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T3P®-assisted esterification and amidation of phosphinic acids☆

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ABSTRACT

A few phosphinic acids, such as phenylphosphinic acids, 1-hydroxy-3-phospholene 1-oxides and 1-hydroxyphospholane oxides are esterified with simple alcohols in the presence of propylphosphonic anhydride (T3P®). If 1.1 equiv of the T3P® reagent is used, the esterifications are fast and efficient at 25° C. In the case of more reactive models it was enough to apply 0.66 equiv of T3P® at 85° C under microwave conditions. The amidation of 1-hydroxy-3-methyl-3-phospholene oxide could also be accomplished under similar conditions.

1. Introduction

Phosphinic derivatives are most often prepared by the reaction of phosphinic chlorides with the corresponding nucleophiles, such as alcohols or amines.[2–4] Regarding phosphinates, we have found that phosphinic acids may undergo direct esterification with alcohols under microwave (MW) conditions.[5–8] However, thioesterification and amidation of phosphinic acids took place only partially on MW irradiation.[9,10] According to another method, phosphinates may also be obtained by the alkylating esterification of phosphinic acids; it was found that the combined use of phase transfer catalysis and the MW technique is advantageous.[8,11] In the last decade, a powerful condensing agent, the trimeric propylphosphonic acid anhydride (the T3P® reagent) emerged that could be used well in many reactions, such as the coupling of amino acids, acylations, esterifications and condensations.[12] The three-component Kabachnik–Fields reaction could also be performed under mild conditions utilizing the T3P® reagent.[13]

We have found that phosphinic acids may also be esterified by alcohols in the presence of the T3P® reagent. Our preliminary results were reported in a communication.[1]

In this article, we show the general applicability of the T3P® reagent in the esterification and amidation of different cyclic phosphinic acids.

2. Results and discussion

2.1. Esterification of phosphinic acids

2.1.1. Optimization of the esterification. At first, two model compounds, phenyl-*H*-phosphinic acid (**1**) and 1-hydroxy-3-methyl-3-phospholene 1-oxide (**2**) were chosen to find the most suitable conditions for the T3P®-mediated esterification with 3 equiv of butanol (Table 1). As was shown in the preliminary communication,[1] the esterification of phosphinic acids is practically quantitative in the presence of 1.1 equiv of the T3P® reagent at room temperature. After a reaction time of 30 min, phosphinates **3e** and **4** were obtained in yields of 95% and 82%, respectively (Table 1, entries 1 and 6). The use of only 0.66 equiv of the T3P® reagent under the same conditions was almost as efficient for the **1**→**3e** transformation, as the application of 1.1 equiv (91%, Table 1, entry 2); however, the esterification of hydroxy-phospholene oxide **2** was, in this case, less efficient, as phosphinate **4** was obtained in only 42% (Table 1, entry 7). Carrying out the **2**→**4** esterification at 85 °C, the yield was somewhat increased, but 56% is still far from quantitative (Table 1, entry 8). The latter variation (85 °C and 0.66 equiv of the reagent) was also performed under MW conditions affording product **4** in a yield of 79% (Table 1, entry 9). In the case of the more reactive phenyl-*H*-phosphinic acid (**1**), the esterification was also tried out using 0.44 equiv of the T3P® reagent. In this instance, phosphinate **3e** was obtained in 79% yield (Table 1, entry 3). Elevating the temperature to 85 °C did not help, but MW irradiation at

☆ See Ref. 1.

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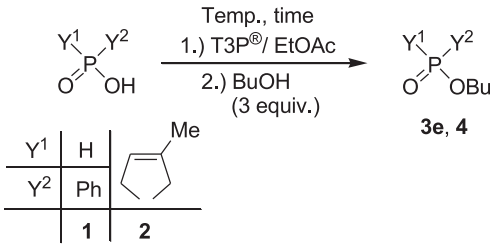
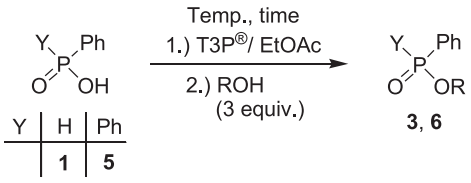
Table 1
Optimization of the esterification of phosphinic acids (**1** and **2**) with butanol in the presence of the T3P® reagent



Entry	Y^1	Y^2	T3P® (equiv)	Temp (°C)	Time (h)	Yield (%)
1	H	Ph	1.1	25	0.5	95 (**3e**)
2	H	Ph	0.66	25	0.5	91 (**3e**)
3	H	Ph	0.44	25	0.5	79 (**3e**)
4	H	Ph	0.44	85 (Δ)	0.25[a]	78 (**3e**)
5	H	Ph	0.44	85 (MW)	0.25[b]	89 (**3e**)
6[1]			1.1	25	0.5	82 (**4**)
7			0.66	25	0.5	42 (**4**)
8			0.66	85 (Δ)	0.5	56 (**4**)
9			0.66	85 (MW)	0.5[b]	79 (**4**)

[a] No change on further heating.
[b] No change on further irradiation.

Table 2
Esterification of phenyl-*H*-phosphinic acid (**1**) and diphenylphosphinic acid (**5**) with a series of alcohols in the presence of T3P®



R = Me (**a**), Et (**b**), Pr (**c**), ^{i}Pr (**d**), Bu (**e**), ^{i}Bu (**f**), ^{s}Bu (**g**),^{t}Bu (**h**)

Entry	Y	ROH	T3P® (equiv)	Temp (°C)	Time (h)	Yield (%)
1	H	MeOH	1.1 (0.66)	25	0.5	82 (80) (**3a**)
2	H	EtOH	1.1 (0.66)	25	0.5	89 (83) (**3b**)
3	H	PrOH	1.1 (0.66)	25	0.5	96 (91) (**3c**)
4	H	^{i}PrOH	1.1 (0.66)	25	1	81 (78) (**3d**)
5	H	BuOH	1.1 (0.66)	25	0.5	95 (91) (**3e**)
6	H	^{t}BuOH	1.1 (0.66)	25	1	91 (86) (**3f**)
7	H	^{s}BuOH	1.1 (0.66)	25	1	83 (81) (**3g**)[a]
8	H	^{t}BuOH	1.1 (0.66)	25	1	82 (78) (**3h**)
9	Ph	MeOH	1.1	85 (MW)	1	45 (**6a**)
10	Ph	EtOH	1.1	85 (MW)	1	45 (**6b**)
11	Ph	PrOH	1.1	85 (MW)	1	47 (**6c**)
12	Ph	BuOH	1.1	85 (MW)	1	49 (**6e**)

[a] As a 54–46% mixture of two isomers.

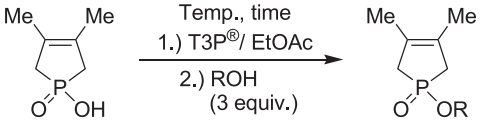
the same temperature was quite efficient and led to a yield of 89% (Table 1, entries 4 and 5, respectively).

It can be seen that from among the three '^{n}PrP(O)O' units of the T3P® reagent, one fragment can be used without any problem. The utilization of the second unit of '^{n}PrP(O)O' is possible with reactive phosphinic acids, such as phenyl-*H*-phosphinic acid (**1**). With less reactive phosphinic acids, like 1-hydroxy-3-phospholene oxide **2**, MW irradiation at 85 °C was necessary to attain a yield of 79%, when 0.66 equiv of the T3P® reagent was used. The esterification using 0.44 equiv of the T3P® reagent was beneficial only with the more reactive phenyl-*H*-phosphinic acid (**1**) under MW conditions.

*2.1.2. Esterification of acyclic phenylphosphinic acids (**1** and **5**).* In the next stage, phenyl-*H*-phosphinic acid (**1**) was esterified with other simple (C_1–C_4) alcohols using 1.1 or 0.66 equiv of the T3P® reagent at 25 °C (Table 2). In the second variation, applying only 0.66 equiv of the T3P® reagent, the yields were 2–6% lower, than using 1.1 equiv of the T3P® reagent. The yields of phosphinates **3a**–**h**, regarding both series of experiments, fall in the range of 80–95% after flash column chromatography (Table 2, entries 1–8). It is worthy of mention that the sterically hindered *tert*-butyl alcohol could be used almost as efficiently as the other alcohols (Table 2, entry 8). The esterification with *sec*-butanol resulted in product **3g** as a 54–46% mixture of two diastereomers. The esterification of the sterically more crowded, and hence not too reactive diphenylphosphinic acid (**5**) was performed in the presence of 1.1 equiv of the T3P® reagent at 85 °C for 1 h under MW irradiation to afford the products in lower yields of 45–49% (Table 2, entries 9–12). The products **3a**–**h**, **6a**–**c** and **6e**, which, with the exception of **3g**, were described earlier, were identified on the basis of ^{31}P NMR and HRMS. Compound **3g** was fully characterized also by ^{13}C and ^{1}H NMR data.

*2.1.3. Esterification of cyclic phosphinic acids (**7**, **9** and **11**).* The T3P®-mediated esterifications were then carried out with 1-hydroxy-3,4-dimethyl-3-phospholene 1-oxide (**7**) (Table 3). Using 1.1 equiv of the T3P® reagent, the reactions with *n*-alcohols were complete at 25 °C after 1 h (Table 3, entries 1, 3, 5, 10), but the esterification with branched alcohols required heating at 85 °C for 1 h (Table 3, entries 8, 13, 16), as the latter

Table 3
Esterification of 1-hydroxy-3,4-dimethyl-3-phospholene 1-oxide (**7**)



R = Me (**a**), Et (**b**), Pr (**c**), ^{i}Pr (**d**), Bu (**e**), ^{i}Bu (**f**), ^{s}Bu (**g**)

Entry	ROH	T3P® (equiv)	Temp (°C)	Time (h)	Yield (%)
1	MeOH	1.1	25	1	84 (**8a**)
2	MeOH	0.66	85 (MW)	1	83 (**8a**)
3	EtOH	1.1	25	1	82 (**8b**)
4	EtOH	0.66	85 (MW)	1	80 (**8b**)
5	PrOH	1.1	25	1	79 (**8c**)
6	PrOH	0.66	85 (MW)	1	80 (**8c**)
7	^{i}PrOH	1.1	25	2[a]	59 (**8d**)
8	^{i}PrOH	1.1	85[b] (Δ)	1[c]	79 (**8d**)
9	^{i}PrOH	0.66	85 (MW)	1	62 (**8d**)
10	BuOH	1.1	25	1	85 (**8e**)
11	BuOH	0.66	85 (MW)	1	79 (**8e**)
12	^{i}BuOH	1.1	25	1	72 (**8f**)
13	^{i}BuOH	1.1	85[b] (Δ)	1[c]	81 (**8f**)
14	^{i}BuOH	0.66	85 (MW)	1	75 (**8f**)
15	^{s}BuOH	1.1	25	2[a]	61 (**8g**)
16	^{s}BuOH	1.1	85[b] (Δ)	1[c]	71 (**8g**)
17	^{s}BuOH	0.66	85 (MW)	1	57 (**8g**)

[a] No change on further stirring.
[b] Temperature of the oil bath.
[c] No change on further heating.

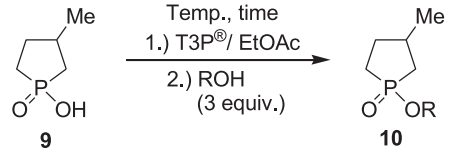
reactions were incomplete at 25 °C after ≤2 h (Table 3, entries 7, 12, 15).

Eventually, the phosphinates **8a**–**g** could be obtained in yields of 71–85% after flash column chromatography. Carrying out the esterifications with *n*-alcohols using only 0.66 equiv of the T3P® reagent at 85 °C under MW, the yields of phosphinates **8a**–**c** and **8e** were 1–6% lower (Table 3, entries 2, 4, 6, 11), while with branched alcohols as the reactant, the yields of esters **8d**, **8f** and **8g** were 6–17% lower (Table 3, entries 9, 14, 17). It can be concluded that in the case of *n*-alcohols as the partners, the use of only 0.66 equiv of the T3P® reagent may be enough, but 85 °C and MW irradiation are necessary.

With the exception of phosphinate **8g**, the other compounds (**8a**–**f**) were described earlier in the literature. The known species were identified on the basis of ^{31}P NMR and HRMS.

Then, 1-hydroxy-3-methylphospholane oxide (**9**) was esterified in a similar manner using 1.1 equiv of the T3P® reagent (Table 4). Reaction of the cyclic phosphinic acid (**9**) with alcohols at 25 °C furnished the phosphinates (**10a**–**g**) in yields of 54–81% after flash column chromatography (Table 4, entries 1, 3, 5, 7, 9, 11, 12). The lowest yields (55/54%) were obtained in the esterifications with isopropyl alcohol, and *sec*-butyl alcohol (Table 4, entries 7, 12). Performing the esterification with isopropyl alcohol at 85 °C did not help much (57%, Table 4, entry 8). Products **10a**–**f** consisted of ca. 1:1 mixtures of two diastereomers, while the *sec*-butyl ester (**10g**) comprised four isomers. Carrying out the esterifications with only 0.66 equiv of the T3P® reagent at 85 °C under MW, the yields of the *n*-alkyl esters (**10a**–**c** and **10e**) were 10–14% lower (Table 4, entries 2, 4, 6, 10), suggesting that in the case of hydroxymethylphospholane oxide **9**, that is of lower reactivity, it is better to use 1.1 equiv of the T3P® reagent to obtain the phosphinates (**10**) in higher yields.

Table 4
Esterification of 1-hydroxy-3-methylphospholane 1-oxide (**9**)



R = Me (**a**), Et (**b**), Pr (**c**), ^{i}Pr (**d**), Bu (**e**), ^{i}Bu (**f**), ^{s}Bu (**g**)

Entry	ROH	T3P® (equiv)	Temp (°C)	Time (h)	Yield[a] (%)
1	MeOH	1.1	25	1	81 (**10a**)
2	MeOH	0.66	85 (MW)	1	67 (**10a**)
3	EtOH	1.1	25	1	71 (**10b**)
4	EtOH	0.66	85 (MW)	1	60 (**10b**)
5	PrOH	1.1	25	1	67 (**10c**)
6	PrOH	0.66	85 (MW)	1	57 (**10c**)
7	^{i}PrOH	1.1	25	2[b]	55 (**10d**)
8	^{i}PrOH	1.1	85[c] (Δ)	1.5[b]	57 (**10d**)
9	BuOH	1.1	25	1	75 (**10e**)
10	BuOH	0.66	85 (MW)	1	61 (**10e**)
11	^{i}BuOH	1.1	25	2	66 (**10f**)
12	^{s}BuOH	1.1	25	2[b]	54 (**10g**)[d]

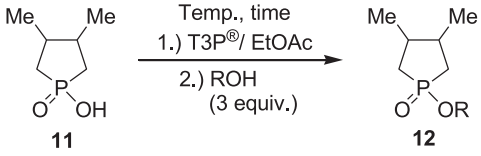
[a] As an ~1:1 mixture of two diastereomers.
[b] No change on further stirring.
[c] Temperature of the oil bath.
[d] As a 23:23:32:22% mixture of four diastereomers (determined on the basis of the relative ^{13}C NMR intensities of the C_5 signals).

1-Hydroxy-dimethylphospholane oxide **11** was also subjected to esterifications (Table 5). The experiences were similar to those observed for the monomethyl derivatives (**9**), however, in this instance, the esterification with isopropyl alcohol and *sec*-butyl alcohol was more efficient at 85 °C for 1.5/2 h (Table 5, entries 7, 8, 12). The phosphinates (**12a**–**g**), formed in this case as a mixture of three isomers, were obtained in yields of 45–75% after flash column chromatography (Table 5, entries 1, 3, 5, 8, 9, 11, 12). It can be seen from the data of Table 5 (entries 2, 4, 6, 10) that the use of only 0.66 equiv of the T3P® reagent led to ca. 11% lower yields of the corresponding phosphinates **12**.

The experience is that the lower reactivity of these saturated derivatives (**9** and **11**) did not justify attempts at the esterification with less T3P®.

The phosphinates **10a**–**d**, **10f** and **10g**, as well as **12a**–**d**, **12f**, and **12g** are new compounds and were fully characterized by ^{31}P, ^{13}C and ^{1}H NMR, as well as HRMS spectroscopy.

Table 5
Esterification of 1-hydroxy-3,4-dimethylphospholane 1-oxide (**11**)[a]



R = Me (**a**), Et (**b**), Pr (**c**), ^{i}Pr (**d**), Bu (**e**), ^{i}Bu (**f**), ^{s}Bu (**g**)

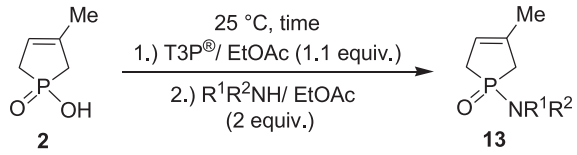
Entry	ROH	T3P® (equiv)	Temp (°C)	Time (h)	Yield (%)	Composition
1	MeOH	1.1	25	1	69 (**12a**)	91:3:6
2	MeOH	0.66	85 (MW)	1	57 (**12a**)	—
3	EtOH	1.1	25	1	72 (**12b**)	92:3:5
4	EtOH	0.66	85 (MW)	1	65 (**12b**)	—
5	PrOH	1.1	25	1	67 (**12c**)	94:3:3
6	PrOH	0.66	85 (MW)	1	55 (**12c**)	—
7	^{i}PrOH	1.1	25	2[b]	35 (**12d**)	—
8	^{i}PrOH	1.1	85[c] (Δ)	1.5	45 (**12d**)	95:3:2
9	BuOH	1.1	25	1	75 (**12e**)	92:5:3
10	BuOH	0.66	85 (MW)	1	63 (**12e**)	—
11	^{i}BuOH	1.1	25	2	54 (**12f**)	94:3:3
12	^{s}BuOH	1.1	85[c] (Δ)	2	45 (**12g**)	47:45:3:5

[a] The starting phosphinic acid comprised a 7:3 mixture of two isomers.
[b] No change on further reaction.
[c] Temperature of the oil bath.

One can see, that in most cases, phosphinic acids may be esterified efficiently with alcohols under mild conditions using 1.1 equiv of the T3P® reagent. With more reactive phosphinic acids, it is enough to apply the T3P® reagent in a quantity of 0.66 equiv, but more forcing conditions are necessary.

*2.1.4. Amidation of 1-hydroxy-3-methyl-3-phospholene 1-oxide (**2**).* We wished to extend the sphere of T3P®-promoted derivatizations of phosphinic acids. For this, 1-hydroxy-3-methyl-3-phospholene oxide **2** was reacted with a series of primary amines (propyl-, butyl-, hexyl- and benzyl-amines) and secondary amines (diethyl-, di-*n*-propyl- and di-*n*-butyl-amine) at 25 °C applying the T3P® reagent in a quantity of 1.1 equiv (Table 6). Depending on the reactivity of the amine, the completion required a reaction time of

Table 6
Amidation of 1-hydroxy-3-methyl-3-phospholene 1-oxide (**2**)



R^1	Pr	^{i}Pr	Bu	^{i}Bu	^{s}Bu	Hex	^{c}Hex	Bn	Et	Pr	Bu
R^2	H	H	H	H	H	H	H	H	Et	Pr	Bu
	(**a**)	(**b**)	(**c**)	(**d**)	(**e**)	(**f**)	(**g**)	(**h**)	(**i**)	(**j**)	(**k**)

Entry	R^1	R^2	Time (h)	Yield (%)
1	Pr	H	0.5	61 (**13a**)
2	^{i}Pr	H	2	60 (**13b**)
3	Bu	H	0.5	65 (**13c**)
4	^{i}Bu	H	0.5	68 (**13d**)
5	^{s}Bu	H	2	62 (**13e**)[a]
6	Hex	H	0.5	86 (**13f**)
7	^{c}Hex	H	2	82 (**13g**)
8	Bn	H	0.5	87 (**13h**)
9	Et	Et	2	65 (**13i**)
10	Pr	Pr	2	61 (**13j**)
11	Bu	Bu	2	70 (**13k**)

[a] As a 1:1 mixture of two diastereomers.

0.5 h or 2 h, and the phosphinic amides (**13a**–**k**) were obtained in a yield of 60–87% after column chromatography (Table 6, entries 1–11). The amide with the *sec*-butyl substituent (**13e**) was obtained as a 1:1 mixture of two diastereomers. The majority of the aminophospholene oxides (**13**) have been described earlier,[21,22] only species **13a**, **13b**, **13e**, **13j** and **13k** are new and were characterized in detail by us.

It can be seen that the T3P® reagent is also suitable to promote efficient amidation of phosphinic acids under mild conditions. This is the first case that a phosphinic acid is converted to amides using the T3P® reagent.

3. Conclusions

It was shown that phosphinic acids that do not undergo direct esterification and amidation with alcohols and amines, respectively, may be derivatized using the corresponding nucleophile in the presence of 1.1 equiv of the T3P® reagent. In the case of more reactive phosphinic acids, it was enough to apply 0.66 equiv of the condensing agent, and in certain cases, it was helpful to accomplish the reactions at 85 °C under MW conditions. The method developed represents an environmentally-friendly approach for the preparation of phosphinic derivatives.

4. Experimental

4.1. General

The MW-assisted reactions were carried out in a 300 W CEM Discover focused reactor equipped with a pressure controller applying 30–50 W under isothermal conditions. Standard 5 mL glass reaction vessels were used distributed by the supplier of the CEM reactor, and the reaction mixtures were stirred magnetically. The ^{13}C and ^{1}H NMR spectra were obtained in $CDCl_3$ solution on a Bruker DRX-500 spectrometer operating at 125.7, and 500.1 MHz, respectively. The ^{13}C and ^{1}H chemical shifts are referred to TMS. ^{31}P NMR spectra were obtained on a Bruker AV-300 spectrometer. Chemical shifts are downfield relative to 85% H_3PO_4. Mass spectrometry was performed on a Thermo LTQ-FT-Ultra spectrometer, or a Waters GCT Premier instrument applying ESI and EI modes of operation, respectively.

4.2. General procedure for esterification of phosphinic acids (1, 2, 5, 7, 9 and 11) in the presence of T3P®

A mixture of the phosphinic acid (0.76 mmol [phenyl-*H*-phosphinic acid (**1**): 0.11 g, 1-hydroxy-3-methyl-3-phospholene 1-oxide (**2**): 0.10 g, diphenylphosphinic acid (**5**): 0.15 g, 1-hydroxy-3,4-dimethyl-3-phospholene 1-oxide (**7**): 0.11 g, 1-hydroxy-3-methylphospholane 1-oxide (**9**): 0.10 g, 1-hydroxy-3,4-dimethylphospholane 1-oxide (**11**): 0.11 g]) and the T3P® reagent (0.55 mL, 0.84 mmol 50 wt % ethyl acetate solution) was stirred for 10 min. To the resulting mixture was added the alcohol (2.3 mmol [methanol: 0.09 mL, ethanol: 0.13 mL, propanol: 0.17 mL, isopropanol: 0.17 mL, butanol: 0.21 mL, isobutanol: 0.21 mL, *sec*-butanol: 0.21 mL, *tert*-butanol: 0.22 mL]) and the contents of the flask were stirred for appropriate time (see Tables 2–5). The excess of the T3P® reagent was hydrolyzed with 10% $NaHCO_3$ solution (15 mL) and the aqueous phase was washed with ethyl acetate (30 mL). The combined organic phase was dried (Na_2SO_4), and concentrated in vacuum to provide the crude product that was passed through a thin (ca. 3–4 cm) layer of silica gel using 3% MeOH in CH_2Cl_2 as the eluent to give the products (**2**, **3**, **6**, **8**, **10** and **12**) in a purity >99% as oils. For details see Tables 1–5. During the optimization procedure and in a part of other experiments, the T3P® reagent was also used in a 0.50 mmol and a 0.33 mmol (0.33 mL and 0.22 mL, respectively) quantity (see the appropriate parts of Tables 1–5).

The following new compounds were thus prepared:

*4.2.1. 1-Methylpropyl phenyl-H-phosphinate (**3g**).* ^{31}P NMR: ($CDCl_3$) δ: 22.2 (54%) and 23.6 (46%); ^{13}C NMR ($CDCl_3$) δ: 9.6 and 9.8 (CH_2CH_3), 21.3 and 21.9 (d, *J* 3.2 and 3.4, $CHCH_3$), 30.7 and 30.8 (d, *J* 4.7, $CHCH_2$), 76.0 and 76.6 (d, *J* 6.8, OCH), 128.8 (d, *J* 13.9, C_2 or C_3), 130.6 (d, *J* 132.5, C_1), 131.0 (d, *J* 11.8, C_3 or C_2), 133.1 (d, *J* 2.0, C_4); ^{1}H NMR ($CDCl_3$) δ: 0.88 and 0.96 (t, *J* 7.4, 3H, CH_2CH_3), 1.30 and 1.37 (d, *J* 6.2, 3H, $OCHCH_3$), 1.50–1.77 (m, 2H, $CHCH_2$), 4.40–4.52 (m, 1H, OCH), 7.60 (d, *J* 558.1, 1H, PH), 7.31–7.62 (m, 3H, ArH), 7.69–7.85 (m, 2H, ArH); IR (neat) 1033, 1234, 1440, 2975 cm^{-1}; $[M+H]^+_{found}$ = 199.0889, $C_{10}H_{16}O_2P$ requires 199.0888.

*4.2.2. 1-(1-Methylpropoxy)-3,4-dimethyl-3-phospholene 1-oxide (**8g**).* ^{31}P NMR: ($CDCl_3$) δ: 68.5; ^{13}C NMR ($CDCl_3$) δ: 9.6 (CH_2CH_3), 16.5 (d, *J* 15.8, C_3–CH_3), 21.7 (d, *J* 2.6, $OCHCH_3$), 30.7 (d, *J* 5.0, $OCHCH_2$), 36.4 and 36.8 (d, *J* 92.1, C_2), 74.3 (d, *J* 6.9, OCH), 127.3 and 127.5 (d, *J* 10.4 and 10.2, C_3); ^{1}H NMR ($CDCl_3$) δ: 0.82 (t, *J* 7.4, 3H, CH_2CH_3), 1.21 (d, *J* 6.2, 3H,$OCHCH_3$), 1.37–1.69 (m, 2H, $OCHCH_2$), 1.61 (s, 6H, C_3–CH_3, C_4–CH_3), 2.20–2.47 (m, 4H, PCH_2), 4.27–4.44 (m, 1H, OCH); IR (neat) 1030, 1244, 1446, 1651, 2973 cm^{-1}; $[M+H]^+_{found}$ = 203.1204, $C_{10}H_{20}O_2P$ requires 203.1201.

*4.2.3. 1-Methoxy-3-methylphospholane 1-oxide (**10a**).* ^{31}P NMR ($CDCl_3$) δ: 81.1; ^{13}C NMR ($CDCl_3$) δ: isomer **A**: 21.1 (d, *J* 7.9, C_3–CH_3), 24.8 (d, *J* 88.0, C_5), 31.1 (d, *J* 9.8, C_4 or C_3), 31.7 (d, *J* 12.9, C_3 or C_4), 32.2 (d, *J* 89.5, C_2 or), 51.0 (d, *J* 6.8, OCH_3); isomer **B**: 21.3 (d, *J*=7.4, C_3–CH_3), 25.5 (d, *J*=87.4, C_5), 31.3 (d, *J*=9.8, C_4 or C_3), 32.0 (d, *J*=12.9, C_3 or C_4), 32.5 (d, *J*=89.0, C_2), 51.0 (d, *J*=6.8, OCH_3); ^{1}H NMR ($CDCl_3$) δ: 1.05 (d, *J* 5.3, 3H, C_3–CH_3), 1.15–2.31 (m, 7H, CH_2, CH), 3.66 (d, *J* 10.8, 3H, OCH_3); IR (neat) 1034, 1228, 1458, 2956 cm^{-1}; $[M+H]^+_{found}$ = 149.0732, $C_6H_{14}O_2P$ requires 149.0732.

*4.2.4. 1-Ethoxy-3-methylphospholane 1-oxide (**10b**).* ^{31}P NMR ($CDCl_3$) δ: 79.4; ^{13}C NMR ($CDCl_3$) δ: isomer **A**: 16.5 (d, *J* 6.0, CH_2CH_3), 21.1 (d, *J* 8.0, C_3–CH_3), 25.4 (d, *J* 88.0, C_5), 31.2 (d, *J* 9.8, C_4 or C_3), 31.8 (d, *J* 13.0, C_3 or C_4), 32.9 (d, *J* 89.6, C_2), 60.45 (d, *J* 6.6, OCH_2); isomer **B**: 16.5 (d, *J* 6.0, CH_2CH_3), 21.3 (d, *J* 7.4, C_3–CH_3), 26.1 (d, *J* 87.6, C_5), 31.3 (d, *J* 9.8, C_4 or C_3), 32.0 (d, *J* 13.0, C_3 or C_4), 33.1 (d, *J* 89.1, C_2), 60.50 (d, *J* 6.5, OCH_2); ^{1}H NMR ($CDCl_3$) δ: 1.04 (d, *J* 6.2, 3H, C_3–CH_3), 1.28 (t, *J* 6.9, 3H, CH_2CH_3), 1.30–2.19 (m, 7H, skeletal CH_2, CH), 3.91–4.09 (m, 2H, OCH_2); IR (neat) 1036, 1228, 1458, 2957 cm^{-1}; $[M+H]^+_{found}$ = 163.0888, $C_7H_{16}O_2P$ requires 163.0888.

*4.2.5. 1-Propoxy-3-methylphospholane 1-oxide (**10c**).* ^{31}P NMR ($CDCl_3$) δ: 79.4; ^{13}C NMR ($CDCl_3$) δ: isomer **A**: 10.0 (CH_2CH_3), 21.2 (d, *J* 15.0, C_3–CH_3), 23.9 (d, *J* 6.1, OCH_2CH_2), 25.3 (d, *J* 88.1, C_5), 31.2 (d, *J* 9.7, C_4 or C_3), 31.8 (d, *J* 12.9, C_3 or C_4), 32.8 (d, *J* 89.6, C_2), 65.98 (d, *J* 6.8, OCH_2); isomer **B** 10.0 (CH_2CH_3), 21.3 (d, *J* 14.3, C_3–CH_3), 23.9 (d, *J* 6.1, OCH_2CH_2), 26.0 (d, *J* 87.6, C_5), 31.4 (d, *J* 9.8, C_4 or C_3), 32.0 (d, *J* 12.9, C_3 or C_4), 33.1 (d, *J* 89.2, C_2), 66.03 (d, *J* 6.8, OCH_2); ^{1}H NMR ($CDCl_3$) δ: 0.91 (t, *J* 7.3, 3H, CH_2CH_3), 1.05 (d, *J* 5.4, 3H, C_3–CH_3), 1.19–2.18 (m, 9H, skeletal CH_2, CH, CH_2CH_3), 3.80–4.00 (m, 2H, OCH_2); IR (neat) 1056, 1228, 1459, 2963 cm^{-1}; $[M+H]^+_{found}$ = 177.1040, $C_8H_{18}O_2P$ requires 177.1039.

*4.2.6. 1-Isopropoxy-3-methylphospholane 1-oxide (**10d**).* ^{31}P NMR ($CDCl_3$) δ: 77.8 (**A**, 54%) and 77.7 (**B**, 46%); ^{13}C NMR ($CDCl_3$) δ: isomer **A**: 21.3 (d, *J* 7.7, C_3–CH_3), 24.3 (d, *J* 4.2, $OCHCH_3$), 26.4 (d, *J* 88.2, C_5), 31.4 (d, *J* 10.0, C_4 or C_3), 32.0 (d, *J* 13.2, C_3 or C_4), 33.9 (d, *J* 89.7, C_2), 69.46 (d, *J* 6.6, OCH); isomer **B**: 21.5 (d, *J* 7.0, C_3–CH_3), 24.4 (d, *J* 4.2, $OCHCH_3$), 27.0 (d, *J* 88.0, C_5), 31.5 (d, *J* 10.9, C_4 or C_3), 32.2 (d, *J* 14.2, C_3 or C_4), 34.1 (d, *J* 89.5, C_2), 69.50 (d, *J* 6.6, OCH); ^{1}H NMR ($CDCl_3$) δ: 1.08 (d, *J*=6.2, 3H, C_3–CH_3), 1.31 (d, *J*=6.1, 6H, $CHCH_3$), 1.34–2.21 (m,

7H, skeletal CH_2, CH), 4.55–4.74 (m, 1H, OCH); IR (neat) 1059, 1229, 1458, 2960 cm^{-1}; $[M+H]^+_{found}$ = 177.1039, $C_8H_{18}O_2P$ requires 177.1039.

*4.2.7. 1-Isobutoxy-3-methylphospholane 1-oxide (**10f**).* ^{31}P NMR ($CDCl_3$) δ: 79.2; ^{13}C NMR ($CDCl_3$) δ: isomer **A**: 18.7 ($CHCH_3$), 21.2 (d, *J* 7.0, C_3-CH_3), 25.2 (d, *J* 88.2, C_5), 29.2 (d, *J* 6.3, OCH_2CH), 31.2 (d, *J* 9.7, C_4 or C_3), 31.8 (d, *J* 13.0, C_3 or C_4), 32.7 (d, *J* 89.8, C_2), 70.46 (d, *J* 6.9, OCH_2); isomer **B**: 18.7 ($CHCH_3$), 21.4 (d, *J* 6.2, C_3-CH_3), 25.9 (d, *J* 87.7, C_5), 29.2 (d, *J* 6.3, OCH_2CH), 31.4 (d, *J* 9.8, C_4 or C_3), 32.0 (d, *J* 13.1, C_3 or C_4), 33.0 (d, *J* 89.3, C_2), 70.51 (d, *J* 6.9, OCH_2); ^1H NMR ($CDCl_3$) δ: 0.79 (d, *J* 6.6) and 0.80 (d, *J* 6.6) total intensity 6H, $CHCH_3$, 0.96 (d, *J* 5.0, 3H, C_3-CH_3), 1.08–2.04 (m, 8H, skeletal CH_2, CH, CH_2CH), 3.52–3.72 (m, 2H, OCH_2); IR (neat) 1023, 1228, 1458, 2959 cm^{-1}; $[M+H]^+_{found}$ = 191.1195, $C_9H_{20}O_2P$ requires 191.1195.

*4.2.8. 1-(1-Methylpropoxy)-3-methylphospholane 1-oxide (**10g**).* ^{31}P NMR ($CDCl_3$) δ: 77.8 (**A** and **B**, 46% [on the basis of the relative ^{13}C NMR intensities of the signals of the C_5 atom, the ratio of **A** and **B** is 1:1]), 78.0 (**C**, 32%) and 77.9 (**D**, 22%); ^{13}C NMR ($CDCl_3$) δ: isomer **A**: 9.7 (CH_2CH_3), 21.3 (d, *J* 15.1, C_3-CH_3), 21.74 (d, *J* 7.9, $CHCH_3$), 26.1 (d, *J* 88.3, C_5), 30.69 (d, *J* 5.2, $CHCH_2$), 31.3 (d, *J* 9.7, C_4 or C_3), 31.9 (d, *J* 13.4, C_3 or C_4), 33.6 (d, *J* 89.9, C_2), 74.06 (d, *J* 7.1, OCH); isomer **B**: 9.7 (CH_2CH_3), 21.3 (d, *J* 15.1, C_3-CH_3), 21.74 (d, *J* 7.9, $CHCH_3$), 26.6 (d, *J* 88.3, C_5), 30.69 (d, *J* 5.2, $CHCH_2$), 31.4 (d, *J* 9.1, C_4 or C_3), 31.94 (d, *J* 13.4, C_3 or C_4), 33.9 (d, *J* 89.5, C_2), 74.08 (d, *J* 6.8, OCH); isomer **C**: 9.7 (CH_2CH_3), 21.4 (d, *J* 14.4, C_3-CH_3), 21.77 (d, *J* 8.0, $CHCH_3$), 26.8 (d, *J* 88.1, C_5), 30.71 (d, *J*~5, $CHCH_2$), 31.5 (d, *J* 9.3, C_4 or C_3), 32.04 (d, *J* 13.0, C_3 or C_4), 34.0 (d, *J* 89.9, C_2), 74.2 (d, *J*=7.1, OCH); isomer **D**: 9.7 (CH_2CH_3), 21.4 (d, *J* 14.4, C_3-CH_3), 21.71 (d, *J* 8.0, $CHCH_3$), 27.3 (d, *J* 88.0, C_5), 30.8 (d, *J*~5, $CHCH_2$), 31.6 (d, *J* 9.7, C_4 or C_3), 32.12 (d, *J* 13.6, C_3 or C_4), 34.4 (d, *J* 89.5, C_2), 74.3 (d, *J* 6.9, OCH); ^1H NMR ($CDCl_3$) δ: 0.88 (t, *J* 7.3, 3H, CH_2CH_3), 1.05 (d, *J* 4.7, 3H, C_3-CH_3), 1.26 (d, *J* 6.1, 3H, $CHCH_3$), 1.10–141 (m, 2H, $CHCH_2$), 1.45–2.15 (m, 7H, skeletal CH_2, CH), 4.27–4.48 (m, 1H, OCH); IR (neat) 1030, 1228, 1458, 2967 cm^{-1}; $[M+H]^+_{found}$ = 191.1196, $C_9H_{20}O_2P$ requires 191.1195.

*4.2.9. 1-Methoxy-3,4-dimethylphospholane 1-oxide (**12a**).* ^{31}P NMR ($CDCl_3$) δ: 74.7 (**A**, 91%), 81.3 (**B**, 6%) and 80.6 (**C**, 3%); ^{13}C NMR ($CDCl_3$) δ: 18.9 (d, *J* 15.7, C_3-CH_3 or C_4-CH_3), 19.1 (d, *J* 14.7, C_4-CH_3 or C_3-CH_3), 33.8 (d, *J* 88.4, C_5 or C_2), 34.1 (d, *J* 87.9, C_2 or C_5), 38.6 (d, *J* 10.8, C_4 or C_3), 38.7 (d, *J* 10.8, C_3 or C_4), 51.1 (d, *J* 6.7, OCH_3); ^1H NMR ($CDCl_3$) δ: 1.05 (br d, *J* 4.7, total intensity 6H, C_3-CH_3/C_4-CH_3), 1.24–2.10 (m, 6H, skeletal CH_2, CH), 3.65 (d, *J* 10.8, 3H, OCH_3); IR (neat) 1033, 1242, 1456, 2961 cm^{-1}; $[M+H]^+_{found}$ = 163.0886, $C_7H_{16}O_2P$ requires 163.0888.

*4.2.10. 1-Ethoxy-3,4-dimethylphospholane 1-oxide (**12b**).* ^{31}P NMR ($CDCl_3$) δ: 72.6 (**A**, 92%), 79.1 (**B**, 5%) and 78.5 (**C**, 3%); ^{13}C NMR ($CDCl_3$) δ: 16.4 (d, *J* 6.0, CH_2CH_3), 18.7 (d, *J* 15.1, C_3-CH_3 or C_4-CH_3), 18.9 (d, *J* 14.2, C_4-CH_3 or C_3-CH_3), 34.3 (d, *J* 88.5, C_5 or C_2), 34.6 (d, *J* 88.1, C_2 or C_5), 38.50 (d, *J* 10.8, C_4 or C_3), 38.54 (d, *J* 10.9, C_3 or C_4), 60.4 (d, *J* 6.5, OCH_2); ^1H NMR ($CDCl_3$) δ: 1.01 (br d, *J*~4.4, total intensity 6H, C_3-CH_3/C_4-CH_3), 1.24 (t, *J* 7.0) and 1.25 (t, *J* 7.0), total intensity 3H, CH_2CH_3, 1.15–2.02 (m, 6H, skeletal CH_2, CH), 3.89–4.10 (m, 2H, OCH_2); IR (neat) 1035, 1242, 1455, 2963 cm^{-1}; $[M+H]^+_{found}$ = 177.1042, $C_8H_{18}O_2P$ requires 177.1039.

*4.2.11. 1-Propoxy-3,4-dimethylphospholane 1-oxide (**12c**).* ^{31}P NMR ($CDCl_3$) δ: 72.6 (**A**, 94%), 78.5 (**B**, 3%) and 79.2 (**C**, 3%); ^{13}C NMR ($CDCl_3$) δ: 10.0 (CH_2CH_3), 18.7 (d, *J* 15.3, C_3-CH_3 or C_4-CH_3), 19.0 (d, *J* 14.4, C_4-CH_3 or C_3-CH_3), 23.8 (d, *J* 6.2, OCH_2CH_2), 33.8 (d, *J* 88.5, C_5 or C_2), 35.0 (d, *J* 88.2, C_2 or C_5), 38.5 (d, *J* 10.8, C_4 or C_3), 38.6 (d, *J* 10.9, C_3 or C_4), 65.9 (d, *J* 6.7, OCH_2); ^1H NMR ($CDCl_3$) δ: 0.91 (t, *J* 7.4, 3H, CH_2CH_3), 1.05 (br d, *J*~4.7, total intensity 6H, C_3-CH_3/C_4-CH_3), 1.29–1.75 (m, 6H, skeletal CH_2, CH), 1.93–2.08 (m, 2H, CH_2CH_3), 3.84–3.96 (m, 2H, OCH_2); IR (neat) 1064, 1243, 1456, 2965 cm^{-1}, $[M+H]^+_{found}$ = 191.1197, $C_9H_{20}O_2P$ requires 191.1195.

*4.2.12. 1-Isopropoxy-3,4-dimethylphospholane 1-oxide (**12d**).* ^{31}P NMR ($CDCl_3$) δ: 70.9 (**A**, 95%), 77.4 (**B**, 3%) and 76.9 (**C**, 2%); ^{13}C NMR ($CDCl_3$) δ: 18.9 (d, *J* 14.9, C_3-CH_3 or C_4-CH_3), 19.1 (d, *J* 14.1, C_4-CH_3 or C_3-CH_3), 24.2 and 24.3 (d, *J* 4.0 and *J* 3.7, $OCHCH_3$), 35.3 (d, *J* 88.6, C_5 or C_2), 35.6 (d, *J* 88.4, C_2 or C_5), 38.7 (d, *J* 10.8, C_3 and C_4), 69.3 (d, *J* 6.6, OCH); ^1H NMR ($CDCl_3$) δ: 1.06 (br d, *J*~4.8) and 1.07 (br d, *J*~4.8, total intensity 6H, C_3-CH_3/C_4-CH_3), 1.31 (br d, *J* 6.2, 6H, $CHCH_3$), 1.31–2.09 (m, 6H, skeletal CH_2, CH), 4.60–4.71 (m, 1H, OCH); IR (neat) 1065, 1244, 1457, 2961 cm^{-1}; $[M+H]^+_{found}$ = 191.1197, $C_9H_{20}O_2P$ requires 191.1195.

*4.2.13. 1-Isobutoxy-3,4-dimethylphospholane 1-oxide (**12f**).* ^{31}P NMR ($CDCl_3$) δ: 72.7 (**A**, 94%), 79.3 (**B**, 3%) and 78.5 (**C**, 3%); ^{13}C NMR ($CDCl_3$) δ: 18.9 ($CHCH_3$), 19.0 (d, *J* 17.1, C_3-CH_3 or C_4-CH_3), 19.2 (d, *J* 14.8, C_4-CH_3 or C_3-CH_3), 29.3 (d, *J* 6.3, OCH_2CH), 34.3 (d, *J* 88.6, C_5 or C_2), 34.7 (d, *J* 88.3, C_2 or C_5), 38.8 (d, *J* 10.8, C_3 and C_4), 70.6 (d, *J* 6.9, OCH_2); ^1H NMR ($CDCl_3$) δ: 0.88 (d, *J* 6.7, 6H, $CHCH_3$), 1.03 (br d, *J*~5.0, 6H, C_3-CH_3/C_4-CH_3), 1.26–2.08 (m, 7H, skeletal CH_2, CH, OCH_2CH), 3.60–3.77 (m, 2H, OCH_2); IR (neat) 1024, 1244, 1456, 2961 cm^{-1}; $[M+H]^+_{found}$ = 205.1355, $C_{10}H_{22}O_2P$ requires 205.1352.

*4.2.14. 1-(1-Methylpropoxy)-3,4-dimethylphospholane 1-oxide (**12g**).* ^{31}P NMR ($CDCl_3$) δ: 71.2 (**A**, 49%), 71.3 (**B**, 47%), 77.3 (**C**, 2%) and 77.8 (**D**, 2%); ^{13}C NMR ($CDCl_3$) δ: isomer **A**: 9.6 (CH_2CH_3), 18.8 (d, *J* 15.3, C_3-CH_3 or C_4-CH_3), 19.1 (d, *J* 14.5, C_4-CH_3 or C_3-CH_3), 21.6 (d, *J* 2.8, $OCHCH_3$), 30.6 (d, *J* 5.3, $CHCH_2$), 35.0 (d, *J* 88.8, C_5 or C_2), 35.4 (d, *J* 88.7, C_2 or C_5), 38.6 (d, *J* 10.9, C_4 or C_3), 38.66 (d, *J* 10.8, C_3 or C_4), 74.0 (d, *J* 7.0, OCH); isomer **B**: 9.6 (CH_2CH_3), 18.8 (d, *J* 15.3, C_3-CH_3 or C_4-CH_3), 19.1 (d, *J* 14.5, C_4-CH_3 or C_3-CH_3), 21.8 (d, *J* 2.4, $OCHCH_3$), 30.7 (d, *J* 5.1, $CHCH_2$), 35.3 (d, *J* 88.5, C_5 or C_2), 35.8 (d, *J* 88.6, C_2 or C_5), 38.66 (d, *J* 10.8, C_4 or C_3), 38.71 (d, *J* 10.6, C_3 or C_4), 74.2 (d, *J* 7.0, OCH); ^1H NMR ($CDCl_3$) δ: 0.90 (t, *J* 7.4, 3H, CH_2CH_3), 1.05 (br d, *J*~4.8) and 1.06 (br d, *J*~4.8, total intensity 6H, C_3-CH_3/C_4-CH_3), 1.28 (d, *J* 6.2, 3H, $CHCH_3$), 1.37–2.04 (m, 8H, skeletal CH_2, CH, $CHCH_2$), 4.30–4.45 (m, 1H, OCH); IR (neat) 1031, 1239, 1457, 2966 cm^{-1}; $[M+H]^+_{found}$ = 205.1352, $C_{10}H_{22}O_2P$ requires 205.1352.

The identification of the known compounds (**3a**–**f**, **3h**, **6a**–**c**, **6e**, **8a**–**f**, **10e** and **12e**) is given in Table 7.

Table 7
Selected spectral data for the known esters (**3a**–**f**, **3h**, **6a**–**c**, **6e**, **8a**–**f**, **10e** and **12e**)

Product	^{31}P NMR ($CDCl_3$)	δ_P (lit.)	$[M+H]^+_{found}$	$[M+H]^+_{requires}$
3a	27.2	27.6 [14]	157.0423	157.0413
3b	25.7	24.7 [15]	171.0575	171.0575
3c	25.0	24.9 [15]	185.0733	185.0731
3d	22.3	22.3 [15]	185.0733	185.0731
3e	25.7	24.9 [15]	199.0888	199.0888
3f	25.2	25.0 [15]	199.0887	199.0888
3h	15.2	15.3 [16]	199.0888	199.0888
6a	33.4	34.5 [17]	233.0737	233.0737
6b	31.4	30.8 [18]	247.0888	247.0888
6c	31.2	33.5 [19]	261.1040	261.1039
6e	31.2	31.2 [15]	275.1196	275.1195
8a	70.5	70.1 [20]	161.0730	161.0731
8b	68.5	68.3 [11]	175.0887	175.0888
8c	68.6	68.5 [15]	188.0955[a]	188.0966[a]
8d	66.8	66.8 [11]	188.0959[a]	188.0966[a]
8e	68.5	68.4 [15]	203.1203	203.1201
8f	67.6	68.5 [15]	203.1204	203.1201
10e	79.4	79.40 (50%)	191.1204	191.1201
		79.38 (50%) [8]		
12e	72.4 (92%)	72.5 (60%)	205.1350	205.1357
	78.3 (3%)	78.4 (20%)		
	79.0 (5%)	79.0 (20%) [8]		

[a] For the unprotonated M.

4.3. General procedure for the amidation of 1-hydroxy-3-methyl-3-phospholene 1-oxide (2) in the presence of T3P®

A mixture of 1-hydroxy-3-methyl-3-phospholene 1-oxide (**2**) (0.76 mmol, 0.10 g) and the T3P® reagent (0.55 mL, 0.84 mmol 50 wt % ethyl acetate solution) was stirred for 10 min. The amine (1.52 mmol [propylamine: 0.12 mL, isopropylamine: 0.13 mL, butylamine: 0.15 mL, isobutylamine: 0.15 mL, *sec*-butylamine: 0.15 mL, hexylamine: 0.20 mL, cyclohexylamine: 0.17 mL, benzylamine: 0.17 mL, diethylamine: 0.17 mL, dipropylamine: 0.21 mL, dibutylamine: 0.26 mL]) was added to the resulting mixture and the contents of the flask were stirred for the appropriate time (see Table 6). The excess of T3P® reagent was hydrolyzed with 10% $NaHCO_3$ solution (7 mL) and the aqueous phase was washed with of ethyl acetate (30 mL). The combined organic phase was dried (Na_2SO_4), filtered and concentrated in vacuum to provide the crude product that was passed through a thin (ca. 3–4 cm) layer of silica gel using 3% MeOH in CH_2Cl_2 as the eluent to give the products (**13**) in a purity >99% as oils. For details, see Table 6.

The following new compounds were thus prepared:

*4.3.1. 1-Propylamino-3-methyl-3-phospholene 1-oxide (**13a**).* ^{31}P NMR: ($CDCl_3$) δ: 63.2; ^{13}C NMR ($CDCl_3$) δ: 11.2 (CH_2CH_3), 20.6 (d, J 12.1, C_3–CH_3), 25.2 (d, J 6.3, CH_2CH_3), 32.1 (d, J 82.1, C_5), 35.0 (d, J 85.6, C_2), 42.4 (d, J 1.7, NCH_2), 120.7 (d, J 9.7, C_4), 136.6 (d, J 15.2, C_3); ^1H NMR ($CDCl_3$) δ: 0.90 (t, J 7.4, 3H, CH_2CH_3), 1.42–1.64 (m, 2H, CH_2), 1.77 (s, 3H, C_3–CH_3), 2.19–2.61 (m, 5H, CH_2, NH), 2.78–2.98 (m, 2H, $NHCH_2$), 5.49 (d, J 33.8, 1H, C_4–H); IR (neat) 773, 1173, 1457, 1649, 2962 cm^{-1}; $[M+H]^+_{found}$=174.1049, $C_8H_{17}NOP$ requires 174.1043.

*4.3.2. 1-Isopropylamino-3-methyl-3-phospholene 1-oxide (**13b**).* ^{31}P NMR: ($CDCl_3$) δ: 61.0; ^{13}C NMR ($CDCl_3$) δ: 20.8 (d, J 12.1, C_3–CH_3), 26.0 ($CHCH_3$), 33.3 (d, J 82.3, C_5), 36.1 (d, J 85.8, C_2), 43.4 (d, J 2.0, NHCH), 120.8 (d, J 9.7, C_4), 136.8 (d, J 15.2, C_3); ^1H NMR ($CDCl_3$) δ: 1.20 (d, J 6.4, 6H, $CHCH_3$), 1.79 (s, 3H, C_3–CH_3), 2.10–2.65 (m, 5H, CH_2, NH), 3.30–3.59 (m, 1H, NHCH), 5.51 (d, J 32.6, 1H, C_4–H); IR (neat) 776, 1173, 1467, 1650, 2966 cm^{-1}; $[M+H]^+_{found}$=174.1054, $C_8H_{17}NOP$ requires 174.1043.

*4.3.3. 1-(1-Methylpropylamino)-3-methyl-3-phospholene 1-oxide (**13e**).* ^{31}P NMR: ($CDCl_3$) δ: 61.3; ^{13}C NMR ($CDCl_3$) δ: isomers **A** and **B** 10.4 (CH_2CH_3), 20.7 (d, J 12.1, C_3–CH_3), 23.4 (d, J 2.1, $CHCH_3$), 32.2 (d, J 4.7, CH_2CH_3), 33.1 and 33.2 (d, J 82.7 and 82.2, C_5), 35.9 and 36.1 (d, J 86.3 and 85.2, C_2), 48.7 (d, J 1.8, CH), 120.7 (d, J 9.7, C_4), 136.7 (d, J 15.3, C_3); ^1H NMR ($CDCl_3$) δ: 0.92 (t, J 7.4, 3H, CH_2CH_3), 1.19 (d, J 6.4, 3H, $CHCH_3$), 1.40–1.55 (m, 2H, CH_2CH_3), 1.79 (s, 3H, C_3–CH_3), 2.17–2.62 (m, 5H, CH_2, NH), 3.06–3.28 (m, 1H, NHCH), 5.52 (d, J 33.2, 1H, C_4–H); IR (neat) 778, 1173, 1467, 1652, 2966 cm^{-1}; $[M+H]^+_{found}$=188.1206, $C_9H_{19}NOP$ requires 188.1204.

*4.3.4. 1-Dipropylamino-3-methyl-3-phospholene 1-oxide (**13j**).* ^{31}P NMR: ($CDCl_3$) δ: 66.3; ^{13}C NMR ($CDCl_3$) δ: 11.2 (CH_2CH_3), 20.6 (d, J 12.1, C_3–CH_3), 21.6 (d, J 2.8, CH_2CH_3), 32.0 (d, J 80.9, C_5), 34.7 (d, J 84.1, C_2), 46.1 (d, J 3.3, NCH_2), 121.2 (d, J 9.7, C_4), 137.0 (d, J 15.2, C_3); ^1H NMR ($CDCl_3$) δ: 0.86 (t, J 7.4, 6H, CH_2CH_3), 1.40–1.61 (m, 4H, CH_2CH_3), 1.78 (s, 3H, C_3–CH_3), 2.18–2.52 (m, 4H, CH_2), 2.71–2.96 (m, 4H, NCH_2), 5.53 (d, J 33.7, 1H, C_4–H); IR (neat) 768, 1195, 1465, 1647, 2963 cm^{-1}; $[M+H]^+_{found}$=216.1517, $C_{11}H_{23}NOP$ requires 216.1517.

*4.3.5. 1-Dibutylamino-3-methyl-3-phospholene 1-oxide (**13k**).*[21] ^{31}P NMR: ($CDCl_3$) δ: 66.3; ^{13}C NMR ($CDCl_3$) δ: 13.8 (CH_2CH_3), 20.1 (CH_2CH_3), 20.6 (d, J 12.1, C_3–CH_3), 30.7 (d, J 2.8, NCH_2CH_2), 32.0 (d, J 80.8, C_5), 34.7 (d, J 84.1, C_2), 44.1 (d, J 3.3, NCH_2), 121.2 (d, J 9.7, C_4), 137.0 (d, J 15.2, C_3); ^1H NMR ($CDCl_3$) δ: 0.89 (t, J 7.3, 6H, CH_2CH_3), 1.15–1.32 (m, 4H, CH_2CH_3), 1.34–1.55 (m, 4H, NCH_2CH_2), 1.76 (s, 3H, C_3–CH_3), 2.26–2.50 (m, 4H, CH_2), 2.79–2.98 (m, 4H, NCH_2), 5.51 (d, J 32.4, 1H, C_4–H); IR (neat) 776, 1186, 1466, 1647, 2959 cm^{-1}; $[M+H]^+_{found}$=244.1838, $C_{13}H_{27}NOP$ requires 244.1825.

The identification of the known compounds (**13c**, **13d** and **13f**–**i**) is given in Table 8.

Table 8
Selected spectral data for the known amides (**13c**, **13d** and **13f**–**i**)

Product	^{31}P NMR ($CDCl_3$)	δ_P (lit.)	$[M+H]^+_{found}$	$[M+H]^+_{requires}$
13c	63.4	63.2 [22]	188.1207	188.1204
13d	63.3	63.6 [22]	188.1207	188.1204
13f	63.7	63.1 [22]	216.1518	216.1517
13g	60.9	60.7 [22]	214.1359	214.1361
13h	63.9	63.5 [22]	222.1046	222.1048
13i	65.8	65.5 [23]	188.1204	188.1204

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