Imide – Amide Rearrangement of Cyclic Phosphorimidates: A Mechanistic Study

Eurico J. Cabrita, Carlos A. M. Afonso, and António Gil de Oliveira Santos*[a]

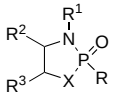
Abstract: Studies aimed at the development of new synthetic pathways for the preparation of chiral cyclic oxaza and diaza phosphoramides suitable for use in asymmetric chemistry led us to the investigation of the imide – amide rearrangement of cyclic phosphorimidates. As a result of this work new types of oligomeric organophosphorus compounds, formed by a novel 1,4-addition type ring opening polymerisation, were identified. These compounds are the stable intermediates of the imide – amide rearrangement, which upon heating yield the previously reported rearranged product. A detailed study of the mechanism of the Lewis acid catalysed imide – amide rearrangement and stereochemical control of the final products is reported. As a result, the full mechanism was elucidated and evidence of retention of configuration at the rearranged carbon atom is presented. Substituent effects were rationalised based on molecular modelling calculations.

Keywords: imide – amide rearrangement · mechanism elucidation · molecular modeling · heterocycles · polymers

Introduction

Chiral organophosphorus compounds have demonstrated an interesting behaviour over the last few years as efficient reagents in a large number of chemical transformations and applications, in addition to their known biological activity (mainly as insecticides and fungicides[1]). Of special interest are their applications in asymmetric synthesis, including their use as catalysts and ligands,[2–8] chiral auxiliaries,[9–12] and resolving agents for the determination of the optical purity of alcohols, thiols, and amines.[13]

Phosphonamides **1** and **2** with R = alkyl or aryl and phosphoramides **1** and **2** with R ≠ alkyl or aryl are the most often reported organophosphorus compounds used either as chiral auxiliaries[9–11] or as Lewis base catalysts.[3, 6, 14] The most prominent among those are the cyclic oxaza (X = O) and diaza (X = NR) phospholidin-2-ones **1** and phosphorinan-2-ones **2**.



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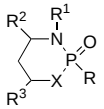

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Recently there has been a growing interest in novel phosphorus containing compounds due to their potential industrial applications as organophosphorus polymers have gained considerable interest as flame retardant additives[15–18] for commercial polymers.[17, 18] The versatility of the phosphorus atom can be used to synthesise a wide range of phosphorus containing polymers which offer an attractive combination of chemical, physical and mechanical properties, such as better resistance to extraction, migration and volatile loss. The increasing number of reports on the synthesis and property evaluation of different types of new flame retardant organophosphorus materials[17] as well as the increasing number of patented organophosphorus polymers,[18] reflects their growing importance.

Our interest in the development of new synthetic pathways for the preparation of chiral cyclic oxaza and diaza phosphoramides suitable for use in asymmetric chemistry, led us to the study of the Lewis acid catalysed imide – amide rearrangement of cyclic phosphorimidates.[19] As a result of this work, we recently reported[20] the identification of new types of oligomeric organophosphorus compounds **3** and **4** formed by a novel 1,4-addition-type ring-opening polymerisation of cyclic phosphorimidates and, for the first time, evidence of the intermolecular nature of this rearrangement. The oligomeric compound **3** was identified as being a stable intermediate which originates, upon heating, the previously reported[21] rearranged product **5**.

The similarity between the isolated oligomers and those reported in the literature as having flame retardancy properties[17] and our interest in the stereochemical control of the

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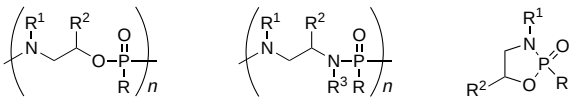


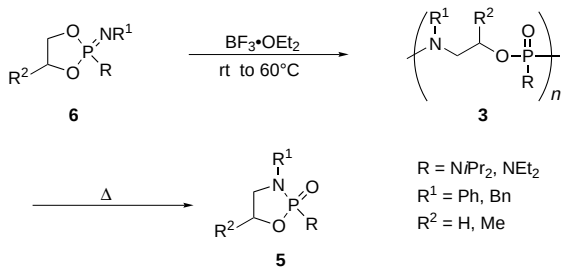
3 4 5

R = N*i*Pr$_2$, NEt$_2$; R^1 = Ph, Bn; R^2 = H, Me; R^3 = Ph, Bn

final products of type **5** was the incentive for a full study of the imide–amide rearrangement of cyclic phosphorimidates, which combined the study of the substrate structure, the reaction conditions and the overall reaction mechanism. We wish to report here the results of this study, supported by NMR spectroscopy, molecular modelling and mass spectrometry, which led us to the optimisation of the reaction conditions, the rational design of more reactive substrates and also the elucidation of the overall mechanism. Evidence of the retention of configuration at the alkoxide carbon atom during the imide–amide rearrangement is presented, based on detailed studies of the "oligomer–monomer" conversion.

Results and Discussion

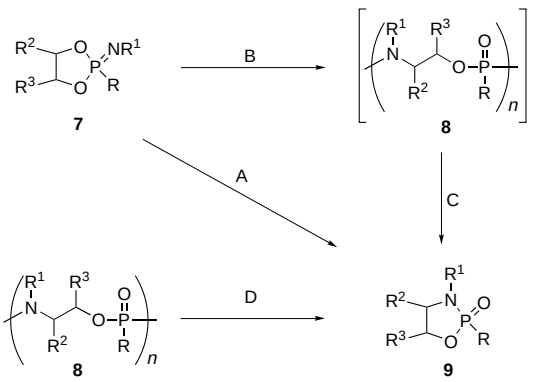
Optimisation of the polymerisation reaction: In a previous paper[20] we reported that the rearrangement of cyclic phosphorimidates **6** proceeds by a two-step process (Scheme 1). In the first step compound **6** undergoes a Lewis acid catalysed 1,4-addition-type ring-opening polymerisation with the formation of the stable oligomeric intermediate **3**. The rearranged monomeric product **5** may then be obtained by heating compound **3** in the presence (80 °C) or absence (>140 °C) of the Lewis acid catalyst. The isolation of the oligomer **3** is strongly dependent on the reaction temperature because of its low thermal stability in the reaction conditions (10 mol % of Lewis acid). If the reaction is carried out at 80 °C the oxazaphospholidinone **5** is directly obtained, in good yields. For temperatures up to 60 °C only the oligomer **3** is formed, which may then be isolated and characterised.



6 3 5

Scheme 1. Rearrangement of cyclic phosphorimidates by an overall two-step process.[20]

Several experiments were made in order to account for the involvement of an oligomeric compound in the overall imide–amide rearrangement mechanism (Scheme 2). We have gathered detailed evidence for the formation of an oligomeric intermediate of type **8**, even when product **9** is directly formed (Scheme 2, path A). For instance, the reaction of compound **7a** in the presence of $BF_3 \cdot OEt_2$ was followed by ^{31}P NMR spectroscopy, at different temperatures (Scheme 2). In one experiment the oligomer **8a** was formed at room temperature by adding $BF_3 \cdot OEt_2$ to a solution of phosphorimidate **7a** (Scheme 2, path B). After the completion of the reaction the solution was heated to 80 °C, which promoted the conversion of the oligomer **8a** into the oxazaphospholidinone **9a** (Scheme 2, path C). The same result was obtained by heating a solution of the oligomer **8a** (prepared from a previously isolated sample of this compound) to 80 °C in the presence of $BF_3 \cdot OEt_2$ (Scheme 2, path D). Following the reaction of the phosphorimidate **7a** in the presence of $BF_3 \cdot OEt_2$ at 80 °C by ^{31}P NMR spectroscopy the almost instantaneous conversion of this compound into oligomer **8a** was observed, followed by the formation of oxazaphospholidinone **9a** (Scheme 2, path A, C). In an experiment to test the thermal stability of compound **8**, samples of the oligomer **8b** were heated at different temperatures (Table 1). ^{31}P NMR spectra were taken after heating for 15 min and the conversions to cyclic phosphoramide **9b** were thus determined. The results compiled in Table 1 show that, in the absence of catalysis, it is necessary to heat the compound to temperatures above 140 °C in order to promote its rearrangement to the



7 8 8 9

	R	R^1	R^2	R^3
a	N*i*Pr$_2$	Ph	H	H
b	NEt$_2$	Ph	H	H
c	NBu$_2$	Ph	H	H
d	Pyr	Ph	H	H
e	Ph	Ph	H	H
f	N*i*Pr$_2$	Bn	H	H
g	N*i*Pr$_2$	4-NO$_2$Bn	H	H
h	N*i*Pr$_2$	*n*-oct	H	H
i	N*i*Pr$_2$	Ts	H	H
j	N*i*Pr$_2$	TMS	H	H
k	NEt$_2$	Ph	H	CH_3
l	N*i*Pr$_2$	Bn	H	CH_3
m	N*i*Pr$_2$	Bn	CH_3	CH_3
n	NEt$_2$	Bn	H	H

Scheme 2. Experiments made in order to account for the involvement of an oligomeric compound in the overall imide–amide rearrangement mechanism. A) $BF_3 \cdot Et_2O$ (10 mol %), 80 °C; B) $BF_3 \cdot Et_2O$ (10 mol %), rt to 60 °C; C) analogous to B) but at 80 °C; D) without $BF_3 \cdot Et_2O$, >140 °C, with $BF_3 \cdot Et_2O$ (10 mol %), 80 °C.

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Table 1. Thermal rearrangement of **8b** without any Lewis acid. (Calculated from the ^{31}P NMR spectra after 15 min of reaction;[22] **8b**: $\delta = 13.0$; **9b**: $\delta = 20.1$.

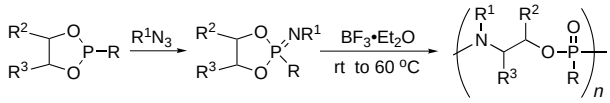
Entry		*T*/°C	Yield/% **(9b)**
100	1		0[a]
120	2		0
140	3		>10[b]
160	4		>10
180	5		≈90

[a] Lower than 10% after 840 min; [b] approx. 80% after 315 min.

cyclic phosphoramide. Above 180 °C the reaction proceeds smoothly, and the conversion is complete after 15 min.

The reactivity of a phosphorimidate with general structure **7** is a result of a balance between the electronic and stereochemical effects of the exocyclic phosphorus atom substituent (R), the nitrogen atom substituent (R^1) and the ring substituents (R^2 and R^3). Table 2 displays the results

Table 2. Dependence of the polymerisation rate on the phosphorimidate **7**, reaction at room temperature, $R^2 = R^3 = H$, unless stated otherwise.



10 **7** **8**

		R	R^1	*t* [min]	Yield [%]	Solvent
1	**7c**	NBu_2	Ph	720	0[a]	$CDCl_3$
2	**7a**	$NiPr_2$	–	720	55	–
3	**7d**	Pyr	–	720	20	–
4	**7e**	Ph	–	720	40	–
5	**7a**	$NiPr_2$	Ph	341	71	C_6D_6
6	**7f**	–	Bn	67	95	–
7	**7g**	–	4-NO_2Bn	61	92	–
8	**7h**	–	*n*-oct	720	0	–
9	**7i**	–	Ts	1058	0	–
10	**7j**	–	TMS	[b]		–
11	**7b**	NEt_2	Ph	222	60	–
12	**7b**	–	–	60	90[a]	–
13	**7k**	–	–	1632	79[a, c]	–
14	**7l**	$NiPr_2$	Bn	1060	68[a, c]	–
15	**7m**	–	–	1440	0[d, e]	[D_8]toluene

[a] Reaction performed at 60 °C; [b] no Staudinger reaction occurred; [c] $R^2 = H$, $R^3 = CH_3$; [d] $R^2 = R^3 = CH_3$; [e] reaction performed at 100 °C.

obtained in the polymerisation reaction of several phosphorimidates bearing different substituents, which will help us to illustrate and discuss the mentioned dependence.

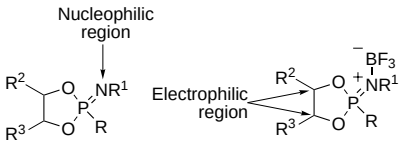
All phosphorimidates were prepared through the Staudinger reaction of the proper phosphorus(III) compound **10** with an azide. The behaviour of the Staudinger reaction was in accordance with the results reported in the literature, which demonstrate that the reaction takes place through the nucleophilic attack of the phosphorus atom to the azide group.[23] As an example, when $R^1 = TMS$ (Table 2, entry 10), no Staudinger reaction occurred, since the azide is a poor electrophile and when $R^1 = Ts$ (Table 2, entry 9) the Staudinger reaction is almost instantaneous and highly exothermic.

We initiated the study of the influence of the various substituents by following the reaction of compound **7** with different exocyclic substituents (R), in the presence of 10 mol% of $BF_3 \cdot OEt_2$ in $CDCl_3$, by ^{31}P NMR spectroscopy (Table 2, entries 1 to 4). All reactions were initially performed at room temperature in order to avoid a possible thermal rearrangement of oligomer **8** to phosphorimidate **9**. As Table 2 shows, when $R = NBu_2$ (entry 1) no polymerisation was observed even after heating at 60 °C for several hours. The best result was obtained when $R = NiPr_2$ (entry 2) at room temperature with a moderate conversion. The results obtained in the series corresponding to entries 1 to 3 suggest that a bulky group in this position enhances the polymerisation rate. However, the result obtained with R = Ph (entry 4), similar to the one reached for $R = NiPr_2$ suggests that the electronic nature of the group is also important.

The influence of the imine nitrogen susbtituent (R^1, entries 5 to 10) was studied using compounds with $R = NiPr_2$, since this group has given the best results in the previous study. The reactions of the phosphorimidates in the presence of 10 mol% of Lewis acid were followed by ^{31}P NMR spectroscopy in C_6D_6 at room temperature. When R^1 = Ph, Bn or 4-NO_2Bn (entries 5 to 7, respectively) a good conversion was observed but for R^1 = alkyl (entry 8) or Ts (entry 9), no conversion occurred. The best result was obtained with the benzyl groups (entries 6 and 7) for which the conversion of the phosphorimidate to oligomer is almost complete after one hour at room temperature.[24] From Table 2 it is also possible to conclude that there is a strong dependence of the reaction rate on the solvent, with the best results obtained in benzene (compare entries 2 and 5).

The presence or absence of substituents at the carbon atoms of the dioxaphospholane ring (R^2 and R^3) has a profound effect on the polymerisation rate (entries 13 to 15). In the case of the monosubstituted compounds **7k** and **7l**, the polymerisation proceeds through the non-substituted carbon atom (Scheme 2, **8k** and **8l**) but, in contrast to the unsubstituted compound **7b** (entry 11), the polymerisation does not occur unless the reaction mixture is heated to 60 °C (entries 13 and 14). When a disubstituted compound is used, no reaction is observed even with the most reactive combination of substituents ($R = NiPr_2$ and R^1 = Bn, **7m**) under prolonged heating (entry 15).

To understand these results compound **7** has to be regarded as a molecule with two opposite and complementary reactive sites (Figure 1), both dependent on the same electronic effects. In fact, the proposed polymerisation mechanism should be favoured by a good nucleophilic imidic nitrogen, which attacks an electrophilic carbon atom in the ring moiety. In principle the electronic effects which increase the electrophilicity of the carbon atom should also reduce the nucleophilicity of the imidic nitrogen, being the opposite equally true. The complexation of a phosphorimidate molecule with the Lewis acid yields an adduct in which the carbon atoms are more electrophilic than in the free compound, being this the first step (initiation) of the polymerisation reaction.[20] The electronic effects of the substituents, both in the free molecule



7 11

	R	R^1	R^2	R^3
a	N*i*Pr$_2$	Ph	H	H
f	N*i*Pr$_2$	Bn	H	H
g	N*i*Pr$_2$	4-NO_2Bn	H	H
i	N*i*Pr$_2$	Ts	H	H
o	N*i*Pr$_2$	Et	H	H

Figure 1. Compound **7** and its complexed form **11**, showing two opposite but interdependent reactive sites.

and in the BF_3 adduct, are responsible for the reactivity observed. For instance, when using compound **7i** the reaction does not occur because the nitrogen atom is deactivated for the nucleophilic attack. The polymerisation only occurs when both the nucleophilicity of the nitrogen atom and the electrophilicity of the carbon alkoxide atom are in good balance. This is strongly dependent on very sensitive electronic effects induced in the phosphorus atom, since there is a direct link between the nucleophilic and electrophilic sides of the molecule. The combination N*i*Pr$_2$/Bn in **7f** seems to be the most balanced combination. Since we proposed a S_N2 type mechanism, it is also expected that an increase in the steric hindrance of the alkoxide carbon atom or of the imine nitrogen moiety will hinder the polymerisation, which might explain the results obtained with the methyl substituted compounds **7k–m** (Table 2, entries 13 to 15).

Minimised structures of the free phosphorimidate **7a, f, g, i, o** and of the corresponding BF_3 adducts **11a, f, g, i, o** at ab initio level[25] showed that the complexation with the Lewis acid through the imidic nitrogen atom is a favourable process, which lowers the energy by a maximum value of about 108 kJ mol^{-1} for adduct **11o** (R^1 = Et) and a minimum value of about 25 kJ mol^{-1} for adduct **11i** (R^1 = Ts) and results in an electrostatic activation of the carbon atoms of the dioxaphospholane ring for nucleophilic attack, when compared with the free phosphorimidate molecule. This activation is nearly the same for all the compounds studied (by a factor of approx. 1.3), thus suggesting that the differences in reactivity are essentially due to differences in the nucleophilic character of the nitrogen atom or to differences in the steric hindrance of the ring carbon atoms.

The greater the stabilisation energy of the complexation of the phosphorimidate with the Lewis acid, the greater its basicity. The calculation of this energy for different imine substituted phosphorimidates allows the prediction of a theoretical sequence of increasing bias towards polymerisation, if we consider that the nucleophilicity follows the same pattern as the basicity (which is acceptable since the structures are all similar): **7i**, R^1 = Ts < **7a**, R^1 = Ph < **7g**, R^1 = 4-NO_2Bn < **7f**, R^1 = Bn < **7o**, R^1 = Et. Compound **7o** was calculated instead of the octyl substituted compound **7h** because its smaller chain size (thus reducing the required calculation time) and because of the fact that the stabilisation energies of these two compounds should be similar since both involve an alkyl substituent. Therefore, the calculated theoretical sequence is confirmed experimentally, except for the octyl substituted compound **7h** (no reaction was observed in this case). The reason for this discrepancy shall be due to larger stereochemical hindrance generated by the octyl chain, when compared with the one generated by the ethyl group. However, calculating the actual energy values of compound **7h** would be of no advantage, since steric hindrance can not be acceptably assessed when large linear structures are involved.

With the aim of determining which set of orbitals might be involved in the polymerisation reaction and how they might be related to the reactivity, we examined the electronic density surfaces and energies of the HOMO to HOMO(−4) and LUMO to LUMO(+4) orbitals of the same compounds (**7a**, **f**, **g**, **i**, **o**) of the free and the BF_3-complexed structures. This examination allowed us to identify the highest occupied molecular orbitals of the free phosphorimidates and the lowest unoccupied molecular orbitals of the BF_3 adducts, which are best suited for the polymerisation reaction in terms of both shape and localisation. We also considered the relative energy of each orbital, before and after the complexation with the Lewis acid. The differences found can be used as an indication of the orbital involvement in the nucleophilic substitution, since the orbitals which participate in the complexation with the BF_3 and those which are involved in the nucleophilic attack of a free phosphoroimidate to a BF_3-activated molecule, should be the same. This analysis indicates that the occupied orbitals are much more affected by the complexation with the Lewis acid than the unoccupied ones despite the fact that they are all stabilised by the complexation with the degree of stabilisation depending on the type of substituents.

For all calculated free phosphorimidates containing aromatic groups (**7a, f, g, i**), the HOMO orbitals have strong aromatic characters and low density over the imidic nitrogen atoms (the lobe over the nitrogen atoms is confined to the interior of the isodensity surfaces (0.002 e$^-$ au^{-3}) of the molecules, indicating difficult accessibility for the interaction with the unoccupied orbitals of the BF_3 adducts). For the same molecules the HOMO(−1) orbitals are essentially aromatic and therefore should not be very important for the reaction; this is in accordance with the fact that the energies of the HOMO(−1) orbitals are almost unaffected by the formation of the complex with the BF_3. The HOMO(−2) orbitals seems to be the most relevant orbitals to consider since they have the highest density over the imidic nitrogen atoms and are the most stabilised upon complexation with the Lewis acid (Figure 2).

The difference in reactivity between the phenyl (**7a**), and benzyl (**7f, g**) derivatives becomes apparent when comparing the relative energies of the HOMO and HOMO(−2) orbitals of these two types of phosphorimidates, before and after the complexation (Figure 3). For the benzyl derivatives **7f, g** these orbitals are closer in energy than they are for the phenyl compound **7a**, being almost degenerated. Since the HOMO(−2) gives a higher contribution to the electronic density over the imidic nitrogen atom, the proximity in energy of the

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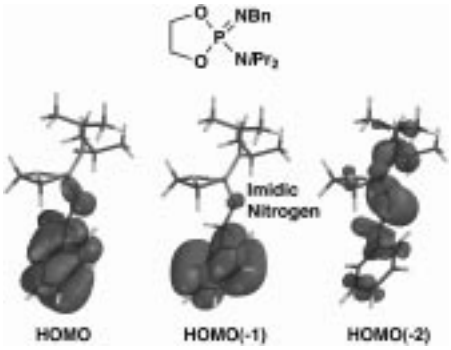


Figure 2. HOMO(−2) to HOMO of compound **7f**, showing the high density of the HOMO(−2) over the imidic nitrogen atom.

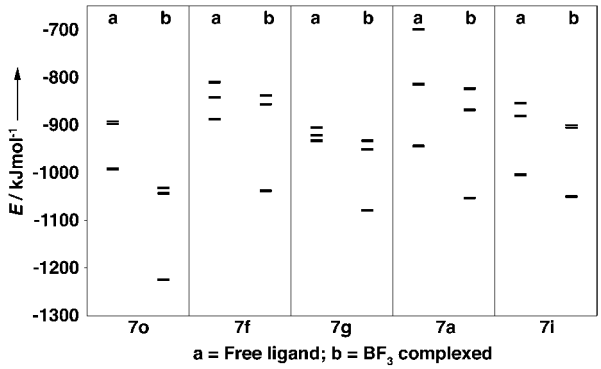


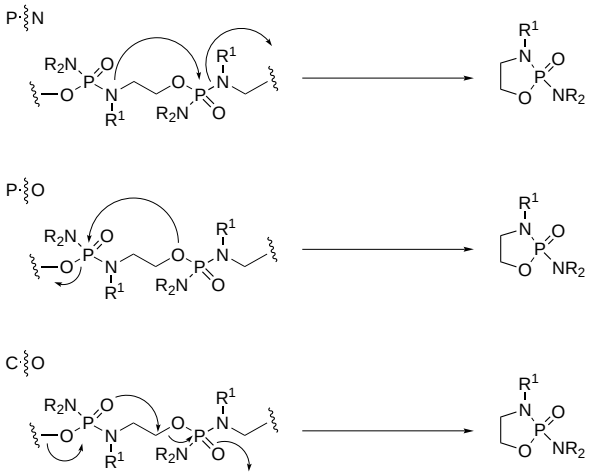
Figure 3. Orbital energies [kJ mol^{-1}] (HOMO(−2) to HOMO) of several free and complexed phosphorimidates, showing the strong participation of the HOMO(−2) into the complexation process.

two orbitals should lead to a higher nucleophilicity of the nitrogen atom of the benzyl compounds which, in turn, leads to an increase in the reactivity towards polymerisation.

Under the assumption that for the same family of compounds, the nucleophilicity depends directly on the basicity, the small change in energy of the HOMO(−2) orbital of the tosyl compound **7i** upon complexation can be seen as a reflection of the low basicity of its imidic nitrogen atom and, therefore, of its lower reactivity.

The study presented herein finds full support in the experimental data and is in agreement with the previous proposed mechanism for the polymerisation reaction,[20] and reflects the importance of the catalyst for the electrophilic activation of the phosphorimidate molecule. However, it also suggests that the reactivity is controlled by the nucleophilicity of the free phosphorimidate. We found that the optimal combination of substituents for the polymerisation reaction (R = N*i*Pr$_2$ and R^1 = Bn) may, in this way, be interpreted as being due to the higher nucleophilicity of this compound when compared to all the others tested.

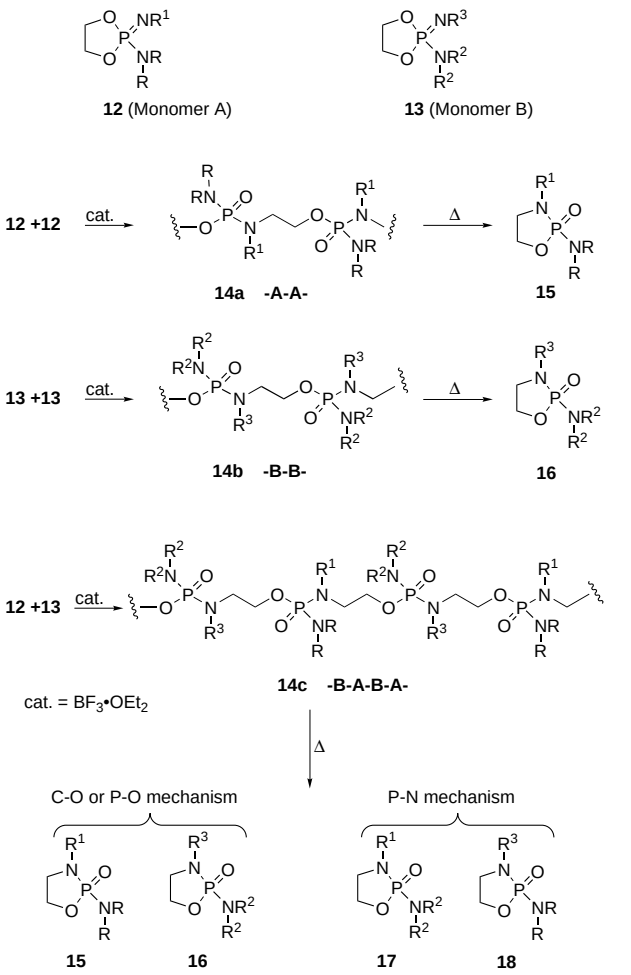
Study of the oligomer–monomer conversion: As was mentioned earlier, the final product of the imide–amide rearrangement may be obtained through the thermal conversion of the stable intermediate oligomer into the rearranged monomer. The "oligomer–monomer" conversion may be intramolecular, intermolecular or a mixture of both. The intermolecular hypothesis was soon ruled out by mixing oligomers **8a** and **8n** in a 1:1 proportion and warming of the solution (180 °C, 15 min) until depolymerisation occurred. Only compounds **9a** and **9n** were obtained from this experiment, which points out the intramolecular nature of the reaction. For the intramolecular conversion several reaction pathways may be drawn, according to the bond of the oligomer chain which is broken. In Scheme 3 the different bond-breaking processes as well as the mechanism hypothesis leading to the monomer conversion are shown.



Scheme 3. Possible pathways for the intramolecular oligomer–monomer conversion.

In all cases a chain reaction is initiated by the intramolecular nucleophilic attack of an oxygen or a nitrogen atom in an SNi reaction. The pathways involving P–O or P–N bond cleavage are more likely, since these are the weakest bonds within the oligomer chain. Nevertheless the phosphoryl oxygen is known to be nucleophilic, which means that the C–O bond cleavage has to be considered as well. If, as depicted in Scheme 4, we consider the thermal rearrangement of a copolymer, obtained from the polymerisation reaction of two phosphorimidates with different 2-*N*-imine (R^1, R^3) and 2-*N*,*N*-amine (R, R^2) substituents, then a careful observation of the products should give important information about the reaction pathway, because this will depend on the copolymer sequence and on the mechanism of the conversion. A copolymer prepared from **12** and **13** may afford any of the sequences depicted in Scheme 4. Thermal rearrangement of the sequence −A−A− (**14a**) will give compound **15**. The sequence −B−B− (**14b**) give compound **16**. The sequence −B−A−B−A− (**14c**) yields both **15** and **16** when the P–O and C–O bond are broken, or **17** and **18**, in the P–N bond-breaking mechanism.

For the preparation of the copolymer we had to consider several aspects. It is important that the two initial phosphorimidates have similar reactivity, which means essentially the same basicity of the imidic nitrogen atoms; this implies very similar substituents, otherwise one would react faster than the other and homopolymers would be mainly obtained. On the other hand, the substituents must be different enough to enable identification of the four possible compounds which



Scheme 4. Possible sequences for a copolymer and products resulting from polymer degradation.

can be formed. This means that the substituents of both the phosphorus amine and imine moiety had to be different, as depicted in Scheme 4. Finding such a system was the main difficulty of this experiment because the reaction is very sensitive to the nature of the phosphorus substituents with small changes causing severe differences in the reaction rates. After several trials, the system shown in Figure 4 was chosen.

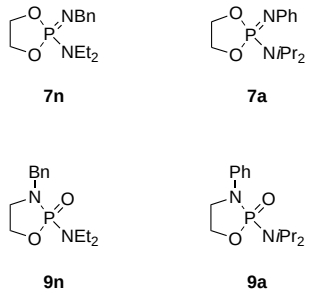


Figure 4. System used to differentiate between C–O, P–O or P–N bond-cleavage mechanism.

The copolymerisation experiment was carried out by mixing equal amounts of **7n** (structure **12**, R = Et, R^1 = Bn) and **7a** (structure **13**, R^2 = *i*Pr, R^3 = Ph) and a catalytic amount of $BF_3 \cdot OEt_2$. The reaction was followed by ^{31}P NMR spectroscopy until completion with the indication that the copolymerization had occurred since only one signal was observed with different chemical shift ($\delta = 17.8$) from the ones of the homopolymers ($\delta = 18.7$ and 13.3, for compounds **8n** and **8a**, respectively). The formation of the copolymer was confirmed by MALDI spectrometry. Unlike the MALDI spectra of the homopolymers, which are composed of single ion peaks separated by the monomer mass, the copolymer spectrum has, for each value of *n*, a multiplet signal corresponding to the statistical monomers combination (Figure 5).

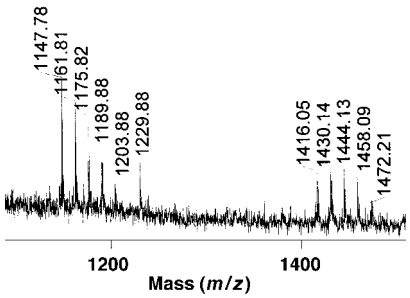
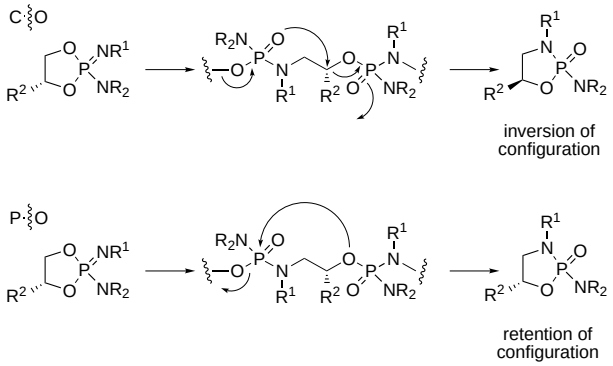


Figure 5. Part of the MALDI spectrum of the copolymerisation product of compounds **7n** and **7a**.

The copolymer was heated to 180 °C and the mixture thus obtained showed only two ^{31}P NMR signals, corresponding to compounds **9n** (structure **15**, R = Et, R^1 = Bn) and **9a** (structure **16**, R^2 = *i*Pr, R^3 = Ph), as was confirmed after separation of the mixture and characterisation of the two isolated compounds by comparison with independently prepared authentic samples. This result indicates that the formation of the monomer occurs by a process involving C–O or P–O bond cleavage. To distinguish between these two pathways another experiment was set based in the observation that in the C–O bond-breaking mechanism the substitution takes place at the carbon atom and in the P–O bond cleavage at the phosphorus atom (Scheme 3). As a result, the two pathways may be distinguished by determining the stereochemistry of the rearranged products in the reaction performed with a chiral substituted phosphorimidate (Scheme 5). If the conversion



Scheme 5. Scheme used to differentiate between a P–O and C–O bond-cleavage mechanism.

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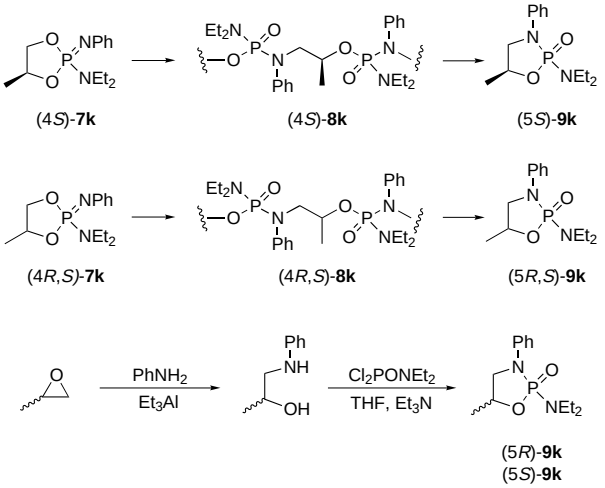
proceeds through the C–O mechanism the inversion at the carbon atom (or at least some degree of racemization) should occur; if this is not the case, retention of configuration should be observed, since the P–O mechanism does not involve that atom.

The polymerisation reactions were carried out with the chiral (*S*) and racemic phosphorimidates (4*S*)-**7k** and (4*R*,*S*)-**7k** (Scheme 6) derived from chiral and racemic 1,2-propanediol, respectively. Chiral phosphoramides to be used as authentic samples (5*S*)-**9k** and (5*R*)-**9k** were also prepared, starting from chiral (*R* or *S*)-propylene oxide (Scheme 6). All

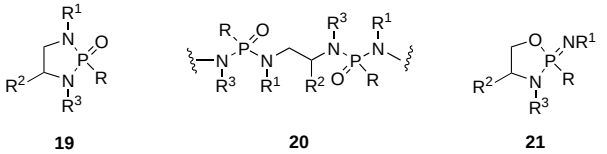


Scheme 6. Polymerisation of chiral and racemic phosphorimidates (4*S*)-**7k** and (4*R*,*S*)-**7k** and preparation of racemic and chiral authentic samples (5*S*)-**9k** and (5*R*)-**9k**.

compounds were purified and caracterized as inseparable mixtures of diastereomers, both in the preparation of authentic samples and in the rearrangment reactions. Experiments with chiral shift reagents allowed the determination of the samples configuration. Comparison of the ^{1}H NMR spectra of the authentic samples (5*S*)-**9k** and (5*R*)-**9k**, racemic sample (5*R*,*S*)-**9k** and chiral sample (5*S*)-**9k** clearly shows that the configuration of the latter is identical to that of the authentic sample (5*S*)-**9k**. The spectrum obtained for an equimolar mixture of chiral sample (5*S*)-**9k** and chiral authentic sample (5*R*)-**9k** is identical to that obtained with the racemic sample. This proves that the configuration proposed for the product of the thermal rearrangement of the chiral oligomer is correct and that the most probable mechanism involves the P–O bond cleavage (Scheme 3 and Scheme 5).

Conclusion

With this study we have elucidated the full mechanism involved in the Lewis acid catalysed imide – amide rearrangement of cyclic phosphorimidates. A new oligomeric material resulting from a novel 1,4-addition-type ring-opening polymerisation of cyclic phosphorimidates was identified as being a stable intermediate of the rearrangment reaction, which occurs with retention of configuration at the carbon atom. The use of molecular modelling enabled the rationalisation of the substituent effects, which is of major importance for the extension of this methodology to the synthesis of interesting phosphoramides and polyphosphoramides of types **19** and **20**. The latter, due to their thermal stability and similarity to known organophosphorus flame retardants, might prove extremely useful. A detailed study of the mechanism and synthetic possibilities of this type of reaction, when applied to compounds of type **21**, is currently under investigation.



Experimental Section

General methods: All dried solvents, amines, $POCl_3$, and PCl_3 were purified/dried before use, according to literature procedures.[26] Thin-layer chromathography (TLC) was performed on aluminium sheets coated with silica gel 60 F_{254} (Merck 5554). Column chromatography was carried out on silica gel 60 (MN 815381, 230–400 mesh). Melting points were determined on an Eletrothermal IA 6304 capillary melting point apparatus and are uncorrected. Size-exclusion chromatography was performed on a Waters Millipore 510 apparatus, equipped with a refraction index detector (Waters differential refractometer R401) and a Ultrastyragel 500 A column, operating at 30 °C with THF as eluent (0.16 % BHT *w/v* as internal reference), at a flow rate of 1 mL min^{-1} and calibrated with polystyrene standards. Observed rotations at the Na–D line were measured at 25 °C using an Optical Activity polarimeter AA-1000. Low- and high-resolution mass spectra were obtained on a Fisons Autospec or Kratos apparatus. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker ARX400 spectrometer. The following compounds were prepared, according to general reported procedures: chlorodioxaphospholane,[27] dichlorodiethylphosphoramidite,[28] diethylphosphoroamidous dichloride,[29] benzylazide,[30] octylazide,[30] 4-nitrobenzylazide,[30] 4-methylphenylazide,[31] phenylazide,[31] tosylazide.[32]

(2*R*)-1-*N*-Phenylamino-2-propanol: Prepared from (*R*)-propylene oxide, following general reported procedure;[33] $[\alpha]_D^{20} = -16.8$ ($c = 1$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.20$ (t, J(H,H) = 7.8 Hz, 2H; -CH, Ar), 6.76 (t, J(H,H) = 7.2 Hz, 1H; -CH, Ar), 6.66 (d, J(H,H) = 7.9 Hz, 2H; -CH, Ar), 4.03 (m, 1H; -OCH-), 3.22 (dd, J(H,H) = 12.9, 3.2 Hz, 1H; -NCH-), 2.99 (dd, J(H,H) = 12.9, 8.5 Hz, 1H, -NCH-), 1.27 (d, J(H,H) = 6.3 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 148.2$ (-C-, Ar), 129.3 (-CH-, Ar), 117.9 (-CH-, Ar), 113.3 (-CH-, Ar), 66.5 (-OCH-), 51.7 (-NCH_2-), 20.86 (-CH_3); IR (film): $\nu_{max} = 3405$ (NH, OH), 2974 (CH), 1610 (C=C, Ar), 1508 (C=C, Ar), 1327 (C–N, Ar), 1247 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 151 (40) $[M]^+$, 106 (100) $[C_6H_5NH{=}CH_2]^+$, 77 (24) $[C_6H_5]^+$; HRMS (EI): calcd for $C_9H_{13}NO$ $[M]^+$: 151.099714; found 151.099126.

(2*S*)-1-*N*-Phenylamino-2-propanol: Prepared from (*S*)-propylene oxide, following general reported procedure;[33] $[\alpha]_D^{20} = +16.4$ ($c = 1$, $CHCl_3$); other spectral data identical to the (2*R*)-isomer.

Preparation of 1,3,2-dioxaphospholanes: All 1,2,3-dioxaphospholanes were prepared following published procedures.[29] Compounds **10a–d** were prepared by the coupling of chlorodioxaphospholane with the proper amine, **10e** by the coupling of dichlorophenylphosphine and 1,2-ethyleneglycol, **10k** by the coupling of dichlorodiethylphosphoramidite with 1,2-propanediol and **10m** by the coupling of *meso*-2-chloro-4,5-dimethyldioxaphospholane[27a] with diisopropylamine.

2-Diisopropylamino-1,3,2-dioxaphospholane (10a): Colourless liquid; b.p. 52 °C (0.3 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.14$ (m, 2H, -OCH_2-), 3.86 (m, ^3J(P,H) = 1.2 Hz, J(H,H) = 9.3 Hz, 2H, -OCH_2-), 3.45 (m, ^3J(P,H) = 9.3 Hz, J(H,H) = 6.68 Hz, 2H, 2 × CH), 1.22 (d, J(H,H) = 6.7 Hz, 12H, -NCH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 63.7$ (d, ^2J(P,C) = 8.0 Hz, -OCH_2-), 44.2 (d, ^2J(P,C) = 11.0 Hz,

-NCH-), 24.7 (-CH_3), 24.65 (d, ^3J(P,C) = 8.0 Hz, -CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 144.7.

2-Diethylamino-1,3,2-dioxaphospholane (10b): Colourless liquid; b.p. 50 °C (0.1 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.12 (m, 2H, -CH_2-), 3.86 (m, 2H, CH_2), 2.99 (q, J(H,H) = 7.1 Hz, 4H, 2 × -CH_2-), 1.03 (t, J(H,H) = 7.1 Hz, 2 × -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 63.9 (d, ^3J(P,C) = 9.0 Hz, -CH_2-), 37.9 (d, ^3J(P,C) = 20.8 Hz, -CH-), 15.1 (d, ^4J(P,C) = 2.6 Hz, -CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 143.6.

2-Dibutylamino-1,3,2-dioxaphospholane (10c): Colourless liquid; b.p. 62 °C (0.3 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.17 – 4.12 (m, 2H, -OCH_2-), 3.92 – 3.86 (m, 2H, -OCH_2-), 2.96 – 2.89 (m, 4H, 2 × -NCH_2-), 1.46 – 1.39 (m, 4H, 2 × -NCH_2CH_2-), 1.28 (m, J(H,H) = 7.3 Hz, 4H, 2 × -$N(CH_2)_2CH_2$-), 0.91 (t, J(H,H) = 7.3 Hz, 6H, 2 × -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 65.3 (-OCH_2-), 60.0 (d, J(P,C) = 8.8, -OCH_2-), 45.4 (d, J(P,C) = 19.0 Hz, -$N(CH_2(CH_2)_2CH_3)_2$), 43.6 (d, J(P,C) = 19.0 Hz, -$N(CH_2(CH_2)_2CH_3)_2$), 31.1 (-$N(CH_2CH_2CH_2CH_3)_2$), 30.5 (-$N(CH_2CH_2CH_2CH_3)_2$), 20.2 (-$N((CH_2)_2CH_2CH_3)_2$), 20.1 (-$N((CH_2)_2CH_2CH_3)_2$), 13.9 (-$N(CH_2)_3CH_3)_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 143.7.

2-Pyrrolidino-1,3,2-dioxaphospholane (10d): Colourless liquid; b.p. 130 °C (0.05 mmHg, Kugelrohr); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.00 – 3.95 (m, 2H, -OCH_2-), 3.80 – 3.73 (m, 2H, -OCH_2-), 3.09 – 2.99 (m, 4H, -CH_2NCH_2-), 1.63 – 1.60 (m, 4H, -CH_2CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 64.5 (d, ^2J(P,C) = 9.4 Hz, -OCH_2CH_2O-), 44.8 (d, ^2J(P,C) = 15.3 Hz, -CH_2NCH_2-), 25.8 (d, J(P,C) = 3.3 Hz, -CH_2CH_2-); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 135.6.

2-Phenyl-1,3,2-dioxaphospholane (10e): Colourless oil; b.p. 70 °C (0.1 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.34 – 7.26 (m, 5H, -CH-, Ar), 3.93 – 3.77 (m, 4H, -OCH_2CH_2O-); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 143.2 (d, ^1J(P,C) = 47.0 Hz, -C-, Ar), 129.8 (-CH-, Ar), 128.2 (d, ^2J(P,C) = 12.3 Hz, -CH-, Ar), 128.1 (-CH-, Ar), 64.1 (d, ^2J(P,C) = 9.7 Hz, -OCH_2CH_2O-); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 162.6.

2-Diethylamino-4-methyl-1,3,2-dioxaphospholane (10k): Colourless liquid; mixture of diastereoisomers (*cis*/*trans*, 36:64, determined by ^{31}P NMR); b.p. 35 °C (0.06 mmHg);[27a] 101.5 – 101.7 °C (25 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.42 – 4.33 (m, J(H,H) = 6.8, 6.3, 6.2, 6.2 Hz, ^3J(P,H) = 1.5 Hz, 1H, -$OCHCH_3$, *trans*), 4.21 (ddd, J(H,H) = 8.4, 6.2 Hz, ^3J(P,H) = 6.2 Hz, 1H, -OCH_2-, *trans*), 4.17 – 4.10 (m, J(H,H) = 10.7, 6.2, 6.0 Hz, ^3J(P,H) = 1.4 Hz, 1H, -$OCHCH_3$, *cis*), 3.91 (ddd, J(H,H) = 9.5, 6.2 Hz, ^3J(P,H) = 14.3 Hz, 1H, -OCH_2-, *cis*), 3.41 (ddd, J(H,H) = 10.7, 9.5 Hz, ^3J(P,H) = 9.0 Hz, 1H, -OCH_2-, *cis*), 3.34 (ddd, J(H,H) = 8.4, 6.8 Hz, ^3J(P,H) = 6.2 Hz, 1H, -OCH_2-, *trans*), 3.09 – 2.95 (m, 2H, -NCH_2CH_3, *cis* and 4H, -$N(CH_2CH_3)_2$, *trans*), 2.78 (q, J(H,H) = 7.2 Hz, 2H, -NCH_2CH_3, *cis*), 1.37 (d, J(H,H) = 6.0 Hz, 3H, -$CHCH_3$, *cis*), 1.21 (d, J(H,H) = 6.3 Hz, 3H, -$CHCH_3$, *trans*), 1.04 (t, J(H,H) = 6.7 Hz, 6H, -$N(CH_2CH_3)_2$, *cis*), 1.02 (t, J(H,H) = 7.1 Hz, 6H, -$N(CH_2CH_3)_2$, *trans*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 72.3 (d, ^2J(P,C) = 6.6 Hz, -$OCH_2CH(CH_3)O$-, *cis*), 71.2 (d, ^2J(P,C) = 9.4 Hz, -$OCH_2CH(CH_3)O$-, *trans*), 70.3 (d, J(P,C) = 7.1 Hz, -$OCH_2CH(CH_3)O$-, *trans*), 69.2 (d, ^2J(P,C) = 6.9 Hz, -$OCH_2CH(CH_3)O$-, *cis*), 38.1 (d, J(P,C) = 3.6 Hz, -NCH_2CH_3, *trans*), 37.9 (d, ^2J(P,C) = 3.4 Hz, -NCH_2CH_3, *cis*), 42.8 (d, ^2J(P,C) = 12.0 Hz, -NCH_2CH_3, *trans*), 39.9 (-NCH_2CH_3, *cis*), 20.1 (d, ^3J(P,C) = 4.1 Hz, -$OCHCH_3$,*trans*), 17.5 (d, ^3J(P,C) = 3.9 Hz, -$OCHCH_3$, *cis*), 15.2 (d, ^3J(P,C) = 3.8 Hz, -NCH_2CH_3, *trans*), 15.2 (d, ^3J(P,C) = 3.1 Hz, -NCH_2CH_3, *trans*), 14.2 (-NCH_2CH_3, *cis*); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 150.5 (*cis*), 145.9 (*trans*).

(2*RS*,4*S*)-2-Diethylamino-4-methyl-1,3,2-dioxaphospholane [(4*S*)-10k]: Colourless liquid; mixture of diastereoisomers (*cis*/*trans*, 36:64, determined by ^{31}P NMR); spectral data identical to the racemic compound **10k**.

***meso*-2-Diisopropylamino-4,5-dimethyl-1,3,2-dioxaphospholane (10m)**: Colourless liquid with only one diastereomer according to the ^{1}H and ^{31}P NMR spectra; b.p. 59 °C (0.1 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.48 – 4.41 (m, 2H, 2 × -$OCHCH_3$), 3.56 – 3.43 (m, 2H, 2 × -$NCH(CH_3)_2$), 1.22 (d, J(H,H) = 6.8 Hz, 12H, 2 × -$NCH(CH_3)_2$), 1.17 (d, J(H,H) = 5.6 Hz, 6H, 2 × -$OCHCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 73.9 (d, ^2J(P,C) = 8.0 Hz, -$OCHCH_3$), 44.4 (d, ^2J(P,C) = 11.0 Hz, -$NCH(CH_3)_2$), 24.7 (d, ^3J(P,C) = 8.0 Hz, -$NCH(CH_3)_2$), 16.2 (d, ^3J(P,C) = 4.0 Hz, -$CH(CH_3)_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 142.7.

Study of the polymerisation mechanism

A) Formation of 2-diisopropylamino-3-*N*-phenyl-1,2,3-λ^5-dioxaphospholidine-2-one (9a):

1) At 80 °C in the presence of $BF_3 \cdot OEt_2$ from poly-O-ethyl-N,N-diisopropylamino-N′-phenylaminophosphoramidate (**8a**) *prepared in situ at room temperature*: Phenylazide (53 mg, 0.44 mmol) was added dropwise to a deuterated toluene solution (0.4 mL) of dioxaphospholane **10a** (85.3 mg, 0.45 mmol) in a dry argon pre-filled NMR tube stopped with a rubber septum. After the complete addition of the azide the reaction proceeded at room temperature until no more evolution of N_2 was observed (ca. 90 min). The complete conversion of **10a** into the Staudinger product **7a** was confirmed by ^{31}P NMR spectroscopy (only one signal at δ = 17.4). $BF_3 \cdot OEt_2$ (5.4 μL, 10 mol %) was added to the solution and the reaction was followed by ^{31}P NMR at room temperature. After 3 h the conversion of the iminophospholane **7a** into oligomer **8a** (δ = 13.0 – 12.8, 9.7, and 9.0 with a 90:5:5 ratio) was complete. The solution was then heated to 80 °C and the conversion of the polyphosphoramidate **8a** into oxazaphospholidinone **9a** (δ = 18.1) was followed. After 80 min, 80 % conversion was reached. After this time no further change in the ratio of the phosphoramide signal at δ = 18.1 and the residual oligomer signals at δ = 13.0 and 9.0 was observed.

2) At 80 °C in the presence of $BF_3 \cdot OEt_2$ from a solution prepared with previously isolated poly-O-ethyl-N,N-diisopropylamino-N′-phenylaminophosphoramidate (***8a***): $BF_3 \cdot OEt_2$ (5.5 μL) was added to a deuterated toluene solution (0.4 mL) of oligomer **8a** (128.0 mg) in an NMR tube at room temperature. This solution was then heated to 80 °C and ^{31}P NMR spectra were acquired every 10 min. After 90 min 80 % conversion of oligomer **8a** (δ = 13.0) into oxazaphospholidinone **9a** (δ = 18.3) was reached. Further heating did not change the ratio of the observed signals.

3) At 80 °C in the presence of $BF_3 \cdot OEt_2$ from a solution of partially polymerised 2-diisopropylamino-2-N-phenylimino-1,2,3-λ^5-dioxaphospholane (***7a***): The procedure was identical to that described in **1)** up to the addition of the Lewis acid. After addition of the $BF_3 \cdot OEt_2$ the reaction was followed at room temperature until about 50 % of the iminophospholane **7a** was converted into oligomer **8a**; at this point the solution was heated to 80 °C and ^{31}P NMR spectra were acquired every 2 min. After 4 min all of the remaining iminophospholane **7a** was converted into oligomer **8a** and after 8 min the signal relative to the oxazaphospholidinone **9a** (δ = 18.3) was observed. As in the previous experiments, 80 % conversion was reached after 80 min.

B) Thermal stability of poly-*O*-ethyl-*N*,*N*-diethylamino-*N*′-phenylaminophosphoramidate (8b): Five flasks containing polyphosphoramidate **8b** (flask 1: 35.9 mg; flask 2: 35.1 mg; flask 3: 36.8 mg; flask 4: 36.3 mg; flask 5: 37.9 mg) were heated to 100, 120, 140, 160, and 180 °C for 15 min each. After this time the content of each flask was dissolved in $CDCl_3$ (0.5 mL) and their ^{31}P NMR spectra were adquired. The percentage of conversion into monomer, presented in Table 1, was determined by the integration of the monomer **9b** (δ = 20.3) and oligomer **8b** (δ = 14.4 and 10.9) signals.

Study of the oligomer – monomer conversion mechanism

A) Cross polymerisation reaction:

1a) Preparation of 2-diisopropylamino-2-N-phenylimino-1,2,3-λ^5-dioxaphospholane (***7a***): Phenylazide (42 mg, 0.352 mmol) was added dropwise to a deuterated benzene solution (0.32 mL) of **10a** (67.5 mg, 0.353 mmol), prepared in a dry, argon pre-filled NMR tube, stopped with a rubber septum. After addition of the azide the solution was left to react at room temperature until no more evolution of N_2 was observed (5 h). A ^{31}P NMR spectra was then acquired to confirm the complete conversion of **10a** (δ = 144.7) into iminodioxaphospholane **7a** (δ = 16.7).

1b) Preparation of 2-N-benzylimino-2-diethylamino-1,2,3-λ^5-dioxaphospholane (***7n***): Benzylazide (55.4 μL, 0.443 mmol) was added dropwise to a deuterated benzene solution (0.4 mL) of **10b** (72.4 mg, 0.443 mmol), prepared in a dry, argon pre-filled NMR tube, stopped with a rubber septum. After the addition of the azide the solution was heated to 40 °C until no more evolution of N_2 was observed (5 h). A ^{31}P NMR spectra was then acquired to confirm the complete conversion of **10b** (δ = 144.2) into iminodioxaphospholane **7n** (δ = 26.2).

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2) Cross polymerisation: $BF_3 \cdot OEt_2$ (5.4 μL, 10 mol %) was added to a solution containing an equimolar mixture of iminophospholanes **7a** and **7n**, prepared by mixing 0.2 mL of each of the previous described solutions, and the reaction was followed by ^{31}P NMR spectroscopy at room temperature. The ^{31}P NMR spectra acquired before the addition of the Lewis acid showed two signals at the characteristic chemical shifts of the two iminodioxaphospholanes (**7n**: $\delta = 26.2$ and **7a**: $\delta = 16.7$) with a relative intensity of 49:51. 60 min after the addition of the Lewis acid only one signal was observed in the ^{31}P NMR spectra ($\delta = 17.8$) with a different chemical shift of the ones of the homopolymers (**8n**: 18.7 and **8a**: $\delta = 13.3$). The solution was then washed with aq sat. solution of $NaHCO_3$ (1 mL) and the aqueous layer extracted with dichloromethane (2 mL). The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent removed in vacuo. The residue obtained was characterised by MALDI-TOF spectrometry and further submitted to thermal isomerisation.

3) Thermal isomerisation of the copolymer: The copolymer obtained in **2)** (42 mg) was weighted in a round-bottom flask and warmed to 180 °C in an oil bath for 15 min. The residue obtained was dissolved in $CDCl_3$ and a ^{31}P NMR spectrum was acquired, showing the disappearance of the copolymer signal and the appearance of two other signals. The residue was purified by thin-layer chromatography (*n*-hexanes/AcOEt 1:1) and two compounds were isolated, which were identified as 2-diisopropylamino-3-*N*-phenyl-1,3,2-λ^5-oxazaphospholidin-2-one (**9a**) (less polar compound, 8.6 mg) and 3-*N*-benzyl-2-diethylamino-1,3,2-λ^5-oxazaphospholidin-2-one (**9n**) (more polar compound, 3.5 mg), with all the spectral data identical to those of the standards prepared by a separate way.

B) Other experiments for the elucidation of the oligomer–monomer conversion mechanism:

Preparation of poly-O-(1-methyl)ethyl-N,N-diethylamino-N′-phenylamino-phosphoramidate (***8k***): Phenylazide (145 mg, 1.21 mmol) was added slowly under argon atmosphere to a stirred solution of **10k** (215 mg, 1.21 mmol) in dry benzene (1.0 mL). The mixture was heated to 40 °C on an oil bath and allowed to react until no more N_2 evolution was observed (approx. 3 h). After this time $BF_3 \cdot OEt_2$ (15.0 μL, 10 mol %) was added and the reaction mixture was heated to 60 °C for 24 h. The solution was washed with sat. aq $NaHCO_3$ solution (1 mL) and the aqueous layer was extracted with dichloromethane (2 × 2 mL). The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent removed under vacuum. The polyphosphoramidate **8k** was obtained as a light yellow oil (327 mg, 100 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.33-6.81$ (br), 6.61 (d, $J = 7.6$ Hz), 6.46 (d, $J = 7.6$ Hz), 6.21 (d, $J = 8.0$ Hz), 5.91 (d, $J = 8.0$ Hz), 4.70–3.32 (m), 3.10–2.90 (m), 2.79–2.68 (m), 1.31–1.05 (m), 0.99 (t, J(H,H) = 7.2 Hz), 0.6–0.4 (m); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 140.2$, 128.9, 128.8–128.5, 117.4, 70.48, 39.7, 39.6, 19.5, 13.9, 13.5; ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 13.6-13.1$, 12.8–12.6, 11.3, 10.9, 10.4; IR (KBr): $\nu_{max} = 2975.6$, 1603.8, 1500.1, 1221.8 (P=O), 1204.8, 1033.4 (P-O-C), 990.1, 960.8 cm^{-1}; SEC: $M_n = 3590$, polydispersion index = 4.69.

Preparation of (1*S*)-poly-*O*-(1-methyl)ethyl-*N*,*N*-diethylamino-*N*′-phenyl-aminophosphoramidate [(1*S*)-8k]: The procedure was identical to the one described for the racemic compound, using dioxaphospholane (4*S*)-**10k** (197 mg, 1.11 mmol) and phenylazide (132 mg, 1.11 mmol) in dry benzene (1.0 mL). The oligomer (1*S*)-**8k** was obtained as a light yellow oil (265 mg, 89 %). Spectral data identical to the racemic compound **8k**.

Preparation of 2-diethylamino-5-methyl-3-*N*-phenyl-1,2,3-λ^5-oxazaphospholidin-2-one (9k) from the thermal rearrangement of poly-*O*-(1-methyl)ethyl-*N*,*N*-diethylamino-*N*′-phenylaminophosphoramidate (8k): Polyphosphoramidate **8k** (67.5 mg) was weighted in a round-bottom flask, which was dipped into a 200 °C oil bath for 15 min. The residue obtained was purified by thin-layer chromatography (*n*-hexanes/AcOEt 1:1) and oxazaphospholidinone **9k** (14.0 mg, 21 %) was isolated as a mixture of diastereomers (*cis*/*trans*, 39:61-determined by ^1H and ^{31}P NMR). ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 19.57$ (39), 19.32 (61); other spectral data identical to the one obtained for the authentic sample of **9k** prepared as a standard by an separate way.

Preparation of (2*RS*,5*S*)-2-*N*′,*N*′-diethylamino-5-methyl-3-*N*-phenyl-1,3,2-λ^5-oxazaphospholidin-2-one (5*S* 9k) from the thermal rearrangement of (1*S*)-poly-1-methylethyl-*N*,*N*-diethylamino-*N*′-phenylaminophosphoramidate [(1*S*)-8k]: The procedure was identical to the one described previously for the racemic compound **9k**, using polyphosphoramidate (1*S*)-**8k** (70 mg). After purification, the oxazaphospholidinone (5*S*)-**9k** (14.3 mg, 20 %) was isolated as a mixture of diastereomers (*cis*/*trans*, 34:66-determined by ^1H and ^{31}P NMR). ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 19.57$ (34), 19.32 (66); other spectral data identical to the one obtained for the authentic sample of **9k** prepared as a standard by separate way. The determination of the absolute configuration (C-5) was done by comparing the ^1H NMR spectrum of compound (5*S*)-**9k** with that of the authentic racemic (2*RS*,5*RS*) and chiral samples (2*RS*,5*S*) and (2*RS*,5*R*) of the corresponding oxazaphospholidinone (**9k**, (5*S*)-**9k** and (5*R*)-**9k**), in the presence of the chiral shift reagent $Eu(hfc)_3$ (hfc: 3-heptafluoropropylhydroxymethylen-(+)-camphorate).

Reactivity studies on the polymerisation of iminodioxaphospholanes of type 7

General method: A solution of dioxaphospholane (0.2 mmol) was prepared in deuterated chloroform, benzene, or toluene (0.4 mL) in a dried and argon-filled NMR tube, stopped with a rubber septum. To this solution the appropriate azide (1.0 equiv) was added dropwise and the Staudinger reaction was followed at room temperaure (unless stated otherwise) by ^{31}P NMR by the observation of the conversion of the ^{31}P NMR signals of the dioxaphospholane **10** into the corresponding iminodioxaphospholane. As soon as the reaction was complete $BF_3 \cdot OEt_2$ (10 mol %) was added and the polymerisation was monitored by ^{31}P NMR. In the cases were polymerisation occured, the conversion was calculated by integration of the ^{31}P NMR signals.

A) Effect of the exocyclic phosphorus substituent

Reaction with 2-dibutylamino-1,2,3-dioxaphospholane (10c): Dioxaphospholane **10c** (41.6 mg, 0.196 mmol) and phenylazide (23.7 mg, 0.199 mmol) in $CDCl_3$ were used, following the general method described above. The Staudinger reaction was monitored by ^{31}P NMR following the conversion of **10c** ($\delta = 143.7$) into iminodioxaphospholane **7c** ($\delta = 25.3$). After 107 min, $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added; however, 12 h after the addition of the Lewis acid still no polymerisation was observed. The NMR tube was then heated to 60 °C but after 12 h there was still no change in the initial phosphorus spectrum.

Reaction with 2-pyrrolidyl-1,3,2-dioxaphospholane (10d): Dioxaphospholane **10d** (31.5 mg, 0.195 mmol) and phenylazide (24.0 mg, 0.201 mmol) in $CDCl_3$ were used following the general method described above. The Staudinger reaction was monitored by ^{31}P NMR following the conversion of **10d** ($\delta = 135.6$) into iminodioxaphospholane **7d** ($\delta = 21.6$). After 124 min, $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added. A conversion of 20 % into oligomer **8d** ($\delta = 24.1$) was observed after 12 h.

Reaction with 2-phenyl-1,3,2-dioxaphospholane (10e): Dioxaphospholane **10e** (31.9 mg, 0.190 mmol) and phenylazide (22.4 mg, 0.188 mmol) in $CDCl_3$ were used, following the general method described above. The Staudinger reaction was monitored by ^{31}P NMR following the conversion of **10e** ($\delta = 162.6$) into iminodioxaphospholane **7e** ($\delta = 37.1$). After 150 min, $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added. A conversion of 40 % into oligomer **8e** ($\delta = 37.1$) was observed after 12 h.

Reaction with 2-diisopropylamino-1,3,2-dioxaphospholane (10a): Dioxaphospholane **10a** (43.2 mg, 0.226 mmol) and phenylazide (26.8 mg, 0.225 mmol) in $CDCl_3$ were used, following the general method described above. The Staudinger reaction was monitored by ^{31}P NMR following the conversion of **10a** ($\delta = 144.7$) into iminodioxaphospholane **7a** ($\delta = 24.5$). After 150 min, $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added. A conversion of 55 % into oligomer **8a** ($\delta = 13.0$) was observed after 12 h.

B) Effect of the imino substituent

Reaction of 2-diisopropyl-2-*N*-phenylimino-1,3,2-λ^5-dioxaphospholane (7a): Dioxaphospholane **10a** (36.1 mg, 0.189 mmol) and phenylazide (22.8 mg, 0.191 mmol) in C_6D_6 were used. After 80 min, the conversion of **10a** into **7a** ($\delta = 18.0$) was complete and $BF_3 \cdot OEt_2$ (2.5 μL, 11 mol %) was added. The formation of polyphosphoramidate **8a** ($\delta = 13.0$) was followed by ^{31}P NMR. (progress of the reaction *t*/ min, (% oligomer **8a**)): 32 (0), 119 (23), 341 (71), 1046 (100).

Reaction of 2-*N*-benzylimino-2-diisopropyl-1,3,2-λ^5-dioxaphospholane (7f): Dioxaphospholane **10a** (33.5 mg, 0.175 mmol) and benzylazide (21.9 μL, 0.175 mmol) in C_6D_6 were used. The conversion of **10a** into **7f** ($\delta = 25.2$) was initially followed at room temperature but, in order to accelerate the Staudinger reaction, the NMR tube was heated to 50 °C. After 320 min, at 50 °C the tube was allowed to cool to room temperature

and $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added. The formation of polyphosphoramidate **8f** ($\delta = 16.9$) was followed by ^{31}P NMR. (*t*/ min, (% oligomer **8f**)): 6 (0), 67 (95), 794 (100).

Reaction of 2-diisopropyl-2-*N*′-(4-nitrobenzyl)imino-1,3,2-λ⁵-dioxaphospholane (7g): Dioxaphospholane **10a** (40.2 mg, 0.210 mmol) and 4-nitrobenzylazide (37.5 μL, 0.210 mmol) in C_6D_6 were used, with the NMR tube heated to 50 °C. The conversion of **10a** into **7g** ($\delta = 27.3$) was complete after 860 min. The tube was allowed to cool to room temperature and $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added. The formation of polyphosphoramidate **8g** ($\delta = 16.8$) was followed by ^{31}P NMR. (*t*/ min, (% oligomer **8g**)): 5 (44), 61 (92), 287 (100).

Reaction of 2-diisopropyl-2-*N*-octylimino-1,3,2-λ⁵-dioxaphospholane (7h): Dioxaphospholane **10a** (36.6 mg, 0.191 mmol) and octylazide (29.0 mg, 0.191 mmol) in C_6D_6 were used. The conversion of **10a** into **7h** ($\delta = 21.8$) was initially followed at room temperature but, in order to accelerate the Staudinger reaction, the NMR tube was heated to 50 °C. After 1080 min, the tube was allowed to cool to room temperature and $BF_3 \cdot OEt_2$ (2.5 μL, 11 mol %) was added. The formation of polyphosphoramidate **8h** was still not observed after 720 min of the addition of $BF_3 \cdot OEt_2$.

Reaction of 2-diisopropyl-2-*N*-tosylimino-1,3,2-λ⁵-dioxaphospholane (7i): Dioxaphospholane **10a** (33.4 mg, 0.175 mmol) and tosylazide (34.4 mg, 0.175 mmol) in C_6D_6 were used. The Staudinger reaction was followed by ^{31}P NMR. After 43 min, the conversion of **10a** into **7i** ($\delta = 26.6$) was complete and $BF_3 \cdot OEt_2$ (2.5 μL, 12 mol %) was added. The formation of polyphosphoramidate **8i** was still not observed after 1058 min of the addition of $BF_3 \cdot OEt_2$.

Tentative of isomerisation of 2-diisopropyl-2-*N*-trimethylsilylimino-1,2,3-λ⁵-dioxaphospholane (7j): Dioxaphospholane **10a** (35.0 mg, 0.191 mmol) and trimetylsilylazide (29.0 mg, 0.191 mmol) in C_6D_6 were used. Even after heating the reaction to 60 °C for 6 h no Staudinger reaction was observed.

C) Effect of substituents at the alkoxy carbon atoms

Reaction with 2-diethylamino-2-*N*-phenylimino-1,3,2-λ⁵-dioxaphospholane (7b): **At room temperature**: The general method was followed using **10b** (36.2 mg, 0.222 mmol) and phenylazide (26.4 mg, 0.222 mmol) in C_6D_6, at 35 °C, until all the dioxaphospholane **10b** ($\delta = 150.9$) was converted into the Staudinger product **7b** ($\delta = 19.9$, approx. 180 min). The tube was cooled to room temperature, $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added and the formation of polyphosphoramidate **8b** ($\delta = 13.6$) followed by ^{31}P NMR. After 220 min of the addition of $BF_3 \cdot OEt_2$ 70 % conversion was reached.

At 60 °C: The general method was followed using **10b** (32.8 mg, 0.201 mmol) and phenylazide (23.4 mg, 0.196 mmol) in C_6D_6 at 35 °C until all the dioxaphospholane **10b** ($\delta = 150.9$) was converted into the Staudinger product **7b** ($\delta = 19.9$, approx. 190 min). $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added and the reaction heated to 60 °C. The formation of polyphosphoramidate **8b** ($\delta = 13.6$) was followed by ^{31}P NMR. (*t*/ min, (% oligomer **8b**)): 13 (34), 26 (69), 60 (90).

Reaction with 2-diethylamino-4-methyl-2-*N*-phenylimino-1,3,2-λ⁵-dioxaphospholane (7k): **At room temperature**: The general method was followed using **10k** (36.5 mg, 0.192 mmol) and phenylazide (25.8 mg, 0.216 mmol) in C_6D_6. The reaction was followed until all dioxaphospholane **10k** ($\delta = 150.9$ and 146.3, initially in a 36:64 ratio) was converted into the Staudinger product **7k** ($\delta = 19.3$ and 18.8, 50:50 ratio, approx. 135 min). $BF_3 \cdot OEt_2$ (2.6 μL, 10 mol %) was added but the formation of polyphosphoramidate **8k** was still not observed after 920 min of the addition of the Lewis acid.

At 60 °C: The general method was followed, using **10k** (34.1 mg, 0.192 mmol) and phenylazide (23.4 mg, 0.196 mmol) in C_6D_6 at 40 °C. The reaction was followed by ^{31}P NMR, until all dioxaphospholane **10k** ($\delta = 150.9$ and 146.3, initially in a 36:64 ratio) was converted into the Staudinger product **7k** ($\delta = 19.3$ and 18.8, 50:50 ratio, approx. 80 min). $BF_3 \cdot OEt_2$ (2.4 μL, 10 mol %) was added and the reaction heated to 60 °C. The formation of polyphosphoramidate **8k** ($\delta = 12-14$) was followed by ^{31}P NMR. (*t*/ min, (% oligomer **8k**)): 257 (0), 1020 (43), 1277 (63), 1361 (67), 1434 (71), 1632 (79).

Reaction with 2-*N*-benzylimino-2-diisopropylamino-4-methyl-1,3,2-λ⁵-dioxaphospholane (7l) at 60 °C: The general method was followed with **10l** (42.5 mg, 0.207 mmol) and benzylazide (26.0 μL, 0.207 mmol) in toluene at 40 °C until all dioxaphospholane **10l** ($\delta = 151.1$ and 146.4, in an initial ratio of 25:75) was converted into the Staudinger product **7l** ($\delta = 24-25$, overlapping diastereomeric signals, approx. 280 min). $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added and the reaction heated to 60 °C. The formation of polyphosphoramidate **8l** ($\delta = 15-16$) was followed by ^{31}P NMR. (*t*/ min, (% oligomer **8l**)): 413 (25), 765 (39), 861 (53), 1060 (68).

Reaction with 2-*N*-benzylimino-2-diisopropylamino-4,5-dimethyl-1,3,2-λ⁵-dioxaphospholane (7m) at 100 °C: The general procedure was followed with a solution of **10m** (129.5 mg, 0.55 mmol) in [D_8]toluene (0.5 mL, instead of [D_6]benzene) and benzylazide (73.8 μL, 0.55 mmol). The mixture heated at 40 °C for 3 h, the time necessary for the total conversion of the dioxaphospholane **10m** ($\delta = 143.4$, only one diastereomer) into the Staudinger product **7m** (two diastereomers, $\delta = 27.1$ and 25.9 in a relative 85:15 proportion). $BF_3 \cdot OEt_2$ (2.5 μL, 10 mol %) was added and the reaction heated to 100 °C. After 12 h the ^{31}P NMR spectra revealed no change in the composition of the mixture and even after 24 h no polymerisation was observed.

Preparation of phosphoramides (9) used as standards

2-Diisopropylamino-3-*N*-phenyl-1,3,2-λ⁵-oxazaphospholidine-2-one (9a): $POCl_3$ (1.47 mL, 15.8 mmol) was added dropwise under argon atmosphere to a stirred ice-cold solution of 2-phenylaminoethanol (2.0 mL, 15.8 mmol) and dry triethylamine (2.2 mL, 31.6 mmol) in dry benzene (60 mL). Once the addition was complete the mixture was allowed to react at room temperature for 2 h. Diisopropylamine was added (4.45 mL, 31.64 mmol) and the mixture was refluxed for 12 h. After cooling, the amine salts were removed by filtration, the solvent removed in vacuo and the residue purified by flash chromatography (SiO_2, *n*-hexanes/AcOEt 1:1). Compound **9a** was obtained as white needles (537 mg, 12 %). M.p. 94–95 °C (AcOEt/*n*-hexanes); ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.28$ (t, $J(H,H) = 11.6$ Hz, 2H, -CH-, Ar), 7.16 (d, $J(H,H) = 8.0$ Hz, 2H, -CH-, Ar), 4.43 (q, $J(H,H) = 8.2$ Hz, 1H, -OCH_2CH$_2$N-), 4.44 (m, 1H, -OCH_2CH$_2$N-), 3.87 (q, $J(H,H) = 8.8$ Hz, 1H, -OCH$_2$CH_2N-), 3.64 (q, $J(H,H) = 7.1$ Hz, 1H, -OCH$_2$CH_2N-), 3.26–3.18 (m, $J(H,H) = 6.7$ Hz, 2H, -N(CH(CH$_3$)$_2$)$_2$), 1.25 (d, $J(H,H) = 6.7$ Hz, 6H, -N(CH(CH_3)$_2$)$_2$), 1.18 (d, $J(H,H) = 6.7$ Hz, 6H, -N(CH(CH_3)$_2$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 141.2$ (-C-, Ar), 128.1 (-CH-, Ar), 121.4 (-CH-, Ar), 116.1 (-CH-, Ar), 62.1 (-OCH_2CH$_2$N-), 46.9 (d, $^2J(P,C) = 14.0$ Hz, -OCH$_2$CH_2N-), 46.4 (-NCH(CH$_3$)$_2$), 22.3 (-NCH(CH_3)$_2$), 22.2 (-NCH(CH_3)$_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 19.3$; IR (KBr): $\nu_{max} =$ 2962.0 (CH), 1304.0 (Ph-N-R), 1247.4 (P=O), 1043.0, 1008.9 (P-O-C), 804.5 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 282 (25) $[M]^+$, 267 (48) $[M - CH_3]^+$, 239 (20) $[M - i\mathrm{Pr}]^+$, 225 (100) $[M - CH_3 - CH_2{=}CHCH_3]^+$, 182 (24) $[M - N i\mathrm{Pr}_2]^+$; HRMS (EI): calcd for $C_{14}H_{23}N_2O_2P$: 282.14972 $[M]^+$; found 282.14970.

3-*N*-Benzyl-2-diisopropylamino-1,3,2-λ⁵-oxazaphospholidine-2-one (9f): Dry diisopropylamine (6.02 mL, 42.9 mmol) was added dropwise under argon atmosphere to a stirred ice-cold solution of $POCl_3$ (2.0 mL, 21.5 mmol) in dry benzene (60.0 mL). After the addition of the amine the mixture was allowed to react at room temperature for 1 h. The mixture was cooled in a ice bath and a mixture of 2-benzylaminoethanol (3.05 mL, 21.5 mmol) and dry triethylamine (6.0 mL, 42.9 mmol) was added dropwise. Once the addition was completed the reaction was heated under reflux for 20 h. After cooling, the amine salts were removed by filtration, the solvent removed under vacuum and the residue purified by flash chromatography (SiO_2, *n*-hexanes/AcOEt 4:6). Compound **9f** was obtained has a viscous oil (902 mg, 14 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.39-7.32$ (m, 4H, -CH-, Ar), 7.27 (t, $J(H,H) = 7.2$ Hz, 1H, -CH-, Ar) 4.31–4.24 (m, 1H, -OCH_2CH$_2$N-), 4.16–4.02 (m, 3H, -OCH_2CH$_2$N-, -CH_2Ph), 3.53–3.36 (m, $J(H,H) = 6.9$ Hz, 2H, -N(CH(CH$_3$)$_2$)$_2$), 3.21–3.09 (m, 2H, -OCH$_2$CH_2N-), 1.30 (d, $J(H,H) = 6.9$ Hz, 6H, -N(CH(CH_3)$_2$)$_2$), 1.27 (d, $J(H,H) = 6.8$ Hz, 6H, -N(CH(CH_3)$_2$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 137.8$ (d, $^3J(P,C) = 7.0$ Hz, -C-, Ar), 128.6 (-CH-, Ar), 127.6 (-CH-, Ar), 127.4 (-CH-, Ar), 63.6 (-OCH$_2$CH$_2$N-), 48.6 (d, $^2J(P,C) = 5.6$ Hz, -NCH$_2$Ph), 46.1 (d, $^2J(P,C) = 5.5$ Hz, -OCH$_2$CH$_2$N-), 45.9 (d, $J(P,C) = 14.0$ Hz, -NCH(CH$_3$)$_2$), 22.9 (-NCH(CH$_3$)$_2$), 22.3 (-NCH(CH$_3$)$_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 27.1$; IR (film): $\nu_{max} = 2965.0$ (CH), 1240.0 (P=O), 1208.4, 1029.8, 1006.9 (P-O-C), 807.4, 731.6 cm^{-1}; MS (EI): *m*/*z* (%): 296 (13) $[M]^+$, 281 (90) $[M - CH_3]^+$, 253 (24) $[M - CH(CH_3)_2]^+$, 239 (67) $[M - CH_3 - CH_2{=}CHCH_3]^+$, 91 (100) $[PhCH_2]^+$; HRMS (EI): calcd for $C_9H_{25}N_2O_2P$: 296.16537 $[M]^+$; found 296.16540.

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General method for the coupling of aminoalcohols with diethylphosphoramidous dichloride: A solution of freshly distilled diethylphosphoramidous dichloride and a catalytic amount of 4-DMAP in THF (3.0 mL) was added dropwise under argon atmosphere to a stirred ice-cold dry THF (10 mL) solution of the respective aminoethanol and dry triethylamine. After stirring for 12 h at room temperature the mixture was filtered and the triethylamine salt washed with diethyl ether. The combined filtrate and washings were concentrated in vacuo and the products purified by flash chromatography (SiO_2) or crystallisation.

3-*N*-Benzyl-2-diethylamino-1,3,2-λ^5-oxazaphospholidine-2-one (9n): The general method was followed using 2-benzylaminoethanol (398 mg, 2.63 mmol), diethylphosphoramidous dichloride (500 mg, 2.63 mmol) and triethylamine (0.735 mL, 5.30 mmol). The yellow oily residue was purified by flash chromatography (SiO_2, AcOEt/*n*-hexanes 3:7, $R_f = 0.25$) to afford **9n** (503 mg, 71 %) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.35$ (m, 4H, -CH-, Ar), 7.29 (m, 1H, -CH-, Ar), 4.32–4.34 (m, 1H, -OC*H*$_2$CH$_2$N-), 4.17–4.09 (m, 1H, -OC*H*$_2$CH$_2$N-), 4.01 (d, J(H,H) = 7.0 Hz, 2H, -C*H*$_2$Ph), 3.26–3.02 (m, 6H, -OCH$_2$C*H*$_2$N-, -N(C*H*$_2$CH$_3$)$_2$), 1.13 (t, J(H,H) = 7.0 Hz, 6H, -N(CH$_2$C*H*$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 137.4$ (-C-, Ar), 128.5 (-CH-, Ar), 128.0 (-CH-, Ar), 127.4 (-CH-, Ar), 63.7 (-NCH$_2$*C*H$_2$O-), 48.5 (d, ^2J(P,C) = 5.0 Hz, -*C*H$_2$Ph), 46.1 (d, ^2J(P,C) = 15.0 Hz, -N*C*H$_2$CH$_2$O-); 39.5 (d, ^2J(P,C) = 5.0 Hz, -N(*C*H$_2$CH$_3$)$_2$), 14.4 (-N(CH$_2$*C*H$_3$)$_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 28.0$; IR (film): $\nu_{max} = 2971.5$ (CH), 1380.0, 1238.8 (P=O), 1210.3, 1027.1 (P-O-C), 809.8 cm^{-1}; MS (FAB): *m*/*z* (%): 269 (100) $[MH]^+$, 253 (10) $[M - CH_3]^+$, 196 (7) $[M - NEt_2]^+$, 91 (60) $[CH_2Ph]^+$; HRMS (FAB): calcd for $C_{13}H_{22}N_2O_2P$: 269.141892 $[MH]^+$; found 269.139793.

2-Diethylamino-3-*N*-phenyl-1,2,3-λ^5-oxazaphospholidine-2-one (9b): The general method was followed starting from anilinoethanol (780 mg, 5.70 mmol), diethylphosphosphoramidous dichloride (1.00 g, 5.70 mmol) and triethylamine (1.58 mL, 11.40 mmol). The residue was purified by flash chromatography (SiO_2, Et_2O, $R_f = 0.25$) to afford **9b** (806 mg, 60 %) as a white solid which was recrystallised from AcOEt/*n*-hexanes. M.p. 85–85.5 °C (AcOEt/*n*-hexanes), lit.[42] 87–87.5 °C (heptane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.06$ (d, J(H,H) = 8 Hz, 2H, -CH-, Ar), 6.97 (t, J(H,H) = 7.2 Hz, 1H, -CH-, Ar), 4.51 (m, J(P,H) = 9.4, J(H,H) = 8.9, 6.2, 2.8 Hz, 1H, -OC*H*$_2$CH$_2$N-), 4.38 (m, J(P,H) = 19.3, J(H,H) = 8.9, 7.1, 2.6 Hz, 1H, -OC*H*$_2$CH$_2$N-), 3.85 (m, J(P,H) = 9.6, J(H,H) = 7.8, 6.2, 2.6 Hz, 1H, -OCH$_2$C*H*$_2$N-), 3.70 (m, J(P,H) = 3.2, J(H,H) = 9.4, 7.8, 7.1 Hz, 1H, -OCH$_2$C*H*$_2$N-), 3.16–2.96 (m, 4H, -N(C*H*$_2$CH$_3$)$_2$), 0.99 (t, J(H,H) = 7.1 Hz, 6H, -N(CH$_2$C*H*$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 141.0$ (-C-, Ar), 129.1 (-CH-, Ar), 121.2 (-CH-, Ar), 115.7 (d, ^2J(P,C) = 4.2 Hz, -CH-, Ar), 62.4 (-NCH$_2$*C*H$_2$O-), 46.5 (d, ^2J(P,C) = 15.2 Hz, -N*C*H$_2$CH$_2$O-), 39.6 (d, ^2J(P,C) = 4.8 Hz, -N(*C*H$_2$CH$_3$)$_2$), 13.8 (-N(CH$_2$*C*H$_3$)$_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 20.1$; IR (KBr): $\nu_{max} = 2977.3$ (CH), 1303.1 (Ph-NR$_2$), 1240.0 (P=O), 1209.5, 1034.3 (P-O-C), 823.9 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 254 (48) $[M]^+$, 239 (100) $[M - CH_3]^+$, 182 (45) $[M - N(C_2H_5)_2]^+$, 119 (35), 72 (35); HRMS (EI): calcd for $C_{12}H_{19}N_2O_2P$: 254.11842 $[M]^+$; found 254.11840.

2-Diethylamino-5-methyl-3-*N*-phenyl-1,3,2-λ^5-oxazaphospholidine-2-one (9k): The general method was followed starting from D,L-1-*N*-phenylamino-2-propanol (1.0 g, 6.6 mmol), diethylphosphosphoramidous dichloride (1.26 g, 6.6 mmol) and triethylamine (1.85 mL, 13.3 mmol). The residue was purified by flash chromatography (SiO_2, *n*-hexanes/AcOEt 7:3) to afford **9k** (547 mg, 31 %) as a white solid mixture of diastereomers (*cis*/*trans*, 39:61); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.21$ (br, 2H, -CH-, Ar, *cis*; 2H, -CH-, Ar, *trans*), 7.02–6.95 (m, 2H, -CH-, Ar, *cis*; 2H, -CH-, *trans*), 6.91–6.86 (m, 1H, -CH-, Ar, *cis*; 1H, -CH-, *trans*), 4.76–4.72 (m, 1H, -OC*H*(CH$_3$)CH$_2$N-, *cis*), 4.67–4.58 (m, 1H, -OC*H*(CH$_3$)CH$_2$N-, *trans*), 3.85 (ddd, J = 8.8, 8.8, 7.1 Hz, 1H, -OCH(CH$_3$)C*H*$_2$N-, *trans*), 3.65 (ddd, J = 10.2, 8.7, 5.9 Hz, 1H, -OCH(CH$_3$)C*H*$_2$N-, *cis*), 3.38–3.26 (m, 1H, -OCH(CH$_3$)C*H*$_2$N-, *cis*; 1H, -OCH(CH$_3$)C*H*$_2$N-, *trans*), 3.16–2.86 (m, 4H, -N(C*H*$_2$CH$_3$)$_2$, *cis*; 4H, -N(C*H*$_2$CH$_3$)$_2$, *trans*), 1.50 (d, J(H,H) = 6.3 Hz, 3H, -OCH(C*H*$_3$)CH$_2$N-, *trans*), 1.42 (d, J(H,H) = 6.1 Hz, 3H, -OCH(C*H*$_3$)CH$_2$N-, *cis*), 0.97 (t, J(H,H) = 7.1 Hz, 6H, -N(CH$_2$C*H*$_3$)$_2$, *trans*), 0.92 (t, J(H,H) = 7.1 Hz, 6H, -N(CH$_2$C*H*$_3$)$_2$, *cis*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 141.1$ (-C-, Ar, *cis*, *trans*),129.1 (-CH-, Ar, *cis*, *trans*), 129.1 (-CH-, Ar, *cis*, *trans*), 121.1 (d, ^3J(P,C) = 13.0 Hz, -CH-, Ar, *cis*, *trans*), 116.0 (d, ^2J(P,C) = 5.2 Hz, -CH-, *para*-Ar, *cis*), 115.6 (d, ^2J(P,C) = 5.0 Hz, -CH-, *para*-Ar, *trans*), 71.5 (-O*C*H(CH$_3$)CH$_2$N-, *cis*), 70.4 (-O*C*H(CH$_3$)CH$_2$N-, *trans*), 54.1 (d, ^2J(P,C) = 13.3 Hz, -OCH(CH$_3$)*C*H$_2$N-, *cis*), 54.4 (d, ^2J(P,C) = 15.3 Hz, -OCH(CH$_3$)*C*H$_2$N-, *trans*), 39.6 (d, ^2J(P,C) = 4.3 Hz, -N(*C*H$_2$CH$_3$)$_2$), 39.6 (d, ^2J(P,C) = 3.6 Hz, -N(*C*H$_2$CH$_3$)$_2$, *cis* and *trans*), 21.9 (d, ^3J(P,C) = 2.4 Hz, -OCH(*C*H$_3$)CH$_2$N-, *trans*), 19.9 (d, ^3J(P,C) = 8.2 Hz, -OCH(*C*H$_3$)CH$_2$N-, *cis*), 14.0 (-N(CH$_2$*C*H$_3$)$_2$, *trans*), 13.9 (-N(CH$_2$*C*H$_3$)$_2$, *cis*); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 19.6$ (*cis*), 19.3 (*trans*); IR (KBr): $\nu_{max} = 2978.1$ (CH), 1331.8, 1310.4 (Ph-NR$_2$), 1245.1 (P=O), 1209.4, 1039.3 (P-O-C), 960.9, 752.0 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 268 (73) $[M]^+$, 253 (100) $[M - CH_3]^+$, 196 (32) $[M - N(C_2H_5)_2]^+$, 146 (22) $[PhNH_2CH_2CH(CH_3)OH]^+$, 132 (38), 106 (19) $[HOP(O)NEt_2]^+$; HRMS (EI): calcd for $C_{13}H_{21}N_2O_2P$: 268.134067 $[M]^+$; found 268.134643.

(2*RS*,5*S*)-2-Diethylamino-5-methyl-3-*N*-phenyl-1,3,2-λ^5-oxazaphospholane-2-one [(5*S*)-9k]: The general method was followed starting from (2*S*)-1-*N*-phenylamino-2-propanol (512 mg, 3.4 mmol), diethylphosphosphoramidous dichloride (643 mg, 3.4 mmol) and triethylamine (0.95 mL, 6.8 mmol). The residue was purified by flash chromatography (SiO_2, *n*-hexanes/AcOEt 7:3) to afford (5*S*)-**9k** (91.5 mg, 10 %) as a white solid mixture of diastereomers (*cis*-(2*R*,5*S*)/*trans*-(2*S*,5*S*) 32:68). All the spectral data identical to the racemic compound.

(2*RS*,5*R*)-2-Diethylamino-5-methyl-3-*N*-phenyl-1,3,2-λ^5-oxazaphospholane-2-one [(5*R*)-9k]: The general method was followed starting from (2*R*)-1-*N*-phenylamino-2-propanol (568 mg, 3.7 mmol), diethylphosphosphoramidous dichloride (714 mg, 3.7 mmol) and triethylamine (1.1 mL, 6.8 mmol). The residue was purified by flash chromatography (SiO_2, *n*-hexanes/AcOEt 7:3) to afford (5*R*)-**9k** (172 mg, 17 %) as a white solid mixture of diastereomers (*cis*-(2*S*,5*R*)/*trans*-(2*R*,5*R*) 32:68). All the spectral data identical to the racemic compound.

General procedure for the preparation of polyphosphoramidates (8): The respective azide (1.0 equiv) was added to a stirred solution (1.1M) of the dioxaphospholane **10** in dry benzene or toluene, under argon atmosphere, and the mixture was allowed to react, at the temperature indicated, until no more evolution of N_2 was observed. $BF_3 \cdot OEt_2$ (10 mol %) was added and, after 12 h, the reaction mixture was washed with aq sat. $NaHCO_3$ solution. The aqueous phase was extracted with dichloromethane, the combined organic layers where dried with $MgSO_4$ and the solvent removed in vacuo. Oligomers **8** where characterised without further purification (attempts to purify some of the samples by flash chromatography lead to decomposition by hydrolysis).

Poly-*O*-ethyl-*N*-benzylamino-*N*′,*N*′-diisopropylaminophosphoramidate (8n): The general method was followed using **10a** (470 mg, 2.46 mmol) and benzylazide (307 μL, 2.46 mmol) in dry benzene (2.7 mL) at 40 °C. After 3 h the mixture was cooled to room temperature and $BF_3 \cdot OEt_2$ (30.2 μL, 10 mol %) was added. The polyphosphoramidate **8n** (736 mg, 101 %) was obtained as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 7.27–7.266 (br, 5H, -C*H*-, Ar), 4.23–3.55 (br, 5H), 3.45–2.90 (br, 3H), 1.21–0.97 (br, 12H, -N(CH(C*H*$_3$)$_2$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 138.32$ (br), 128.16 (br), 127.78 (br), 127.16, 126.94, 62.4–61.9 (br), 51.2–50.9 (br), 45.7–45.5 (br), 22.64, 22.22; ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 17.2–16.9$; IR (film): $\nu_{max} = 2968.9$, 1239.6 (P=O), 1203.9, 1000.0 (P-O-C), 948.9 cm^{-1}; SEC: $M_n = 9727$, polydispersion index = 5.30.

Poly-*O*-ethyl-*N*,*N*-diisopropylamino-*N*′-(4-nitrobenzylamino)phosphoramidate (8g): The general method was followed using **10a** (558 mg, 2.92 mmol) and 4-nitrobenzylazide (520 mg, 2.92 mmol) in dry benzene (2.5 mL) at 40 °C. After 6 h the mixture was cooled to room temperature and $BF_3 \cdot OEt_2$ (30.2 μL, 10 mol %) was added. The polyphosphoramidate **8g** (744 mg, 75 %) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.22–8.06$ (br, 2H), 7.61–7.50 (br, 2H), 4.42–3.60 (br, 5H), 3.60–2.91 (3H, br), 1.3–1.1 (br, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 147.1$, 146.4, 128.4–127.9, 123.8–123.5, 62.7–62.3, 51.5–50.9, 22.9–22.7, 22.3, 22.2; ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 18.33$, 16.86, 16.64, 16.49, 16.27; IR (KBr): $\nu_{max} =$ 2971.0, 1522.1 (NO_2), 1345.8 (NO_2), 1245.8 (P=O), 1204.2, 1001.4 cm^{-1}; SEC: $M_n = 3395$, polydispersion index = 2.70.

Poly-*O*-ethyl-*N*,*N*-diethylamino-*N*′-phenylaminophosphoramidate (8b): The general method was followed using **10b** (500 mg, 3.1 mmol) and phenylazide (865 mg, 3.1 mmol) in dry benzene (3.0 mL) at room temperature. After 3 h $BF_3 \cdot OEt_2$ (37 μL, 10 mol %) was added. The polyphos-

phoramidate **8b** (789 mg, 87%) was obtained as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.19-6.60$ (br, 5H), 4.28–3.24 (br, 4H), 2.98–2.70 (br, 4H), 0.89–0.68 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 147.8$, 128.9–128.7 (br), 126.4, 125.1, 117.3, 63.3 (-OCH_2CH_2N-), 49.9 (-OCH_2CH_2N-), 39.5–39.3 (br), 13.9, 13.6; ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 14.4-14.0$ (br, approx. 70%), 10.9 (br); IR (KBr): $\nu_{max} = 2973.2$, 1602.4, 1495.3, 1222.1 (P=O), 1201.6, 1029.8 (P-O-C), 958.9 cm^{-1}; SEC: $M_n = 1374$, polydispersion index = 1.39; MS (FAB): *m*/*z* (%): 644 (2), 555 (2), 509 (16), 436 (17), 390 (34), 384 (20), 300 (46), 281 (52), 255 (78).

Poly-*O*-ethyl-*N*,*N*-diisopropylamino-*N*′-phenylaminophosphoramidate (8a): The general method was followed using **10a** (511 mg, 2.7 mmol) and phenylazide (318 mg, 2.7 mmol) in dry benzene (2.42 mL) at room temperature. After 3 h $BF_3 \cdot OEt_2$ (33 μL, 10 mol%) was added. The polyphosphoramidate **8a** (629 mg, 83%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.06$ (br, 4H), 6.98 (br, 1H), 3.80 (br, 2H), 3.36 (br, 2H), 3.14 (br, 2H), 1.08–0.70 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 142.9$ (br), 128.5 (br), 126.3 (br), 125.0 (br), 63.0 (br), 49.6 (br), 45.9 (br), 22.7 (br), 22.6 (br), 22.0 (br); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): $\delta = 12.9-12.3$ (>85%), 9.74, 9.41; IR (KBr): $\nu_{max} = 2969.4$, 1598.1, 1223.5 (P=O), 1026.1 (P-O-C), 992.2 cm^{-1}; SEC: $M_n = 3996$, polydispersion index = 3.92; MS (FAB): *m*/*z* (%): 710 (2), 658 (3), 565 (5), 464 (19), 446 (17), 402 (30), 327 (41), 309 (48), 283 (81); MS (MALDI): repeating unit: 282 ± 2 Da; $M_n = 1924$, polydispersion index = 1.14 (high intensity distribution) and $M_n = 1815$, polydispersion index = 1.14 (low intensity distribution).

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