Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 2101–2123

TETRAHEDRON

# New ketone homoenolate anion equivalents derived from (alkenyl)pentamethyl phosphoric triamides

Claude Grison,* Antoine Thomas,† Frédéric Coutrot and Philippe Coutrot*

*Laboratoire de Chimie Organique Biomoléculaire, Institut Nancéien de Chimie Moléculaire, FR CNRS 1742, UMR 7565, Université Henri Poincaré, Nancy 1, BP 239, 54506 Vandoeuvre-les-Nancy cedex, France*

Received 23 October 2002; revised 19 December 2002; accepted 3 February 2003

**Abstract**—Lithiated ambident anions derived from (1-alkyl-2-propenyl)- or (1-phenyl-2-propenyl)-pentamethyl phosphoric triamides undergo regioselectively γ-reaction with various alkylating reagents and isobutyraldehyde. Further hydrolysis of adducts releases the ketone under acid conditions. Number of synthetic applications clearly show the ketone homoenolate behaviour of these new carbanions. 

## 1. Introduction

One of the most important applications of heterosubstituted allyl anions has been found in the umpolung of carbonyl compounds. They allow the introduction of electrophiles at the β position of a carbonyl moiety and they constitute homoenolate equivalents.[1,2]

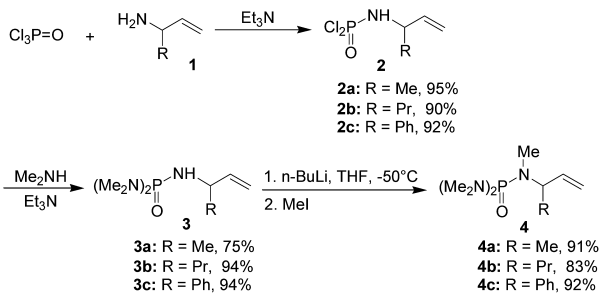
The main difficulties of the methodology are the regioselectivity in the reaction with electrophilic reagents, a problem inherent to the ambident structure of the allyl anions and the accessibility to various substituted allyl precursors allowing structural variations in the target carbonyl compound.[3] From this last point of view, most of the works has been carried out on aldehyde homoenolate equivalents and information on ketone homoenolate equivalents is limited, probably because the requisite substituted suitable allylic precursors are not easily available.[1,2b,4] To remedy these limitations, a new route to ketone homoenolates using (alkenyl)pentamethyl phosphoric triamide method has been devised. Numerous ketones and dicarbonyl compounds have been prepared to demonstrate the utility of this route.

## 2. Results and discussion

### 2.1. Preparation of the *N*-phosphoramide precursors 4

We have previously described the formation and the utility of lithium anions derived from allylphosphoramides as aldehyde homoenolate equivalents.[5] (Allyl)pentamethyl phosphoric triamides have been prepared in high yields by reaction between pentamethyl phosphoric triamide anion, generated with butyllithium or sodium hydride, and chloro or bromo allylic compounds.[5c] Analogously, the direct generation of (1-alkyl-2-propenyl)- or (1-phenyl-2-propenyl)-phosphoramides **4** from secondary chloro or bromo allylic compounds was considered, but unsuccessful, due to side $SN_2'$ reaction.

Other attempts to prepare **4** from secondary allylamines and phosphoryl trichloride were tested. Unfortunately, the steric hindrance generated around the phosphorus atom by the secondary allylamine moiety limited the further introduction of the two dimethylamino groups; the substitution of a sole chlorine being actually observed.[6] Finally, the required precursor **4** was conveniently prepared in a three-step sequence from primary allylamines 1-alkyl- or 1-phenyl-2-propenylamine[8] **1** and $POCl_3$ (Scheme 1). In a first step,




**Scheme 1.** Preparation of the phosphoramides **4**.

*Keywords*: homoenolate anion; ketone homoenolate anion; (alkenyl)pentamethyl phosphoric triamide; 1,*n*-diketone; phosphoramidedithioester.

* Corresponding authors. Tel.: +33-3-83-68-43-61; fax: +33-3-83-68-43-63; e-mail: philippe.coutrot@incm.uhp-nancy.fr

† Part of the thesis of author; Thomas, A. Thesis, University Henri Poincaré, Nancy 1, France, 2002.

0040–4020/03/$ - see front matter 
doi:10.1016/S0040-4020(03)00188-1

**Table 1**. Preparation of the phosphoramide **4** and $^{31}P$ NMR data

| R | 2 | Yield (%) | $^{31}P$ NMR ($CDCl_3$) $\delta$ (ppm) | 3 | Yield (%) | $^{31}P$ NMR ($CDCl_3$) $\delta$ (ppm) | 4 | Yield (%) | $^{31}P$ NMR ($CDCl_3$) $\delta$ (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| Me | **2a** | 95[a] | 10.8 | **3a** | 75[a] | 18.6 | **4a** | 91[b] | 21.0 |
| Pr | **2b** | 90[a] | 11.3 | **3b** | 94[a] | 18.7 | **4b** | 83[b] | 21.0 |
| Ph | **2c** | 92[a] | 10.8 | **3c** | 94[a] | 18.8 | **4c** | 92[b] | 20.9 |

[a] Determined on the crude product.
[b] Determined on the distilled product.

1-alkyl- or 1-phenyl-2-propenylamine **1** reacted with $POCl_3$ in THF, in the presence of triethylamine to yield dichlorophosphoramide **2** (90–95%). Further treatment of **2** with an excess of dimethylamine/triethylamine (4:3) in THF led to (bis-dimethylamino) phosphoramides **3** (75–94%). Subsequent deprotonation of **3** with *n*-BuLi (1 equiv.) at −50°C in THF afforded the expected lithium phosphoramide. After 10 min at −50°C, iodomethane was added. The reaction mixture was stirred at −50°C for 2 h, and then hydrolysed. Allylphosphoramides **4** were obtained with very good yield from **3** (83–92%), and good overall yield from allylamine **1** (70–80%). It is noteworthy that the last methylation step is very sensitive to experimental conditions and it is necessary to be stringent with conditions mentioned.

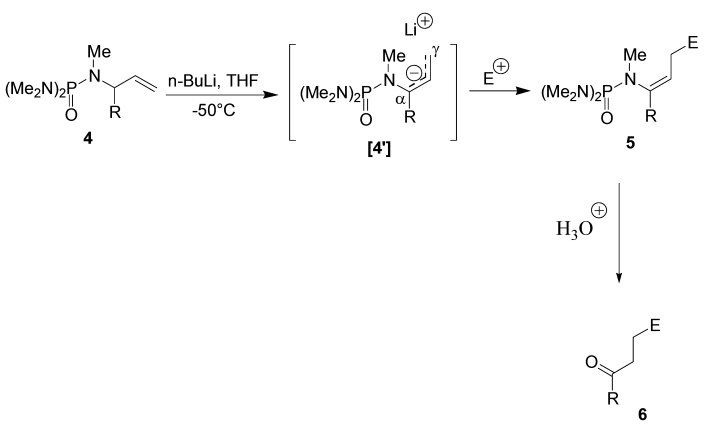
The three steps were easily monitored by $^{31}P$ NMR spectroscopy (Table 1). The crude products **4** may be used without purification. Nevertheless, a distillation was possible in the cases R=Me, Pr. In these conditions, (1-alkyl-2-propenyl)pentamethyl phosphoric triamides **4a-b** were obtained in good yields after distillation whereas (1-phenyl-2-propenyl)pentamethyl phosphoric triamide **4c**, which is thermally unstable was directly used in the following step without any further purification (Table 1).

## 2.2. Preparation of lithium anions [4′] derived from 4 and reactivity of 4′ with electrophiles

The reaction of **4** with *n*-BuLi (1 equiv.) at −50°C in THF led to a deprotonation at the α-allylic position to yield the carbanion [**4′**]. Interestingly, the time for the metallation of **4** depends on the α-substituent R and can be observed in $^{31}P$ NMR. A very fast deprotonation occurred for the methyl compound **4a** (characterized by a $^{31}P$ NMR signal at 21.0 ppm in THF) and phenyl compound **4c** (characterized by a $^{31}P$ NMR signal at 20.9 ppm in THF) leading to the instantaneous formation of the corresponding carbanion [**4′a**] (characterized by a $^{31}P$ NMR singlet at 21.9 ppm) and [**4′c**] which has an intense green color, indicating extensive charge delocalization (characterized by a $^{31}P$ NMR singlet at 22.7 ppm). From those results, the conditions of metallation of the unsubstituted α-allylphosphoramide (R=H) were revisited since we have previously described its complete metallation with *n*-BuLi in THF, at −50°C for 1 h 30 min. We have verified that such a long reaction time was not necessary since the $^{31}P$ NMR study of the reaction medium demonstrated that, in this case also, total metallation was complete just at the time where the dropwise introduction of *n*-BuLi was achieved. On the contrary, complete metallation of **4b** (characterized by a $^{31}P$ NMR signal at 21.0 ppm in THF) occurred only after stirring for 1 h at −50°C on the addition of *n*-BuLi before it could be observed in the $^{31}P$ NMR spectrum a sole singlet at 22.6 ppm characteristic of the carbanion [**4′b**].

Hydrolysis and deuterolysis of carbanion [**4′**] gave the fully transposed enephosphoramide **5** (E=H or D) as the sole product that confirmed the complete formation of the carbanion [**4′**] in the above conditions. Analogously, carbanion [**4′**] reacted exclusively at the γ-position with various alkylating agents providing the enephosphoramide **5** (E=alkyl). Different reasons can account for the easy deprotonation of **4** and for the γ-regiospecificity.

Stereoelectronic effects at phosphorus seem to be important: at one, both dimethylamine substituents appear essential to promote the α-deprotonation,[9] and at the same time, the bulkiness of the *N*-methyl-bis-dimethylphosphoramide moiety makes the alkylation reaction easier at the γ-carbon. Moreover, as for hydrolysis, the alkylation is kinetically controlled, consequently the γ-transition state that leads to the enephosphoramide **5** has a more stable trisubstituted double bond character (and, in addition, conjugated in




**Scheme 2.** Preparation of the γ-alkylated enephosphoramides **5** and ketones **6**.

**Table 2**. Reactions of lithium anions **4′** with electrophiles and hydrolysis of adducts **5** into ketones **6**

| Entry | Reagent | E | R | **5** | % Conversion[a] | *Z*/*E* | **6** | % Yield[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | $H_2O$ | H | Me | **5aa** | 96 | 96/4 | **6aa** | 75 |
| 2 | | | Pr | **5ba** | 100 | 100/0 | **6ba** | 69 |
| 3 | | | Ph | **5ca** | 91 | 100/0 | **6ca** | 85 |
| 4 | $D_2O$ | D | Me | **5ab** | 98 | 90/10 | **6ab** | 78 |
| 5 | | | Pr | **5bb** | 100 | 100/0 | **6bb** | 78 |
| 6 | | | Ph | **5cb** | 100 | 100/0 | **6cb** | 79 |
| 7 | MeI | Me | Me | **5ac** | 100 | 88/12 | **6ac** | 87 |
| 8 | | | Pr | **5bc** | 100 | 100/0 | **6bc** | 83 |
| 9 | | | Ph | **5cc** | 99 | 100/0 | **6cc** | 70 |
| 10 | $Me_2SO_4$ | Me | Me | **5ac** | 100 | 98/8 | **6ac** | 87 |
| 11 | | | Pr | **5bc** | 100 | 100/0 | **6bc** | 83 |
| 12 | | | Ph | **5cc** | 86 | 100/0 | **6cc** | 69 |
| 13 | $C_5H_{11}Cl$ | $C_5H_{11}$ | Me | **5ad** | 100 | 53/47 | **6ad** | 86 |
| 14 | | | Pr | **5bd** | 100 | 100/0 | **6bd** | 83 |
| 15 | | | Ph | **5cd** | 75 | 100/0 | **6cd** | 64 |
| 16 | $C_5H_{11}I$ | $C_5H_{11}$ | Me | **5ad** | 100 | 87/13 | **6ad** | 83 |
| 17 | | | Pr | **5bd** | 100 | 100/0 | **6bd** | 90 |
| 18 | | | Ph | **5cd** | 78 | 100/0 | **6cd** | 67 |
| 19 | BnCl | Bn | Me | **5ae** | 97 | 90/10 | **6ae** | 91 |
| 20 | | | Pr | **5be** | 100 | 100/0 | **6be** | 93 |
| 21 | | | Ph | **5ce** | 98 | 100/0 | **6ce** | 84 |
| 22 | $iC_3H_7I$ | $iC_3H_7$ | Me | **5af** | 100 | 80/20 | **6af** | 90 |
| 23 | | | Pr | **5bf** | 96 | 100/0 | **6bf** | 62 |
| 24 | | | Ph | **5cf** | 94 | 100/0 | **6cf** | 70 |
| 25 | $MeOCH_2Cl$ | $MeOCH_2$ | Me | **5ag** | 95 | 95/5 | **6ag** | 78 |
| 26 | | | Pr | **5bg** | 76 | 100/0 | **6bg** | 76 |
| 27 | | | Ph | **5cg** | 74 | 100/0 | **6cg** | 61 |
| 28 | $CH_2{=}CHCH_2Br$ | $CH_2{=}CH{-}CH_2$ | Me | **5ah** | 96 | 90/10 | **6ah** | 83 |
| 29 | | | Pr | **5bh** | 100 | 100/0 | **6bh** | 80 |
| 30 | | | Ph | **5ch** | 84 | 100/0 | **6ch** | 63 |
| 31 | *i*Pr CHO | *i*Pr CHOH | Me | **5ai** | 75 | 100/0 | **6ai** | – |
| 32 | | | Pr | **5bi** | 70 | 100/0 | **6bi** | – |
| 33 | | | Ph | **5ci** | 100 | 100/0 | **6ci** | – |

[a] Percentage was determined by NMR measurements and based on the conversion of the starting substrate **4**.
[b] Yields of pure products evaluated on starting substrates **4**.

the case R=Ph) than the α-transition state that provides α-alkylation where the double bond remains terminal. Compared with the earlier results of α-unsubstituted allylphosphoramides where hydrolysis leads to a mixture of transposed and not transposed enephosphoramide[5e–g] the more substituted double-bond character of the γ-transition state appears here as the essential factor since only the complete transposed product is observed.

Neither the bulkiness of the electrophile or the nature of its leaving group, nor the nature of the α-substituent R, affected dramatically the results (Scheme 2, Table 2). However, we observed that the reaction was easier with R=alkyl than with R=Ph. In this last case the nucleophilicity of [**4′c**] decreased because of the extensive charge delocalisation and alkylations required thus much longer time. As a result, reaction times varied from 1 h at −50°C with R=alkyl to 2 h at +20°C with R=Ph.

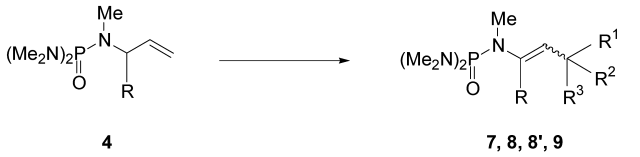
Reactions of lithium anion [**4′**] with isobutyraldehyde, as model of carbonyl compound, showed the same γ-regioselectivity than for alkylation and gave exclusively the respective γ-products **5ai–ci**. Hence, in contrast to already published results using other heteroatom-stabilised allyl anions,[1] the nature of the electrophile did not modify the γ-regioselectivity of the nucleophilic attack of the phosphoramide ambident anion [**4′**]. Interestingly, before hydrolysis of the reaction mixture leading to **5ai–ci**, internal addition of the alcoholate onto the double bond of the intermediate γ-hydroxyalkylated enephosphoramide, which would lead to the formation of tetrahydrofuran ring, was not observed, in contrast to previous results reported by us with unsubstituted α-allylphosphoramides.[5d] In the present case, we assumed that steric hindrance carried by the α-substituent prevents this reaction. The $^1H$, $^{13}C$, and $^{31}P$ NMR data allowed assignment of the different products. Enephosphoramides **5** were easily distinguished from the starting enephosphoramides **4**. In the $^1H$ NMR spectra, the Cα–N-*Me* signal was observed as a doublet at 2.42–2.46 ppm for **4** ($^3J_{H-P}$=8.9–9.5 Hz) whereas in the transposed product **5** this doublet appeared in all cases downfield at 2.62–2.94 ppm ($^3J_{H-P}$=8.0–8.7 Hz). Moreover, the $^1H$ NMR spectra of **4b** and **4c** presented two separate doublets at 2.63 ppm (6H) and 2.66 ppm (6H) corresponding to the resonances of the inequivalent $(Me_2N)_2$. In the transposed product **5** the $(Me_2N)_2$ are equivalent and a sole doublet (12H) was observed upfield, at 2.5–2.67 ppm.

Not only the reaction of anions [**4′**] with different electrophiles resulted in the exclusive formation of γ-products **5**, but also the stereochemistry was preferentially *Z*. To explain this result, a five-membered intermediate structure is postulated, in which the lithium cation is kept between the γ-carbon atom of the ambident anion and the nitrogen of the phosphoramide moiety (see [**4′**] in Scheme 2).

Treatment of enephosphoramide **5** with an aqueous acid solution afforded the expected ketone **6** in good yields,

but we observed that hydrolysis of such α-substituted phosphoramide **5** revealed obviously slower than unsubstituted analogue (R=H) which provided aldehyde in 1 h at room temperature.[5c] Here, the rate of cleavage of the C–N bond in phosphoramide **5** was dependent on the nature of R. When R=Me, Pr the cleavage was carried out with a 2N HCl aqueous/ether solution and was complete after stirring 4 h at room temperature. When R=Ph, the hydrolysis required heating at reflux for 4 h with a 6N $H_2SO_4$ aqueous/benzene solution. A large number of unsymmetrical ketones **6** were obtained except hydroxyketones **6ai–ci** that were the only compounds that could not be obtained by this process because degradation occurred during hydrolysis (Table 2). It is noteworthy that γ-deuterated ketones have been so prepared in high yields by acid hydrolysis of deuterated enephosphoramides **5ab–cb** (entries 4–6).

Encouraged by the precedent results, we investigated a new method for the synthesis of masked diketones and unsymmetrical diketones using phosphoramide anions [**4′**].




**7** : $R^1$ = SMe $R^2$ = H $R^3$ = H — **7a** : R = Me **7b** : R = Pr **7c** : R = Ph
**8** : $R^1$ = SMe $R^2$ = SMe $R^3$ = H — **8a** : R = Me **8b** : R = Pr **8c** : R = Ph
**8'** : $R^1$ = SMe $R^2$ = SMe $R^3$ = Me — **8'a** : R = Me **8'b** : R = Pr **8'c** : R = Ph
**9** : $R^1$ = SMe $R^2$ = SMe $R^3$ = SMe — **9a** : R = Me **9b** : R = Pr **9c** : R = Ph

**Scheme 3.** γ-Enephosphoramides **7**, **8**, **8′**, **9**.

## 2.3. Synthesis of masked dicarbonyl compounds and unsymmetrical dicarbonyl compounds

Two approaches were studied: the first approach was the disulfanylation of anions [**4′**] and the second was the introduction of a ketal moiety from the reaction between [**4′**] and halogeno ketals.

**2.3.1. Sulfanylation of anions [4′].** The reaction between phosphoramide anions [**4′**] and two sulfur electrophiles (dimethyldisulfide and *S*-methyl methanethiosulfonate) was investigated in order to prepare conjugate enephosphoramides containing one, two or three methylsulfanyl groups at γ-C (Scheme 3, Table 3).

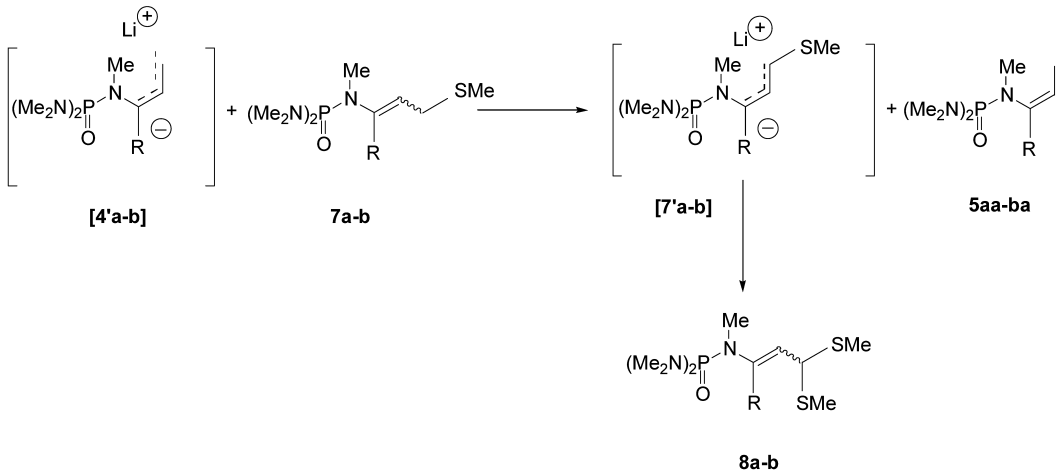
On the contrary of unsubstituted α-allylphosphoramide anion [**4′**] (R=H) where α-selectivity sometimes was observed,[5e] α-substituted anion [**4′**] (R=Me, Pr, Ph) reacted with $MeSSO_2Me$ and MeSSMe exclusively at the γ-position. In analogous experimental alkylation conditions, carbanion [**4′c**] reacted with $MeSSO_2Me$ faster than with MeSSMe (Table 3, entries 5, 6). Treatment of this anion with 1 equiv. of $MeSSO_2Me$ exclusively yielded the γ-mono product **7c**. With [**4′a**] and [**4′b**], the rate of sulfanylation decreased with the two sulfur electrophiles. The thioethers **7a** and **7b** were obtained accompanied of dithioacetals **8a** and **8b**, and transposed enephosphoramides **5aa** and **5ba** (Table 3, entries 1–4). It was noticed that dithioacetals **8a** and **8b** and transposed enephosphoramides **5aa** and **5ba** were obtained in the same proportion (entries 1, 3). The formation of **5aa** and **5ba** could be due to the hydrolysis of unreacted carbanion [**4′a-b**] (see above Scheme 2, Table 2), or another possible explanation would be that ambident carbanion [**4′a-b**] is able to γ-deprotonate, in situ, the thioether **7a-b** formed in the reaction, leading to the new carbanion [**7′a-b**] and

**Table 3**. Sulfanylation of anions **4′**

| Entry | R | Sulfanylation conditions | Starting material **4** | **5** (%)[a] | **7** (%)[a] | **8** (%)[a] | **9** (%)[a] | **8′** (%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | Me | (i) BuLi<br>(ii) $MeSSO_2Me$<br>(iii) $H_2O$ | **4a** | **5aa** (20) | **7a** (60) | **8a** (20) | **9a** (0) | – |
| 2 | Me | (i) BuLi<br>(ii) MeSSMe<br>(iii) $H_2O$ | **4a** | **5aa** (12) | **7a** (64) | **8a** (24) | **9a** (0) | – |
| 3 | Pr | (i) BuLi<br>(ii) $MeSSO_2Me$<br>(iii) $H_2O$ | **4b** | **5ba** (22) | **7b** (56) | **8b** (22) | **9b** (0) | – |
| 4 | Pr | (i) BuLi<br>(ii) MeSSMe<br>(iii) $H_2O$ | **4b** | **5ba** (8) | **7b** (79) | **8b** (13) | **9b** (0) | – |
| 5 | Ph | (i) BuLi<br>(ii) $MeSSO_2Me$<br>(iii) $H_2O$ | **4c** | **5ca** (0) | **7c** (100) | **8c** (0) | **9c** (0) | – |
| 6 | Ph | (i) BuLi<br>(ii) MeSSMe<br>(iii) $H_2O$ | **4c** | **5ca** (16) | **7c** (74) | **8c** (10) | **9c** (0) | – |
| 7 | Me | Procedure A | **4a** | **5aa** (13) | **7a** (0) | **8a** (69) | **9a** (18) | – |
| 8 | Pr | Procedure A | **4b** | **5ba** (5) | **7b** (0) | **8b** (84) | **9b** (11) | – |
| 9 | Me | Procedure B | **4a** | **5aa** (9) | **7a** (0) | **8a** (64) | **9a** (27) | – |
| 10 | Pr | Procedure B | **4b** | **5ba** (6) | **7b** (0) | **8b** (74) | **9b** (20) | – |
| 11 | Me | Procedure B′ | **4a** | **5aa** (11) | **7a** (0) | **8a** (15) | **9a** (0) | **8′a** (74) |
| 12 | Pr | Procedure B′ | **4c** | **5ba** (12) | **7b** (0) | **8b** (20) | **9b** (0) | **8′b** (68) |

Procedure A: (i) BuLi; (ii) MeSSMe; (iii) $H_2O$; (iv) BuLi; (v) MeSSMe; (vi) $H_2O$. Procedure B: (i) BuLi; (ii) MeSSMe; (iii) BuLi; (iv) MeSSMe; (v) $H_2O$. Procedure B′: (i)BuLi; (ii) MeSSMe; (iii) BuLi; (iv) MeSSMe; (v) BuLi; (vi) MeI.

[a] Percentage was determined by NMR measurements and based on the conversion of the starting substrate **4**.

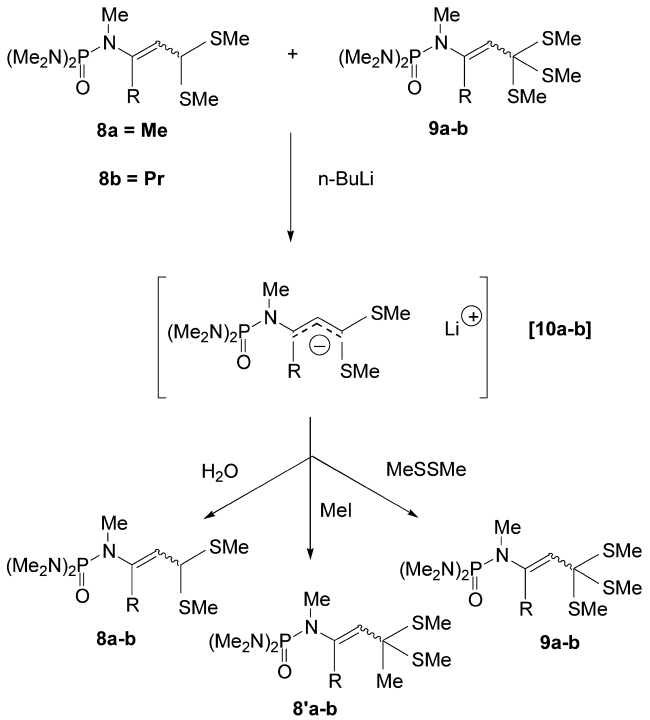



**Scheme 4.** Obtention of dithioacetals **8a-b** accompanied of transposed enephosphoramides **5aa-ba**.

the transposed enephosphoramide **5aa-ba**. The fact that carbanions derived from allylsulfides can react with electrophiles preferentially at α-C position of the sulphur, cumulated with the γ-effect of the phosphoramide moiety into [**7′a-b**] provided an exclusive γ-reaction of [**7′a-b**] with dimethyldisulfide and gave the dithioacetal product **8a-b** in approximately the same proportion than **5aa-ba** (Scheme 4).

Given the trend to the bis-sulfanylation observed in above stoichiometric conditions, we then looked for the best conditions for the introduction of the dithioacetal group.

Initially, we used the sequenced procedure A that consisted to begin with the preparation of thioether **7** in the above conditions, then to effect the metalation of **7** with *n*-BuLi at −50°C, followed by addition of MeSSMe and subsequent hydrolysis. In these conditions, the phosphoramide **8** was obtained in rather good yield in mixture with the trisulfanyl compound **9** (Table 3, entries 7–8). Otherwise, we developed a simpler one-pot sequence (procedure B) for the preparation of phosphoramide **8**, by treating, in situ, the γ-monomethylsulfanyl phosphoramide **7** with *n*-BuLi for 10 min followed by addition of dimethyldisulfide, and subsequent hydrolysis. An analogous procedure B′ allowed to obtain **8′** after successive addition, in situ, of *n*-BuLi to the precedent phosphoramide **8** and iodomethane (Table 3, entries 11–12).

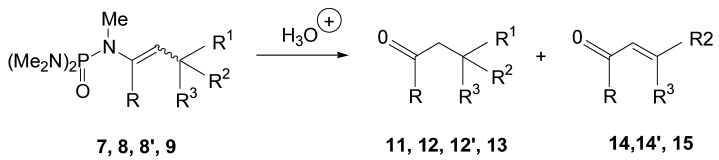



**Scheme 5.** Chemoselective preparation of dithioacetal **8a-b**, dithioketal **8′a-b** and γ-trisulfanyl enephosphoramide **9a-b**.

Similar results were obtained from the two procedures A and B, but dithioacetal **8** was always accompanied by a little amount of trisulfanyl product **9** and transposed enephosphoramide **5aa-ba** (entries 7–10, Table 3). Finally, we found the following solution to improve the chemoselective obtention of either γ-dithioacetal phosphoramide **8**, either γ-dithioketal phosphoramide **8′**, or γ- trimethylsulfanyl phosphoramide **9** in optimal conditions. A mixture of **8a-b**, **9a-b** and **5aa-ba** obtained according to procedure A or B was treated with 1 equiv. of *n*-BuLi and led to the lithium enephosphoramide dithioacetal [**10a-b**] through, respectively, hydrogen–metal exchange on **8a-b** and sulfur–metal exchange on **9a-b**. The new ambident carbanion [**10a-b**] reacted with $H_2O$, or MeI, or MeSSMe to afford, respectively, **8a-b**, or **8′a-b** or **9a-b** in high conversion. It was noteworthy that **5aa-ba** was recovered unchanged in the three experiences, that could mean *n*-BuLi was unable to deprotonate **5aa-ba** (Scheme 5, Table 4).

**Table 4**. Chemoselective preparation of dithioacetal **8a-b**, dithioketal **8′a-b** and γ-trisulfanyl enephosphoramide **9a-b**

| Starting mixture | Reagent | | | | |
|---|---|---|---|---|---|
| **5aa/8a/9a** (5/58/37) | | **5aa** (%) | **8a** (%) | **8′a** (%) | **9a** (%) |
| | $H_2O$ | 5 | 90 | 0 | 0 |
| | MeI | 5 | 0 | 94 | 0 |
| | MeSSMe | 5 | 0 | 0 | 81 |
| **5ba/8b/9b** (8/64/28) | | **5ba** (%) | **8b** (%) | **8′b** (%) | **9b** (%) |
| | $H_2O$ | 8 | 92 | 0 | 0 |
| | MeI | 8 | 0 | 94 | 0 |
| | MeSSMe | 8 | 0 | 0 | 85 |




**7, 8, 8', 9** **11, 12, 12', 13** **14,14', 15**

**11**: $R^1$ = SMe $R^2$ = H $R^3$ = H
**12** : $R^1$ = SMe $R^2$ = SMe $R^3$ = H
**12'** : $R^1$ = SMe $R^2$ = SMe $R^3$ = Me
**13** : $R^1$ = SMe $R^2$ = SMe $R^3$ = SMe
**14**: $R^2$ = SMe $R^3$ = H
**14'**: $R^2$ = SMe $R^3$ = Me
**15:** $R^2$ = SMe $R^3$ = SMe

**11a** : R = Me **11b** : R = Pr **11c** : R = Ph
**12a** : R = Me **12b** : R = Pr
**12'a** : R = Me **12'b** : R = Pr
**13a :** R = Me **13b** : R = Pr
**14a :** R = Me **14b** : R = Pr
**14'a :** R = Me **14'b** : R = Pr
**15a :** R = Me **15b** : R = Pr

**Scheme 6.** Hydrolysis of enephosphoramides **7**, **8**, **8′** and **9**.

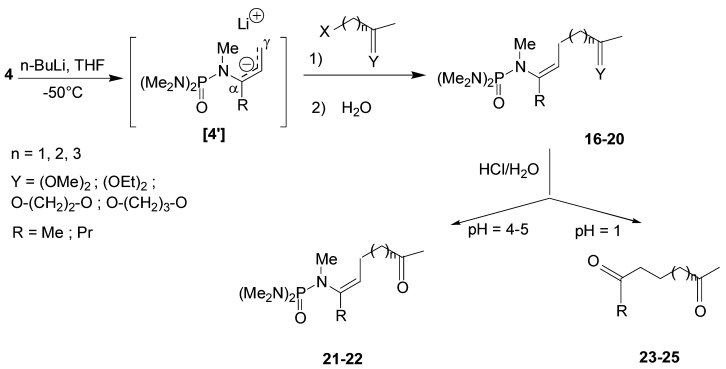
**Table 5**. Hydrolysis of enephosphoramides **7**, **8**, **8′** and **9**

| Entry | R | Starting material[a] | **11** (%) | **12** (%)[b] | **14** (%)[b] | **14′** (%)[b] | **15** (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | Ph | **7c** (**4c**) | **11c** (70) | – | – | – | – |
| 2 | Me | **7a** (**4a**) | **11a** (51) | – | – | – | – |
| 3 | Pr | **7b** (**4b**) | **11b** (36) | | | | |
| 4 | Me | **8a** (**4a**) | – | **12a** (67) | **14a** 17 (*E*/*Z*:94/6) | – | – |
| 5 | Pr | **8b** (**4b**) | | **12b** (34) | **14b** 48 (*E*/*Z*:95/5) | | |
| 6 | Me | **8′a** (**4a**) | – | – | – | **14′a** (90) (*E*/*Z*:80/20) | – |
| 7 | Pr | **8′b** (**4b**) | – | – | – | **14′b** (92) (*E*/*Z*:85/15) | |
| 8 | Me | **9a** (**4a**) | – | | – | | **15a** (38) |
| 9 | Pr | **9b** (**4b**) | – | | – | – | **15b** (45) |

[a] Pure or major γ-sulfanylated enephosphoramide obtained from (enephosphoramide **4a**–**c**).
[b] Yields of pure products after chromatography and evaluated from the starting substrate **4a**–**c**.

**2.3.2. Hydrolysis of γ-sulfanyl phosphoramides 7, 8, 8′ and 9 into corresponding γ-sulfanyl ketones 11, 12, 12′, 13 and/or enonesulfides 14, 14′, 15.** The enephosphoramide moiety of mixture of sulfanyl phosphoramides **7**, **8**, **8′** and **9** previously obtained as indicated above (Table 3) was cleanly cleaved by acidolysis to afford γ-sulfanyl ketones **11**, **12**, **12′**, **13** and/or enonesulfides **14**, **14′**, **15** (Scheme 6, Table 5). The hydrolysis of the γ-methylsulfanyl enephosphoramide **7c** (R=Ph) prepared from **4c** as a sole product (entry 5, Table 3), was complete after stirring for 4 h at reflux with 6N $H_2SO_4$ and afforded β-methylsulfanyl ketone **11c** as the sole product (70% yield) (entry 1, Table 5). Hydrolysis of **7a**-**b** (R=Me, Pr) was easier and achieved after 4 h at room temperature at pH=2 for R=Me and at pH=1.5 for R=Pr. The nature of the major hydrolysis product was dependent on the composition of the sulfanylated mixture obtained from **4a**-**b**. In the case of γ-methylsulfanyl enephosphoramide **7a** (entry 2, Table 3) or **7b** (entry 4, Table 3) respectively, obtained from **4a** or **4b** as the major product, it was possible to obtain the pure corresponding γ-methylsulfanyl ketone **11a** and **11b** in modest yield after a chromatographic purification on silicagel (51% yield from **4a** and 36% yield from **4b**) (entries 2–3, Table 5). In the cases of practically pure γ-dimethylsulfanyl enephosphoramides **8a**-**b** or **8′a**-**b**, or γ-trimethylsulfanyl enephosphoramides **9a**-**b**, which were prepared from the mixture **5aa**-**ba**/**8a**-**b**/**9a**-**b** according to the Scheme 6, acid hydrolysis of **8a**-**b** led to ketone dithioacetal **12a**-**b** accompanied with the enone sulfide **14a**-**b** (entries 4–5, Table 5). This last product was the result of a partial elimination of methanethiol from ketone dithioacetal **12a**-**b** in acidic medium. If the final target of the enephosphoramide route is the preparation of 2-oxobutanal or 2-oxopentanal, such hydrolysis product mixture was not a problem, since enone sulfide may be regarded as a masked carbonyl group comparable to a dithioacetal. On the other hand, if enone sulfide **14a**-**b** or ketone dithioacetal **12a**-**b** is the target, those compounds could be easily separated by chromatography. Hydrolysis of practically pure **8′a**-**b** afforded enone sulfide **14′a**-**b** in excellent yield after purification by chromatography (85–90% overall yield from **4a**-**b**) (entries 6–7, Table 5) whereas hydrolysis of **9a**-**b** into α-oxoketenedithioketal **15a**-**b** was less convenient (entries 8–9, Table 5). In these last cases, the sole hydrolysis products **14′a**-**b** and **15a**-**b** that have been isolated after purification also resulted from an elimination of methanethiol into dimethysulfanylketone **12′a**-**b** or trimethysulfanylketone **13a**-**b** which were the first intermediates of the hydrolysis. Presumably, such elimination of methanethiol from di- or trimethysulfanylketones presented $E_1$ character since the vinylsulfide was the major product in the hydrolysis of those tertiary C-methylsulfanyl structures (entries 6–9, Table 5). Thus, a series of β-methylsulfanylketones (entries 1–3), ketone dithioketals and/or enonesulfides (entries 4–7) and oxoketenedithioacetals (entries 8–9) were synthetised and characterized. Structures of products were confirmed by NMR ($^1$H, $^{13}$C), IR and by mass spectroscopy.

**2.3.3. Reaction between [4′] and halogenoketals.** A simple and efficient protocol for the construction of 1,5-, 1,6- and 1,7-diketones has been developed using the reaction




**Scheme 7.** Reaction between [**4′**] and halogenoketals: a route to the preparation of diketones and masked diketones.

**Table 6**. Preparation of enephosphoramide ketals **16–20** and hydrolysis into enephosphoramide ketones **21–22** or diketones **23–25**

| Entry | R | *n* | Y | X | **16–20** | % Conversion[a] | **21–22**[b] | % Conversion[a,c] | **23–25**[d] | % Yield[e] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Me | 1 | $(OMe)_2$ | Br | **16a** | 55 | **21a** | 46 (84) | **23a** | 19 |
| 2 | Me | 1 | $(OMe)_2$ | Br[f] | **16a** | 49 | | | | |
| 3 | Pr | 1 | $(OMe)_2$ | Br | **16b** | 47 | **21b** | 39 (83) | **23b** | 27 |
| 4 | Pr | 1 | $(OMe)_2$ | Br[f] | **16b** | 37 | | | | |
| 5 | Me | 2 | $O-(CH_2)_2-O$ | I | **17a** | 91 | | | **24a** | 51 |
| 6 | Pr | 2 | $O-(CH_2)_2-O$ | I | **17b** | 91 | | | **24b** | 40 |
| 7 | Me | 3 | $(OEt)_2$ | I | **18a** | 91 | **22a** | 91 (100) | **25a** | 47 |
| 8 | Pr | 3 | $(OEt)_2$ | I | **18b** | 76 | **22b** | 76 (100) | **25b** | 33 |
| 9 | Me | 3 | $O-(CH_2)_2-O$ | I | **19a** | 91 | | | **25a** | 37 |
| 10 | Pr | 3 | $O-(CH_2)_2-O$ | I | **19b** | 85 | | | **25b** | 36 |
| 11 | Me | 3 | $O-(CH_2)_3-O$ | Cl | **20a** | 70 | | | **25a** | 51 |
| 12 | Pr | 3 | $O-(CH_2)_3-O$ | Cl | **20b** | 60 | | | **25b** | 40 |

[a] Percentage was determined by NMR and based on the conversion of the starting substrate **4**.
[b] Obtained at pH=4 or 5.
[c] (Percentage) was determined by NMR and based on the conversion of **16–20**.
[d] Directly obtained from **4** by alkylation and then hydrolysis at pH=1 without isolation of intermediates.
[e] Yields of pure products after chromatography and evaluated on the starting substrate **4**.
[f] With 1 equiv. NaI.

between [**4′**] and halogenoketals. We assumed that the simultaneous or successive hydrolysis of the ketal and the conjugate enephosphoramide moieties into the alkylated enephosphoramide ketal could provide a new approach to diketones and masked diketones. As the hard hydrolysis conditions for the α-phenyl enephosphoramide moiety could afford a product degradation, the study was only investigated to the enephosphoramide **4a-b**. With this aim, the alkylation of the lithio anion [**4′a-b**] derived from phosphoramide **4a-b** was examined using various halogenoketals including a dioxan, dioxolan, diethoxy or dimethoxy group at the β,γ or δ position. (Scheme 7, Table 6).

As previously observed, the reaction was completely γ-regioselective and gave the enephosphoramide ketals **16–20** in 37–91% conversion from enephosphoramides **4a-b**. All those compounds presented a *Z*-double bond configuration.

It appears that the aptitude for substitution decreased in the following order, according to $n=3\sim2>1$, with the best results with iodine as leaving group. These results are both the consequence of the hindrance of the ketal moiety in analogous neopentyl position ($n=1$) and the relative stability of dimethylketal in the basic reaction conditions (entries 1–4, Table 6).

Removal of the enephosphoramide group was achieved in the second hydrolysis step. A chemoselective or a complete acid hydrolysis of enephosphoramide ketals **16–20** was possible, dependent on the nature of the protecting group and the hydrolysis pH.

Acyclic ketal group (dimethylketal or diethylketal) was more sensitive to acid hydrolysis than the enephosphoramide moiety. The dimethoxy group of **16a-b** or the diethoxy group of **18a-b** was chemoselectively removed at pH=5 and 4, respectively, to give the corresponding enephosphoramide ketone **21a-b** (entries 1, 3; Table 6) or **22a-b** (entries 7, 8; Table 6). Hydrolysis was conveniently carried out, in a biphasic medium $Et_2O$ (20 ml)–aqueous HCl solution (40 ml, pH=4 or 5), at ambient temperature by stirring for 4 h. The reaction was monitored by IR, following the appearance and the evolution of the C=O absorption. The pH was adjusted each 30 min, using a pH meter, with a few drops of aqueous $10^{-2}$N HCl, up to the end of the reaction. After usual treatment, crude ketone phosphoramide **21a-b** or **22a-b** was isolated in good yields (39–91%). It was noted that efficient chemoselective hydrolysis of ketal moiety was dependent on the surroundings hindrance, the best results being obtained with enephosphoramide ketal **18a-b** where the ketal moiety was 7C away from the bulky phosphoramide group. As a result, the method seemed particularly interesting for the

preparation of such monoprotected 1,7 dicarbonyl compounds. Access to monoprotected 1,5 dicarbonyl compounds could be nevertheless used in the cases where these last compounds were difficult to obtain with other methods.

Increasing the acidity increased the cleavage. Whatever the ketal moiety, complete hydrolysis of the enephosphoramide ketals **16**–**20** was effective with a 2N HCl aqueous solution and stirring for 4 h at 20°C. Corresponding diketones **23**–**25** were obtained this way, in relatively modest overall yield of purified product after two steps from **4**. Nevertheless, the method allowed the access to pure 1,6 and 1,7 diketones with 33–40% range (R=Pr) and with 37–51% range in the case R=Me. It could lead also to pure 1,5 diketones, but in poor yields.

## 3. Conclusion

We have demonstrated that the lithiated anions [**4′**] derived from *N*-methyl-[(1-alkyl- or 1-phenyl)-2-propenyl)]-phosphoric triamides **4** can be used as new ketone homoenolate equivalents. The proposed route allowed for the preparation of various ketones with an umpolung strategy compared to other routes based on Friedel–Crafts reaction (in the case R=Ph) or Michael addition of organocuprates on α-enones. In the case R=Ph, the results in alkylation reactions are comparable to those described with the long known analogous approach using the lithium carbanion of 1-(*N*-methyl-*N*-phenylamino)-1-phenyl-1-propene as the homoenolate equivalent of propiophenone.[10] In this case, the precursor is simply the *N*-methylanilino enamine of propiophenone, probably easier to prepare than the enephosphoramide **4c**. However, the present strategy is more general since it can be applied to α-alkyl as well as α-aryl substituted precursors, which did not seem to be possible with the precedent cited route. Compared with another route[2b] which recently describes the enantioselective lithiation of *N*-Boc-*N*-(*p*-methoxyphenyl)cinnamylamine as a ketone, acid or ester homoenolate synthon, this approach appeared potentially complementary. A straight advantage of the enephosphoramide group lies in the γ-regioselectivity of the reaction of anions [**4′**] with various electrophiles as alkyl halides, isobutyraldehyde or dialkyldisulfides. The synthesis of different unsymmetrical ketones, deuterated ketones, methylsulfanylketones, ketone dithioketals, oxoketenedithioacetals and diketones illustrates the versatility of the method. These new tools favourably complete the aldehyde homoenolate equivalents derived from α-unsubstituted allyl phosphoramides that we have proposed a long time ago.

## 4. Experimental

Thin layer chromatography (TLC) was carried out on aluminium-backed silica gel-coated plates (Kieselgel 60-$F_{254}$, Merck). Spots were identified under UV lamp ($\lambda$=254 nm), by iodine or developed with spraying sulfuric acid followed by calcination. Column chromatographies were performed on silicagel 60 (230–400 mesh) with indicated eluent wich was dried and distilled shortly before use. IR spectra of solids were recorded as KBr pellets, and IR spectra of liquids were recorded as thin films on NaCl plates with a Nicolet 210 FT-IR spectrophotometer. All NMR experiments were recorded on a Brucker AC-250 spectrometer [250.13 MHz ($^1$H), 62.896 MHz ($^{13}$C) and 101.256 MHz ($^{31}$P)]. Chemicals shifts were given as $\delta$ ppm values and $J$ values are given in Hertz (Hz). Data for $^1$H NMR spectra are reported in $\delta$ units downfield from internal $Me_4Si$. $^{13}$C NMR spectra were referenced to the $CDCl_3$ peak at 77 ppm relative to $Me_4Si$. Orthophosphoric acid (85%) was used as an external standard for $^{31}$P NMR. Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Mass spectra (EI, 70 eV and CI) were obtained on a Fison Trio 1000 spectrometer. Solvents were purified by standard procedures just before use. *N*-Butyllithium was purchased from Aldrich and was titrated using the Watson–Eastham procedure.

### 4.1. Preparation of the *N*-phosphoramide precursors 4

**4.1.1. 3-Buten-2-amine hydrochloride 1a.** IR (KBr pellet, $cm^{-1}$): $\nu_{max}$=3000, 1603, 1425 and 1385; $^1$H NMR ($D_2O$): $\delta_H$=1.39 (d, $^3J_{H-H}$=6.6 Hz, 3H, $CH_3$–CH), 3.95 (q, $^3J_{H-H}$=6.8 Hz, 1H, $CH_3$–C*H*), 5.36 (d, $^3J_{H-H}$=10.7 Hz, 1H, CH=CH*H*), 5.38 (d, $^3J_{H-H}$=17.5 Hz, 1H, CH=CH*H*), 5.93 (ddd, $^3J_{H-H}$=17.5 Hz, $^3J_{H-H}$=10.7 Hz and $^3J_{H-H}$=6.8 Hz, CH–C*H*=$CH_2$); $^{13}$C NMR ($D_2O$): $\delta_C$=20.7 (*C*$H_3$–CH), 52.1 ($CH_3$–*C*H–CH), 121.4 (CH=*C*$H_2$), 137.5 (CH–*C*H=$CH_2$).

**4.1.2. 1-Hexen-3-amine 1b.** Colourless oil, bp 113°C. IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3364, 3282, 3076, 2958, 2872, 1640 and 1423; $^1$H NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=6.7 Hz, 3H, $CH_3$–$CH_2$), 1.27 (s, 2H, CH–N$H_2$), 1.31–1.43 (m, 4H, $CH_3$–C$H_2$–C$H_2$), 3.24–3.32 (m, 1H, $CH_2$–C*H*–CH=), 5.00 (ddd, $^3J_{H-H}$=10.3 Hz, $^4J_{H-H}$=1.4 Hz and $^2J_{H-H}$=1.4 Hz, 1H, CH=CH*H*), 5.09 (ddd, $^3J_{H-H}$=17.0 Hz, $^4J_{H-H}$=1.4 Hz and $^2J_{H-H}$=1.4 Hz, 1H, CH=CH*H*), 5.78 (ddd, $^3J_{H-H}$=17.0 Hz, $^3J_{H-H}$=10.3 Hz and $^3J_{H-H}$=6.7 Hz, 1H, CH=CH*H*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.6 (*C*$H_3$–$CH_2$), 18.9 ($CH_3$–*C*$H_2$), 39.5 ($CH_3$–$CH_2$–*C*$H_2$), 53.9 ($CH_2$–*C*H–CH), 112.7 (CH–CH=*C*$H_2$), 143.3 (CH–*C*H=$CH_2$).

**4.1.3. 1-Phenyl-2-propen-1-amine 1c.** IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3366, 3088, 3061, 3026, 2977 and 1637; $^1$H NMR ($CDCl_3$): $\delta_H$=1.55 (s, 2H, N$H_2$), 4.52 (d, $^3J_{H-H}$=6.1 Hz, 1H, $NH_2$–C*H*), 5.11 (d, $^3J_{H-H}$=10.4 Hz, 1H, CH=CH*H*), 5.24 (dd, $^3J_{H-H}$=17.1 Hz and $^2J_{H-H}$=1.2 Hz, 1H, CH=CH*H*), 6.02 (ddd, $^3J_{H-H}$=17.1 Hz, $^3J_{H-H}$=10.4 Hz and $^3J_{H-H}$=6.1 Hz, 1H, C*H*=$CH_2$), 7.24–7.35 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=58.3 ($NH_2$–*C*H), 113.6 (CH=*C*$H_2$), 126.5, 127.0, 128.4 (*Ph*), 142.1 (*C*H=$CH_2$).

### 4.2. Typical procedure for the preparation of dichloroenephosphoramides 2

To a stirred solution of phosphorus oxychloride (9.2 g, 60 mmol) in $Et_2O$ (40 ml) at −5°C under nitrogen atmosphere was added a mixture of allylamine **1** (60 mmol) and triethylamine (6.07 g, 60 mmol). The solution was stirred for 15 min at −5°C, and 1 h at room temperature and then filtered. The filtrate was concentrated

to afford a crude yellow oil which was used without further purification.

**4.2.1. (3-Buten-2-yl)amidophosphoric dichloride 2a.** Pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3177, 2981, 2852, 1639, 1376, 1321; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.37 (d, $^3J_{H-H}$= 6.8 Hz, 3H, C*H*$_3$–CH), 3.96–4.16 (m, 1H, NH–C*H*–CH=CH$_2$), 4.45–4.69 (m, 1H, P(O)–N*H*–CH), 5.16 (d, $^3J_{H-H}$=10.3 Hz, 1H, CH=CH*H*), 5.27 (d, $^3J_{H-H}$=17.1 Hz, 1H, CH=CH*H*), 5.87 (ddd, $^3J_{H-H}$=17.1 Hz, $^3J_{H-H}$= 10.3 Hz and $^3J_{H-H}$=5.5 Hz, 1H, CH–C*H*=CH$_2$); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=21.8 (d, $^3J_{C-P}$=7.6 Hz, *C*H$_3$–CH), 51.2 (NH–*C*H–CH), 114.9 (CH=*C*H$_2$), 138.7 (d, $^3J_{C-P}$= 6.2 Hz, CH–*C*H=CH$_2$); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=10.8; MS ($EI^+$) *m*/*z* calculated for $C_4H_8NOPCl_2$ $[M]^+$ 188.0 found 188 [$[M]^+$, 5%], 172 [$[M-1-CH_3]^+$, 66%], 117 [$[M-2Cl]^+$, 25%], 70 [$[M-Cl_2PO]^+$, 100%].

**4.2.2. (1-Hexen-3-yl)amidophosphoric dichloride 2b.** Pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3177, 2960, 2930, 2873, 1645, 1450, 1381, 1260; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.95 (t, $^3J_{H-H}$=7.1 Hz, 3H, C*H*$_3$–CH$_2$–CH$_2$–), 1.35–1.49 (m, 2H, CH$_3$–C*H*$_2$–CH$_2$–), 1.52–1.64 (m, 2H, CH$_3$–CH$_2$–C*H*$_2$–), 3.83–4.00 (m, 1H, NH–C*H*(Pr)–CH=), 4.14 (s, 1H, P(O)–N*H*–CH), 5.20 (ddd, $^3J_{H-H}$=10.0 Hz, $^2J_{H-H}$=1.2 Hz and $^4J_{H-H}$=1.2 Hz, 1H, CH–CH=CH*H*), 5.27 (ddd, $^3J_{H-H}$=17.0 Hz, $^2J_{H-H}$= 1.2 Hz and $^4J_{H-H}$=1.2 Hz, 1H, CH–CH=CH*H*), 5.78 (ddd, $^3J_{H-H}$=17.0 Hz, $^3J_{H-H}$=10.0 Hz and $^3J_{H-H}$= 6.5 Hz, 1H, CH–C*H*=CH$_2$); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.6 (*C*H$_3$–CH$_2$–CH$_2$–), 18.7 (CH$_3$–*C*H$_2$–CH$_2$–), 38.1 (CH$_3$–CH$_2$–*C*H$_2$–), 55.8 (NH–*C*H(Pr)–CH), 115.9 (–CH=*C*H$_2$), 137.7 (d, $^3J_{C-P}$=4.2 Hz, CH–*C*H=CH$_2$); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=11.3; MS ($EI^+$) *m*/*z* calculated for $C_6H_{12}NOPCl_2$ $[M]^+$ 216.0 found 216 [$[M]^+$, 14%], 172 [$[M-Pr]^+$, 100%].

**4.2.3. (1-Phenyl-2-propen-1-yl)amidophosphoric dichloride 2c.** Pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3172, 3031, 2981, 2860, 1644, 1602, 1269, 1053; $^1H$ NMR ($CDCl_3$): $\delta_H$=4.68–4.78 (m, 1H, P(O)–N*H*–CH), 5.02–5.14 (m, 1H, NH–C*H*(Ph)–CH), 5.33 (d, $^3J_{H-H}$= 10.5 Hz, 1H, CH=CH*H*), 5.35 (dd, $^3J_{H-H}$=17.0 Hz, $^2J_{H-H}$=0.9 Hz, 1H, CH=CH*H*), 6.03 (ddd, $^3J_{H-H}$= 17.0 Hz, $^3J_{H-H}$=10.5 Hz, $^3J_{H-H}$=5.5 Hz, 1H, CH–C*H*=CH$_2$), 7.31–7.41 (Ph); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=59.0 (NH–*C*H(Ph)–CH), 116.8 (CH=*C*H$_2$), 126.9, 128.0, 128.6, 128.8, 139.4 (Ph), 136.9 (d, $^3J_{C-P}$=7.2 Hz, CH(Ph)–*C*H=CH$_2$); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=10.8; MS ($EI^+$) *m*/*z* calculated for $C_9H_{10}NOPCl_2$ $[M]^+$ 250.1 found 250.0 [$[M]^+$, 6%], 223.0 [$[M-CH=CH_2]^+$, 12%].

### 4.3. Typical procedure for the preparation of *N*-allyl-*N*-bisdimethylaminophosphoramide 3

To a stirred solution of dimethylamine (9 g, 200 mmol) in $Et_2O$ (100 ml) at −20°C under nitrogen atmosphere, was added successively triethylamine (15.2 g, 150 mmol) and dichlorophosphoramide **2** (50 mmol). The mixture was then allowed to warm to room temperature. Progress of the reaction was monitored by $^{31}P$ NMR sweep-off mode. When total disappearance of the dichlorophosphoramide **2** was observed, the solution was filtered, and the solvent evaporated under reduced pressure. The so-obtained crude product was worked-up with $Et_2O$ (20 ml) and stored at 0°C a few hours to precipitate a maximum of triethylamine hydrochloride. The mixture was then filtered and concentrated.

**4.3.1. [(3-Buten-2-yl)]tetramethyl phosphoric triamide 3a.** Pale yellow paste; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$= 3199, 3080, 2882, 2802, 1641, 1459, 1295; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.25 (d, $^3J_{H-H}$=6.7 Hz, 3H, C*H*$_3$–CH), 1.95–2.11 (m, 1H, N*H*–CH), 2.65 [d, $^3J_{H-P}$=9.8 Hz, 6H, (C*H*$_3$)$_2$–N–P], 2.66 [d, $^3J_{H-P}$=9.8 Hz, 6H, (C*H*$_3$)$_2$–N–P], 3.73–3.87 [m, 1H, NH–C*H*(Me)–CH], 5.02 (d, $^3J_{H-H}$= 10.0 Hz, 1H, CH=CH*H*), 5.16 (d, $^3J_{H-H}$=17.0 Hz, 1H, CH=CH*H*), 5.88 (ddd, $^3J_{H-H}$=17.0 Hz, $^3J_{H-H}$=10.0 Hz, $^3J_{H-H}$=5.5 Hz, 1H, CH–C*H*=CH$_2$); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=22.9 (*C*H$_3$–CH), 36.4 [d, $^2J_{C-P}$=3.0 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 48.1 [NH–*C*H(Me)–CH], 111.9 (CH=*C*H$_2$), 142.1 (CH–*C*H=CH$_2$); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.6; MS ($EI^+$) *m*/*z* calculated for $C_8H_{20}N_3OP$ $[M]^+$ 205.2 found 205 [$[M]^+$, 18%], 190 [$[M-CH_3]^+$, 12%], 135 [$[(Me_2N)_2PO]^+$, 100%], 70 [$[M-(Me_2N)_2PO]^+$, 100%].

**4.3.2. [(1-Hexen-3-yl)]tetramethyl phosphoric triamide 3b.** Pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3198, 3075, 2924, 2872, 2800, 1641, 1455, 2378, 1292; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.91 (t, $^3J_{H-H}$=7.3 Hz, 2H, C*H*$_3$–CH$_2$–CH$_2$), 1.25–1.62 (m, 4H, CH$_3$–C*H*$_2$–C*H*$_2$), 2.02–2.10 (m, 1H, N*H*–CH), 2.64 [d, $^3J_{H-P}$=9.7 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 3.55–3.71 [m, 1H, NH–C*H*(Pr)–CH], 5.05 (ddd, $^3J_{H-H}$= 10.3 Hz, $^2J_{H-H}$=1.2 Hz, $^4J_{H-H}$=1.2 Hz, 1H, CH–CH=CH*H*), 5.15 (ddd, $^3J_{H-H}$=17.3 Hz, $^2J_{H-H}$=1.2 Hz, $^4J_{H-H}$=1.2 Hz, 1H, CH–CH=CH*H*), 5.76 (ddd, $^3J_{H-H}$= 17.3 Hz, $^3J_{H-H}$=10.3 Hz, $^3J_{H-H}$=6.7 Hz, 1H, CH–C*H*=CH$_2$); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=12.9 (*C*H$_3$–CH$_2$–CH$_2$), 17.9 (CH$_3$–*C*H$_2$–CH$_2$), 35.9 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 38.6 (d, $^3J_{C-P}$=5.2 Hz, CH$_3$–CH$_2$–*C*H$_2$), 52.4 [NH–*C*H(Pr)–CH], 112.5 (CH–CH=*C*H$_2$), 140.6 (d, $^3J_{C-P}$=3.7 Hz, CH–*C*H=CH$_2$); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.7; MS ($EI^+$) *m*/*z* calculated for $C_{10}H_{24}N_3OP$ $[M]^+$ 233.3 found 234 [$[M+1]^+$, 100%], 135 [$[(Me_2N)_2PO]^+$, 22%], 190 [$[M-CH_2-CH_2-CH_3]^+$, 31%].

**4.3.3. [(1-Phenyl-2-propen-1-yl)]tetramethyl phosphoric triamide 3c.** White solid; mp 85°C; IR (KBr pellets, $cm^{-1}$): $\nu_{max}$=3199, 3058, 3027, 3002, 2884, 2803, 1639, 1598, 1475, 1454, 1296; $^1H$ NMR ($CDCl_3$): $\delta_H$=2.53 [d, $^3J_{H-P}$= 9.9 Hz, 6H, (C*H*$_3$)$_2$–N–P], 2.59 [d, $^3J_{H-P}$=9.9 Hz, 6H, (C*H*$_3$)$_2$N–P], 4.77–4.88 [m, 1H, NH–C*H*(Ph)–CH], 5.16 (d, $^3J_{H-H}$=10.4 Hz, 1H, CH=CH*H*), 5.22 (d, $^3J_{H-H}$= 17.0 Hz, 1H, CH=CH*H*), 6.02 (ddd, $^3J_{H-H}$=17.0 Hz, $^3J_{H-H}$=10.4 Hz, $^3J_{H-H}$=5.5 Hz, 1H, CH–C*H*=CH$_2$), 7.20–7.37 (m, 5H, Ph); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=36.3 [d, $^3J_{C-P}$=3.6 Hz, 2C, (*C*H$_3$)$_2$N–P], 36.4 [d, $^3J_{C-P}$=3.4 Hz, 2C, (*C*H$_3$)$_2$N–P], 56.7 [NH–*C*H(Ph)–CH], 113.9 [NH–*C*H(Ph)–CH], 126.4, 126.6, 128.0, 142.7 (Ph), 140.2 (d, $^3J_{C-P}$=6.0 Hz, *C*H=CH$_2$); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.8; MS ($EI^+$) *m*/*z* calculated for $C_{13}H_{22}N_3OP$ $[M]^+$ 267.3 found 267 [$[M]^+$, 31%], 237 [$[M-1-2CH_3]^+$, 56%], 178 [$[M-2\times(Me_2N)_2]^+$, 58%],

131 [[M−$(Me_2N)_2PO$]$^+$, 100%], 116 [[M−$(Me_2N)_2$-P(O)NH]$^+$, 71%].

### 4.4. Typical procedure for the preparation of phosphoramides 4

To a solution of phosphoramide **3** (43 mmol) in THF (100 ml) was added dropwise at −50°C, under nitrogen atmosphere, a solution of *n*-butyllithium (18.1 ml, 45 mmol, 2.5 M in hexane) in hexane. After 10 min stirring at the same temperature, 6.72 g (47 mmol) of iodomethane was added and the mixture was stirred for 2 h at −50°C before it was allowed to warm to room temperature and quenched with 50 ml of a saturated NaCl aqueous solution. The aqueous layer was extracted with dichloromethane (3×40 ml). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Further distillation in vacuum of the crude product through a short column gave phosphoramides **4a** and **4b** as yellow oil. Phosphoramide **4c** was obtained as a crude product and was used without further purification.

**4.4.1. [(3-Buten-2-yl)]pentamethyl phosphoric triamide 4a.** Yield: 8.58 g (91%); yellow oil; bp 90°C ($4\times10^{-3}$ mmHg); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3083, 2929, 2806, 1638, 1457, 1296; $^1$H NMR ($CDCl_3$): $\delta_H$=1.24 (d, $^3J_{H-H}$=6.9 Hz, 3H, C$H_3$–CH), 2.44 (d, $^3J_{H-P}$=9.5 Hz, 3H, C$H_3$–N–CH), 2.66 [d, $^3J_{H-P}$=9.4 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 4.18–4.28 [m, 1H, C$H$(Me)–CH=CH$_2$], 5.12 (d, $^3J_{H-H}$=17.1 Hz, 1H, CH=CH$H$), 5.14 (d, $^3J_{H-H}$=10.6 Hz, 1H, CH=CH$H$), 5.88 (ddd, $^3J_{H-H}$=17.1 Hz, $^3J_{H-H}$=10.6 Hz, $^3J_{H-H}$=5.5 Hz, 1H, C$H$=CH$_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=16.2 (*C*H$_3$–CH), 26.6 [d, $^2J_{C-P}$=3.1 Hz, *C*H$_3$–N–CH(Ph)], 36.1 [d, $^2J_{C-P}$=3.4 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 50.8 [d, $^3J_{C-P}$=4.5 Hz, *C*H(Me)–CH=CH$_2$], 114.3 (CH=*C*H$_2$), 139.1 (d, $^3J_{C-P}$=3.6 Hz, *C*H=CH$_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=22.74; MS (EI$^+$) *m/z* calculated for $C_9H_{22}N_3OP$ [M]$^+$ 219.3 found 219 [[M]$^+$, 9%], 204 [[M−H]$^+$, 16%], 190 [[M−H−$CH_3$]$^+$, 38%], 135 [[$(Me_2N)_2PO$]$^+$, 100%], 131 [[M−2($Me_2N$)]$^+$, 49%], 84 [[M−$(Me_2N)_2PO$]$^+$, 84%].

**4.4.2. [(1-Hexen-3-yl)]pentamethyl phosphoric triamide 4b.** Yield: 8.83 g (83%); yellow oil; bp 80°C ($2\times10^{-2}$ mmHg); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3078, 2929, 2802, 1644, 1459, 1419, 1295; $^1$H NMR ($CDCl_3$): $\delta_H$=0.94 (t, $^3J_{H-H}$=7.1 Hz, 3H, C$H_3$–CH$_2$–CH$_2$), 1.23–1.44 (m, 2H, CH$_3$–C$H_2$–CH$_2$), 1.47–1.59 (m, 2H, CH$_3$–CH$_2$–C$H_2$), 2.46 [d, $^3J_{H-P}$=9.5 Hz, 3H, C$H_3$–N–CH(Pr)], 2.63 [d, $^3J_{H-P}$=9.5 Hz, 6H, (C$H_3$)$_2$N–PO], 2.64 [d, $^3J_{H-P}$=9.5 Hz, 6H, (C$H_3$)$_2$N–PO], 3.94–4.06 [m, 1H, C$H$(Pr)–CH=CH$_2$], 5.11–5.19 (m, 2H, CH=C$H_2$), 5.86 [ddd, $^3J_{H-H}$=17.6 Hz, $^3J_{H-H}$=10.2 Hz, $^3J_{H-H}$=6.3 Hz, 1H, CH(Pr)–C$H$=CH$_2$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.8 (*C*H$_3$–CH$_2$–CH$_2$), 19.4 (CH$_3$–*C*H$_2$–CH$_2$), 27.4 [d, $^2J_{C-P}$=3.5 Hz, *C*H$_3$–N–CH(Pr)], 33.1 (d, $^3J_{C-P}$=3.4 Hz, CH$_3$–CH$_2$–*C*H$_2$), 36.8 [d, $^2J_{C-P}$=3.8 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 56.7 [d, $^3J_{C-P}$=4.3 Hz, N–*C*H(Pr)–CH=CH$_2$], 116.1 (CH=*C*H$_2$), 137.4 (*C*H=CH$_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=22.68; MS (EI$^+$) *m/z* calculated for $C_{11}H_{26}N_3OP$ [M]$^+$ 247.3 found 247 [[M]$^+$, 4%], 204 [[M−Pr]$^+$, 50%], 135 [[$(Me_2N)_2PO$]$^+$, 100%], 112 [[M−$(Me_2N)_2PO$]$^+$, 12%].

**4.4.3. [(1-Phenyl-2-propen-1-yl)]pentamethyl phosphoric triamide 4c.** Yield: 11.13 g (92%); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3078, 3062, 2927, 2883, 2807, 1634, 1598, 1492, 1453, 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=2.42 [d, $^3J_{H-P}$=8.9 Hz, 3H, (C$H_3$)–N–CH(Ph)], 2.63 [d, $^3J_{H-P}$=9.5 Hz, 6H, [(C$H_3$)$_2$N]$_2$PO], 2.66 [d, $^3J_{H-P}$=9.3 Hz, 6H, [(C$H_3$)$_2$N]$_2$PO], 5.36 (m, 3H, C$H$–CH=C$H_2$), 6.16 [ddd, $^3J_{H-H}$=17.0 Hz, $^3J_{H-H}$=10.7 Hz, $^3J_{H-H}$=6.4 Hz, 1H, CH(Ph)–C$H$=CH$_2$], 7.24–7.40 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=28.9 [d, $^3J_{C-P}$=3.7 Hz, (*C*H$_3$)–N–CH(Ph)], 36.8 [d, $^2J_{C-P}$=3.7 Hz, 2C, (*C*H$_3$)$_2$N–P], 36.9 [d, $^2J_{C-P}$=4.9 Hz, 2C, (*C*H$_3$)$_2$N–P], 60.9 [d, $^3J_{C-P}$=4.9 Hz, *C*H(Ph)–CH=CH$_2$], 117.7 (CH=*C*H$_2$), 126.9, 128.0, 128.2 (C$^2$, C$^3$ and C$^4$ of Ph), 135.9 [d, $^3J_{C-P}$=2.4 Hz, CH(Ph)–*C*H=CH$_2$], 139.9 (d, $^3J_{C-P}$=3.7 Hz, C$^1$ of Ph); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=22.80; MS (EI$^+$) *m/z* calculated for $C_{14}H_{24}N_3OP$ [M]$^+$ 281.3 found 281 [[M]$^+$, 20%], 146 [[M−$(Me_2N)_2PO$]$^+$, 73%], 135 [[$(Me_2N)_2PO$]$^+$, 100%], 77 [[Ph]$^+$, 21%].

### 4.5. Preparation of enephosphoramides 5. General procedure for the preparation of the phosphoramides 5aa–ca

To a stirred solution of phosphoramide **4a**–**c** (4.5 mmol) in THF (10 ml) at −50°C was added a solution of *n*-butyllithium (2.0 ml, 5 mmol, 2.5 M in hexane). After stirring under nitrogen atmosphere at −50°C for 5 min (or 1 h for phosphoramide **4b**), the mixture was rapidly hydrolysed with water (15 ml) at this temperature. The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford the phosphoramide **5aa**–**ca**.

**4.5.1. [(2-Buten-2-yl)]pentamethyl phosphoric triamide 5aa.** Yield: 96%; pale yellow oil (*Z*/*E*: 96/4); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2915, 2803, 1673, 1457, 1376 and 1297; MS (EI$^+$) *m/z* calculated for $C_9H_{22}N_3OP$ [M]$^+$ 219.3 found 219 [[M]$^+$, 27%], 135 [[$(Me_2N)_2PO$]$^+$, 50%], 84 [[M−$(Me_2N)_2PO$]$^+$, 32%].

*Z isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=1.65 [m, 3H, N–C(Me)=CH–C$H_3$], 1.84 [m, 3H, C$H_3$–C(N)=CH], 2.67 (d, $^3J_{H-P}$=9.1 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.72 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–CH(Me)], 5.24 [q, $^3J_{H-H}$=6.8 Hz, 1H, C(Me)=C$H$–CH$_3$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=12.3 [C(Me)=CH–*C*H$_3$], 20.5 [*C*H$_3$–C(N)=CH], 34.6 [d, $^2J_{C-P}$=3.4 Hz, *C*H$_3$–N–CH(Pr)], 36.3 [d, $^2J_{C-P}$=3.4 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 120.3 [d, $^3J_{C-P}$=5.9 Hz, C(Me)=*C*H–CH$_3$], 138.5 [d, $^3J_{C-P}$=1.3 Hz, N–*C*(Me)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.19.

*E isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=1.61 [m, 3H, N–C(Me)=CH–C$H_3$], 1.81 [m, 3H, C$H_3$–C(N)=CH], 2.64 (d, $^3J_{H-P}$=9.1 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.76 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–CH(Me)], 5.30 [m, 1H, C(Me)=C$H$–CH$_3$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.1 [C(Me)=CH–*C*H$_3$], 21.1 [*C*H$_3$–C(N)=CH], 35.5 [d, $^2J_{C-P}$=4.9 Hz, *C*H$_3$–N–CH(Pr)], 37.0 [d, $^2J_{C-P}$=4.9 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 117.2 [d, $^3J_{C-P}$=3.7 Hz, C(Me)=*C*H–CH$_3$], 138.4 [d, $^3J_{C-P}$=2.4 Hz, N–*C*(Me)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=19.40.

**4.5.2. [(2-Hexen-3-yl)]pentamethyl phosphoric triamide 5ba.** Yield: 100%; pale yellow oil; (*Z*/*E*: 100/0); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2955, 2930, 2872, 2802, 1666, 1458, 1377 and 1297; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.5 Hz, 3H, C*H*$_3$–$CH_2$–$CH_2$), 1.50 (m, 2H, $CH_3$–C*H*$_2$–$CH_2$), 1.68 [ddt, $^3J_{H-H}$=6.7 Hz, $^5J_{H-P}$=2.0 Hz and $^5J_{H-H}$=1.6 Hz, 3H, C(Pr)=CH–C*H*$_3$], 2.15 (td, $^3J_{H-H}$=7.5 Hz, $^5J_{H-H}$=1.6 Hz, 2H, $CH_3$–$CH_2$–C*H*$_2$), 2.67 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.76 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–CH(Me)], 5.21 [q, $^3J_{H-H}$=6.7 Hz, 1H, C(Pr)=C*H*–$CH_3$]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=12.7 [C(Pr)=CH–*C*H$_3$], 13.7 (*C*H$_3$–$CH_2$–$CH_2$), 20.7 ($CH_3$–*C*H$_2$–$CH_2$), 36.2 [d, $^2J_{C-P}$=3.7 Hz, *C*H$_3$–N–CH(Pr)], 36.8 [d, $^2J_{C-P}$=4.9 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 38.1 ($CH_3$–$CH_2$–*C*H$_2$), 119.0 [C(Pr)=*C*H–$CH_3$], 143.3 [N–*C*(Pr)=CH]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.13; MS ($EI^+$) *m*/*z* calculated for $C_{11}H_{26}N_3OP$ $[M]^+$ 247.3 found 247 [$[M]^+$, 17%], 204 [$[M-Pr]^+$, 18%], 135 [$[(Me_2N)_2PO]^+$, 100%], 112 [$[M-(Me_2N)_2PO]^+$, 69%].

**4.5.3. [(1-Phenyl-1-propen-1-yl)]pentamethyl phosphoric triamide 5ca.** Yield: 91%; pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3026, 2923, 1637, 1592, 1490, 1454 and 1299; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.94 (dd, $^3J_{H-H}$=6.6 Hz and $^5J_{H-P}$=2.3 Hz, 3H, C=CH–C*H*$_3$), 2.56 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.93 [d, $^3J_{H-P}$=8.5 Hz, 3H, C*H*$_3$–N–CH(Pr)], 5.85 (q, $^3J_{H-H}$=6.6 Hz, 1H, C=C*H*–$CH_3$), 7.19–7.51 (m, 5H, *Ph*); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.9 (C=CH–*C*H$_3$), 36.7, 36.8, 36.9 [[(*C*H$_3$)$_2$N]$_2$PO and *C*H$_3$–N–CH(Pr)], 122.8 (C=*C*H–$CH_3$), 126.2, 127.1, 127.9, 140.5 (*Ph*), 143.5 [N–*C*(Pr)=CH–$CH_3$]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.0.

### 4.6. General procedure for the preparation of the phosphoramides 5ab–cb

To a stirred solution of phosphoramide **4a–c** (4.5 mmol) in THF (10 ml) at −50°C was added a solution of *n*-butyllithium (2.0 ml, 5 mmol, 2.5 M in hexane). After stirring under nitrogen atmosphere at −50°C for 5 min (or 1 h for phosphoramide **4b**), the mixture was rapidly hydrolysed with deuterium oxide (1.5 ml) at this temperature followed by an addition of 15 ml of a NaCl aqueous saturated solution. The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford the phosphoramide **5ab–cb**.

**4.6.1. [(2-Buten-*4d*$_1$-2-yl)]pentamethyl phosphoric triamide 5ab.** Yield: 98%; pale yellow oil; (*Z*/*E*: 90/10); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2918, 2881, 2803, 1671, 1458, 1376, 1297; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.60–1.66 [m, 2H, C(Me)=CH–C*H*$_2$D), 1.84–1.85 [m, 3H, C*H*$_3$–C(N)=CH], 2.67 [d, $^3J_{H-H}$=9.1 Hz, 12H, (C*H*$_3$)$_2$N]$_2$PO], 2.72 [d, $^3J_{H-H}$=8.7 Hz, 3H, C*H*$_3$–N–CH(Pr)], 5.24 [t, $^3J_{H-H}$=7.0 Hz, 1H, C(Me)=C*H*–$CH_2$D]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=12.2 (t, $^1J_{C-D}$=19.4 Hz, C=CH–*C*H$_2$D), 20.7 [$CH_3$–C(N)=CH], 34.8 [d, $^2J_{C-P}$=3.7 Hz, *C*H$_3$–N–CH(Me)], 36.4 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 120.5 [d, $^3J_{C-P}$=5.7 Hz, C=*C*H–$CH_2$D), 138.7 [N–*C*(Me)=CH–$CH_2$D]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.17; MS ($EI^+$) *m*/*z* calculated for $C_9H_{21}DN_3OP$ $[M]^+$ 220.3 found 220 [$[M]^+$, 21%], 135 [$[(Me_2N)_2PO]^+$, 100%], 85 [$[M-(Me_2N)_2PO]^+$, 37%].

**4.6.2. [(2-Hexen-*1d*$_1$-3-yl)]pentamethyl phosphoric triamide 5bb.** Yield: 100%; pale yellow oil; (*Z*/*E*: 100/0); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2955, 2914, 2874, 2802, 1664, 1458 and 1297; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, C*H*$_3$–$CH_2$–$CH_2$), 1.42–1.58 (m, 2H, $CH_3$–C*H*$_2$–$CH_2$), 1.65–1.68 [m, 2H, C(Pr)=CH–C*H*$_2$D], 2.15 (t, $^3J_{H-H}$=7.7 Hz, 2H, $CH_3$–$CH_2$–C*H*$_2$), 2.67 [d, $^3J_{H-P}$=9.3 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.76 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Pr)=CH], 5.21 [t, $^3J_{H-H}$=6.5 Hz, 1H, C(Me)=C*H*–$CH_2$D]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=12.3 [t, $^1J_{C-D}$=19.5 Hz, C(Pr)=CH–*C*H$_2$D], 13.6 (*C*H$_3$–$CH_2$–$CH_2$), 20.5 ($CH_3$–*C*H$_2$–$CH_2$), 36.0 [d, $^2J_{C-P}$=3.7 Hz, *C*H$_3$–N–CH(Me)], 36.7 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 38.0 ($CH_3$–$CH_2$–*C*H$_2$), 118.9 [d, $^3J_{C-P}$=6.1 Hz, C(Pr)=*C*H–$CH_2$D], 143.2 [N–*C*(Pr)=CH–$CH_2$D]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.15; MS ($EI^+$) *m*/*z* calculated for $C_{11}H_{25}DN_3OP$ $[M]^+$ 248.3 found 248 [$[M]^+$, 41%], 135 [$[(Me_2N)_2PO]^+$, 60%], 113 [$[M-(Me_2N)_2PO]^+$, 77%], 84 [$M-(Me_2N)_2P(O)N-CH_3]^+$, 16%].

**4.6.3. [(1-Phenyl-1-propen-*3d*$_1$-1-yl)pentamethyl phosphoric triamide 5cb.** Yield: 100%; pale yellow oil; (*Z*/*E*: 100/0); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3026, 2923, 2151, 1637, 1592, 1490, 1454 and 1299; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.92 (m, 2H, C=CH–C*H*$_2$–D), 2.55 [d, $^3J_{H-P}$=9.0 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.93 [d, $^3J_{H-P}$=8.6 Hz, 3H, C*H*$_3$–N–CH(Ph)], 5.82 [t, $^3J_{H-H}$=6.8 Hz, 1H, C(Ph)=C*H*–$CH_2$D], 7.19–7.51 (m, 5H, *Ph*); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.6 (t, $^1J_{C-D}$=19.0 Hz, C=CH–*C*H$_2$D), 36.7, 36.8 [[(C*H*$_3$)$_2$N]$_2$PO and C*H*$_3$–N–CH(Pr)], 122.6 (d, $^3J_{C-P}$=5.0 Hz, C=*C*H–$CH_2$D), 126.0, 126.9, 127.8, 140.4 (*Ph*), 143.3 [N–*C*(Ph)=CH–$CH_2$D]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.97; MS ($EI^+$) *m*/*z* calculated for $C_{14}H_{23}DN_3OP$ $[M]^+$ 282.3 found 282 [$[M]^+$, 70%], 147 [$[M-(Me_2N)_2PO]^+$, 78%], 135 [$[(Me_2N)_2PO]^+$, 100%].

### 4.7. Typical procedure for the preparation of other phosphoramide 5ac–ai, 5bc–bi, 5cc–ci

To a stirred solution of phosphoramide **4** (4.5 mmol) in THF (15 ml) at −50°C under inert atmosphere was added a solution of *n*-butyllithium (2.0 ml, 5 mmol, 2.5 M in hexane). After stirring for 10 min (1 h for **4b**) at this temperature, 1.15 equiv. of electrophile was added. The mixture was stirred for another 1 h at −50°C and then allowed to warm to room temperature where it was rapidly hydrolysed with 15 ml of a NaCl saturated aqueous solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure.

**4.7.1. [(2-Penten-2-yl)]pentamethyl phosphoric triamide 5ac.** Yield: 100% ($E^+$=$CH_3I$), 100% ($E^+$=$Me_2SO_4$); pale yellow oil; (*Z*/*E*: 88/12); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2920, 2878, 2804, 1668, 1460, 1376 and 1297; MS ($EI^+$) *m*/*z* calculated for $C_{10}H_{24}N_3OP$ $[M]^+$ 233.3 found 233 [$[M]^+$, 27%], 135 [$[(Me_2N)_2PO]^+$, 91%], 98 [$[M-(Me_2N)_2PO]^+$, 98%].

*Z isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=0.97 (t, $^3J_{H-H}$=7.5 Hz, 3H, C=CH–$CH_2$–$CH_3$), 1.85 [m, 3H, $CH_3$–C(N)=CH], 2.07–2.19 (m, 2H, C=CH–$CH_2$–$CH_3$), 2.67 [d, $^3J_{H-P}$= 9.1 Hz, 12H, [$(CH_3)_2N]_2PO$], 2.73 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Me)=CH], 5.13 [t, $^3J_{H-H}$=6.9 Hz, 1H, C=C*H*–$CH_2$–$CH_3$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.4 (C=CH–$CH_2$–*C*$H_3$), 20.2 (C=CH–*C*$H_2$–$CH_3$), 20.7 [*C*$H_3$–C(N)–CH], 35.3 [d, $^2J_{C-P}$=3.5 Hz, *C*$H_3$–N–C(Me)], 36.4 [d, $^2J_{C-P}$=3.4 Hz, [(*C*$H_3)_2N]_2PO$], 128.3 (d, $^3J_{C-P}$=5.9 Hz, C=*C*H–$CH_2$–$CH_3$), 137.1 [(Me)N–*C*(Me)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.11.

*E isomer*: $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=19.39.

**4.7.2. [(3-Hepten-4-yl)]pentamethyl phosphoric triamide 5bc.** Yield: 100% ($E^+$=$CH_3I$), 100% ($E^+$=$Me_2SO_4$); pale yellow oil; (*Z*/*E*: 100/0); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2959, 2930, 2873, 2802, 1662, 1458 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.93 (t, $^3J_{H-H}$=7.3 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 0.99 (t, $^3J_{H-H}$=7.5 Hz, 3H, C=CH–$CH_2$–C*H*$_3$), 1.43–1.62 (m, 2H, $CH_3$–*C*$H_2$–$CH_2$), 2.09–2.22 (m, 4H, $CH_3$–$CH_2$–*C*$H_2$ and C=CH–*C*$H_2$–$CH_3$), 2.67 [d, $^3J_{H-P}$=9.1 Hz, 12H, [$(CH_3)_2N]_2PO$], 2.76 [d, $^3J_{H-P}$= 8.7 Hz, $CH_3$–N–C(Me)=CH], 5.09 (t, $^3J_{H-H}$=7.1 Hz, 1H, C=C*H*–$CH_2$–$CH_3$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.5 (C=CH–$CH_2$–*C*$H_3$), 13.7 (*C*$H_3$–$CH_2$–$CH_2$), 20.3 (C=CH–*C*$H_2$–$CH_3$), 20.5 ($CH_3$–*C*$H_2$–$CH_2$), 36.2, 36.6, 36.7 [(*C*$H_3)_2N]_2PO$ and *C*$H_3$–C(N)–CH], 37.9 ($CH_3$–$CH_2$–*C*$H_2$), 126.7 (d, $^3J_{C-P}$=6.1 Hz, C=*C*H–$CH_2$–$CH_3$), 141.6 [(Me)N–*C*(Pr)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.03; MS ($EI^+$) *m*/*z* calculated for $C_{12}H_{28}N_3OP$ $[M]^+$ 261.3 found 262 $[[M+1]^+$, 29%], 135 $[(Me_2N)_2PO]^+$, 80%], 126 $[M-(Me_2N)_2PO]^+$, 49%].

**4.7.3. [(1-Phenyl-1-buten-1-yl)]pentamethyl phosphoric triamide 5cc.** Yield: 99% ($E^+$=$CH_3I$), 86% ($E^+$=$Me_2SO_4$); pale yellow oil; (*Z*/*E*: 100/0); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3045, 2928, 2806, 1637, 1598, 1491, 1456 and 1300; $^1$H NMR ($CDCl_3$): $\delta_H$=1.1 (t, $^3J_{H-H}$= 7.4 Hz, 3H, C=CH–$CH_2$–C*H*$_3$), 2.33–2.48 (m, 2H, C=CH–C*H*$_2$–$CH_3$), 2.54 [d, $^3J_{H-P}$=8.9 Hz, 12H, [(C*H*$_3)_2N]_2PO$], 2.94 [d, $^3J_{H-P}$=8.5 Hz, 3H, C*H*$_3$–N–C(Ph)=CH], 5.69 [t, $^3J_{H-H}$=7.2 Hz, 1H, C(Ph)=C*H*–$CH_2$–$CH_3$], 7.21–7.52 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.9 (C=CH–$CH_2$–*C*$H_3$), 21.6 (C=CH–*C*$H_2$–$CH_3$), 36.4, 36.6, 36.9, 37.0 [(*C*$H_3)_2N]_2PO$ and *C*$H_3$–N–CH(Ph)], 126.3, 127.2, 128.0 (*C*$^2$, *C*$^3$, *C*$^4$ of *Ph*), 130.6 (d, $^3J_{C-P}$= 5.4 Hz, C=*C*H–$CH_2$–$CH_3$), 140.7 (*C*$^1$ of *Ph*), 141.9 [(Me)N–*C*(Ph)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.86; MS ($EI^+$) *m*/*z* calculated for $C_{15}H_{26}N_3OP$ $[M]^+$ 295.3 found 295 $[[M]^+$, 29%], 160 $[[M-(Me_2N)_2PO]^+$, 100%], 135 $[(Me_2N)_2PO]^+$, 71%], 77 $[[Ph]^+$, 23%], 44 $[[Me_2N]^+$, 40%].

**4.7.4. [(2-Nonen-2-yl)]pentamethyl phosphoric triamide 5ad.** Yield: 100% ($E^+$=PeCl; *Z*/*E*: 53/47), 100% ($E^+$=PeI; *Z*/*E*: 87/13); pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2923, 2803, 1664, 1459, 1378 and 1297; MS ($EI^+$) *m*/*z* calculated for $C_{14}H_{32}N_3OP$ $[M]^+$ 289.4 found 289 $[[M]^+$, 13%], 154 $[[M-(Me_2N)_2PO]^+$, 75%], 135 $[[(Me_2N)_2PO]^+$, 100%].

*Z isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=0.88 [t, $^3J_{H-H}$=7.0 Hz, 3H, C=CH–$(CH_2)_5$–C*H*$_3$], 1.22–1.37 [m, 8H, C=CH–$CH_2$–$(CH_2)_4$–$CH_3$], 1.85 [m, 3H, C*H*$_3$–C(N)=CH–$(CH_2)_5$–$CH_3$], 2.09 [q, $^3J_{H-H}$=7.3 Hz and $^3J_{H-H}$=7.0 Hz, 2H, C=CH–C*H*$_2$–$(CH_2)_4$–$CH_3$], 2.67 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3)_2N]_2PO$], 2.72 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Me)=CH], 5.16 [t, $^3J_{H-H}$=7.3 Hz, 1H, C=C*H*–$(CH_2)_5$–$CH_3$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.5 [C=CH–$(CH_2)_5$–*C*$H_3$], 20.7 [*C*$H_3$–C(N)=CH–$(CH_2)_5$–$CH_3$], 22.1 [C=CH–$(CH_2)_4$–*C*H–$CH_3$], 27.0, 28.8, 28.9, 31.2 [C=CH–(*C*$H_2)_4$–$CH_2$–$CH_3$], 35.2 [d, $^2J_{C-P}$=5.2 Hz, *C*$H_3$–N–C(Me)=CH], 36.4 [d, $^2J_{C-P}$=3.3 Hz, [(*C*$H_3)_2N]_2PO$], 126.7 (d, $^3J_{C-P}$=5.7 Hz, C=*C*H–$(CH_2)_5$–$CH_3$), 137.4 (*C*=CH–$(CH_2)_5$–$CH_3$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.09.

*E isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=0.88 [t, $^3J_{H-H}$=7.0 Hz, 3H, C=CH–$(CH_2)_5$–C*H*$_3$], 1.22–1.37 [m, 8H, C=CH–$CH_2$–$(CH_2)_4$–$CH_3$], 1.81 [s, 3H, C*H*$_3$–C(N)=CH–$(CH_2)_5$–$CH_3$], 1.98 [q, $^3J_{H-H}$=7.0 Hz and $^3J_{H-H}$=7.0 Hz, 2H, C=CH–C*H*$_2$–$(CH_2)_4$–$CH_3$], 2.64 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3)_2N]_2PO$], 2.76 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Me)=CH], 5.24 [tq, $^3J_{H-H}$=7.5 Hz and $^4J_{H-H}$=1.2 Hz, 1H, C=C*H*–$(CH_2)_5$–$CH_3$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.5 [C=CH–$(CH_2)_5$–*C*$H_3$], 20.7 [*C*$H_3$–C(N)=CH–$(CH_2)_5$–$CH_3$], 22.1 [C=CH–$(CH_2)_4$–*C*H–$CH_3$], 27.3, 28.5, 29.2, 31.2 [C=CH–(*C*$H_2)_4$–$CH_2$–$CH_3$], 35.2 [d, $^2J_{C-P}$=5.2 Hz, *C*$H_3$–N–C(Me)=CH], 36.0 [d, $^2J_{C-P}$=3.0 Hz, [(*C*$H_3)_2N]_2PO$], 122.6 [d, $^3J_{C-P}$=4.3 Hz, C=*C*H–$(CH_2)_5$–$CH_3$], 137.4 (*C*=CH–$(CH_2)_5$–$CH_3$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=19.31.

**4.7.5. (4-Undecen-4-yl)pentamethyl phosphoric triamide 5bd.** Yield: 100% ($E^+$=PeCl; *Z*/*E*: 60/40), 100% ($E^+$=PeI; *Z*/*E*: 100/0); pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2925, 2863, 2803, 1659, 1459, 1377 and 1297; MS ($EI^+$) *m*/*z* calculated for $C_{16}H_{36}N_3OP$ $[M]^+$ 317.4 found 317 $[[M]^+$, 12%], 274 $[[M-Pr]^+$, 12%], 182 $[[M-(Me_2N)_2PO]^+$, 82%], 135 $[[(Me_2N)_2PO]^+$, 100%].

*Z isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=0.85–0.99 [m, 6H, C*H*$_3$–$CH_2$–$CH_2$–C=CH and C=CH–$(CH_2)_5$–C*H*$_3$], 1.28–1.35 [m, 8H, C=CH–$CH_2$–(*C*$H_2)_4$–$CH_3$], 1.44–1.56 [m, 2H, $CH_3$–*C*$H_2$–$CH_2$–C=CH], 1.97–2.20 [m, 4H, $CH_3$–$CH_2$–C*H*$_2$–C=CH–C*H*$_2$–$(CH_2)_4$–$CH_3$], 2.67 [d, $^3J_{H-P}$= 9.1 Hz, 12H, [(C*H*$_3)_2N]_2PO$], 2.75 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Me)=CH], 5.12 [t, $^3J_{H-H}$=7.1 Hz, 1H, C=C*H*–$(CH_2)_5$–$CH_3$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.7 [*C*$H_3$–$CH_2$–$CH_2$–C=CH], 13.8 [C=CH–$(CH_2)_5$–*C*$H_3$], 20.7 [$CH_3$–*C*$H_2$–$CH_2$–C=CH], 22.4 [C=CH–$(CH_2)_4$–*C*H–$CH_3$], 27.3, 28.3, 29.1, 32.2 [C=CH–(*C*$H_2)_4$–$CH_2$–$CH_3$], 38.0 [$CH_3$–$CH_2$–*C*$H_2$–C=CH], 36.7–37.0 [[(*C*$H_3)_2N]_2PO$ and *C*$H_3$–N–C(Me)=CH], 125.3 [d, $^3J_{C-P}$=5.7 Hz, C=*C*H–$(CH_2)_5$–$CH_3$], 142.0 (*C*=CH–$(CH_2)_5$–$CH_3$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.04.

*E isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=0.85–0.99 [m, 6H, C*H*$_3$–$CH_2$–$CH_2$–C=CH and C=CH–$(CH_2)_5$–C*H*$_3$], 1.28–1.35 [m, 8H, C=CH–$CH_2$–(*C*$H_2)_4$–$CH_3$], 1.44–1.56 [m, 2H, $CH_3$–*C*$H_2$–$CH_2$–C=CH], 1.97–2.20 [m, 4H, $CH_3$–$CH_2$–C*H*$_2$–C=CH–C*H*$_2$–$(CH_2)_4$–$CH_3$], 2.65 [d, $^3J_{H-P}$= 9.1 Hz, 12H, [(C*H*$_3)_2N]_2PO$], 2.79 [d, $^3J_{H-P}$=9.6 Hz, 3H, C*H*$_3$–N–C(Me)=CH], 5.23 [td, $^3J_{H-H}$=7.1 Hz and

$^5J_{H-P}$=2.0 Hz, 1H, C=C*H*–$(CH_2)_5$–$CH_3$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.8 [C=CH–$(CH_2)_5$–*C*$H_3$], 14.1 [*C*$H_3$–$CH_2$–$CH_2$–C=CH], 21.4 [$CH_3$–*C*$H_2$–$CH_2$–C=CH], 22.4 [C=CH–$(CH_2)_4$–*C*H–$CH_3$], 27.5, 28.9, 29.8, 31.5 [C=CH–(*C*$H_2$)$_4$–$CH_2$–$CH_3$], 38.0 [$CH_3$–$CH_2$–*C*$H_2$–C=CH], 36.7–37.0 [[(*C*$H_3$)$_2$N]$_2$PO and *C*$H_3$–N–C(Me)=CH], 123.4 [d, $^3J_{C-P}$=4.0 Hz, C=*C*H–$(CH_2)_5$–$CH_3$], 142.3 (*C*=CH–$(CH_2)_5$–$CH_3$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=19.51.

**4.7.6. [(1-phenyl-1-octen-1-yl)]pentamethyl phosphoric triamide 5cd.** Yield: 75% ($E^+$=PeCl), 78% ($E^+$=PeI); pale yellow oil; isomer *Z* only; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2924, 2802, 1638 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.83–0.96 [m, 3H, C=CH–$(CH_2)_5$–C*H*$_3$], 1.25–1.48 [m, 6H, C=CH–$CH_2$–$CH_2$–(C*H*$_2$)$_3$–$CH_3$], 1.75–1.86 [m, 2H, C=CH–$CH_2$–C*H*$_2$–$(CH_2)_3$–$CH_3$], 2.33–2.41 [m, 2H, C=CH–C*H*$_2$–$(CH_2)_4$–$CH_3$], 2.54 [d, $^3J_{H-P}$=9.0 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.93 [d, $^3J_{H-P}$=8.5 Hz, 3H, C*H*$_3$–N–C(Ph)=CH], 5.71 [d, $^3J_{H-H}$=7.2 Hz, 1H, C=C*H*–$CH_2$–$(CH_2)_4$–$CH_3$], 7.26–7.52 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.9 [C=CH–$(CH_2)_5$–*C*$H_3$], 22.4 [C=CH–$(CH_2)_4$–*C*$H_2$–$CH_3$], 28.2, 29.2, 29.3, 31.6 [C=CH–(*C*$H_2$)$_4$–$CH_2$–$CH_3$], 36.8 [d, $^2J_{C-P}$=3.6 Hz, [(*C*$H_3$)$_2$N]$_2$PO], 37.4 [d, $^2J_{C-P}$=3.9 Hz, *C*$H_3$–N–C(Ph)=CH], 126.1, 127.0, 127.9, 128.8, 128.9 [C=*C*H–$(CH_2)_5$–$CH_3$ and *C*$^2$, *C*$^3$, *C*$^4$ of *Ph*], 140.6 (*C*$^1$ of *Ph*), 142.16 [d, $^2J_{C-P}$=1.9 Hz, *C*(Ph)=CH–$(CH_2)_5$–$CH_3$]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.90; MS ($EI^+$) *m/z* calculated for $C_{19}H_{34}N_3OP$ $[M]^+$ 351.5 found 351 [$[M]^+$, 48%], 336 [$[M-CH_3]^+$, 14%], 216 [$[M-(Me_2N)_2PO]^+$, 100%], 135 [$[(Me_2N)_2PO]^+$, 92%], 77 [$[Ph]^+$, 25%], 44 [$[(Me_2)N]^+$, 71%].

**4.7.7. [(5-Phenyl-2-penten-2-yl)]pentamethyl phosphoric triamide 5ae.** Yield: 97% (*Z*/*E*: 90/10); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3026, 2920, 2804, 1670, 1603, 1495, 1454, 1375 and 1297; MS ($EI^+$) *m/z* calculated for $C_{16}H_{28}N_3OP$ $[M]^+$ 309.4 found 309 [$[M]^+$, 6%], 218 [$[M-CH_2Ph]^+$, 86%], 135 [$[(Me_2N)_2PO]^+$, 100%], 91 [$[CH_2Ph]^+$, 40%].

*Z isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=1.84–1.85 [m, 3H, C*H*$_3$–C(N)=CH–$CH_2$–$CH_2$Ph], 2.39–2.50 (m, 2H, C=CH–C*H*$_2$–$CH_2$Ph), 2.62 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Me)=CH), 2.64–2.69 (m, 2H, C=CH–$CH_2$–C*H*$_2$Ph), 2.65 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 5.21 (t, $^3J_{H-H}$=6.9 Hz, 1H, C=C*H*–$CH_2$–$CH_2$Ph), 7.17–7.33 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=20.3 [*C*$H_3$C(N)=CH–$CH_2$–$CH_2$Ph], 28.7 (C=CH–*C*$H_2$–$CH_2$Ph), 34.8 (C=CH–$CH_2$–*C*$H_2$Ph), 36.1 [d, $^2J_{C-P}$=3.7 Hz, [(*C*$H_3$)$_2$N]$_2$PO and *C*$H_3$–N–C(Me)=CH], 124.9, 127.4, 127.6 (*C*$^2$, *C*$^3$, *C*$^4$ of *Ph*), 125.2 (C=*C*H–$CH_2$–$CH_2$Ph), 137.8 (*C*$^1$ of *Ph*), 141.2 (*C*=CH–$CH_2$–$CH_2$Ph); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.97.

*E isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=1.80–1.82 [m, 3H, C*H*$_3$–C(N)=CH–$CH_2$–$CH_2$Ph], 2.39–2.50 (m, 2H, C=CH–C*H*$_2$–$CH_2$Ph), 2.62 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Me)=CH), 2.64–2.69 (m, 2H, C=CH–$CH_2$–C*H*$_2$Ph), 2.65 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 5.04 (t, $^3J_{H-H}$=7.3 Hz, 1H, C=C*H*–$CH_2$–$CH_2$Ph), 7.17–7.33 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=20.3 [*C*$H_3$C(N)=CH–$CH_2$–$CH_2$Ph], 28.7 (C=CH–*C*$H_2$–$CH_2$Ph), 34.8 (C=CH–$CH_2$–*C*$H_2$Ph), 36.1 [d, $^2J_{C-P}$=3.7 Hz, [(*C*$H_3$)$_2$N]$_2$PO and *C*$H_3$–N–C(Me)=CH], 124.9, 127.4, 127.6 (*C*$^2$, *C*$^3$, *C*$^4$ of *Ph*), 125.2 (C=*C*H–$CH_2$–$CH_2$Ph), 137.8 (*C*$^1$ of *Ph*), 141.2 (*C*=CH–$CH_2$–$CH_2$Ph); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=19.38.

**4.7.8. [(1-Pheny-3-hepten-4-yl)]pentamethyl phosphoric triamide 5be.** Yield: 100% (*Z*/*E*: 100/0); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3063, 3027, 3000, 2958, 2929, 2805, 1663, 1603, 1454, 1376 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.5 Hz, 3H, C*H*$_3$–$CH_2$–$CH_2$–C=CH), 1.49 (m, $^3J_{H-H}$=7.5 Hz and $^3J_{H-H}$=7.5 Hz, 2H, $CH_3$–C*H*$_2$–$CH_2$–C=CH), 2.14 (t, $^3J_{H-H}$=7.5 Hz, 2H, $CH_3$–$CH_2$–C*H*$_2$–C=CH), 2.41–2.51 (m, 2H, C=CH–C*H*$_2$–$CH_2$Ph), 2.64–2.73 (m, 2H, C=CH–$CH_2$–C*H*$_2$Ph), 2.64 [d, $^3J_{C-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.65 [d, $^3J_{C-P}$=8.0 Hz, 3H, C*H*$_3$–N–C(Pr)=CH], 5.17 (t, $^3J_{H-H}$=6.9 Hz, 1H, C=C*H*–$CH_2$–$CH_2$Ph), 7.17–7.30 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.6 (*C*$H_3$–$CH_2$–$CH_2$–C=CH), 20.5 ($CH_3$–*C*$H_2$–$CH_2$–C=CH), 29.2 (C=CH–*C*$H_2$–$CH_2$Ph), 35.4 (C=CH–$CH_2$–*C*$H_2$Ph), 36.4 [d, $^2J_{C-P}$=3.7 Hz, *C*$H_3$–N–C(Pr)=CH], 36.6 [d, $^2J_{C-P}$=3.7 Hz, [(*C*$H_3$)$_2$N]$_2$PO], 37.8 ($CH_3$–$CH_2$–*C*$H_2$–C=CH), 124.0 (d, $^3J_{C-P}$=6.1 Hz, C=*C*H–$CH_2$–$CH_2$Ph), 125.4, 127.9, 128.1 (*C*$^2$, *C*$^3$, *C*$^4$ of *Ph*), 141.7 (*C*$^1$ of *Ph*), 142.6 (*C*=CH–$CH_2$–$CH_2$Ph); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.92; MS ($EI^+$) *m/z* calculated for $C_{18}H_{32}N_3OP$ $[M]^+$ 337.4 found 338 [$[M+1]^+$, 65%], 246 [$[M-CH_2Ph]^+$, 90%], 202 [$[M-(Me_2N)_2PO]^+$, 28%], 135 [$[(Me_2N)_2PO]^+$, 100%].

**4.7.9. [(1,4-Diphenyl-1-buten-1-yl)]pentamethyl phosphoric triamide 5ce.** Yield: 98%; *Z*/*E*: 100/0; yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3026, 2924, 1636, 1600, 1492, 1453 and 1299; $^1$H NMR ($CDCl_3$): $\delta_H$=2.50 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.69–2.77 (m, 2H, C=CH–C*H*$_2$–$CH_2$Ph), 2.77–2.84 (m, 2H, C=CH–$CH_2$–C*H*$_2$Ph), 2.82 [d, $^3J_{H-P}$=8.6 Hz, 3H, C*H*$_3$–N–C(Ph)=CH], 5.72 (t, $^3J_{H-H}$=6.8 Hz, 1H, C=C*H*–$CH_2$–$CH_2$Ph), 7.17–7.48 (m, 10H, 2×*Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=30.1 (C=CH–*C*$H_2$–$CH_2$–Ph), 35.6 (C=CH–$CH_2$–*C*$H_2$–Ph), 36.9 [d, $^2J_{C-P}$=3.7 Hz, [(C*H*$_3$)$_2$N]$_2$PO], 37.3 [d, $^2J_{C-P}$=3.7 Hz, C*H*$_3$–N–C(Ph)=CH], 125.8, 126.3, 127.2, 128.0, 128.3, 128.5, 140.5, 141.7 (2×*Ph*), 142.9 (d, $^3J_{C-P}$=2.4 Hz, *C*=CH–$CH_2$–$CH_2$–Ph); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.83; MS ($EI^+$) *m/z* calculated for $C_{21}H_{30}N_3OP$ $[M]^+$ 371.5 found 371 [$[M]^+$, 8%], 280 [$[M-CH_2Ph]^+$, 53%], 235 [$[M-(Me_2N)_2PO]^+$, 18], 135 [$[(Me_2N)_2PO]^+$, 100%], 91 [$[CH_2Ph]^+$, 25%].

**4.7.10. [(5-Methyl-2-hexen-2-yl)]pentamethyl phosphoric triamide 5af.** Yield: 100% (*Z*/*E*: 80/20); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2897, 2842, 2805, 1669, 1460, 1377 and 1298; MS ($EI^+$) *m/z* calculated for $C_{12}H_{28}N_3OP$ $[M]^+$ 261.3 found 261 [$[M]^+$, 19%], 218 [$[M-iPr]^+$, 58%], 135 [$[(Me_2N)_2PO]^+$, 100%], 126 [$[M-(Me_2N)_2PO]^+$, 52%].

*Z isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=0.90 [d, $^3J_{H-H}$=6.7 Hz, 6H, C=CH–$CH_2$–CH(C*H*$_3$)$_2$], 1.53–1.69 [m, 1H, C=CH–$CH_2$–C*H*(C*H*$_3$)$_2$], 1.85–1.86 [m, 3H, C*H*$_3$–C(N)=CH], 1.96–2.03 [m, 2H, C=CH–C*H*$_2$–CH(C*H*$_3$)$_2$], 2.67 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO],

2.72 [d, $^3J_{H-P}$=8.7 Hz, C$H_3$–N–C(Me)=CH], 5.19 [t, $^3J_{H-H}$=7.0 Hz, C=C$H$–CH$_2$–CH(CH$_3$)$_2$]; $^{13}$C NMR (CDCl$_3$): $\delta_C$=20.8 [$C$H$_3$–C(N)=CH], 22.2 [C=CH–CH$_2$–CH($C$H$_3$)$_2$], 27.9 [C=CH–CH$_2$–$C$H(CH$_3$)$_2$], 35.3 [d, $^2J_{C-P}$=2.4 Hz, $C$H$_3$–N–C(Me)=CH], 36.2 [C=CH–$C$H$_2$–CH(CH$_3$)$_2$], 36.5 [d, $^2J_{C-P}$=2.4 Hz, [($C$H$_3$)$_2$N]$_2$PO], 125.6 [d, $^3J_{C-P}$=5.6 Hz, C=$C$H–CH$_2$–CH(CH$_3$)$_2$], 138.0 [$C$=CH–CH$_2$–CH(CH$_3$)$_2$]; $^{31}$P NMR (101.256 MHz, CDCl$_3$): $\delta_P$=18.12.

*E isomer*: $^1$H NMR (CDCl$_3$): $\delta_H$=0.90 [d, $^3J_{H-H}$=6.7 Hz, 6H, C=CH–CH$_2$–CH(C$H_3$)$_2$], 1.53–1.69 [m, 1H, C=CH–CH$_2$–C$H$(CH$_3$)$_2$], 1.80 [s, 3H, C$H_3$–C(N)=CH], 1.96–2.03 [m, 2H, C=CH–C$H_2$–CH(CH$_3$)$_2$], 2.67 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.72 [d, $^3J_{H-P}$=8.7 Hz, C$H_3$–N–C(Me)=CH], 5.19 [t, $^3J_{H-H}$=7.0 Hz, C=C$H$–CH$_2$–CH(CH$_3$)$_2$]; $^{13}$C NMR (CDCl$_3$): $\delta_C$=20.8 [$C$H$_3$–C(N)=CH], 22.2 [C=CH–CH$_2$–CH($C$H$_3$)$_2$], 27.9 [C=CH–CH$_2$–$C$H(CH$_3$)$_2$], 35.3 [d, $^2J_{C-P}$=2.4 Hz, $C$H$_3$–N–C(Me)=CH], 36.2 [C=CH–$C$H$_2$–CH(CH$_3$)$_2$], 36.5 [d, $^2J_{C-P}$=2.4 Hz, [($C$H$_3$)$_2$N]$_2$PO], 125.6 [d, $^3J_{C-P}$=5.6 Hz, C=$C$H–CH$_2$–CH(CH$_3$)$_2$], 138.0 [$C$=CH–CH$_2$–CH(CH$_3$)$_2$]; $^{31}$P NMR (101.256 MHz, CDCl$_3$): $\delta_P$=19.35.

**4.7.11. [(2-Methyl-4-octen-5-yl)]pentamethyl phosphoric triamide 5bf.** Yield: 96% (*Z*/*E*: 100/0); pale yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2930, 2873, 2812, 1660, 1459, 1368 and 1297; $^1$H NMR (CDCl$_3$): $\delta_H$=0.91 [d, $^3J_{H-H}$=6.7 Hz, 6H, C=CH–CH$_2$–CH(C$H_3$)$_2$], 0.93 (t, $^3J_{H-H}$=7.9 Hz, 3H, C$H_3$–CH$_2$–CH$_2$–C=CH), 1.52 (m, 2H, CH$_3$–C$H_2$–CH$_2$–C=CH), 1.63 [m, 1H, C=CH–CH$_2$–C$H$(CH$_3$)$_2$], 2.02 [m, 2H, C=CH–C$H_2$–CH(CH$_3$)$_2$], 2.16 (t, $^3J_{H-H}$=7.9 Hz, 2H, CH$_3$–CH$_2$–C$H_2$–C=CH), 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.75 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–C(Pr)=CH], 5.15 [t, $^3J_{H-H}$=6.9 Hz, 1H, C=C$H$–CH$_2$–CH(CH$_3$)$_2$]; $^{13}$C NMR (CDCl$_3$): $\delta_C$=13.5 ($C$H$_3$–CH$_2$–CH$_2$–C=CH), 20.5 (CH$_3$–$C$H$_2$–CH$_2$–C=CH), 22.3 [C=CH–CH$_2$–CH($C$H$_3$)$_2$], 28.0 [C=CH–CH$_2$–$C$H(CH$_3$)$_2$], 36.1 [C=CH–$C$H$_2$–CH(CH$_3$)$_2$], 36.4 [d, $^2J_{C-P}$=4.9 Hz, $C$H$_3$–N–C(Pr)=CH], 36.6 [d, $^2J_{C-P}$=3.7 Hz, [($C$H$_3$)$_2$N]$_2$PO], 37.8 (CH$_3$–CH$_2$–$C$H$_2$–C=CH), 123.7 [d, $^3J_{C-P}$=6.1 Hz, C=$C$H–CH$_2$–CH(CH$_3$)$_2$], 142.3 [$C$=CH–CH$_2$–CH(CH$_3$)$_2$]; $^{31}$P NMR (101.256 MHz, CDCl$_3$): $\delta_P$=18.04; MS (EI$^+$) *m*/*z* calculated for $C_{14}H_{32}N_3OP$ [M]$^+$ 289.4 found 289 [[M]$^+$, 6%], 246 [[M−iPr]$^+$, 23%], 154 [[M−(Me$_2$N)$_2$PO]$^+$, 38%], 135 [[(Me$_2$N)$_2$PO]$^+$, 100%].

**4.7.12. [(4-Methyl-1-phenyl-1-penten-1-yl)] pentamethyl phosphoric triamide 5cf.** Yield: 94% (*Z*/*E*: 100/0); pale yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=3062, 2954, 2926, 1633, 1592, 1491, 1456 and 1299; $^1$H NMR (CDCl$_3$): $\delta_H$=0.99 [d, $^3J_{H-H}$=6.6 Hz, 6H, C=CH–CH$_2$–CH(C$H_3$)$_2$], 1.70–1.85 [m, 1H, C=CH–CH$_2$–C$H$(CH$_3$)$_2$], 2.28 [m, 2H, C=CH–C$H_2$–CH(CH$_3$)$_2$], 2.54 [d, $^3J_{H-P}$=9.0 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.92 [d, $^3J_{H-P}$=8.6 Hz, 3H, C$H_3$–N–C(Ph)=CH], 5.73 [t, $^3J_{H-H}$=7.0 Hz, 1H, C=C$H$–CH$_2$–CH(CH$_3$)$_2$], 7.19–7.53 (m, 5H, *Ph*); $^{13}$C NMR (CDCl$_3$): $\delta_C$=22.5 [C=CH–CH$_2$–CH(C$H_3$)$_2$], 28.4 [C=CH–CH$_2$–$C$H(CH$_3$)$_2$], 36.8 [d, $^2J_{C-P}$=3.7 Hz, [($C$H$_3$)$_2$N]$_2$PO], 37.1 [C=CH–$C$H$_2$–CH(CH$_3$)$_2$], 37.2 [d, $^2J_{C-P}$=3.7 Hz, $C$H$_3$–N–C(Ph)=CH], 126.2, 127.0, 127.8 ($C^2$, $C^3$, $C^4$ of *Ph*), 127.5 [d, $^3J_{C-P}$=6.1 Hz, C=$C$H–CH$_2$–CH(CH$_3$)$_2$], 140.6 ($C^1$ of *Ph*), 142.7 [d, $^2J_{C-P}$=2.4 Hz, $C$=CH–CH$_2$–CH(CH$_3$)$_2$],; $^{31}$P NMR (101.256 MHz, CDCl$_3$): $\delta_P$=17.92; MS (EI$^+$) *m*/*z* calculated for $C_{17}H_{30}N_3OP$ [M]$^+$ 323.4 found 323 [[M]$^+$, 82%], 280 [[M−iPr]$^+$, 58%], 188 [[M−(Me$_2$N)$_2$PO]$^+$, 84%], 135 [[(Me$_2$N)$_2$PO]$^+$, 100%].

**4.7.13. [(5-Methoxy-2-penten-2-yl)]pentamethyl phosphoric triamide 5ag.** Yield: 95% (*Z*/*E*: 95/5); yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2889, 2805, 1670, 1459, 1377, 1297 and 1117; $^1$H NMR (CDCl$_3$): $\delta_H$=1.87 (m, 3H, C$H_3$–C=CH–CH$_2$–CH$_2$–O–CH$_3$), 2.37–2.46 (m, 2H, CH$_3$–C=CH–C$H_2$–CH$_2$–O–CH$_3$), 2.67 [d, $^3J_{H-P}$=9.4 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.74 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–C(Me)=CH], 3.34 (s, 3H, CH$_3$–C=CH–CH$_2$–CH$_2$–O–C$H_3$), 3.41 (t, $^3J_{H-H}$=6.8 Hz, 2H, CH$_3$–C=CH–CH$_2$–C$H_2$–O–CH$_3$), 5.22 (t, $^3J_{H-H}$=6.9 Hz, 1H, CH$_3$–C=C$H$–CH$_2$–CH$_2$–O–CH$_3$); $^{13}$C NMR (CDCl$_3$): $\delta_C$=20.6 ($C$H$_3$–C=CH–CH$_2$–CH$_2$–O–CH$_3$), 27.5 (CH$_3$–C=CH–$C$H$_2$–CH$_2$–O–CH$_3$), 35.2 [d, $^2J_{C-P}$=2.3 Hz, $C$H$_3$–N–C(Me)=CH], 36.3 [d, $^2J_{C-P}$=2.9 Hz, (C$H_3$)$_2$N]$_2$PO], 57.9 (CH$_3$–C=CH–CH$_2$–CH$_2$–O–$C$H$_3$), 71.5 (CH$_3$–C=CH–CH$_2$–$C$H$_2$–O–CH$_3$), 122.5 (d, $^3J_{C-P}$=5.8 Hz, CH$_3$–C=$C$H–CH$_2$–CH$_2$–O–CH$_3$), 139.3 ($C$H$_3$–C=CH–CH$_2$–CH$_2$–O–CH$_3$); $^{31}$P NMR (101.256 MHz, CDCl$_3$): $\delta_P$=17.90; MS (EI$^+$) *m*/*z* calculated for $C_{11}H_{26}N_3O_2P$ [M]$^+$ 263.3 found 264 [[M+1]$^+$, 100%], 232 [[M−OCH$_3$]$^+$, 20%], 218 [[M−CH$_2$OCH$_3$]$^+$, 20%], 135 [[(Me$_2$N)$_2$PO]$^+$, 34%].

**4.7.14. [(7-Methoxy-4-hepten-4-yl)] pentamethyl phosphoric triamide 5bg.** Yield: 76% (*Z*/*E*: 100/0); yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2955, 2924, 2873, 2842, 2805, 1664, 1458, 1379, 1297 and 1116; $^1$H NMR (CDCl$_3$): $\delta_H$=0.93 (t, $^3J_{H-H}$=7.5 Hz, 3H, C$H_3$–CH$_2$–CH$_2$–C=CH), 1.52 (m, 2H, CH$_3$–C$H_2$–CH$_2$–C=CH), 2.17 (m, 2H, CH$_3$–CH$_2$–C$H_2$–C=CH), 2.43 (m, 2H, C=CH–C$H_2$–CH$_2$–O–CH$_3$), 2.67 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.77 [d, $^3J_{H-P}$=8.3 Hz, 3H, C$H_3$–N–C(Pr)=CH], 3.34 (s, 3H, C=CH–CH$_2$–CH$_2$–O–C$H_3$), 3.42 (t, $^3J_{H-H}$=7.5 Hz, C=CH–CH$_2$–C$H_2$–O–CH$_3$); $^{13}$C NMR (CDCl$_3$): $\delta_C$=13.5 ($C$H$_3$–CH$_2$–CH$_2$–C=CH), 20.4 (CH$_3$–$C$H$_2$–CH$_2$–C=CH), 27.7 (C=CH–$C$H$_2$–CH$_2$–O–CH$_3$), 36.6 [d, $^2J_{C-P}$=3.4 Hz, $C$H$_3$–N–C(Pr)=CH and (C$H_3$)$_2$N]$_2$PO], 37.7 (CH$_3$–CH$_2$–$C$H$_2$–C=CH), 58.1 (C=CH–CH$_2$–CH$_2$–O–$C$H$_3$), 71.8 (C=CH–CH$_2$–$C$H$_2$–O–CH$_3$), 120.8 (d, $^3J_{C-P}$=6.1 Hz, C=$C$H–CH$_2$–CH$_2$–O–CH$_3$), 143.8 ($C$=CH–CH$_2$–CH$_2$–O–CH$_3$); $^{31}$P NMR (101.256 MHz, CDCl$_3$): $\delta_P$=17.83; MS (EI$^+$) *m*/*z* calculated for $C_{13}H_{30}N_3O_2P$ [M]$^+$ 291.4 found 292 [[M+1]$^+$, 100%], 260 [[M−OCH$_3$]$^+$, 47%], 135 [[(Me$_2$N)$_2$PO]$^+$, 65%].

**4.7.15. [(4-Methoxy-1-phenyl-1-buten-1-yl)]pentamethyl phosphoric triamide 5cg.** Yield: 74% (*Z*/*E*: 100/0); yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=3052, 2924, 2878, 1634, 1593, 1491, 1454, 1299 and 1115; $^1$H NMR (CDCl$_3$): $\delta_H$=2.55 [d, $^3J_{H-P}$=9.0 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.63–2.73 (m, 2H, C=CH–C$H_2$–CH$_2$–O–CH$_3$), 2.94 [d, $^3J_{H-P}$=9.0 Hz, 3H, C$H_3$–N–C(Ph)=CH], 3.37 (s, 3H, C=CH–CH$_2$–CH$_2$–O–C$H_3$), 3.53 (t, $^3J_{H-H}$=6.4 Hz, 2H, C=CH–C$H_2$–CH$_2$–O–CH$_3$), 5.78 (t, $^3J_{H-H}$=6.8 Hz, 1H, C=C$H$–CH$_2$–CH$_2$–O–CH$_3$); $^{13}$C NMR (CDCl$_3$): $\delta_C$=28.2 (C=CH–$C$H$_2$–CH$_2$–O–CH$_3$), 36.3 [d, $^2J_{C-P}$=3.5 Hz,

[$(CH_3)_2N]_2PO$], 36.8 [d, $^2J_{C-P}$=3.3 Hz, $CH_3$–N–C(Ph)=CH], 57.9 (C=CH–$CH_2$–$CH_2$–O–$CH_3$), 71.2 (C=CH–$CH_2$–$CH_2$–O–$CH_3$), 124.3 (d, $^3J_{C-P}$=5.3 Hz, C=CH–$CH_2$–$CH_2$–O–$CH_3$), 125.7, 126.7, 127.4 ($C^2$, $C^3$, $C^4$ of *Ph*), 139.7 ($C^1$ of *Ph*), 143.1 (C=CH–$CH_2$–$CH_2$–O–$CH_3$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.70; MS ($EI^+$) *m/z* calculated for $C_{16}H_{28}N_3O_2P$ $[M]^+$ 325.4 found 326 $[[M+1]^+$, 19%], 135 $[[(Me_2N)_2PO]^+$, 100%].

**4.7.16. [(2,6-Heptadien-2-yl)]pentamethyl phosphoric triamide 5ah.** Yield: 96% (*Z*/*E*: 90/10); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3078, 2915, 2845, 2805, 1667, 1639, 1456, 1376 and 1298; MS ($EI^+$) *m/z* calculated for $C_{12}H_{26}N_3OP$ $[M]^+$ 259.3 found 260 $[[M+1]^+$, 8%], 218 $[[M-(CH_2-CH_2-CH=CH_2)]^+$, 38%], 135 $[[(Me_2N)_2PO]^+$, 100%], 124 $[[(Me_2N)_2PO]^+$, 17%].

*Z isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=1.85–1.87 (m, 3H, $CH_3$–C=CH–$CH_2$), 2.07–2.26 (m, 4H, C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 2.67 [d, $^3J_{H-P}$=9.5 Hz, 12H, $[(CH_3)_2N]_2PO$], 2.73 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Me)=CH], 4.96 (d, $^3J_{H-H}$=11.9 Hz, $CH_2$–$CH_2$–CH=CH*H*), 5.02 (d, $^3J_{H-H}$=18.2 Hz, $CH_2$–$CH_2$–CH=CH*H*), 5.17 (t, $^3J_{H-H}$=6.7 Hz, C=C*H*–CH2), 5.74–5.91 (m, 1H, $CH_2$–$CH_2$–C*H*=$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=20.73 ($CH_3$–C=CH–$CH_2$), 26.4 ($CH_2$–$CH_2$–CH=$CH_2$), 33.0 (C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 35.3 [d, $^3J_{C-P}$=3.3 Hz, $CH_3$–N–C(Me)=CH], 36.5 [d, $^3J_{C-P}$=3.3 Hz, $[(CH_3)_2N]_2PO$], 114.2 ($CH_2$–$CH_2$–CH=$CH_2$), 125.7 (C=CH–$CH_2$), 137.9 ($CH_2$–$CH_2$–CH=$CH_2$), 138.1 (C=CH–$CH_2$–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.98.

*E isomer*: $^1$H NMR ($CDCl_3$): $\delta_H$=1.79–1.82 (m, 3H, $CH_3$–C=CH–$CH_2$), 2.07–2.26 (m, 4H, C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 2.64 [d, $^3J_{H-P}$=9.5 Hz, 12H, $[(CH_3)_2N]_2PO$], 2.72 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Me)=CH], 4.96 (d, $^3J_{H-H}$=11.9 Hz, $CH_2$–$CH_2$–CH=CH*H*), 5.02 (d, $^3J_{H-H}$=18.2 Hz, $CH_2$–$CH_2$–CH=CH*H*), 5.17 (t, $^3J_{H-H}$=6.7 Hz, C=C*H*–CH2), 5.74–5.91 (m, 1H, $CH_2$–$CH_2$–C*H*=$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=20.73 ($CH_3$–C=CH–$CH_2$), 26.4 ($CH_2$–$CH_2$–CH=$CH_2$), 33.0 (C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 35.3 [d, $^2J_{C-P}$=3.3 Hz, $CH_3$–N–C(Me)=CH], 36.5 [d, $^2J_{C-P}$=3.3 Hz, $[(CH_3)_2N]_2PO$], 114.2 ($CH_2$–$CH_2$–CH=$CH_2$), 125.7 (C=CH–$CH_2$), 137.9 ($CH_2$–$CH_2$–CH=$CH_2$), 138.1 (C=CH–$CH_2$–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=19.37.

**4.7.17. [(1,5-nonadien-6-yl)]pentamethyl phosphoric triamide 5bh.** Yield: 100% (*Z*/*E*: 100/0); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3078, 2990, 2929, 2874, 2802, 1663, 1639, 1458 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.93 (t, $^3J_{H-H}$=7.3 Hz, $CH_3$–$CH_2$–$CH_2$–C=CH), 1.43–1.58 (m, 2H, $CH_3$–$CH_2$–$CH_2$–C=CH), 2.67 [d, $^3J_{H-P}$=9.1 Hz, 12H, $[(CH_3)_2N]_2PO$], 2.73 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Me)=CH], 4.94–5.07 (m, 2H, $CH_2$–$CH_2$–CH=C$H_2$), 5.14 (t, $^3J_{H-H}$=6.5 Hz, C=C*H*–$CH_2$–$CH_2$), 5.83 (ddt, $^3J_{H-H}$=17.0 Hz, $^3J$ $^3J_{H-H}$=10.3 Hz and $^3J_{H-H}$=6.3 Hz, 1H, $CH_2$–$CH_2$–C*H*=$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.7 ($CH_3$–$CH_2$–$CH_2$–C=CH), 20.7 ($CH_3$–$CH_2$–$CH_2$–C=CH), 26.6 (C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 33.4 (C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 36.6, 36.8, 36.9 [$[(CH_3)_2N]_2PO$] and $CH_3$–N–C(Me)=CH], 38.0 ($CH_3$–$CH_2$–$CH_2$–C=CH), 114.5 (C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 124.3 (d, $^3J_{C-P}$=6.1 Hz, C=CH–$CH_2$–$CH_2$), 138.2 (C=CH–$CH_2$–$CH_2$–CH=$CH_2$), 142.6 (C=CH–$CH_2$–$CH_2$–CH=$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.91; MS ($EI^+$) *m/z* calculated for $C_{14}H_{30}N_3OP$ $[M]^+$ 287.4 found 288 $[[M+1]^+$, 100%], 246 $[[M-(CH_2-CH=CH_2)]^+$, 65%], 135 $[[(Me_2N)_2PO]^+$, 62%].

**4.7.18. [(1-Phenyl-1,5-hexadien-1-yl)] pentamethyl phosphoric triamide 5ch.** Yield: 84% (*Z*/*E*: 100/0); yellow oil, IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3052, 2923, 2847, 2806, 1639, 1598, 1491 and 1300; $^1$H NMR ($CDCl_3$): $\delta_H$=2.25 (m, 2H, $CH_2$–C$H_2$–CH=$CH_2$), 2.40–2.60 (m, 2H, C$H_2$–$CH_2$–CH=$CH_2$), 2.55 [d, $^3J_{H-P}$=9.1 Hz, 12H, $[(CH_3)_2N]_2PO$], 2.92 [d, $^3J_{H-P}$=8.6 Hz, 3H, $CH_3$–N–C(Ph)=CH], 5.01 (d, $^3J_{H-H}$=10.2 Hz, 1H, $CH_2$–$CH_2$–CH=CH*H*), 5.08 (dd, $^3J_{H-H}$=17.1 Hz and $^2J_{H-H}$=1.6 Hz, 1H, $CH_2$–$CH_2$–CH=CH*H*), 5.71 (t, $^3J_{H-H}$=7.1 Hz, 1H, C=C*H*–$CH_2$), 5.80–5.94 (m, 1H, $CH_2$–$CH_2$–C*H*=$CH_2$), 7.22–7.52 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=27.5 (C=CH–$CH_2$), 33.4 ($CH_2$–$CH_2$–CH=$CH_2$), 36.9 [d, $^2J_{C-P}$=3.6 Hz, $[(CH_3)_2N]_2PO$], 37.4 [d, $^2J_{C-P}$=3.4 Hz, $CH_3$–N–C(Ph)=CH], 115.0 ($CH_2$–$CH_2$–CH=$CH_2$), 126.3, 127.2, 128.0 ($C^2$, $C^3$, $C^4$ of *Ph*), 127.8 (d, $^3J_{C-P}$=6.1 Hz, C=CH–$CH_2$), 138.0 ($CH_2$–$CH_2$–$CH$=$CH_2$), 140.5 ($C^1$ of *Ph*), 142.7 (C=CH–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.84; MS ($EI^+$) *m/z* calculated for $C_{17}H_{28}N_3OP$ $[M]^+$ 321.4 found 321 $[[M]^+$, 16%], 280 $[[M-(CH_2-CH_2-CH=CH_2)]^+$, 47%], 135 $[[(Me_2N)_2PO]^+$, 100%], 77 $[[Ph]^+$, 20%].

**4.7.19. [(5-Hydroxy-6-methyl-2-hepten-2-yl)]pentamethyl phosphoric triamide 5ai.** Yield: 75% (*Z*/*E*: 100/0); pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3342, 2940, 2877, 2807, 1673, 1462, 1377 and 1298; $^1$H NMR ($CDCl_3$): $\delta_H$=0.91 [d, $^3J_{H-H}$=7.1 Hz, 3H, $CH_2$–CH(OH)–CH(Me)–C$H_3$], 0.93 [d, $^3J_{H-H}$=6.7 Hz, 3H, $CH_2$–CH(OH)–CH(Me)–C$H_3$], 1.59–1.75 (m, 1H, $CH_2$–CH(OH)–C*H*(Me)–$CH_3$], 1.84 (d, $^4J_{H-P}$=1.2 Hz, 3H, $CH_3$–C=CH–$CH_2$), 2.32–2.46 [m, 2H, C=CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 2.67 [d, $^3J_{H-P}$=9.1 Hz, 6H, $[(CH_3)_2N]PO$], 2.68 [d, $^3J_{H-P}$=9.9 Hz, 6H, $[(CH_3)_2N]PO$], 2.76 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Me)=CH], 3.32–3.43 [m, 1H, $CH_2$–C*H*(OH)–CH(Me)–$CH_3$], 5.25–5.37 [m, 1H, C=C*H*–$CH_2$–CH(OH)–CH(Me)–$CH_3$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=17.6 [C=CH–$CH_2$–CH(OH)–CH(Me)–*C*$H_3$], 18.1 [C=CH–$CH_2$–CH(OH)–CH(Me)–*C*$H_3$], 20.1 ($CH_3$–C=CH–$CH_2$), 31.2 [C=CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 33.8 [C=CH–$CH_2$–CH(OH)–*C*H(Me)–$CH_3$], 35.5 [d, $^2J_{C-P}$=3.7 Hz, $CH_3$–N–C(Me)=CH], 36.3 [d, $^2J_{C-P}$=3.7 Hz, $[(CH_3)_2N]PO$], 36.5 [d, $^2J_{C-P}$=4.9 Hz, $[(CH_3)_2N]PO$], 74.9 [C=CH–$CH_2$–*C*H(OH)–CH(Me)–$CH_3$], 125.3 [d, $^3J_{C-P}$=4.9 Hz, C=*C*H–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 138.3 [*C*=CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.72; MS ($EI^+$) *m/z* calculated for $C_{13}H_{30}N_3O_2P$ $[M]^+$ 291.4 found 292 $[[M+1]^+$, 100%], 274 $[[M-OH]^+$, 17%], 135 $[[(Me_2N)_2PO]^+$, 27%].

**4.7.20. [(7-Hydroxy-9-methyl-4-nonen-4-yl)]pentamethyl phosphoric triamide 5bi.** Yield: 70% (*Z*/*E*: 100/0); pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3335, 2956, 2873, 2805, 1666, 1463, 1379, 1365 and 1298; $^1$H NMR ($CDCl_3$):

$\delta_H$=0.90–0.97 [m, 9H, $CH_2$–CH(OH)–CH($CH_3$)$_2$ and $CH_3$–$CH_2$–$CH_2$–C═CH], 1.46–1.57 [m, 1H, $CH_2$–CH(OH)–$CH$($CH_3$)$_2$], 1.61–1.75 [m, 2H, $CH_3$–$CH_2$–$CH_2$–C═CH], 2.09–2.18 [m, 2H, $CH_3$–$CH_2$–$CH_2$–C═CH], 2.34–2.48 [m, 2H, $CH_2$–CH(OH)–CH($CH_3$)$_2$], 2.67 [d, $^3J_{H-P}$=9.5 Hz, 6H, [($CH_3$)$_2$N]PO], 2.68 [d, $^3J_{H-P}$= 9.5 Hz, 6H, [($CH_3$)$_2$N]PO], 2.78 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Pr)═CH], 3.31–3.43 [m, 1H, $CH_2$–$CH$(OH)–CH($CH_3$)$_2$], 5.24–5.30 [m, 1H, C═$CH$–$CH_2$–CH(OH)–CH($CH_3$)$_2$]; $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.8 ($CH_3$–$CH_2$–$CH_2$–C═CH), 18.0 [$CH_2$–CH(OH)–CH(Me)–$CH_3$], 18.5 [$CH_2$–CH(OH)–CH(Me)–$CH_3$], 20.6 ($CH_3$–$CH_2$–$CH_2$–C═CH), 31.5 [$CH_2$–CH(OH)–CH($CH_3$)$_2$], 34.2 [$CH_2$–CH(OH)–$CH$($CH_3$)$_2$], 36.7–36.8 [($CH_3$)$_2$N]$_2$PO and $CH_3$–N–C(Pr)═CH], 36.9 ($CH_3$–$CH_2$–$CH_2$–C═CH), 75.5 [$CH_2$–$CH$(OH)–CH($CH_3$)$_2$], 123.9 [d, $^3J_{C-P}$=4.9 Hz, C═$CH$–$CH_2$–CH(OH)–CH($CH_3$)$_2$], 143.0 (C═CH–$CH_2$–CH(OH)–CH($CH_3$)$_2$]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.76; MS (EI$^+$) *m/z* calculated for $C_{15}H_{34}N_3O_2P$ [M]$^+$ 319.4 found 320 [[M+1]$^+$, 44%], 302 [M−OH]$^+$, 13%], 135 [[($Me_2N$)$_2$PO]$^+$, 100%], 44 [[$Me_2N$]$^+$, 37%].

**4.7.21. [(4-Hydroxy-5-methyl-1-phenyl-1-hexen-1-yl)]-pentamethyl phosphoric triamide 5ci.** Yield: 100% (*Z*/*E*: 100/0); pale yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=3334, 3056, 2927, 2807, 1638, 1592, 1490, 1459, 1382, 1364 and 1299; $^1$H NMR ($CDCl_3$): $\delta_H$=0.96 [d, $^3J_{H-H}$=6.7 Hz, 3H, $CH_2$–CH(OH)–CH(Me)–$CH_3$], 0.99 [d, $^3J_{H-H}$=6.7 Hz, 3H, $CH_2$–CH(OH)–CH(Me)–$CH_3$], 1.68–1.79 (m, 1H, $CH_2$–CH(OH)–$CH$(Me)–$CH_3$], 2.34–2.45 [m, 2H, C═CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 2.55 [d, $^3J_{H-P}$=9.1 Hz, 6H, [($CH_3$)$_2$N]PO], 2.68 [d, $^3J_{H-P}$= 9.9 Hz, 6H, [($CH_3$)$_2$N]PO], 2.88 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Me)═CH], 3.43–3.57 [m, 1H, $CH_2$–$CH$(OH)–CH(Me)–$CH_3$], 5.79–5.86 [m, 1H, C═$CH$–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 7.23–7.45 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=17.7 [C═CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 18.4 [C═CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 32.5 [C═CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 34.12 [C═CH–$CH_2$–CH(OH)–$CH$(Me)–$CH_3$], 36.7 [d, $^2J_{C-P}$=3.7 Hz, [($CH_3$)$_2$N]PO], 36.8 [d, $^2J_{C-P}$=3.7 Hz, [($CH_3$)$_2$N]PO], 37.2 [d, $^2J_{C-P}$=3.7 Hz, $CH_3$–N–C(Me)═CH], 75.5 [C═CH–$CH_2$–$CH$(OH)–CH(Me)–$CH_3$], 126.3, 126.9, 127.8 ($C^2$, $C^3$, $C^4$ of *Ph*), 127.1 [d, $^3J_{C-P}$=4.9 Hz, C═$CH$–$CH_2$–CH(OH)–CH(Me)–$CH_3$], 140.1 ($C^1$ of *Ph*), 142.8 [C═CH–$CH_2$–CH(OH)–CH(Me)–$CH_3$]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.13; MS (EI$^+$) *m/z* calculated for $C_{18}H_{32}N_3O_2P$ [M]$^+$ 353.4 found 354 [[M+1]$^+$, 21%], 281 [[M−[CH(OH)CH($CH_3$)$_2$]]$^+$, 42%], 135 [[($Me_2N$)$_2$PO]$^+$, 100%].

### 4.8. Typical procedure for the preparation of ketones 6

To a solution of enephosphoramide **5** (4 mmol) in benzene (25 ml) was added 20 ml of a 6N aqueous solution of $H_2SO_4$. The mixture was heated at reflux for 4 h. The aqueous layer was then saturated with NaCl and extracted with $Et_2O$ (3×20 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by chromatography on a silica gel column.

Butanone **6aa**, 3-hexanone **6ba**, 1-phenyl-1-propanone **6ca**, 2-pentanone **6ac**, 4-heptanone **6bc**, 1-phenyl-1-butanone **6cc**, 2-nonanone **6ad**, 4-undecanone **6bd**, 1-phenyl-1-octanone **6cd**, 5-phenyl-2-pentanone **6ae**, 1,4-diphenyl-1-butanone **6ce**, 5-methyl-2-hexanone **6af**, 7-methyl-4-octanone **6bf**, 4-methyl-1-phenyl-1-pentanone **6cf**, are commercially available. They were characterized by a comparison of their spectral data with those authentic samples.

The compounds 2-butanone-*4*-$d_1$ **6ab**,[11] 1-phenyl-1-propanone-*3*-$d_1$ **6cb**,[12] 1-phenyl-4-heptanone **6be**,[13] 5-methoxy-2-pentanone **6ag**,[14] 4-methoxy-1-phenyl-1-butanone **6cg**,[15] 6-hepten-2-one **6ah**,[16] 8-nonen-4-one **6bh**,[17] 1-phenyl-5-hexen-1-one **6ch**,[18] have already been reported and were identified by NMR, IR, and MS spectra.

All new compounds are characterized below.

**4.8.1. 3-Hexanone-1-$d_1$ 6bb.** Yield: 78%; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2966, 2930, 2876, 2254, 1712, 1458, 1413 and 1381; $^1$H NMR ($CDCl_3$): $\delta_H$=0.91 (t, $^3J_{H-H}$=7.3 Hz, 3H, $CH_3$–$CH_2$–$CH_2$–CO), 0.99–1.08 (m, 2H, CO–$CH_2$–$CH_2$–D), 1.53–1.68 (m, 2H, $CH_3$–$CH_2$–$CH_2$–CO), 2.38 (t, $^3J_{H-H}$=7.1 Hz, 2H, $CH_3$–$CH_2$–$CH_2$–CO), 2.44 (t, $^3J_{H-H}$=7.1 Hz, 2H, CO–$CH_2$–$CH_2$–D); $^{13}$C NMR ($CDCl_3$): $\delta_C$=7.4 (t, $^3J_{H-H}$=19.5 Hz, CO–$CH_2$–$CH_2$–D), 13.9 ($CH_3$–$CH_2$–$CH_2$–CO), 17.2 ($CH_3$–$CH_2$–$CH_2$–CO), 35.6 (CO–$CH_2$–$CH_2$D), 44.1 ($CH_3$–$CH_2$–$CH_2$–CO), 211.5 (C═O).

**4.8.2. 1-Methoxy-4-heptanone 6bg.** Yield: 76%; bp 76°C/30 mmHg; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2961, 2932, 2875, 2828, 1713, 1459, 1412, 1374 and 1120; $^1$H NMR ($CDCl_3$): $\delta_H$=0.91 (t, $^3J_{H-H}$=7.2 Hz, 3H, $CH_3$–$CH_2$–$CH_2$–CO), 1.52–1.68 (m, 2H, $CH_3$–$CH_2$–$CH_2$–CO), 1.78–1.90 (m, 2H, $CH_2$–$CH_2$–O–$CH_3$), 2.38 (t, $^3J_{H-H}$=7.3 Hz, 2H, $CH_3$–$CH_2$–$CH_2$–CO), 2.48 [d, $^3J_{H-H}$=7.1 Hz, 2H, C(O)–$CH_2$–$CH_2$–$CH_2$–O–$CH_3$], 3.31 (s, 3H, O–$CH_3$), 3.37 (t, $^3J_{H-H}$=6.1 Hz, 2H, $CH_2$–O–$CH_3$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.6 ($CH_3$–$CH_2$–$CH_2$–CO), 17.2 ($CH_3$–$CH_2$–$CH_2$–CO), 23.6 ($CH_2$–$CH_2$–$CH_2$), 39.1 [C(O)–$CH_2$–$CH_2$–$CH_2$–O–$CH_3$], 44.7 ($CH_3$–$CH_2$–$CH_2$–CO), 58.3 (O–$CH_3$), 71.6 ($CH_2$–O–$CH_3$), 210.7 (C═O).

### 4.9. Typical procedure for the preparation of monosulfanylenephosphoramides 7

To a stirred solution of phosphoramide **4** (4.5 mmol) in THF (15 ml) at −50°C under inert atmosphere was added a solution of *n*-butyllithium (2.0 ml, 5 mmol, 2.5 M in hexane). After stirring for 10 min (1 h for **4b**) at this temperature, 1.15 equiv. of dimethyldisulfide (or *S*-methyl-methanethiosulfonate) was added. The mixture was stirred for another hour at −50°C and then allowed to warm to room temperature where it was rapidly hydrolysed with 15 ml of a NaCl saturated solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure.

**4.9.1. [(4-Methylsulfanyl-2-buten-2-yl)]pentamethyl phosphoric triamide 7a.** Yield: 60% ($MeSSO_2Me$) and 64% (MeSSMe); yellow oil; IR (NaCl plates, cm$^{-1}$):

$\nu_{max}$=2915, 2837, 2803, 1662, 1458, 1375 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=1.89–1.90 [m, 3H, C*H*$_3$–C(N)=CH], 2.11 (s, 3H, S–C*H*$_3$), 2.68 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.77 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Ph)=CH], 3.26 (d, $^3J_{H-H}$=7.5 Hz, 2H, C*H*$_2$–S–CH$_3$), 5.32 [t, $^3J_{H-H}$=7.5 Hz, 1H, C(Me)=C*H*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=15.4 (S–*C*H3), 21.0 [*C*H$_3$–C(N)=CH], 30.9 (*C*H$_2$–S–CH$_3$), 36.0 [d, $^2J_{C-P}$=2.4 Hz, *C*H$_3$–N–C(Me)=CH], 36.9 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 123.0 [d, $^3J_{C-P}$=6.1 Hz, C(Me)=*C*H], 140.6 [*C*(Me)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.83.

**4.9.2. [(1-Methylsulfanyl-2-hexen-3-yl)]pentamethyl phosphoric triamide 7b.** Yield: 56% ($MeSSO_2Me$) and 79% (MeSSMe); Yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2950, 2916, 2868, 2803, 1655, 1458 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.95 (t, $^3J_{H-H}$=7.3 Hz, 3H, C*H*$_3$–CH$_2$–CH$_2$), 1.46–1.62 (m, 2H, CH$_3$–C*H*$_2$–CH$_2$), 2.11 (s, 3H, S–C*H*$_3$), 2.19 (t, $^3J_{H-H}$=7.5 Hz, 2H, CH$_3$–CH$_2$–C*H*$_2$), 2.67 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.79 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Pr)=CH], 3.28 (dd, $^3J_{H-H}$=7.3 Hz and $^5J_{H-H}$=0.9 Hz, 2H, C*H*$_2$–S–CH$_3$), 5.29 [td, $^3J_{H-H}$=7.3 Hz and $^4J_{H-H}$=0.8 Hz, 1H, C(Pr)=C*H*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.6 (*C*H$_3$–CH$_2$–CH$_2$), 15.1 (S–*C*H$_3$), 20.4 (CH$_3$–*C*H$_2$–CH$_2$), 30.6 (*C*H$_2$–S–CH$_3$), 36.7 [d, $^2J_{C-P}$=3.7 Hz, *C*H$_3$–N–C(Me)=CH and [(*C*H$_3$)$_2$N]$_2$PO], 37.4 (CH$_3$–CH$_2$–*C*H$_2$), 121.2 [d, $^3J_{C-P}$= 4.9 Hz, C(Pr)=*C*H], 144.7 [*C*(Pr)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.70.

**4.9.3. [(3-Methylsulfanyl-1-phenyl-1-propen-1-yl)]pentamethyl phosphoric triamide 7c.** Yield: 100% ($MeSSO_2Me$) and 74% (MeSSMe); pale yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3056, 2917, 2804, 1633, 1603, 1490, 1446 and 1299; $^1$H NMR ($CDCl_3$): $\delta_H$=2.18 (s, 3H, S–C*H*$_3$), 2.61 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.89 [d, $^3J_{H-P}$=8.3 Hz, 3H, C*H*$_3$–N–C(Ph)=CH], 3.52 (dd, $^3J_{H-H}$=7.7 Hz and $^5J_{H-P}$=1.7 Hz, 2H, C*H*$_2$–S–CH$_3$), 5.81 [td, $^3J_{H-H}$=7.7 Hz and $^4J_{H-P}$=1.6 Hz, 1H, C(Ph)=C*H*], 7.26–7.53 (m, 5H, *Ph*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=15.3 (S–*C*H$_3$), 31.4 (*C*H$_2$–S–CH$_3$), 37.4 [d, $^2J_{C-P}$=2.8 Hz, *C*H$_3$–N–C(Ph)=CH], 36.8 [d, $^2J_{C-P}$=1.8 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 123.8 [d, $^3J_{C-P}$=4.8 Hz, C(Ph)=*C*H], 126.5, 127.6, 128.0 (*C*$^2$, *C*$^3$, *C*$^4$ of *Ph*), 139.4 (*C*$^1$ of *Ph*), 144.1 [*C*(Ph)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.99; MS ($EI^+$) *m/z* calculated for $C_{15}H_{26}N_3OPS$ $[M]^+$ 327.4 found 326 $[[M-1]^+$, 5%], 280 $[[M-SCH_3]^+$, 30%], 192 $[[M-(Me_2N)_2PO]^+$, 5%), 135 $[[(Me_2N)_2PO]^+$, 100%].

### 4.10. Typical procedure for the preparation of dithiocetal enephosphoramides 8

*Procedure A*. To a stirred solution of phosphoramide **7** (4.5 mmol) in THF (15 ml) at −50°C under inert atmosphere was added 2.0 ml (5 mmol, 1.1 equiv.) of a 2.5 M *n*-butyllithium solution in hexane. After stirring for 10 min for **7a** or for 1 h for **7b** at −50°C, 1.15 equiv. of dimethyldisulfide was added. The mixture was stirred for another hour at −50°C and then allowed to warm to room temperature where it was rapidly hydrolysed with 15 ml of a NaCl saturated solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford a mixture of **5**, **8** and **9**, with **8** as the major product. *Procedure B*: To a stirred solution of phosphoramide **4a-b** (4.5 mmol) in THF (15 ml) at −50°C under nitrogen atmosphere was added 1.9 ml (4.95 mmol, 1.05 equiv.) of a 2.5 M *n*-butyllithium solution in hexane. After stirring for 10 min (with **4a**) or 1 h (with **4b**), 466 mg (1.1 equiv.) of dimethyldisulfide was added. The mixture was stirred 1 h at −50°C and supplementary 1.9 ml (4.95 mmol, 1.05 equiv.) of a 2.5 M *n*-butyllithium solution in hexane was added. The mixture was then stirred 10 min (for **4a**) or 1 h (for **4b**) and additionnal 466 mg (1.1 equiv.) of dimethyldisulfide were added. After stirring 1 h at −50°C the solution was rapidly hydrolysed at this temperature with 15 ml of a NaCl saturated solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford as a yellow oil a mixture of **5**, **8** and **9**, with **8** as the major product.

### 4.11. Obtention of dithiocetal enephosphoramide 8 as a practically pure crude product

To a stirred solution of a mixture **5aa/8a/9a** (5/58/37) or **5ba/8b/9b** (8/64/28) obtained with the procedure B (4.0 mmol) in THF (15 ml) at −50°C under inert atmosphere was added 1.8 ml (4.5 mmol) of a 2.5 M *n*-butyllithium solution in hexane. After stirring at −50°C for 5 min (**a**), or 1 h (**b**) the mixture was hydrolysed with 15 ml of a NaCl saturated aqueous solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$), and the solvent was removed under reduce pressure to yield crude **8a** or **8b** accompanied with small amounts of **5aa** (5%) or **5ba** (8%).

**4.11.1. [(1,1-Dimethylsulfanyl-2-buten-3-yl)]pentamethyl phosphoric triamide 8a.** Yield: 90%; yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2916, 2837, 2805, 1654, 1456, 1435, 1376 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=1.91–1.92 [m, 3H, C*H*$_3$–C(N)=CH], 2.16 (s, 6H, 2×S–C*H*$_3$), 2.69 [d, $^3J_{H-P}$= 9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.84 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Ph)=CH], 4.77 [d, $^3J_{H-H}$=10.7 Hz, 1H, C*H*–(S–Me)$_2$], 5.28 [d, $^3J_{H-H}$=10.7 Hz, 1H, C(Me)=C*H*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=12.9 (S–*C*H3), 20.9 [*C*H$_3$–C(N)=CH], 36.0 [d, $^2J_{C-P}$=2.4 Hz, *C*H$_3$–N–C(Me)=CH], 36.7 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 48.2 [*C*H(S–Me)$_2$], 123.8 [d, $^3J_{C-P}$=6.1 Hz, C(Me)=*C*H], 140.0 [*C*(Me)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.43.

**4.11.2. [(1,1-Dimethylsulfanyl-2-hexen-3-yl)]pentamethyl phosphoric triamide 8b.** Yield: 92%; yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2955, 2917, 2873, 2803, 1648, 1458 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.95 (t, $^3J_{H-H}$=7.3 Hz, 3H, C*H*$_3$–CH$_2$–CH$_2$), 1.46–1.61 (m, 2H, CH$_3$–C*H*$_2$–CH$_2$), 2.17 (s, 6H, 2×S–C*H*$_3$), 2.21 (t, $^3J_{H-H}$=7.5 Hz, 2H, CH$_3$–CH$_2$–C*H*$_2$), 2.69 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.87 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Pr)=CH], 4.78 [d, $^3J_{H-H}$=10.3 Hz, 1H, C*H*(SMe)$_2$], 5.24 [d, $^3J_{H-H}$=10.3 Hz, 1H, C(Pr)=C*H*); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.1 (S–*C*H$_3$), 13.7 (*C*H$_3$–CH$_2$–CH$_2$), 20.5 (CH$_3$–*C*H$_2$–CH$_2$), 36.7 [d, $^2J_{C-P}$=3.7 Hz, *C*H$_3$–N–C(Pr)=CH and [(*C*H$_3$)$_2$N]$_2$PO], 37.7 (CH$_3$–CH$_2$–*C*H$_2$), 48.4 [*C*H(SMe)$_2$], 122.4 [d, $^3J_{C-P}$=4.9 Hz, C(Pr)=*C*H], 144.2 [*C*(Pr)=CH]; $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.33.

### 4.12. Typical procedure for the preparation of dithiocetal enephosphoramide 8′as a practically pure crude product

To a stirred solution of a mixture **5aa/8a/9a** (5/58/37) or **5ba/8b/9b** (8/64/28) obtained with the procedure B (4.0 mmol) in THF (15 ml) at −50°C under inert atmosphere was added 1.8 ml (4.5 mmol) of a 2.5 M *n*-butyllithium solution in hexane. After stirring for 5 min at −50°C (**a**), or 1 h (**b**) iodomethane (735 mg, 5 mmol) was added. The mixture was stirred 3 h at −50°C and rapidly hydrolysed at this temperature with 15 ml of a NaCl saturated aqueous solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford as a yellow oil **8′a** or **8′b** accompanied with small amounts of **5aa** (5%) or **5ba** (8%).

**4.12.1. (4,4-Dimethylsulfanyl-2-penten-2-yl) pentamethyl phosphoric triamide 8′a.** Yield: 94%; yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2919, 2867, 2805, 1647, 1458, 1428 and 1298; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.92 [s, 3H, CH–C(SMe)$_2$–C$H_3$], 1.94–1.97 (m, 3H, C$H_3$–C(N)=CH], 2.10 [s, 6H, CH–C(SC$H_3$)$_2$–Me], 2.69 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.84 [d, $^3J_{H-P}$=9.5 Hz, 3H, C$H_3$–N–C(Me)=CH], 5.32 [d, $^4J_{H-P}$=1.2 Hz, 1H, C(Me)=C*H*]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=12.4 [CH–C(S*C*H$_3$)$_2$–Me], 22.3 [*C*H$_3$–C(N)=CH], 25.6 [CH–C(SMe)$_2$–*C*H$_3$], 36.4 [d, $^2J_{C-P}$=3.5 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 36.9 [*C*H$_3$–N–C(Me)=CH], 56.2 [CH–*C*(SMe)$_2$–CH$_3$], 127.6 [d, $^3J_{C-P}$=7.3 Hz, C(Me)=*C*H], 139.7 [*C*(Me)=CH]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.57; MS ($EI^+$) *m/z* calculated for $C_{12}H_{28}N_3OPS_2$ $[M]^+$ 325.5 found 278 [[M−SMe]$^+$, 34%], 135 [[(Me$_2$N)$_2$PO]$^+$, 100%].

**4.12.2. [(2,2-Dimethylsulfanyl-3-hepten-4-yl)]pentamethyl phosphoric triamide 8′b.** Yield: 94%; yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2950, 2917, 2873, 2804, 1643, 1485, 1455 and 1297; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.95 (t, $^3J_{H-H}$=7.1 Hz, 3H, C$H_3$–CH$_2$–CH$_2$), 1.47–1.62 (m, 2H, CH$_3$–C$H_2$–CH$_2$), 1.92 [s, 3H, CH–C(SMe)$_2$–C$H_3$], 2.11 (s, 6H, 2×SC$H_3$), 2.25 (t, $^3J_{H-H}$=7.5 Hz, 2H, CH$_3$–CH$_2$–C$H_2$), 2.69 [d, $^3J_{H-P}$=9.1 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.88 [d, $^3J_{H-P}$=9.1 Hz, 3H, C$H_3$–N–C(Pr)=CH], 5.24 [s, 1H, C(Pr)=C*H*); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=12.4 [CH–C(S*C*H$_3$)$_2$–Me], 13.2 (*C*H$_3$–CH$_2$–CH$_2$), 21.2 (CH$_3$–*C*H$_2$–CH$_2$), 25.6 [CH–C(SMe)$_2$–*C*H$_3$], 38.8 (CH$_3$–CH$_2$–*C*H$_2$), 36.0–37.0 [*C*H$_3$–N–C(Pr)=CH and (*C*H$_3$)$_2$N]$_2$PO], 56.2 [CH–*C*(SCH$_3$)$_2$–Me], 125.8 [d, $^3J_{C-P}$=7.3 Hz, C(Pr)=*C*H], 143.5 [*C*(Pr)=CH]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.50.

### 4.13. Typical procedure for the preparation of trisulfanyl enephosphoramide 9 as a practically pure crude product

To a stirred solution of a mixture **5aa/8a/9a** (5/58/37) obtained with the procedure B (4.0 mmol) in THF (15 ml) at −50°C under inert atmosphere was added 1.8 ml (4.5 mmol) of a 2.5 M *n*-butyllithium solution in hexane. After stirring for 5 min at −50°C (**a**), or 1 h (**b**) dimethyldisulfide (400 mg, 4.2 mmol) was added. Stirring was maintained for 1 h at −50°C and then the mixture was allowed to warm to room temperature where it was hydrolysed with 15 ml of a NaCl saturated solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford as a yellow oil **9a** accompanied with small amounts of **5aa** (5%).

**4.13.1. [(1,1,1-Trimethylsulfanyl-2-buten-3-yl)]pentamethyl phosphoric triamide 9a.** Yield: 81%; yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2915, 2842, 2806, 1646, 1456, 1435, 1372, 1347 and 1299; $^1H$ NMR ($CDCl_3$): $\delta_H$=2.00–2.03 [m, 3H, C$H_3$–C(N)=CH], 2.18 (s, 9H, 3×SC$H_3$), 2.71 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.89 [d, $^3J_{H-P}$=9.1 Hz, 3H, C$H_3$–N–C(Me)=CH], 5.28 (s, 1H, C=C*H*); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.8 (S*C*H$_3$), 23.2 [*C*H$_3$–C(N)=CH], 36.7 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 37.9 [*C*H$_3$–N–C(Me)=CH], 68.1 [*C*(SCH$_3$)$_3$], 124.4 [d, $^3J_{C-P}$=8.5 Hz, C(Me)=*C*H], 142.4 [*C*(Me)=CH]; $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.91.

### 4.14. Typical procedure for the preparation of monosulfanyl ketone 11c

To a solution of enephosphoramide **7a** (4 mmol) in benzene (25 ml) was added 20 ml of a 6N aqueous solution of $H_2SO_4$. The mixture was heated at reflux for 4 h. The aqueous layer was then saturated with NaCl and extracted with $Et_2O$ (3×20 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel.

3-Methylsulfanyl-1-phenyl-1-propanone **11c** is commercially available. It was characterized by a comparison of spectral data with an authentic sample.

### 4.15. Typical procedure for the preparation of ketones 11, 12, 14, 14′ and 15

To a HCl aqueous solution (20 ml) at pH 2.00 (R=Me) or pH 1.5 (R=Pr), was added a solution of sulfanyl phosphoramides with **7**, **8**, **8′**, or **9**, is the major product (4 mmol) in $Et_2O$ (25 ml). The mixture was stirred for 4 h at room temperature whereas pH was ajusted with a few drops of HCl each hour. The aqueous layer was then saturated with NaCl and extracted with $Et_2O$ (3×15 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel.

4-Methylsulfanyl-2-butanone **11a** is commercially available. It was characterized by a comparison of spectral data with an authentic sample.

The compounds: 4,4-dimethylsulfanyl-2-butanone **12a**,[19] 1,1-dimethylsulfanyl-3-hexanone **12b**,[20] 4-methylsulfanyl-3-buten-2-one **14a**,[19] 4-methylsulfanyl-3-penten-2-one **14′a**,[21] 4,4-dimethylsulfanyl-3-buten-2-one **15a**,[22] have already been reported and were identified by NMR, IR, and MS spectra.

**4.15.1. 1-Methylsulfanyl-3-hexanone 11b.** Yield: 46% (from **7b** obtained as major product from **4b**, Table 4,

entry 4), overall yield (from **4b**): 36%; $R_f$: 0.30 (1:14 AcOEt–Hep); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2962, 2918, 2875, 1713, 1458, 1427, 1410 and 1370; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.54–1.70 (m, 2H, $CH_3$–$CH_2$–$CH_2$), 2.11 (s, 3H, S–$CH_3$), 2.41 (t, $^3J_{H-H}$=7.3 Hz, 2H, $CH_3$–$CH_2$–$CH_2$), 2.70–2.73 [m, 4H, C(O)–$CH_2$–$CH_2$]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.6 ($CH_3$–$CH_2$–$CH_2$), 15.7 (S–$CH_3$), 17.1 ($CH_3$–$CH_2$–$CH_2$), 27.9 [C(O)–$CH_2$–$CH_2$], 42.3 [C(O)–$CH_2$–$CH_2$], 44.9 ($CH_3$–$CH_2$–$CH_2$), 209.1 (C=O).

**4.15.2. 1-Methylsulfanyl-1-hexen-3-one 14b.** Yield: 48% (from **4b**); $R_f$: 0.24 (1:14 AcOEt–Hep); (*Z*/*E*: 5/95); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2961, 2930, 2873 and 1655; MS ($EI^+$) *m*/*z* calculated for $C_7H_{12}OS$ $[M]^+$ 144.2 found 144 [$[M]^+$, 5%], 101 [$[M-Pr]^+$, 100%], 73 [$[M-(Pr-CO)]^+$, 16%].

*E isomer*: $^1H$ NMR ($CDCl_3$): $\delta_H$=0.94 (t, $^3J_{H-H}$=7.4 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.58–1.73 (m, 2H, $CH_3$–$CH_2$–$CH_2$), 2.35 (s, 3H, CH=CH–S$CH_3$), 2.48 (t, $^3J_{H-H}$=7.3 Hz, 2H, $CH_3$–$CH_2$–$CH_2$), 6.04 [d, $^3J_{H-H}$=15.1 Hz, 1H, C(O)C*H*=CH–SMe], 7.69 [d, $^3J_{H-H}$=15.1 Hz, 1H, C(O)C*H*=CH–SMe]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.7 ($CH_3$–$CH_2$–$CH_2$), 14.3 (CH=CH–S$CH_3$), 17.8 ($CH_3$–$CH_2$–$CH_2$), 42.5 ($CH_3$–$CH_2$–$CH_2$), 122.1 [C(O)–*C*H=CH–SMe], 145.9 [C(O)–CH=*C*H–SMe], 196.6 (*C*=O).

*Z isomer*: $^1H$ NMR ($CDCl_3$): $\delta_H$=0.94 (t, $^3J_{H-H}$=7.4 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.58–1.73 (m, 2H, $CH_3$–$CH_2$–$CH_2$), 2.38 (s, 3H, CH=CH–S$CH_3$), 2.48 (t, $^3J_{H-H}$=7.3 Hz, 2H, $CH_3$–$CH_2$–$CH_2$), 6.30 [d, $^3J_{H-H}$=15.1 Hz, 1H, C(O)C*H*=CH–SMe], 7.02 [d, $^3J_{H-H}$=15.1 Hz, 1H, C(O)C*H*=CH–SMe]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.7 ($CH_3$–$CH_2$–$CH_2$), 14.3 (CH=CH–S$CH_3$), 17.7 ($CH_3$–$CH_2$–$CH_2$), 44.8 ($CH_3$–$CH_2$–$CH_2$), 119.7 [C(O)–*C*H=CH–SMe], 151.1 [C(O)–CH=*C*H–SMe], 199.4 (*C*=O).

**4.15.3. 2-Methylsulfanyl-2-hepten-4-one 14′b.** Yield: 92% (*E*/*Z*: 85/15) (from **8′b** obtained as major product from **4b**, Table 5); IR (KBr pellets, $cm^{-1}$): $\nu_{max}$=2959, 2921, 2872, 1676, 1425 and 1375; MS ($EI^+$) *m*/*z* calculated for $C_8H_{14}OS$ $[M]^+$ 158.3 found 158 [$[M]^+$, 12%], 143 [$[M-Me]^+$, 25%], 115 [$[M-Pr]^+$, 100%], 87 [$[M-PrCO]^+$, 30%], 71 [$[PrCO]^+$, 38%].

*Z isomer*: $R_f$: 0.57 (1:8 $Et_2O$–Pe); $^1H$ NMR ($CDCl_3$): $\delta_H$=0.94 (t, $^3J_{H-H}$=7.3 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.57–1.71 (m, 2H, $CH_3$–$CH_2$–$CH_2$), 2.30 [s, 3H, CH=C(Me)S$CH_3$], 2.40 [s, 3H, CH=C(SMe)$CH_3$], 2.41 (t, $^3J_{H-H}$=7.5 Hz, 2H, $CH_3$–$CH_2$–$CH_2$), 5.85 [s, 1H, C(O)C*H*=C]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.6 ($CH_3$–$CH_2$–$CH_2$), 14.9 [CH=C(Me)S$CH_3$], 17.8 ($CH_3$–$CH_2$–$CH_2$), 21.3 [CH=C(SMe)$CH_3$], 46.0 ($CH_3$–$CH_2$–$CH_2$), 115.5 [C(O)*C*H=C], 159.2 [CH=*C*(SMe)$CH_3$], 197.0 (*C*=O).

*E isomer*: $R_f$: 0.17 (1:8 $Et_2O$–Pe); $^1H$ NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.55–1.73 (m, 2H, $CH_3$–$CH_2$–$CH_2$), 2.23 [s, 3H, CH=C(SMe)$CH_3$], 2.33 [s, 3H, CH=C(Me)S$CH_3$], 2.39 (t, $^3J_{H-H}$=7.3 Hz, 2H, $CH_3$–$CH_2$–$CH_2$), 6.29 [s, 1H, C(O)C*H*=C]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.8 ($CH_3$–$CH_2$–$CH_2$), 14.2 [CH=C(Me)S$CH_3$], 18.0 ($CH_3$–$CH_2$–$CH_2$), 23.6 [CH=C(SMe)$CH_3$], 44.9 ($CH_3$–$CH_2$–$CH_2$), 119.9 [C(O)*C*H=C], 158.7 [CH=*C*(SMe)$CH_3$], 198.6 (*C*=O).

**4.15.4. 1,1-Dimethylsulfanyl-1-hexen-3-one 15b.** Yield: 45%; (from **9b** obtained as major product from **4b**, Table 5), $R_f$: 0.15 (1:14 AcOEt–Hep); IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=3052, 2962, 2924, 2873, 1646 and 1488; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.94 (t, $^3J_{H-H}$=7.5 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.58–1.73 (m, 2H, $CH_3$–$CH_2$–$CH_2$), 2.42 (t, $^3J_{H-H}$=7.4 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 2.44, 2.46 [CH=C($SCH_3$)$_2$], 6.03 (s, 1H, C(O)–C*H*=C(SMe)$_2$]; $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.9 ($CH_3$–$CH_2$–$CH_2$), 14.7 (CH=CH–S–$CH_3$), 17.1 (CH=CH–S–$CH_3$), 18.3 ($CH_3$–$CH_2$–$CH_2$), 45.1 ($CH_3$–$CH_2$–$CH_2$), 112.6 [C(O)–*C*H=C], 162.7 [CH=*C*(SMe)$_2$], 195.6 (*C*=O); MS ($EI^+$) *m*/*z* calculated for $C_8H_{14}OS_2$ $[M]^+$ 190.3 found 190 [$[M]^+$, 11%], 175 [$[M-Me]^+$, 20%], 147 [$[M-Pr]^+$, 100%], 143 [$[M-SMe]^+$, 11%], 71 [$[Pr-CO]^+$, 58%].

### 4.16. Typical procedure for the preparation of phosphoramides 16–20

To a stirred solution of phosphoramide **4** (4.5 mmol) in THF (20 ml) at −50°C under inert atmosphere was added 1.9 ml (1.05 equiv.) of a 2.5 M *n*-butyllithium solution in hexane. The mixture was stirred 10 min (**4a**) or 1 h (**4b**) at this temperature, followed by addition of 4.95 mmol (1.1 equiv.) of halogenoketal. The mixture was stirred 2 h at −50°C and then hydrolysed with 20 ml of a NaCl saturated aqueous solution. The aqueous layer was extracted with dichloromethane (3×20 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure.

**4.16.1. [(6,6-Dimethoxy-2-hepten-2-yl)]pentamethyl phosphoric triamide 16a.** Yield: 55 and 47% (NaI); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2991, 2940, 2882, 2842, 2803, 1668, 1457, 1376, 1297, 1110 and 1053; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.28 [s, 3H, $CH_2$–C(OMe)$_2$–$CH_3$], 1.62–1.70 [m, 2H, $CH_2$–C(OMe)$_2$–$CH_3$], 1.82–1.88 [m, 3H, $CH_3$–C(N)=CH], 2.10–2.30 (m, 2H, C=CH–$CH_2$), 2.66 [d, $^3J_{H-P}$=9.1 Hz, 12H, [($CH_3$)$_2$N]$_2$PO], 2.73 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Me)=CH], 3.17 (s, 6H, 2×$CH_3$O), 5.06–5.23 (m, 1H, C=C*H*–$CH_2$); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=20.5 [$CH_3$–C(N)=CH], 20.8 [$CH_2$–C(OMe)$_2$–$CH_3$], 22.0 [$CH_2$–C(OMe)$_2$–$CH_3$], 35.4 [d, $^2J_{C-P}$=3.7 Hz, $CH_3$–N–C(Me)=CH], 35.6 (C=CH–$CH_2$), 36.6 [[($CH_3$)$_2$N]$_2$PO], 47.6 ($CH_3$–O), 101.0 [$CH_2$–*C*(OMe)$_2$–$CH_3$], 126.0 (d, $^3J_{C-P}$=6.1 Hz, C=*C*H–$CH_2$), 138.1 (*C*=CH–$CH_2$); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.90.

**4.16.2. [(8,8-Dimethoxy-4-nonen-4-yl)] pentamethyl phosphoric triamide 16b.** Yield: 47 and 37% (NaI); yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2986, 2930, 2868, 2837, 2802, 1662, 1459, 1376, 1297, 1112 and 1053; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.29 [s, 3H, $CH_2$–C(OMe)$_2$–$CH_3$], 1.44–1.55 (m, 2H, $CH_3$–$CH_2$–$CH_2$), 1.63–1.71 [m, 2H, $CH_2$–C(OMe)$_2$–$CH_3$], 2.12–2.23 (m, 2H, $CH_2$–C=CH–$CH_2$), 2.66 [d, $^3J_{H-P}$=9.1 Hz, 12H, [($CH_3$)$_2$N]$_2$PO], 2.76 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Pr)=CH], 3.17 (s, 6H,

2×C$H_3$–O), 5.02–5.22 (m, 1 h, C═C$H$–$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.1 ($CH_3$–$CH_2$–$CH_2$), 20.0 ($CH_3$–$CH_2$–$CH_2$), 20.2 [$CH_2$–C(OMe)$_2$–$CH_3$], 21.6 (C═CH–$CH_2$–$CH_2$), 35.3 (C═CH–$CH_2$–$CH_2$), 36.0–36.5 [[($CH_3$)$_2$N]$_2$PO and $CH_3$–N–C(Pr)═CH], 37.4 ($CH_3$–$CH_2$–$CH_2$), 47.1 ($CH_3$–O), 100.5 [$CH_2$–$C$(OMe)$_2$–$CH_3$], 123.9 (d, $^3J_{C-P}$= 6.1 Hz, C═CH–$CH_2$), 141.9 (C═CH–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.83.

**4.16.3. [6-(2-Methyl-1,3-dioxolan-2-yl)-2-hexen-2-yl]pentamethyl phosphoric triamide 17a.** Yield: 91%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2981, 2930, 2879, 2804, 1670, 1457, 1376 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=1.31 [s, 3H, $CH_2$–C[O–(CH$_2$)$_2$–O]–C$H_3$], 1.35–1.41 [m, 2H, C═CH–$CH_2$–C$H_2$–(CH$_2$)$_2$–C], 1.60–1.67 [m, 2H, C═CH–(CH$_2$)$_2$–C$H_2$–$CH_2$–C], 1.80–2.00 [m, 2H, C═CH–(CH$_2$)$_2$–$CH_2$–C$H_2$–C], 1.84 [s, 3H, C$H_3$–C(N)═CH], 2.09–2.18 [m, 2H, C═CH–C$H_2$–$CH_2$–(CH$_2$)$_2$–C], 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.72 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–C(Me)═CH], 5.16 (t, $^3J_{H-H}$=6.7 Hz, 1H, C═C$H$–$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=21.1 [$CH_3$–C(N)═CH], 23.6 [$CH_2$–C[O–(CH$_2$)$_2$–O]–$CH_3$], 24.0 (C═CH–C$H_2$), 27.5 [C═CH–$CH_2$–$CH_2$–(CH$_2$)$_2$–C], 29.6 [C═CH–(CH$_2$)$_2$–$CH_2$–$CH_2$–C], 35.7 [d, $^2J_{C-P}$=3.7 Hz, $CH_3$–N–C(Me)═CH], 36.9 [d, $^2J_{C-P}$=3.7 Hz, [($CH_3$)$_2$N]$_2$PO], 39.1 [C═CH–(CH$_2$)$_2$–$CH_2$–$CH_2$–C], 64.5 (O–$CH_2$–$CH_2$–O), 110.0 [$CH_2$–C[O–(CH$_2$)$_2$–O]–$CH_3$], 126.9 (d, $^3J_{C-P}$=6.1 Hz, C═CH–$CH_2$), 138.0 (C═CH–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.09; MS (EI$^+$) *m/z* calculated for $C_{16}H_{34}N_3O_3P$ [M]$^+$ 347.4 found 347 [[M+1]$^+$, 8%], 332 [[M−Me]$^+$, 6%], 212 [[M−(Me$_2$N)$_2$PO]$^+$, 40%], 135 [[(Me$_2$N)$_2$PO]$^+$, 100%].

**4.16.4. [8-(2-Methyl-1,3-dioxolan-2-yl)-4-octen-4-yl] pentamethyl phosphoric triamide 17b.** Yield: 91%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2930, 2873, 2805, 1663, 1459, 1375, 1297 and 1066; $^1$H NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, C$H_3$–$CH_2$–$CH_2$), 1.31 [s, 3H, $CH_2$–C(O–$CH_2$–$CH_2$–O)–C$H_3$], 1.35–1.57 (m, 4H, $CH_3$–C$H_2$–$CH_2$ and C═CH–$CH_2$–C$H_2$–$CH_2$), 1.60–1.72 (m, 2H, C═CH–$CH_2$–$CH_2$–C$H_2$), 2.09–2.21 [m, 4H, C$H_2$–C(N)═CH–C$H_2$], 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.75 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–C(Pr)═CH], 3.90–3.96 (m, 4H, O–C$H_2$–C$H_2$–O), 5.12 (t, $^3J_{H-H}$=6.5 Hz, 1H, C═C$H$–$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.7 ($CH_3$–$CH_2$–$CH_2$), 20.6 ($CH_3$–$CH_2$–$CH_2$), 23.5 [$CH_2$–C(O–$CH_2$–$CH_2$–O)–$CH_3$], 23.7 (C═CH–$CH_2$–$CH_2$–$CH_2$), 27.3 (C═CH–$CH_2$–$CH_2$–$CH_2$), 36.6–36.8 [[($CH_3$)$_2$N]$_2$PO and C$H_3$–N–C(Pr)═CH], 37.9 ($CH_3$–$CH_2$–$CH_2$), 38.9 (C═CH–$CH_2$), 64.3 (O–$CH_2$–$CH_2$–O), 109.7 [$CH_2$–$C$(O–$CH_2$–$CH_2$–O)–$CH_3$], 124.9 (d, $^3J_{C-P}$= 9.1 Hz, C═CH–$CH_2$), 142.3 (C═CH–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.01.

**4.16.5. [8-(8,8-Diethoxy-2-nonen-2-yl)pentamethyl phosphoric triamide 18a.** Yield: 91%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2971, 2931, 2873, 2805, 1669, 1456, 1375, 1297 and 1058; $^1$H NMR ($CDCl_3$): $\delta_H$=1.16 (t, $^3J_{H-H}$=7.0 Hz, 6H, 2×C$H_3$–$CH_2$–O), 1.27 [s, 3H, $CH_2$–C(OEt)$_2$–C$H_3$], 1.28–1.39 [m, 4H, C═CH–$CH_2$–(C$H_2$)$_2$–$CH_2$], 1.54–1.67 [m, 2H, C═CH–(CH$_2$)$_3$–C$H_2$], 1.84 [s, 3H, C$H_3$–C(N)═CH], 2.04–2.18 (m, 2H, C═CH–C$H_2$), 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.72 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–C(Me)═CH], 3.35–3.52 (m, 4H, 2×$CH_3$–C$H_2$–O), 5.15 (t, $^3J_{H-H}$=7.0 Hz, 1H, C═C$H$–$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=15.1 (2×$CH_3$–$CH_2$–O), 20.9 [$CH_3$–C(N)═CH], 21.7 [$CH_2$–C(OEt)$_2$–$CH_3$], 24.0 [C═CH–(CH$_2$)$_2$–$CH_2$–$CH_2$], 27.2 [C═CH–$CH_2$–$CH_2$–(CH$_2$)$_2$], 29.4 [C═CH–(CH$_2$)$_3$–$CH_2$], 35.5 [d, $^2J_{C-P}$=3.7 Hz, $CH_3$–N–C(Me)═CH], 36.6 [d, $^2J_{C-P}$=3.7 Hz, [($CH_3$)$_2$N]$_2$PO], 37.1 (C═CH–$CH_2$), 55.0 (2×$CH_3$–$CH_2$–O), 101.0 [$CH_2$–$C$(OEt)$_2$–$CH_3$], 126.6 (d, $^3J_{C-P}$=6.1 Hz, C═CH–$CH_2$), 137.7 (C═CH–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.08; MS (EI$^+$) *m/z* calculated for $C_{18}H_{40}N_3O_3P$ [M]$^+$ 377.5 found 362 [[M−Me]$^+$, 4%], 332 [[M−EtO]$^+$, 53%], 135 [[(Me$_2$N)$_2$PO]$^+$, 100%].

**4.16.6. (10,10-Diethoxy-4-undecen-4-yl)pentamethyl phosphoric triamide 18b.** Yield: 76%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2929, 2868, 2804, 1662, 1457, 1374, 1297 and 1058; $^1$H NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, C$H_3$–$CH_2$–$CH_2$), 1.16 (t, $^3J_{H-H}$= 7.1 Hz, 6H, 2×C$H_3$–$CH_2$–O), 1.28 [s, 3H, $CH_2$–C(OEt)$_2$–C$H_3$], 1.28–1.67 [m, 8H, $CH_3$–C$H_2$–$CH_2$ and C═CH–$CH_2$–(C$H_2$)$_3$], 2.08–2.19 [m, 4H, C$H_2$–C(N)═CH–C$H_2$], 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.75 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–C(Pr)═CH], 3.35–3.53 (m, 4H, 2×$CH_3$–C$H_2$–O), 5.12 (t, $^3J_{H-H}$=6.9 Hz, 1H, C═C$H$–$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.6 ($CH_3$–$CH_2$–$CH_2$), 15.1 (2×$CH_3$–$CH_2$–O), 20.6 ($CH_3$–$CH_2$–$CH_2$), 21.7 [$CH_2$–C(OEt)$_2$–$CH_3$], 24.1 [C═CH–(CH$_2$)$_2$–$CH_2$–$CH_2$], 27.2 [C═CH–$CH_2$–$CH_2$–(CH$_2$)$_2$], 29.5 [C═CH–(CH$_2$)$_3$–$CH_2$], 36.5 [d, $^2J_{C-P}$= 3.7 Hz, $CH_3$–N–C(Pr)═CH], 36.7 [d, $^2J_{C-P}$=3.7 Hz, [($CH_3$)$_2$N]$_2$PO], 37.2 (C═CH–$CH_2$), 37.9 ($CH_3$–$CH_2$–$CH_2$), 55.1 (2×$CH_3$–$CH_2$–O), 101.1 [$CH_2$–$C$(OEt)$_2$–$CH_3$], 125.0 (d, $^3J_{C-P}$=6.1 Hz, C═CH–$CH_2$), 141.9 (C═CH–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$= 18.04; MS (EI$^+$) *m/z* calculated for $C_{20}H_{44}N_3O_3P$ [M]$^+$ 405.6 found 360 [[M−OEt]$^+$, 10%], 270 [[M−(Me$_2$N)$_2$PO]$^+$, 4%], 135 [[(Me$_2$N)$_2$PO]$^+$, 100%].

**4.16.7. [7-(2-Methyl-1,3-dioxolan-2-yl)-2-hepten-2-yl]-pentamethyl phosphoric triamide 19a.** Yield: 91%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2981, 2930, 2879, 2804, 1670, 1457, 1376 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=1.31 [s, 3H, $CH_2$–C[O–(CH$_2$)$_2$–O]–C$H_3$], 1.35–1.41 [m, 2H, C═CH–$CH_2$–C$H_2$–(CH$_2$)$_2$–C], 1.60–1.67 [m, 2H, C═CH–(CH$_2$)$_2$–C$H_2$–$CH_2$–C], 1.80–2.00 [m, 2H, C═CH–(CH$_2$)$_2$–$CH_2$–C$H_2$–C], 1.84 [s, 3H, C$H_3$–C(N)═CH], 2.09–2.18 [m, 2H, C═CH–C$H_2$–$CH_2$–(CH$_2$)$_2$–C], 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C$H_3$)$_2$N]$_2$PO], 2.72 [d, $^3J_{H-P}$=8.7 Hz, 3H, C$H_3$–N–C(Me)═CH], 5.16 (t, $^3J_{H-H}$=6.7 Hz, 1H, C═C$H$–$CH_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=21.1 [$CH_3$–C(N)═CH], 23.6 [$CH_2$–C[O–(CH$_2$)$_2$–O]–$CH_3$], 24.0 (C═CH–C$H_2$), 27.5 [C═CH–$CH_2$–$CH_2$–(CH$_2$)$_2$–C], 29.6 [C═CH–(CH$_2$)$_2$–$CH_2$–$CH_2$–C], 35.7 [d, $^2J_{C-P}$=3.7 Hz, $CH_3$–N–C(Me)═CH], 36.9 [d, $^2J_{C-P}$=3.7 Hz, [($CH_3$)$_2$N]$_2$PO], 39.1 [C═CH–(CH$_2$)$_2$–$CH_2$–$CH_2$–C], 64.5 (O–$CH_2$–$CH_2$–O), 110.0 [$CH_2$–$C$[O–(CH$_2$)$_2$–O]–$CH_3$], 126.9 (d, $^3J_{C-P}$=6.1 Hz, C═CH–$CH_2$), 138.0 (C═CH–$CH_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.09; MS (EI$^+$) *m/z* calculated for $C_{16}H_{34}N_3O_3P$ [M]$^+$ 347.4 found 347 [[M+1]$^+$,

8%], 332 [[M−Me]$^+$, 6%], 212 [[M−$(Me_2N)_2PO$]$^+$, 40%], 135 [[$(Me_2N)_2PO$]$^+$, 100%].

**4.16.8. [9-(2-Methyl-1,3-dioxolan-2-yl)-4-nonen-4-yl]-pentamethyl phosphoric triamide 19b.** Yield: 85%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2932, 2868, 2803, 1663, 1458, 1375 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, C*H*$_3$–CH$_2$–CH$_2$), 1.31 [s, 3H, CH$_2$–C[O–(CH$_2$)$_2$–O]–C*H*$_3$], 1.38–1.70 [m, 6H, C=CH–CH$_2$–(C*H*$_2$)$_3$], 1.43–1.58 [m, 2H, CH$_3$–C*H*$_2$–CH$_2$), 2.07–2.20 [m, 4H, C*H*$_2$–C(N)=CH–C*H*$_2$], 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.75 [d, $^3J_{H-P}$= 8.7 Hz, 3H, C*H*$_3$–N–C(Pr)=CH], 3.89–3.96 (m, 4H, O–C*H*$_2$–C*H*$_2$–O), 5.12 (t, $^3J_{H-H}$=6.9 Hz, 1H, C=C*H*–CH$_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.7 (*C*H$_3$–CH$_2$–CH$_2$), 20.7 (CH$_3$–*C*H$_2$–CH$_2$), 23.6 [CH$_2$–C[O–(CH$_2$)$_2$–O]–*C*H$_3$], 24.0 [C=CH–(CH$_2$)$_2$–*C*H$_2$–CH$_2$], 27.3 [*C*H$_2$–C[O–(CH$_2$)$_3$–O]–CH$_3$], 29.6 [C=CH–CH$_2$–*C*H$_2$–(CH$_2$)$_2$], 36.8–36.9 [*C*H$_3$–N–C(Pr)=CH and [(*C*H$_3$)$_2$N]$_2$PO], 38.0 (CH$_3$–CH$_2$–*C*H$_2$), 39.0 (C=CH–*C*H$_2$), 64.4 (O–*C*H$_2$–*C*H$_2$–O), 109.8 [CH$_2$–*C*[O–(CH$_2$)$_2$–O]–CH$_3$], 125.0 (d, $^3J_{C-P}$=4.9 Hz, C=*C*H–CH$_2$), 142.2 (*C*=CH–CH$_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.02; MS (EI$^+$) *m/z* calculated for $C_{18}H_{38}N_3O_3P$ [M]$^+$ 375.5 found 375 [[M]$^+$, 22%], 360 [[M−Me]$^+$, 29%], 332 [[M−Pr]$^+$, 29%], 240 [[M−$(Me_2N)_2PO$]$^+$, 72%].

**4.16.9. [(7-(2-Methyl-1,3-dioxan-2-yl)-2-hepten-2-yl]-pentamethyl phosphoric triamide 20a.** Yield: 70%; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2924, 2868, 2805, 1670, 1458, 1374, 1297 and 1211; $^1$H NMR ($CDCl_3$): $\delta_H$=1.37 [s, 3H, CH$_2$–C[O–(CH$_2$)$_3$–O]–C*H*$_3$], 1.52–1.95 [m, 8H, C=CH–CH$_2$–(C*H*$_2$)$_3$–C and O–CH$_2$–C*H*$_2$–CH$_2$–O], 1.85 [s, 3H, C*H*$_3$–C(N)=CH], 2.00–2.17 (m, 2H, C=CH–C*H*$_2$), 2.67 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.72 [d, $^3J_{H-P}$=8.7 Hz, 3H, C*H*$_3$–N–C(Me)=CH], 3.81–3.99 (m, 4H, O–C*H*$_2$–CH$_2$–C*H*$_2$–O), 5.16 (t, $^3J_{H-H}$=6.7 Hz, 1H, C=C*H*–CH$_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=20.6 [*C*H$_3$–C(N)=CH], 21.0 [CH$_2$–C[O–(CH$_2$)$_3$–O]–*C*H$_3$], 23.3 (C=CH–*C*H$_2$), 25.3 [*C*H$_2$–C[O–(CH$_2$)$_3$–O]–CH$_3$], 27.4 (C=CH–CH$_2$–*C*H$_2$), 29.6 [C=CH–CH$_2$–*C*H$_2$–(CH$_2$)$_2$–C], 36.8 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 36.9 [d, $^2J_{C-P}$=3.7 Hz, *C*H$_3$–N–C(Me)=CH], 38.0 (O–CH$_2$–*C*H$_2$–CH$_2$–O), 59.5 (O–*C*H$_2$–CH$_2$–*C*H$_2$–O), 99.0 [CH$_2$–*C*[O–(CH$_2$)$_3$–O]–Me], 126.8 (d, $^3J_{C-P}$=6.1 Hz, C=*C*H–CH$_2$), 137.9 (*C*=CH–CH$_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.01; MS (EI$^+$) *m/z* calculated for $C_{17}H_{36}N_3O_3P$ [M]$^+$ 361.4 found 362 [[M+1]$^+$, 8%], 346 [[M−Me]$^+$, 4%], 135 [[$(Me_2N)_2PO$]$^+$, 100%], 101 [[C(O–(CH$_2$)$_3$–O)–Me]$^+$, 44%].

**4.16.10. [9-(2-Methyl-1,3-dioxan-2-yl)-4-nonen-4-yl]pentamethyl phosphoric triamide 20b.** Yield: 60%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2955, 2935, 2863, 2805, 1664, 1459, 1371 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.93 (t, $^3J_{H-H}$=7.3 Hz, 3H, C*H*$_3$–CH$_2$–CH$_2$), 1.38 [s, 3H, CH$_2$–C[O–(CH$_2$)$_3$–O]–C*H*$_3$], 1.45–1.95 [m, 10H, C=CH–CH$_2$–(C*H*$_2$)$_3$, CH$_3$–C*H*$_2$–CH$_2$ and O–CH$_2$–C*H*$_2$–CH$_2$–O], 2.10–2.20 [m, 4H, C*H*$_2$–C(N)=CH–C*H*$_2$], 2.66 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.75 [d, $^3J_{H-P}$= 9.5 Hz, 3H, C*H*$_3$–N–C(Pr)=CH], 3.82–3.99 (m, 4H, O–C*H*$_2$–CH$_2$–C*H*$_2$–O), 5.12 (t, $^3J_{H-H}$=7.1 Hz, 1H, C=C*H*–CH$_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.7 (*C*H$_3$–CH$_2$–CH$_2$), 20.5 [CH$_2$–C[O–(CH$_2$)$_3$–O]–*C*H$_3$], 20.7 (CH$_3$–*C*H$_2$–CH$_2$), 23.3 (C=CH–*C*H$_2$), 25.3 (O–CH$_2$–*C*H$_2$–CH$_2$–O), 27.4 [*C*H$_2$–C[O–(CH$_2$)$_3$–O]–CH$_3$], 29.7 [C=CH–CH$_2$–*C*H$_2$–(CH$_2$)$_2$], 36.8–37.0 [*C*H$_3$–N–C(Pr)=CH and [(*C*H$_3$)$_2$N]$_2$PO], 37.9 (C=CH–*C*H$_2$), 38.0 (CH$_3$–CH$_2$–*C*H$_2$), 59.4 (O–*C*H$_2$–CH$_2$–*C*H$_2$–O), 98.9 [CH$_2$–*C*[O–(CH$_2$)$_3$–O]–CH$_3$], 125.0 (d, $^3J_{C-P}$=4.9 Hz, C=*C*H–CH$_2$), 142.1 (*C*=CH–CH$_2$); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=18.00; MS (EI$^+$) *m/z* calculated for $C_{19}H_{40}N_3O_3P$ [M]$^+$ 389.5 found 390 [[M+1]$^+$, 16%], 374 [[M−Me]$^+$, 33%], 135 [[$(Me_2N)_2PO$]$^+$, 100%].

## 4.17. Typical procedure for the preparation of ketone phosphoramides 21,22

To 20 ml of a HCl aqueous solution at pH 5.00 [Y=$(OMe)_2$] or pH=4.00 [Y=$(OEt)_2$], was added a solution of phosphoramide **16** or **18** (4 mmol) in $Et_2O$ (25 ml). The mixture was stirred for 4 h at room temperature and pH was monitored and adjusted each hour. The aqueous layer was then saturated with NaCl and extracted with dichloromethane (3×15 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure.

**4.17.1. (2-Oxo-5-hepten-6-yl)pentamethyl phosphoric triamide 21a.** Yield: 46%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2991, 2887, 2848, 2804, 1713, 1670, 1374 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=1.74–1.80 [m, 3H, C*H*$_3$–C(N)=CH], 2.07 (s, 3 h, CO–C*H*$_3$), 2.23–2.38 (m, 2H, C=CH–C*H*$_2$), 2.43–2.54 (C*H*$_2$–CO–CH$_3$), 2.60 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.67 [d, $^3J_{H-P}$= 8.7 Hz, 3H, C*H*$_3$–N–C(Me)=CH], 5.02–5.16 (m, 1H, C=C*H*–CH$_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=20.75 [*C*H$_3$–C(N)=CH), 21.3 (C=CH–*C*H$_2$), 29.8 (CO–*C*H$_3$), 35.4 [*C*H$_3$–N–C(Me)=CH], 36.5 [d, $^2J_{C-P}$=3.7 Hz, [(*C*H$_3$)$_2$N]$_2$PO], 42.7 (*C*H$_2$–CO–CH$_3$), 124.8 (d, $^3J_{C-P}$= 6.1 Hz, C=*C*H–CH$_2$), 138.6 (*C*=CH–CH$_2$), 208.4 (*C*=O); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.66; MS (EI$^+$) *m/z* calculated for $C_{12}H_{26}N_3O_2P$ [M]$^+$ 275.3 found 275 [[M]$^+$, 16%], 232 [[M−$COCH_3$]$^+$, 26%], 140 [[M−$(Me_2N)_2PO$]$^+$, 39%], 135 [[$(Me_2N)_2PO$]$^+$, 100%].

**4.17.2. (2-Oxo-5-nonen-6-yl)pentamethyl phosphoric triamide 21b.** Yield: 39%; yellow oil; IR (NaCl plates, cm$^{-1}$): $\nu_{max}$=2990, 2960, 2929, 2874, 2804, 1716, 1664, 1458, 1363 and 1297; $^1$H NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.1 Hz, 3H, C*H*$_3$–CH$_2$–CH$_2$), 1.41–1.59 (m, 2H, CH$_3$–C*H*$_2$–CH$_2$), 2.10–2.20 (m, 2H, CH$_3$–CH$_2$–C*H*$_2$), 2.14 (s, 3H, CO–C*H*$_3$), 2.33–2.45 (m, 2H, C=CH–C*H*$_2$), 2.53 (t, $^3J_{H-H}$=7.5 Hz, 2H, C*H*$_2$–CO–CH$_3$), 2.67 [d, $^3J_{H-P}$=9.5 Hz, 12H, [(C*H*$_3$)$_2$N]$_2$PO], 2.77 [d, $^3J_{H-P}$= 8.7 Hz, 3H, C*H*$_3$–N–C(Pr)=CH], 5.05–5.28 (m, 1H, C=C*H*–CH$_2$); $^{13}$C NMR ($CDCl_3$): $\delta_C$=13.0 (*C*H$_3$–CH$_2$–CH$_2$), 20.8 (CH$_3$–*C*H$_2$–CH$_2$), 29.0 (CO–*C*H$_3$), 35.5–36.4 [C*H*$_3$–N–C(Pr)=CH and [(C*H*$_3$)$_2$N]$_2$PO], 37.0 (C=CH–*C*H$_2$), 37.3 (CH$_3$–CH$_2$–*C*H$_2$), 42.3 (*C*H$_2$–CO–CH$_3$), 122.6 (d, $^3J_{C-P}$=4.9 Hz, C=*C*H–CH$_2$), 142.4 (*C*=CH–CH$_2$), 207.2 (*C*=O); $^{31}$P NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.63.

**4.17.3. (2-Oxo-7-nonen-8-yl)pentamethyl phosphoric triamide 22a.** Yield: 91%: yellow oil; IR (NaCl plates,

$cm^{-1}$): $\nu_{max}$=2930, 2873, 2805, 1715, 1670, 1458, 1360 and 1297; $^1H$ NMR ($CDCl_3$): $\delta_H$=1.26–1.43 [m, 2H, C=CH–$CH_2$–$CH_2$–$(CH_2)_2$], 1.50–1.67 [m, 2H, C=CH–$(CH_2)_2$–$CH_2$–$CH_2$], 1.84–1.85 [m, 3H, $CH_3$–C(N)=CH], 2.11–2.17 (m, 2H, C=CH–$CH_2$), 2.13 (s, 3H, CO–$CH_3$), 2.44 (t, $^3J_{H-H}$=7.3 Hz, 2H, $CH_2$–CO–$CH_3$), 2.67 [d, $^3J_{H-P}$=9.5 Hz, 12H, $[(CH_3)_2N]_2PO$], 2.72 [d, $^3J_{H-P}$= 8.7 Hz, 3H, $CH_3$–N–C(Me)=CH], 5.15 (t, $^3J_{H-H}$= 6.9 Hz, 1H, C=C*H*–$CH_2$); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=20.6 [$CH_3$–C(N)=CH], 23.1 [C=CH–$(CH_2)_2$–$CH_2$–$CH_2$], 26.7 [C=CH–$CH_2$–$CH_2$–$(CH_2)_2$], 28.3 (C=CH–$CH_2$), 29.3 (CO–$CH_3$), 35.2 [d, $^2J_{C-P}$=3.3 Hz, $CH_3$–N–C(Me)=CH], 36.3 [d, $^2J_{C-P}$=3.1 Hz, $[(CH_3)_2N]_2PO$), 42.9 ($CH_2$–CO–$CH_3$), 126.0 (d, $^3J_{C-P}$=5.7 Hz, C=CH–$CH_2$), 137.7 (C=CH–$CH_2$), 208.2 (C=O); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.95; MS ($EI^+$) *m/z* calculated for $C_{14}H_{30}N_3O_2P$ $[M]^+$ 303.4 found 303 $[[M]^+$, 14%], 288 $[[M-Me]^+$, 4%], 168 $[[M-(Me_2N)_2PO]^+$, 72%], 135 $[[(Me_2N)_2PO]^+$, 100%].

**4.17.4. (2-Oxo-7-undecen-8-yl)pentamethyl phosphoric triamide 22b.** Yield: 76%; yellow oil; IR (NaCl plates, $cm^{-1}$): $\nu_{max}$=2930, 2868, 2803, 1716, 1663, 1456, 1362 and 1296; $^1H$ NMR ($CDCl_3$): $\delta_H$=0.92 (t, $^3J_{H-H}$=7.3 Hz, 3H, $CH_3$–$CH_2$–$CH_2$), 1.25–1.69 [m, 6H, $CH_3$–$CH_2$–$CH_2$ and C=CH–$CH_2$–$(CH_2)_2$–$CH_2$], 2.11–2.17 [m, 4H, $CH_2$–C(N)=CH–$CH_2$], 2.13 [s, 3H, $CH_2$–CO–$CH_3$], 2.67 [d, $^3J_{H-P}$=9.5 Hz, 12H, $[(CH_3)_2N]_2PO$], 2.75 [d, $^3J_{H-P}$=8.7 Hz, 3H, $CH_3$–N–C(Pr)=CH], 5.11 (t, $^3J_{H-H}$= 6.5 Hz, 1H, C=C*H*–$CH_2$); $^{13}C$ NMR ($CDCl_3$): $\delta_C$=13.1 ($CH_3$–$CH_2$–$CH_2$), 20.0 ($CH_3$–$CH_2$–$CH_2$), 22.9 [C=CH–$(CH_2)_2$–$CH_2$–$CH_2$], 26.5 [C=CH–$CH_2$–$CH_2$–$(CH_2)_2$], 28.2 (C=CH–$CH_2$), 29.0 (CO–$CH_3$), 36.0 [d, $^2J_{C-P}$= 3.7 Hz, $CH_3$–N–C(Pr)=CH], 36.2 [d, $^2J_{C-P}$=3.7 Hz, $[(CH_3)_2N]_2PO$], 37.4 ($CH_3$–$CH_2$–$CH_2$), 42.6 ($CH_2$–CO–$CH_3$), 124.1 (d, $^3J_{C-P}$=5.6 Hz, C=CH–$CH_2$), 141.8 (C=CH–$CH_2$), 207.7 (C=O); $^{31}P$ NMR (101.256 MHz, $CDCl_3$): $\delta_P$=17.92; MS ($EI^+$) *m/z* calculated for $C_{16}H_{34}N_3O_2P$ $[M]^+$ 331.4 found 331 $[[M]^+$, 15%], 196 $[[M-(Me_2N)_2PO]^+$, 36%], 135 $[[(Me_2N)_2PO]^+$, 100%].

### 4.18. Typical procedure for the preparation of diketones 23–25

To a solution of enephosphoramide **16-20** (4 mmol) in $Et_2O$ (25 ml) was added 20 ml of a 2N aqueous solution of HCl. The mixture was stirred for 4 h at room temperature. The aqueous layer was then saturated with NaCl and extracted with $Et_2O$ (3×15 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel.

The compounds 2,6-heptandione **23a**,[23] 2,6-nonandione **23b**,[24] 2,7-octandione **24a**,[25] 2,7-decandione **24b**,[26] 2,8-nonandione **25a**,[27] 2,8-undecadione 25b,[28] have already been reported and were identified by NMR, IR, and MS spectra.

## References


1. For reviews, see: (a) Ahlbrecht, H.; Beyer, U. *Synthesis* **1999**, 365–390. (b) Katrizky, A. R.; Piffl, M.; Lang, H.; Anders, E. *Chem. Rev.* **1999**, *99*, 665–722. (c) Crimmins, M. T.; Nantermet, P. G. *Org. Prep. Proced.* **1993**, *25*, 41–81. (d) Kuwajima, I.; Nakamura, E. *Top. Curr. Chem.* **1990**, *155*, 1–39. (e) Stowell, J. C. *Chem. Rev.* **1984**, *84*, 409–436. (f) Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205–268.
2. (a) Okamoto, S.; Teng, X.; Fujii, S.; Takayama, Y.; Sato, F. *J. Am. Chem. Soc.* **2001**, *123*, 3462–3471. (b) Whisler, M. C.; Soli, E. D.; Beak, P. *Tetrahedron Lett.* **2000**, *41*, 9527–9531.
3. (a) Nakamura, E.; Shimada, J.; Kuwajima, I. *Organometallics* **1985**, *4*, 641–646. (b) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368–3370. (c) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360–7362. (d) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192–7194. (e) Goswami, R.; Corcoran, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 7182–7183. (f) Goswami, R.; Corcoran, D. E. *Tetrahedron Lett.* **1982**, *23*, 1463–1466. (g) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1978**, *19*, 883–886.
4. (a) Ahlbrecht, H.; Weber, P. *Synthesis* **1992**, 1018–1025. (b) Ahlbrecht, H.; Schmitt, C.; Kornetzky, D. *Synthesis* **1991**, 637–640. (c) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932–948. (d) De Lombaert, S.; Lesur, B.; Ghosez, L. *Tetrahedron Lett.* **1982**, *23*, 4251–4254. (e) Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1980**, *102*, 5004–5011.
5. (a) Coutrot, Ph.; Grison, C.; Bomont, C. *J. Organomet. Chem.* **1999**, *586*, 208–217. (b) Coutrot, Ph.; Grison, C.; Bomont, C. *Tetrahedron Lett.* **1994**, *35*, 8381–8384. (c) Coutrot, Ph.; Grison, C.; Bomont, C. *Phosphorus Sulfur, Silicon* **1993**, *77*, 195. (d) Coutrot, Ph.; Dormoy, J. R.; Moukimou, A. *J. Organomet. Chem.* **1983**, *258*, C25–C28. (e) Coutrot, Ph.; Savignac, Ph. *J. Chem. Res. (S)* **1977**, 3401. (f) Coutrot, Ph.; Savignac, Ph. *J. Chem. Res. (M)* **1977**, 3401–3409. (g) Coutrot, Ph.; Dreux, M.; Savignac, Ph. *C.R. Acad. Sci.* **1975**, *281*, 131–133. (h) Savignac, Ph.; Coutrot, Ph.; Leroux, Y. *C.R. Acad. Sci.* **1974**, *279*, 609–611.
6. The following reaction sequence has been studied: *N*-methyl-*N*-(α-phenyl-allyl) amine was allowed to react with phosphoryl trichloride in the presence of triethylamine and yielded the expected *N*-methyl-*N*-(1-phenylprop-2-enyl)-phosphoryl dichloride (94%). Further addition of an excess of dimethylamine hydrochloride in the presence of triethylamine led to a mono chlorine substitution at the phosphorus and yielded the *N*-methyl-*N'*-dimethylamido-*N*-(1-phenylprop-2-enyl)-phosphoryl chloride (95%). Other attempts based on the reaction between lithium amide derived from *N*-methyl-*N*-(α-phenyl-allyl) amine[7] and (bis-dimethylamido) phosphoryl chloride gave a mixture of **4** and the transposed product **5** (E=H) in poor yield (50%).
7. Ficini, J.; Normant, H. *Bull. Soc. Chim. Fr.* **1957**, 1454–1458.
8. (a) Cheikh, R. B.; Chaabouni, R.; Laurent, A.; Mison, P.; Nafti, A. *Synthesis* **1983**, 685–700. (b) Overman, L. E. *J. Am. Chem. Soc.* **1976**, *98*, 2901–2910.
9. The change of a bis-dimethylamine group by an ethoxy group, or, a fortiori, the replacement of the two bis-dimethylamine groups by two ethoxy groups at phosphorus into **4**, led to phosphoramides that were not deprotonated by *n*-BuLi.
10. (a) Ahlbrecht, H.; Rauchschwalbe, G. *Synthesis* **1973**, 417. (b) Ahlbrecht, H. *Chimia* **1977**, *31*, 391–403.
11. Smadja, W.; Valéry, J. M.; Ville, G.; Bernassau, J. M. *J. Mol. Catal.* **1985**, *30*, 389–394.
12. Gazzard, L. J.; Motherwell, W. B.; Sandham, D. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 979–994.

13. Bentley, T. W.; Howle, L. M.; Wareham, P. J.; Jones, R. V. H. *Tetrahedron* **1992**, *48*, 7869–7878.
14. Osei-Twum, E. Y.; McCallion, D.; Nazran, A. S.; Panicucci, R.; Risbood, P. A.; Warkentin, J. *J. Org. Chem.* **1984**, *49*, 336–342.
15. Mihel, I.; Sistek, J.; Borcic, S.; Humski, K.; Sunko, D. E. *J. Org. Chem.* **1979**, *44*, 4091–4096.
16. Lee, P. H.; Lee, K.; Sung, S.; Chang, S. *J. Org.Chem.* **2001**, *66*, 8646–8649.
17. O'Shea, M. G.; Kitching, W. *Tetrahedron* **1989**, *45*, 1177–1186.
18. Caddick, S.; Murtagh, L.; Weaving, R. *Tetrahedron* **2000**, *56*, 9365–9373.
19. Rao, C. S.; Chakrasali, R. T.; Hiriyakkanavar, I.; Hiriyakkanavar, J. *Tetrahedron* **1990**, *46*, 2195–2204.
20. Prilezhaeva, E. N.; Mikhelashvili, I. L. *Zh. Org. Khim.* **1973**, *9*, 1129–1133, *Chem. Abstr.* 79:78306.
21. Dieter, R. K.; Silks, L. A.; Fishpaugh, J. R.; Kostner, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 4679.
22. Maignan, J.; Vialle, J. *Bull. Soc. Chim. Fr.* **1973**, 2388–2392.
23. Ross, N. C.; Levine, R. *J. Org. Chem.* **1964**, *29*, 2341–2346.
24. Ramon, D. J.; Yus, M. *J. Org. Chem.* **1991**, *56*, 3825–3831.
25. Satoh, T.; Taguchi, D.; Suzuki, C.; Fujisawa, S. *Tetrahedron* **2001**, *57*, 493–500.
26. Vaskan, R. N.; Kovalev, B. G. *Zh. Org. Khim.* **1973**, *9*, 493–496, *Chem. Abstr.* 78:158849.
27. Yamashita, M.; Matsumiya, K.; Morimoto, H.; Suemitsu, R. *Bull. Chem. Soc. Jpn* **1989**, *62*, 1668–1670.
28. Bel'skii, I. F.; Minashkina, Z. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, *10*, 2338–2343.