.44(d, $^{3}J_{PC}$=18.3 Hz), 86.49 (d, $^{1}J_{PC}$=80.9 Hz), 127.25 (d, $^{1}J_{PC}$= 109.7 Hz), 128.95 (d, $^{2}J_{PC}$=13.0 Hz), 132.35 (d, $^{3}J_{PC}$= 10.7 Hz), 132.90 (d, $^{4}J_{PC}$=3.1 Hz), 149.66 (d, $^{2}J_{PC}$= 8.4 Hz), 168.62 (d, $^{2}J_{PC}$=20.6 Hz), 170.55, 171.56 (d, $^{3}J_{PC}$=6.1 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.55. Anal. Calcd for $C_{21}H_{20}NO_5P$: C, 63.48; H, 5.07; N, 3.52. Found: C, 63.52; H, 5.04; N, 3.51%. MS (EI) *m/z*: 397 (M^+, 100%), 350 (29%), 337 (33%).

4.3.2. 1*H*-2,2-Diphenyl-4,5-dimethoxycarbonyl-3-ethyl-1,2-azaphosphinin-6-one (12b). White solid. Yield 91%. Mp (°C): 130–131. IR (KBr), ν (cm^{-1}): 1729, 1620, 1591. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.58 (t, $^3J_{HH}$=7.1 Hz, 3H), 2.15 (dq, $^3J_{HH}$=7.1, $^3J_{PH}$=23.7 Hz, 2H), 3.72 (s, 3H), 3.83 (s, 3H), 7.47–7.68 (m, 10H^{ar}), 13.98 (s, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 14.78, 22.25 (d, $^2J_{PC}$=8.8 Hz), 51.71, 51.98, 81.98 (d, $^3J_{PC}$=20.9 Hz), 93.22 (d, $^1J_{PC}$=77.9 Hz), 127.82 (d, $^1J_{PC}$= 109.2 Hz), 128.91 (d, $^3J_{PC}$=12.9 Hz), 132.45 (d, $^2J_{PC}$= 10.4 Hz), 132.92 (d, $^4J_{PC}$=2.4 Hz), 149.22 (d, $^2J_{PC}$= 8.8 Hz), 168.53 (d, $^2J_{PC}$=20.9 Hz), 170.64, 171.60 (d, $^3J_{PC}$=6.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.67. Anal. Calcd for $C_{22}H_{22}NO_5P$: C, 64.23; H, 5.39; N, 3.40. Found: C, 64.26; H, 5.41; N, 3.44%. MS (EI) *m/z*: 411 (M^+, 100%), 364 (67%), 335 (92%).

4.3.3. 1*H*-2,2-Diphenyl-4,5-dimethoxycarbonyl-3-propyl-1,2-azaphosphinin-6-one (12c). White solid. Yield 90%. Mp (°C): 160–161. IR (KBr), ν (cm^{-1}): 1745, 1620, 1567. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.62 (t, $^3J_{HH}$=7.2 Hz, 3H), 0.94 (m, 2H), 2.07 (m, 2H), 3.77 (s, 3H), 3.90 (s, 3H), 7.30–7.70 (m, 10H^{ar}), 14.02 (s, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 14.00, 23.60, 31.27 (d, $^2J_{PC}$=8.4 Hz), 51.66, 51.92, 81.53 (d, $^3J_{PC}$= 19.12 Hz), 91.92 (d, $^1J_{PC}$=78.4 Hz), 127.72 (d, $^1J_{PC}$= 109.2 Hz), 128.83 (d, $^2J_{PC}$=13.0 Hz,), 132.36 (d,$^3J_{PC}$= 11.8 Hz), 132.87 (d, $^4J_{PC}$=2.7 Hz), 149.33 (d, $^2J_{PC}$=8.7 Hz), 168.55 (d, $^2J_{PC}$=20.6 Hz), 170.59, 171.56 (d, $^3J_{PC}$=5.1 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.98. Anal. Calcd for $C_{23}H_{24}NO_5P$: C, 64.94; H, 5.69; N, 3.29. Found: C, 64.90; H, 5.65; N, 3.31%. MS (EI) *m/z*: 425 (M^+, 40%), 364 (29%), 335 (55%).

4.3.4. 1*H*-2,2-Diphenyl-4,5-dimethoxycarbonyl-3-isopropyl-1,2-azaphosphinin-6-one (12d). White solid. Yield 91%. Mp (°C): 147–148. IR (KBr), ν (cm^{-1}): 1745, 1625, 1556. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm):0.73 (d, $^3J_{HH}$=7.2 Hz, 6H), 2.62 (m, 1H), 3.64 (s, 3H), 3.87 (s, 3H), 7.41–7.69 (m, 10H^{ar}), 12.68 (s, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 22.07, 30.12 (d, $^2J_{PC}$= 8.6 Hz), 51.45, 51.72, 82.02 (d, $^3J_{PC}$=19.70 Hz), 96.20 (d, $^1J_{PC}$=74.3 Hz), 127.66 (d, $^1J_{PC}$=108.5 Hz), 128.52 (d, $^3J_{PC}$=12.9 Hz), 132.60 (d, $^2J_{PC}$ 10.2 Hz), 132.7, 148.21 (d, $^2J_{PC}$=9.2 Hz), 168.81 (d, $^2J_{PC}$=21.1 Hz), 170.45, 171.56 (d, $^3J_{PC}$=4.5 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.71. Anal. Calcd for $C_{23}H_{24}NO_5P$: C, 64.94; H, 5.69; N, 3.29. Found: C, 64.92; H, 5.71; N, 3.30%. MS (EI) *m/z*: 425 (M^+, 40%), 410 (100%), 378 (34%).

4.3.5. 1*H*-2,2-Diphenyl-4,5-dimethoxycarbonyl-3-propenyl-1,2-azaphosphinin-6-one (12e). White solid. Yield 75%. Mp (°C): 167–168. IR (KBr), ν (cm^{-1}): 1740, 1623, 1545. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 2.92 (dd, $^3J_{PH}$=11.3 Hz), 3.76 (s, 3H), 3.82 (s, 3H), 4.63 (dq, $^3J_{HH}$=17.0 Hz, $^2J_{HH}$=$^4J_{HH}$=1.2 Hz, 1H), 4.65 (dq, $^3J_{HH}$= 9.4 Hz, $^2J_{HH}$=$^4J_{HH}$=1.2 Hz, 1H), 5.30 (ddd, $^3J_{HH}$= 17.0 Hz, $^3J_{HH}$=9.4 Hz, $^3J_{HH}$=6.5 Hz, 1H), 7.49–7.56 (m, 5H^{ar}) 7.60–7.70 (m, 5H^{ar}), 13.91 (s, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 32.71 (d, $^2J_{PC}$=8.4 Hz), 51.72, 51.90, 82.48 (d, $^3J_{PC}$=18.6 Hz), 89.06 (d, $^1J_{PC}$=89.06 Hz), 115.87, 127.38 (d, $^1J_{PC}$=109.9 Hz), 128.83 (d, $^3J_{PC}$=13.2 Hz), 132.61 (d, $^2J_{PC}$=10.8 Hz), 132.93 (d, $^4J_{PC}$=2.4 Hz), 134.85 (d, $^4J_{PC}$=1.0 Hz), 150.34 (d, $^2J_{PC}$=9.0 Hz), 168.28 (d, $^2J_{PC}$=20.4 Hz), 170.66, 171.68 (d, $^3J_{PC}$=5.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 27.37. Anal. Calcd for $C_{23}H_{22}NO_5P$: C, 65.25; H, 5.24; N, 3.31. Found: C, 65.21; H, 5.27; N, 3.29%. MS (EI) *m/z*: 424 (M^++1, 100%), 392 (34%).

4.3.6. 1*H*-2,2-Diphenyl-4,5-dimethoxycarbonyl-3-phenylmethyl-1,2-azaphosphinin-6-one (12f). White solid. Yield 75%. Mp (°C): 180–181. IR (KBr), ν (cm^{-1}): 1730, 1625, 1492. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 3.71 (5H), 3.80 (s, 3H), 6.50 (m, 5H^{ar}), 7.50–8.06 (m, 10H^{ar}), 14.01 (s, 1H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 34.45 (d, $^2J_{PC}$=16.6 Hz), 51.76, 51.88, 82.48 (d, $^2J_{PC}$=19.0 Hz), 90.05 (d, $^1J_{PC}$=79.5 Hz), 125.98, 126.18, 127.14, 127.64, 128.01 (d, $^1J_{PC}$=102.2 Hz), 128.69 (d, $^3J_{PC}$=13.1 Hz), 132.45.(d, $^2J_{PC}$=10.9 Hz), 137.85, 150.67, 168.52 (d, $^2J_{PC}$=21.4 Hz), 170.66, 171.73. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.77. Anal. Calcd for $C_{27}H_{24}NO_5P$: C, 68.49; H, 5.11; N, 2.96. Found: C, 68.52; H, 5.09; N, 2.99%. MS (EI) *m/z*: 473 (M^+, 40%), 391 (100%), 354 (20%).

4.3.7. 2-[Diphenyl(*N*-methoxycarbonyl)phosphoraniliden]-5-phenylpent-4-in-3-one (16)/Diphenyl(ethyliden)-(*N*-methoxycarbonyl)phophoranyl]-*N*-methoxycarbonyl-3-phenylpropargyl amide (15). Isolated as a 55:45 mixture. Oil. Yield 70%. IR (neat), ν (cm^{-1}): 1725, 1620. NMR data for **15**. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.70 (d, $^3J_{PH}$=14.5 Hz, 3H), 3.57 (s, 3H), 7.21–7.92 (m, 15H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 9.90 (d, $^2J_{PC}$=3.2 Hz), 52.05, 86.78, 92.98, 118.96–133.33 (18C^{ar}+PC=), 161.5, 182.12. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 35.65.

4.3.8. Diphenyl(ethyliden)(*N*-methoxycarbonyl)phophoranyl]-*N*-methoxycarbonyl-3-phenylpropargyl amide (16). Isolated as a 55:45 mixture. Oil. Yield 70%. IR (neat), ν (cm^{-1}): 1725, 1620. NMR data for **16**. Oil. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.54 (dd, $^3J_{HH}$=10.1, $^3J_{PH}$=7.0 Hz 3H), 3.54 (s, 3H), 4.49 (dq, $^3J_{HH}$=7.0, $^2J_{PH}$=27.3 Hz, 1H), 7.21–7.92 (m, 15H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 10.37 (C-5), 52.05, 83.35 (d, $^3J_{PC}$=21.8 Hz), 86.50 (d, $^1J_{PC}$=115.5 Hz), 92.90, 118.96–133.33 (18C^{ar}), 159.45, 161.57. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.55.

4.3.9. (2*S,1′*R**)-Dimethyl 2-[1-[diphenyl(*N*-methoxycarbonyl)phosphoranyl]-ethyl]-butanedioate (17a).** Oil. Yield 85%. IR (neat), ν (cm^{-1}): 1740, 1642, 1298. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.17 (dd, $^3J_{HH}$= 7.3, $^3J_{PH}$=16.8 Hz, 3H), 2.41 (dd, $^2J_{HH}$=17.0, $^3J_{HH}$= 2.5 Hz, 1H), 2.59 (dd, $^2J_{HH}$=17.0, $^3J_{HH}$=11.2 Hz, 1H), 3.35 (tt, $^3J_{HH}$=2.5 and 11.2, $^3J_{PH}$=11.2 Hz, 1H), 3.47 (ddq, $^3J_{HH}$=2.5 and 7.3, $^2J_{PH}$=14.3 Hz, 1H), 3.55 (s, 3H), 3.56 (s, 3H), 3.67 (s, 3H), 7.37–7.61 (m, 6H^{ar}), 7.73–7.85 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 9.56 (d, $^2J_{PC}$=1.9 Hz), 30.62 (d, $^1J_{PC}$=68.3 Hz), 30.68, 39.64, 51.58, 52.42, 52.64 (d, $^4J_{PC}$=3.3 Hz), 125.84 (d, $^1J_{PC}$=95.6 Hz), 126.47–132.52 (10C^{ar}), 162.29, 171.99, 173.28 (d, $^3J_{PC}$=17.5 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 28.72. Anal. Calcd for $C_{22}H_{26}NO_6P$: C, 61.25; H, 6.07; N, 3.25. Found: C, 61.22; H, 6.10; N, 3.28%. MS (EI), *m/z*: 430 (M^+−1, 10%), 414 (30%), 529 (70%), 202 (100%).

4.3.10. (2*S,1′*R**)-Dimethyl 2-[1-[diphenyl(*N*-methoxycarbonyl)phosphoranyl]-propyl]-butanodioate (17b).** Oil. Yield 83%. IR (neat), ν (cm^{-1}): 1732, 1627, 1296. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.28 (t, $^3J_{HH}$=6.0 Hz, 3H), 1.81 (m, 2H), 2.60 (m, $^2J_{HH}$=17.1, $^3J_{HH}$=2.4, $^3J_{HH}$=11.2 Hz, 2H), 3.50 (m, 2H), 3.63 (s, 3H), 3.64 (s, 3H), 3.73 (s, 3H), 7.49–7.62 (m, 6H), 7.83–7.93 (m, 4H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 12.95 (d, $^3J_{PC}$=14.2 Hz), 18.49, 30.56, 37.21, 37.64 (d, $^1J_{PC}$=66.5 Hz), 51.72, 52.56, 52.75 (d, $^3J_{PC}$=3.3 Hz), 126.11 (d, $^1J_{PC}$=97.0 Hz), 128.82 (d, $^3J_{PC}$=11.9 Hz), 132.29 (d, $^2J_{PC}$=12.0 Hz), 132.53, 162.38, 172.15, 174.12 (d, $^3J_{PC}$=178.6 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 29.11. Anal. Calcd for $C_{23}H_{28}NO_6P$: C, 62.02; H, 6.34; N, 3.14. Found: C, 62.05; H, 6.31; N, 3.18%. MS (EI) *m/z*: 417 (M^+-1, 10%), 416 (20%), 400 (75%), 391 (100%).

4.3.11. (2*R,1′*R**)-Dimethyl 2-[1-[1-diphenyl[(*N*-methoxycarbonyl)phosphoranyl]-ethyl]-butyl]-propanedioate (18).** Oil. Yield 60%. IR (neat), ν (cm^{-1}): 1738, 1640, 1300. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.68 (t, $^3J_{HH}$=7.0 Hz, 3H), 1.01(m, 2H), 1.20 (dd, $^3J_{HH}$=7.0, $^3J_{PH}$=17.8 Hz, 3H), 1.47 (m, 1H), 2.66 (m, 1H), 2.96 (ddc, $^3J_{HH}$=7.0 and 1.7, $^2J_{PH}$=14.4 Hz, 3H), 3.54 (s, 3H), 3.55 (s, 3H), 3.60 (s, 3H), 3.95 (d, $^3J_{HH}$=2.6 Hz, 1H), 7.30–7.83 (m, 10H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 9.43(d, $^2J_{PC}$=2.2 Hz), 13.42, 20.56, 31.86 (d, $^3J_{PC}$ 12.4 Hz), 32.11 (d, $^1J_{PC}$=66.7 Hz), 36.36 (d, $^2J_{PC}$=2.2 Hz), 51.37, 51.87, 51.90, 52.34, 126.10 (d, $^1J_{PC}$=90.4 Hz), 126.69 (d, $^1J_{PC}$=93.8 Hz), 128.37–132.40 (10C^{ar}), 162.42, 169.47, 169.52. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 29.46. Anal. Calcd for $C_{25}H_{32}NO_6P$: C, 63.42; H, 6.76; N, 2.96. Found: C, 63.47; H, 6.81; N, 2.30. MS (EI) *m/z*: 473 (M^+, 100%,), 443(50%), 417(10%).

4.4. General procedure for the synthesis of β-hydroxyphosphazenes 19 and 20

To a solution of 0.5 mmol of the appropriated phosphazene in THF (25 mL) was added a solution of ^{n}BuLi (0.38 mL of a 1.6 M solution in hexane, 0.6 mmol) at −30°C. After 30 min of metallation, the temperature was lowered at −80°C and was added the corresponding aldehyde (0.5 mmol). The reaction mixture was stirred for 2 h. Addition of water (25 mL) followed by extraction with ethyl acetate (3×15 mL) and solvent evaporation under vacuum afforded a crude product which was purified by precipitation from diethyl ether.

4.4.1. (1*R,2*S**)-2-[diphenyl(*N*-methoxycarbonyl)phosphoranyl]-1-phenyl-1-propanol (19a).** White solid. Yield 80%. IR (KBr), ν (cm^{-1}): 3499, 1630. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.00 (dd, $^3J_{HH}$=6.7, $^3J_{PH}$=13.6 Hz, 3H), 2.71 (m, 1H), 3.66 (s, 3H), 5.26 (d, $^3J_{PH}$=9.7 Hz, 1H), 7.17–7.43 (m, 15H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 5.49, 39.50 (d, $^1J_{PC}$=63.3 Hz), 52.95 (d, $^4J_{PC}$=3.6 Hz), 69.06 (d, $^2J_{PC}$=2.0 Hz), 125.30–142.19 (18C^{ar}), 162.93. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 29.78. Anal. Calcd for $C_{32}H_{24}NO_3P$: C, 70.22; H, 6.15; N, 3.56. Found: C, 70.25; H, 6.11; N, 3.52. MS (EI) *m/z*: 394 (M^++1, 100%), 219 (20%), 201 (25%).

4.4.2. (1*S,2*S**)-2-[Diphenyl(*N*-methoxycarbonyl)phosphoranyl]-1-phenyl-1-propanol (20a).** White solid. Yield 80%. IR (KBr), ν (cm^{-1}): 3499, 1630. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.55 (dd, $^3J_{HH}$=9.4, $^3J_{PH}$=17.1 Hz, 3H), 3.10 (m, 1H), 3.52 (s, 3H), 4.50 (dd, $^3J_{PH}$=9.4, $^3J_{HH}$=17.1 Hz), 4.75 (s, 1H), 7.17–7.43 (m, 15H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 11.60, 37.50 (d, $^1J_{PC}$=68.6 Hz), 52.70 (d, $^4J_{PC}$=4.0 Hz), 74.79 (d, $^2J_{PC}$=3.8 Hz), 125.30–142.19 (18C^{ar}), 162.21. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 32.64. MS (EI) *m/z*: 394 (M^++1, 100%), 219 (20%), 201 (25%).

4.4.3. (1*R,2*S**)-1,3-Diphenyl-2-[diphenyl(*N*-methoxycarbonyl)phosphoranyl]-1-propanol (19b).** Oil. Yield 95%. IR (KBr), ν (cm^{-1}): 3260, 1647, 1613, 1308. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 2.91–3.35 (m, 3H), 3.79 (s, 3H), 5.43 (d, $^3J_{HH}$=10.5 Hz, 1H), 6.13–6.81 (m, 5H^{ar}), 7.21–7.98 (m, 15H^{ar}, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 26.87, 47.53 (d, $^1J_{PC}$=81.0 Hz), 53.22 (d, $^4J_{PC}$=3.4 Hz), 69.20 (d, $^2J_{PC}$=9.2 Hz), 125.11–142.20 (23C^{ar}), 142.20 (d, $^3J_{PC}$=3.7 Hz), 163.08. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 32.64. Anal. Calcd for $C_{32}H_{24}NO_3P$: C, 74.19; H, 6.01; N, 2.98. Found: C, 74.21; H, 6.05; N, 3.01. MS (EI) *m/z*: 470 (M^+, 100%), 201 (15%).

4.4.4. (1*R,2*S**)-1-Ciclohexyl-2-[*P*-diphenyl(*N*-methoxycarbonyl)phosphoranyl]-1-propanol (19c)/(1*S**,2*S**)-1-Ciclohexyl-2-[*P*-diphenyl(*N*-methoxycarbonyl)phosphoranyl]-1-propanol (20c). 19c/20c** Isolated as a 86:14 mixture. White solid. Yield 90%. IR (KBr), ν (cm^{-1}): 3260, 1650.1322.

NMR data for **19c**. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.80–2.12 (m, 11H, Cy), 1.15 (dd, $^3J_{PH}$=25.2, $^3J_{HH}$=7.2 Hz, 3H), 2.79 (m, 1H), 3.63 (s, 3H), 3.72 (dd, $^3J_{PH}$=9.0, $^3J_{HH}$=9.2 Hz, 1H), 5.15 (s, OH), 7.45–7.53 (m, 6H^{ar}), 7.75–7.82 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 6.36 (d, $^2J_{PC}$=1.6 Hz), 26.22, 26.44, 26.60, 29.67, 30.28, 33.87 (d, $^1J_{PC}$=67.0 Hz), 40.06 (d, $^2J_{PC}$=8.8 H), 53.62 (d, $^4J_{PC}$=3.3 Hz), 72.0 (d, $^2J_{PC}$=4.1 Hz), 126.79 (d, $^1J_{PC}$=86.7 Hz), 127.04 (d, $^1J_{PC}$=98.6 Hz), 128.71 (d, $^3J_{PC}$=11.9 Hz), 128.99 (d, $^3J_{PC}$=11.4 Hz), 131.95 (d, $^2J_{PC}$=8.3 Hz), 131.98 (d, $^2J_{PC}$=8.8 Hz), 132.18 (d, $^4J_{PC}$=3.1 Hz), 132.41 (d, $^4J_{PC}$=2.6 Hz), 163.16. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 31.72.

NMR data for **20c**. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.80–2.12 (m, 11H, Cy), 0.97 (dd, $^3J_{PH}$=18.5, $^3J_{HH}$=7.5 Hz, 3H), 3.06 (m, 1H), 3.57 (dd, $^3J_{PH}$=8.8, $^3J_{HH}$=15.8 Hz, 1H), 3.60 (s, 3H), 3.57 (dd, $^3J_{PH}$=9.0, $^3J_{HH}$=9.2 Hz, 1H), 4.8 (s, OH), 7.45–7.53 (m, 6H^{ar}), 7.75–7.82 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 12.51, 25.49, 26.78, 26.90, 30.70, 30.98, 34.58 (d, $^1J_{PC}$=70.6 Hz), 39.83 (d, $^2J_{PC}$=11.0 Hz), 53.47 (d, $^4J_{PC}$=3.3 Hz), 75.92 (d, $^4J_{PC}$=4.1 Hz), 128.29–133.22 (10C^{ar}), 162.44. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.23. MS (API-ES) *m/z*: 398 (M^+).

4.4.5. (1*R,2*S**)-(*p*-Chlorophenyl)-2-[(*P*-diphenyl)(*N*-methoxycarbonyl)phosphoranyl]-1-propanol (19d)/(1*S**,2*S**)-(*p*-chlorophenyl)-2-[(*P*-diphenyl)(*N*-methoxycarbonyl)-phosphoranyl]-1-propanol (20d). 19d/20d** Isolated as a

86:14 mixture. White solid. Yield 87%. IR (KBr), ν (cm^{-1}): 3291, 1650, 1322.

NMR data for **19d**. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.09 (dd, $^3J_{PH}$=16.9, $^3J_{HH}$=7.1 Hz, 3H), 2.72 (dq, $^2J_{PH}$=14.7, $^3J_{HH}$=7.5 Hz, 1H), 3.72 (s, 3H), 5.29 (d, $^3J_{PH}$=9.7 Hz, 1H), 6.42 (s, OH), 7.34–7.56 (m, 10H^{ar}), 7.71–7.80 (m, 2H^{ar}), 7.83–7.90 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 5.89, 39.56 (d, $^1J_{PC}$=39.5 Hz), 53.24 (d, $^4J_{PC}$=3.6 Hz), 68.93, 126.24 (d, $^1J_{PC}$=95.5 Hz), 126.54 (d, $^1J_{PC}$=86.0 Hz), 127.11, 128.20, 128.80 (d, $^3J_{PC}$=12.6 Hz), 131.94 (d, $^2J_{PC}$=9.6 Hz), 132.09 (d, $^2J_{PC}$=9.6 Hz), 132.44 (d, $^4J_{PC}$=2.9 Hz), 133.44, 141.06 (d, $^3J_{PC}$=14.4 Hz), 163.12. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 30.40.

NMR data for **20d**. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.61 (dd, $^3J_{PH}$=17.9, $^3J_{HH}$=7.3 Hz, 3H), 3.10 (m, 1H), 3.57 (s, 3H), 4.5 (dd, $^3J_{PH}$=8.1, $^3J_{HH}$=17.6 Hz, 1H), 6.60 (s, OH), 7.34–7.56 (m, 10H^{ar}), 7.71–7.80 (m, 2H^{ar}), 7.83–7.90 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 11.83, 37.72 (d, $^1J_{PC}$=37.7 Hz), 52.89 (d, $^4J_{PC}$=3.6 Hz), 74.41, 125.0 (d, $^1J_{PC}$=97.3 Hz), 126.32 (d, $^1J_{PC}$=88.3 Hz), 127.97–129.3 (5C^{ar}), 128.62 (d, $^3J_{PC}$=11.4 H C-13), 132.49 (d, $^2J_{PC}$=8.4 Hz), 132.61 (d, $^2J_{PC}$=8.4 Hz), 132.72 (d, $^4J_{PC}$=2.9 Hz), 140.44 (d, $^3J_{PC}$=12.6 Hz), 162.39. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.11. MS (API-ES) *m/z*: 428 (M^++1, 100%), 201 (40%).

4.4.6. (1*R,2*S**)-1-(*p*-Chlorophenyl)-2-[*P*-diphenyl(*N*-methoxycarbonyl)phosphoranyl]-3-phenyl-1-propanol (19e).** White solid. Yield 95%. Mp (°C): 124. IR (KBr), ν (cm^{-1}): 3279,1633, 1318. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 2.86–3.30 (m, 3H), 3.81 (s, 3H), 5.37 (d, $^3J_{PH}$=10.7 Hz, 1H), 6.42 (s, OH), 6.23–7.60 (m, 15H^{ar}), 7.71–7.77 (m, 2H^{ar}), 7.90–7.97 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 27.35, 47.85 (d, $^1J_{PC}$=61.3 Hz), 53.52 (d, $^4J_{PC}$=2.9 Hz), 60.02 (d, $^3J_{PC}$=2.2 Hz), 127.18, 127.90, 139.43 (d, $^3J_{PC}$=5.4 Hz), 126.42–132.75 (17C^{ar}), 140.96 (d, $^3J_{PC}$=14.4 Hz), 163.33. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 29.30. Anal. Calcd for $C_{29}H_{27}NO_3PCl$: C, 69.13; H, 5.36; N, 2.78. Found: C, 69.16; H, 5.37; N, 2.74. MS (API-ES) *m/z*: 503 (M^+, 4%), 472 (10%), 201 (100%).

4.4.7. 2-[*P*-Diphenyl(*N*-methoxycarbonyl)phosphoranyl]-1-phenyl-2-methyl-1-propanol (19f). White solid. Yield 90%. Mp (°C): 136. IR (KBr), ν (cm^{-1}): 3541, 1658, 1332. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.84 (d, $^3J_{PH}$=17.8 Hz, 3H), 1.28 (d, $^3J_{PH}$=16.5 Hz, 3H), 3.63 (s, 3H), 5.05 (d, $^3J_{PH}$=8.1 Hz, 1H), 7.10 (s, OH), 7.27–7.66 (m, 11H^{ar}), 7.95–8.05 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.60, 21.80, 42.16 (d, $^1J_{PC}$=69.2 Hz), 53.07 (d, $^4J_{PC}$=3.6 Hz), 76.93, 125.64 (d, $^1J_{PC}$=90.0 Hz), 126.26 (d, $^1J_{PC}$=76.8 Hz), 127.59, 127.72, 128.63, 128.76 (d, $^2J_{PC}$=8.1 Hz), 128.61 (d, $^2J_{PC}$=8.1 Hz), 132.39 (d, $^4J_{PC}$=3.0 Hz), 132.52 (d, $^4J_{PC}$=2.5 Hz), 133.40 (d, $^3J_{PC}$= 8.6 Hz), 133.83 (d, $^3J_{PC}$=9.1 Hz), 138.87 (d, $^3J_{PC}$= 12.2 Hz), 162.47. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 39.54. Anal. Calcd for $C_{24}H_{26}NO_3P$: C, 70.76; H, 6.39; N, 3.44. Found: C, 70.71; H, 6.41; N, 3.47. MS (API-ES) *m/z*: 407 (M^+, 10%), 334 (26%), 201 (100%), 183 (100%).

4.4.8. 1-(*p*-Chlorophenyl)-2-[*P*-diphenyl(*N*-methoxycarbonyl)phosphoranyl]-2-methyl-1-propanol (19g). White solid. Yield 95%. Mp (°C): 194 (decomposed). IR (KBr), ν (cm^{-1}): 3408, 1666, 1284. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.93 (d, $^3J_{PH}$=18.2 Hz, 3H), 1.35 (d, $^3J_{PH}$=15.3, 3H), 3.72 (s, 3H), 5.11 (d, $^3J_{PH}$=7.7 Hz, 1H), 7.35–7.73 (m, 10H^{ar}), 8.05–8.11 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.43, 21.61, 41.85 (d, $^1J_{PC}$=69.5 Hz), 53.00 (d, $^4J_{PC}$=3.6 Hz), 75.69, 125.32 (d, $^1J_{PC}$=89.9 Hz), 125.44 (d, $^1J_{PC}$=78.9 Hz), 132.41 (d, $^4J_{PC}$=2.5 Hz), 132.55 (d, $^4J_{PC}$=2.5 Hz), 128.04, 128.48 (d, $^3J_{PC}$=10.9 Hz), 128.62 (d, $^3J_{PC}$=10.9 Hz), 129.85, 133.28 (d, $^2J_{PC}$=8.7 Hz), 133.49 (d, $^2J_{PC}$=9.1 Hz), 137.38 (d, $^3J_{PC}$=12.5 Hz), 162.30. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 39.36. Anal. Calcd for $C_{24}H_{26}NO_3PCl$: C, 61.71; H, 5.57; N, 2.79. Found: C, 61.67; H, 5.59; 2.81. MS (API-ES) *m/z*: 441 (M^+, 4%), 367 (10%), 201 (61%), 183 (100%).

4.4.9. 1-Ethyl-2-[*P*-diphenyl(*N*-methoxycarbonyl)phosphoranyl]-2-methyl-1-propanol (19h). White solid. Yield 75%. Mp (°C): 185. IR (KBr), ν (cm^{-1}): 3460, 1647, 1289. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.00 (d, $^3J_{PH}$=18.2 Hz, 3H), 1.04 (t, $^3J_{HH}$=8.9 Hz, 3H), 1.33 (d, $^3J_{PH}$=16.7 Hz, 3H), 3.61 (s, 3H), 1.43–1.50 (m, 2H), 3.82 (ddd, $^3J_{PH}$=12.6, $^3J_{HH}$=8.1, $^3J_{HH}$=4.4 Hz, 1H), 6.50 (s, OH), 7.50–7.58 (m, 6H^{ar}), 7.82–7.88 (m, 2H^{ar}), 7.95–8.01 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 11.28, 17.16, 21.45, 23.26 (d, $^3J_{PC}$=9.5 Hz), 43.10 (d, $^1J_{PC}$= 67.4 Hz), 53.00 (d, $^4J_{PC}$=3.7 Hz), 75.06 (d, $^2J_{PC}$=3.3 Hz), 126.33 (d, $^1J_{PC}$=94.7 Hz), 126.62 (d, $^1J_{PC}$=77.8 Hz), 128.37 (d, $^3J_{PC}$=11.2 Hz), 132.05 (d, $^4J_{PC}$=2.9 Hz), 132.12 (d, $^4J_{PC}$=2.9 Hz), 133.33 (d, $^2J_{PC}$=8.3 Hz), 132.72 (d, $^2J_{PC}$=8.7 Hz), 162.56. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 38.89. Anal. Calcd for $C_{20}H_{26}NO_3P$: C, 66.86; H, 7.24; N, 3.9. Found: C, 66.82; H, 7.26; N, 3.92. MS (API-ES) *m/z*: 360 (M^++1, 100%), 285 (48%), 201 (23%).

4.4.10. 2-[*P*-Diphenyl(*N*-methoxycarbonyl)phosphoranyl]-1,2di-methyl-1-propanol (19i). White solid. Yield 70% Mp (°C): 152. IR (KBr), ν (cm^{-1}): 3459, 1646, 1270. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.95 (d, $^3J_{PH}$=17.5 Hz, 3H), 1.35 (d, $^3J_{PH}$=16.5 Hz, 3H), 1.62–1.72 (m, 1H), 1.75–1.86 (m, 1H), 2.60–2.70 (m, 1H), 2.98–3.07 (m, 1H), 3.63 (s, 3H), 3.98 (ddd, $^3J_{PH}$=10.2, $^3J_{HH}$=8.1, $^4J_{HH}$=1.8 Hz), 6.64 (s, OH), 7.18–7.30 (m, 5H^{ar}), 7.50–7.59 (m, 6H^{ar}), 7.80–7.83 (m, 2H^{ar}), 7.95–8.02 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 17.20, 21.42, 32.37 (d, $^3J_{PC}$=9.0 Hz), 32.63, 43.17 (d, $^1J_{PC}$=66.7 Hz), 53.00 (d, $^4J_{PC}$=3.6 Hz), 72.45 (d, $^2J_{PC}$=3.0 Hz), 125.72, 126.28 (d, $^1J_{PC}$=95.5 Hz), 126.70 (d, $^1J_{PC}$=75.5 Hz), 128.26, 128.37 (d, $^3J_{PC}$=12.0 Hz), 128.41 (d, $^3J_{PC}$=11.4 Hz), 128.57, 132.10 (d, $^4J_{PC}$=4.0 Hz), 132.13 (d, $^4J_{PC}$=3.0 Hz), 133.28 (d, $^2J_{PC}$=8.4 Hz), 133.76 (d, $^2J_{PC}$=9.0 Hz), 142.24, 162.62. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 38.94. Anal. Calcd for $C_{26}H_{30}NO_3P$: C, 71.72; H, 6.90; N, 3.22. Found: C, 71.76; H, 6.87; N, 3.21. MS (API-ES) *m/z*: 436 (M^++1, 100%), 361 (23%), 201 (5%).

4.5. General method for the synthesis of oxazaphosphinin-2-ones 21

To a solution of phosphazene **10h** (0.15 g, 0.5 mmol) in

diethyl ether (15 mL) was added a solution of ^{n}BuLi (0.38 mL of a 1.6 M solution in hexane, 0.6 mmol) in THF (15 mL) at −35°C. The mixture was stirred for 1 h. Then, the temperature was lowered at −80°C and was added the corresponding aldehyde (0.5 mmol). The reaction was allowed to reach ambient temperature and stirred for 14 h. Solvents elimination under vacuum and addition of Et_2O afforded heterocycles **21a** and **21d** as white solids. Compounds **21b–c** were obtained in the same way except for the solvent used. In this case phosphazene **10h** was dissolved in THF.

4.5.1. 4-Diphenyl-6-phenyl-5,5-dimethyl-1,3,4-oxazaphosphinin-2-one (21a). White solid. Yield 77%. Mp (°C): 144 (decomposed). IR (KBr), ν (cm^{-1}): 1663, 1291. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.09 (d, $^3J_{PH}$=16.5 Hz, 3H), 1.15 (d, $^3J_{PH}$=15.2 Hz, 3H), 5.28 (d, $^3J_{PH}$=9.9 Hz, 1H), 7.26–7.33 (m, 5H^{ar}), 7.60–7.70 (m, 6H^{ar}), 8.00–8.08 (m, 2H^{ar}), 8.12–8.19 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.49, 21.87, 33.81 (d, $^1J_{PC}$=47.2 Hz), 80.21, 125.25 (d, $^1J_{PC}$=105.9 Hz), 125.83 (d, $^1J_{PC}$=97.1 Hz), 127.74, 128.46, 129.96–133.11 (3C^{ar}), 133.32 (d, $^3J_{PC}$=11.4 Hz), 157.02. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.20. Anal. Calcd for $C_{23}H_{22}NO_2P$: C, 73.60; H, 5.87; N, 3.73. Found: C, 73.64; H, 5.86; N, 3.70. MS (API-ES) *m/z*: 376 (100%, M$^+$+1), 244 (15%), 202 (27%).

4.5.2. 6-*p*-Chlorophenyl-4,4-diphenyl-5,5-dimethyl-1,3,4-oxazaphosphin-2-one (21b). White solid. Yield 42%. Mp (°C): 146 (decomposed). IR (KBr), ν (cm^{-1}): 1663, 1291. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.06 (d, $^3J_{PH}$=7.5 Hz, 3H), 1.13 (d, $^3J_{PH}$=8.6 Hz, 3H), 5.25 (d, $^3J_{PH}$=9.6 Hz, 1H), 7.18–7.31 (m, 4H^{ar}), 7.53–7.67 (m, 3H^{ar}), 8.0–8.20 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.48, 21.80, 33.78 (d, $^1J_{PC}$=46.86 Hz), 79.59, 125.06 (d, $^1J_{PC}$=106.3 Hz), 125.65 (d, $^1J_{PC}$=98.0 Hz), 129.14, 131.18, 156.61. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.90. Anal. Calcd for $C_{23}H_{21}NO_2PCl$: C, 67.40; H, 5.13; N, 3.42. Found: C, 67.43; H, 5.14; N, 3.39. MS (API-ES) *m/z*: 409 (M$^+$, 27%), 410 (M$^+$+1, 33%), 407 (100%), 201 (22%).

4.5.3. 6-Ethyl-5,5-dimethyl-4,4-diphenyl-1,3,4-oxazaphosphin-2-one (21c). White solid. Yield 65%. Mp (°C): 148 (decomposed). IR (KBr), ν (cm−1): 1651, 1290. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.09 (t, $^3J_{HH}$=7.7 Hz, 3H), 1.15 (d, $^3J_{PH}$=16.2 Hz, 3H), 1.26 (d, $^3J_{PH}$=15.4 Hz, 3H), 4.04 (dt, $^3J_{PH}$=$^3J_{HH}$=9.5, $^4J_{HH}$=2.6 Hz, 1H)), 7.52–7.58 (m, 6H^{ar}), 7.77–7.95 (m, 2H^{ar}), 8.05– 8.11 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 10.86, 15.99, 20.46 (d, $^3J_{PC}$=8.4 Hz), 49.33 (d, $^1J_{PC}$=48.1 Hz), 79.84, 125.35 (d, $^1J_{PC}$=104.5 H), 126.03 (d, $^1J_{PC}$=97.3 Hz), 128.86 (d, $^3J_{PC}$=12.0 Hz), 129.07 (d, $^3J_{PC}$=12.0 Hz), 131.85 (d, $^2J_{PC}$=9.0 Hz), 132.23 (d, $^3J_{PC}$=2.6 Hz), 132.92 (d, $^2J_{PC}$=9.6 Hz), 157.39. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.37. Anal. Calcd for $C_{19}H_{22}NO_2P$: C, 69.72; H, 6.73; N, 4.28. Found: C, 69.70; H, 6.71; N, 4.32. MS (API-ES) *m/z*: 328 (100%, M$^+$+1), 285 (14%), 201 (23%).

4.5.4. 5,5-Dimethyl-4,4-diphenyl-6-(2phenylethyl)- 1,3,4-oxazaphosphin-2-one (21d). White solid. Yield 64%. Mp (°C): 152 (decomposed). IR (KBr), ν (cm^{-1}): 1649, 1291. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.13 (d, $^3J_{PH}$=17.7 Hz, 6H), 1.60–1.70 (m, 1H), 1.82–1.94 (m, 1H), 2.62–2.72 (m, 1H), 3.02–3.12 (m, 1H), 4.14 (dt, $^3J_{PH}$=$^3J_{HH}$=10.5, $^4J_{HH}$=1.3 Hz, 1H), 7.18–7.21 (m, 5H^{ar}), 7.43–7.58 (m, 6H^{ar}), 7.75–7.82 (m, 2H^{ar}), 8.04–8.11 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.96 (d, $^2J_{PC}$=2.3 Hz), 21.13, 29.09 (d, $^3J_{PC}$=8.4 Hz), 31.85, 32.74 (d, $^1J_{PC}$=48.78.4 Hz), 77.05, 124.87 (d, $^1J_{PC}$=105.11 Hz), 125.73 (d, $^1J_{PC}$=97.9 Hz), 125.97, 128.40, 128.56, 128.82 (d, $^3J_{PC}$=12.0 Hz), 129.10 (d, $^3J_{PC}$=12.0 Hz), 131.87 (d, $^2J_{PC}$=8.4 Hz), 132.77 (d, $^2J_{PC}$=9.6 Hz), 133.07 (d, $^4J_{PC}$=2.4 Hz), 141.14, 157.25. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 25.94. Anal. Calcd for $C_{25}H_{26}NO_2P$: C, 74.44; H, 6.45; N, 3.48. Found: C, 74.46; H, 6.46; N, 3.45. MS (API-ES) *m/z*: 404 (100%, M$^+$+1), 361 (24%), 201 (25%).

4.5.5. 1-*p*-Chlorophenyl-2-methyl-2-diphenylphosphoryl-1-propanol (22b). Isolated as a by-product in the synthesis of **21b** by fractional precipitation of the crude reaction in Et_2O. White solid. Yield 83%. Mp (°C): 176. IR (KBr), ν (cm^{-1}): 3415, 1164. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 0.96 (d, $^3J_{PH}$=17.0 Hz, 3H), 1.18 (d, $^3J_{PH}$=15.3 Hz, 3H), 4.96 (d, $^3J_{PH}$=8.8 Hz, 1H), 6.05 (s, OH), 7.19–7.32 (m, 4H^{ar}), 7.53–7.67 (m, 3H^{ar}), 8.00–8.12 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.0, 21.64, 76.32, 40.72 (d, $^1J_{PC}$=66.7 Hz), 125.06 (d, $^1J_{PC}$=106.3 Hz), 127.65, 128.63 (d, $^3J_{PC}$=11.3 Hz), 128.67 (d, $^1J_{PC}$=10.9 Hz), 129.71, 131.97 (d, $^2J_{PC}$=8.5 Hz), 132.15 (d, $^4J_{PC}$=2.8 Hz), 132.19 (d, $^4J_{PC}$=2.8 Hz), 132.33 (d, $^2J_{PC}$=8.5 Hz), 137.04 (d, $^3J_{PC}$=12.6 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 45.44. Anal. Calcd for $C_{22}H_{22}O_2PCl$: C, 68.67; H, 5.72. Found: C, 68.66; H, 5.73. MS (API-ES) *m/z*: 386 (M$^+$+1, 100%), 201 (25%).

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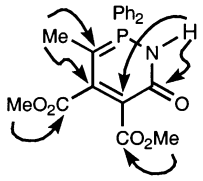
16. Structural elucidation of **12a**: The molecular ion of the mass spectrum matched the molecular weight of one molecule of **10b** plus one molecule of DMAD with loss of methanol (*m/z* 397, M^+ 100%). Accordingly, the ^{1}H spectrum showed only two methoxy groups at δ 3.53 and 3.90. The methyl protons of the phosphazene appeared as a doublet ($^3J_{PH}$=12.1 Hz) at δ 1.71, a value consistent with a methyl group bonded to a sp^2 carbon. The amide proton was assigned to the broad singlet at δ 14.02 (doublet of $^2J_{PH}$=5.6 Hz in DMSO-d_6). The most relevant signals of the ^{13}C spectrum were the nonaromatic quaternary carbons. Particularly, the singlet at δ 81.14 and the doublets at 86.49 ($^1J_{PC}$=105.6 Hz) and 149.46 ($^2J_{PC}$=20.7 Hz). The ^{31}P, ^{13}C couplings observed are characteristics for nuclei separated by one and two bonds, respectively.[17] The spectrum showed also three carbonyl signals at δ 168.49 ($^2J_{PC}$=8.7 Hz), 170.41, and 171.39 ($^3J_{PC}$=6.0 Hz). The structure was finally established through the analysis of the 2D HMBC spectrum. The methyl and NH proton correlations allowed identification of the connectivity of the six-membered ring as indicated in Fig. 1. The assignment of the methoxycarbonyl groups was achieved by identifying in the 2D HMQC spectrum, the direct connection between the respective proton and carbon of each methoxy group and then the long range correlation of the corresponding pair of proton and carbonyl carbon.



12a

Figure 1. Selected long range ^{1}H, ^{13}C correlations observed in the 400.13 MHz gHMBC spectrum of **12a** revealing key connectivities in the heterocyclic ring and the methoxycarbonyl substituents.

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20. The use of dimethyl fumarate as electrophile also afforded **17a** although in lower yield compared to the reaction with the *cis* isomer.
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22. Determined by integration of the inverse-gated proton decoupled ^{31}P NMR spectra of the crude reactions using a pulse width of 15° and a relaxation delay of 10 s. Whenever possible the diastereomeric ratio thus obtained was corroborated with the integrals measured in the ^{1}H spectra for well resolved signals of each isomer.
23. The calculated dihedral angle $H^{\alpha}CCH^{\beta}$ (MM, ChemWindow 6.0 Bio-Rad Laboratories, Sadtler 1998) for the minimal energy conformations of compounds **19a**–**20a** gave values of 87° for **19a** and 180° for **20a**, which implies that, respectively, a vanishing small and a very large $^3J_{H^{\alpha}H^{\beta}}$ vicinal couplings should be observed in excellent agreement with the values experimentally measured for both compounds.
24. Compound **22a** has been previously synthesised by reaction of the corresponding phosphine oxide and benzaldehyde in the presence of ^{n}BuLi. Davidson, A. H.; Earnshaw, C.; Grayson, J. I.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1452. The spectroscopic data of **22a** match those previously reported.
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