Phosphorylation of Arylureas and Arylcarbamates: A New Prospect

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Abstract: *N*,*N*′-Diarylureas having electron-donating substituents at appropriate positions react with phosphorus(III) bromide forming the new heterocyclic system 2,4,1-benzodiazaphosphinan-3-one. *N*-(5-Pyrazolyl), *N*′-arylureas, and *N*,*O*-diarylcarbamates also undergo an analogous heterocyclization affording 1*H*-pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one and 2,4,1-benzoxazaphosphinan-3-one ring systems.

Key words: *N*,*N*′-diarylureas, *N*-(5-pyrazolyl) , *N*′-arylureas, *N*,*O*-diarylcarbamates, phosphorus(III) halides, phosphorylation, heterocyclization

Phosphorus-containing heterocycles are a less numerous and more inaccessible class of compounds in comparison with classic nitrogen or sulfur heterocycles.[1] However, interest in this class of compounds, especially those containing an endocyclic P–C bond, has increased due to their recent use in a wide variety of areas as model substrates,[2] as ligands for new catalysts,[3] for modifying properties of materials,[4] and as important building blocks for drug discovery,[5] etc.

Direct phosphorylation of electron-rich aromatic[6] and heteroaromatic[7] substances with phosphorus halides has proved to be a straightforward route to fused phospha-heterocycles. Electrophilic attack of phosphorus halide as a polydentate reagent results in the binding of two nucleophilic centers of a substrate via the phosphorus atom in one step. We successfully applied this approach to the synthesis of a series of novel fused phosphorus-incorporated heterocyclic systems.[8] Our most recent work was devoted to the study of the binding through a phosphorus atom of a C-nucleophilic center of a ring and an amide functional group.[9] In continuation of our research on the phospha-heterocyclization of substrates with an amide group we investigated phosphorylation of substrates having a C-nucleophilic center and an additional ureido or uretano group on a side chain with phosphorus halides. Earlier, it has been shown that ureas are efficient bis-N,N-nucleophiles for the construction of phosphorus-incorporated heterocycles.[10] Herein, we wish to report the C-phosphorylation of electron-rich diarylureas and diarylcarbamates bearing a ureido or uretano group *ortho* to the C-nucleophilic center of an aromatic or heteroaromatic moiety. Various derivatives of fused 1,5,2-diazaphosphinines and 1,3,4-oxazaphosphinines can be prepared by this method.

The synthesis of monocyclic 1,5,2-diazaphosphinines was reported,[11] however, we were interested in the synthesis of phospha-analogues of biologically active compounds bearing a pyrimidine scaffold, due to the fact that the phosphorus atom in the heterocycle could regulate important biological activity and increase the biological activity of these type of compounds. Phospha-analogues of other biologically active compounds have been found to have increased biological activity,[12] as exemplified in the synthesis of enzymatic inhibitors **I** and **II** having a 1,5,2-diazaphosphinine ring (Figure 1).[13] Also, there is one report on the preparation of benzo-fused compound **III**, patented as a herbicide (Figure 1).[14] The lack of a convenient and flexible method for the synthesis of these heterocycles has limited their use, as they were synthesized in several steps using poorly accessible starting materials.

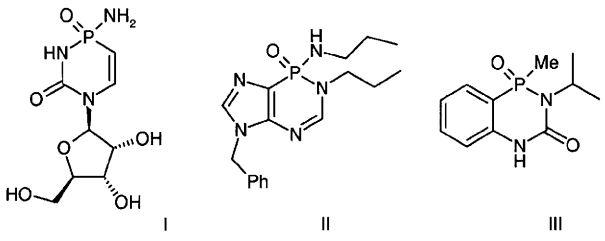

Figure 1

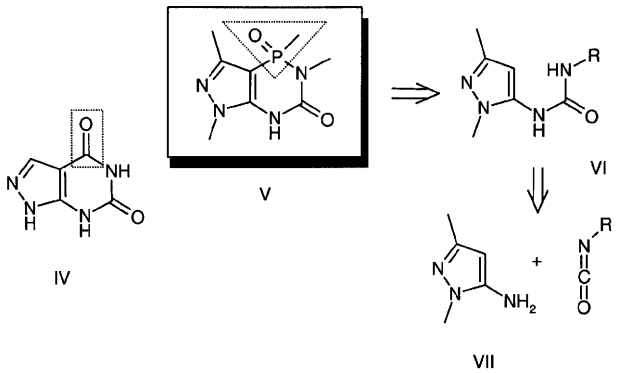

Figure 2

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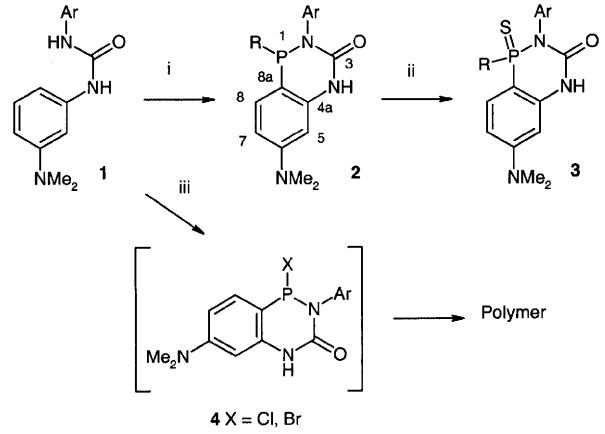
Herein, we describe a one-step procedure for the synthesis of phospha-heterocycles starting from readily available ureas. Retrosynthetic analysis of pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one ring system **V**, which is the phospha-analogue of 1*H*-pyrazolo[3,4-*d*]pyrimidine-4,6(5*H*,7*H*)-dione **IV**, which also posesses enzymatic inhibitor activity, is given in Figure 2.[15]

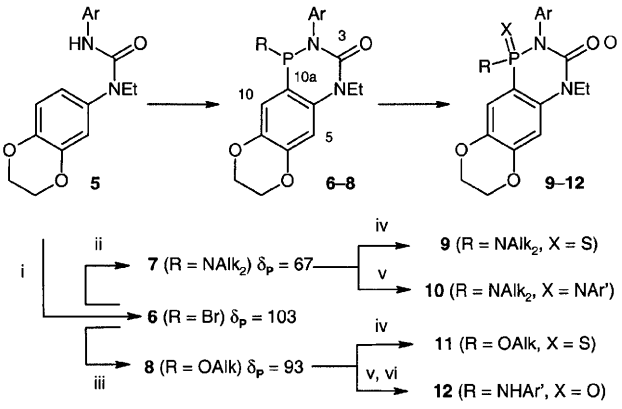
Urea **1** was reacted with aryldibromophosphines forming 2,4,1-benzodiazaphosphinan-3-one ring system **3**.[16] The heterocyclization is carried out in pyridine at room temperature and is complete in 48 hours. Our attempts to carry out the cyclization with phosphorus(III) trihalides were unsuccessful; this can result from the very low stability of cyclic phosphorus acid halides **4** bearing a nucleophilic NH-fragment at the diazaphosphinanone ring (Scheme 1).



Scheme 1 *Reagents and conditions*: (i) 5-methyl-2-furyl–PBr_2, pyridine, r.t., 48 h; (ii) S, pyridine; (iii) PCl_3 or PBr_3, pyridine

A range of spectral methods confirmed the formation of the diazaphosphinanone ring. The ^{1}H NMR spectrum of thiooxide **3** revealed the absence of a signals corresponding to the NH of the ureido group, as well as the absence of one H from the aniline moiety. As well as this, the character of the signals changed, a doublet of doublets appeared corresponding to C(8) on the diazaphosphinanone ring (Figure 3; $\delta = 7.5$, $^3J_{HH} = 8.7$ Hz, $^3J_{PH} = 15.6$ Hz). Further confirmation was obtained from the ^{13}C NMR spectrum where the signal for C(8a) appeared at 96.5 ppm and exhibited considerable coupling with the P atom ($^1J_{PC} = 117.4$ Hz). Besides NMR techniques an intensive IR absorption was observed at 1678 cm^{-1} (C=O) providing convincing evidence of the formation of the diazaphosphinanone ring.

Besides the dialkylamino group, alkoxy groups attached to benzene rings activate these compounds sufficiently to undergo heterocylclization. At the same time, the reduced C-nucleophilicity of these compounds compared to dialkylamino analogous requires the use of a more active phosphorylating agent such as PBr_3. To increase the nucleophilicity of the starting urea **5**, derived from benzodioxane and to avoid any possible complications during the reaction, an ethyl group was introduced at the nitrogen atom. Urea **5** reacts with PBr_3 in pyridine solution in the presence of Et_3N as a base in 48 hours forming cyclic acid bromide **6**.[16] This heterocyclization is the first example of a direct, non-catalytic phosphorylation of a benzodioxane moiety with phosphorus(III) halides.[17] However, the reaction does not occur with less active aryldibromophosphines.



Scheme 2 *Reagents and conditions*: (i) PBr_3, Et_3N, pyridine, r.t., 48 h; (ii) Alk_2NH, pyridine; (iii) AlkOH, pyridine; (iv) S, pyridine; (v) Ar′N_3, pyridine, 50 °C, 3 h; (vi) H_2O, pyridine

On the basis of the cyclic bromoanhydride **6** a series of air-stable phosphorus(V) derivatives **9–12** were synthesized (Scheme 2, Table 2). It should be noted that phosphonimides of benzodiazaphosphinanones **10** are more hydrolytically stable in comparison with phosphonimides of benzoxazaphosphinines.[9a]

The structure of 1λ^5-diazaphosphinan-3-ones **9–12** obtained was confirmed by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. The absence of the signal for the ureido proton and the appearance of spectral lines corresponding to the benzodioxane fragment provided evidence for the formation of the heterocycles. The ^{1}H NMR spectra revealed the two protons attached to C(5) and C(10) of the ring appear at 6.8 and 7.3 ppm ($^4J_{PH} = 6.3$ Hz and $^3J_{PH} = 13.8$ Hz, respectively). While the ^{13}C NMR spectra showed that the signal corresponding to C(10a) appeared at 108.5 ppm with $^1J_{PC} = 140.1$ Hz, which is typical for **11**.

It should be noted that our attempts to extend the reaction to the corresponding thioureas were unsuccessful probably due to the affinity of the phosphorus atom for the sulfur atom in such reactions.[18]

Like *N*,*N*-diarylureas, ureas **13**, derivatives of 5-aminopyrazole underwent the reaction affording 1*H*-pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one ring system **14**, which is the hydrogenated analogue of 2,5-dihydro-1*H*-pyrazolo[4,3-*c*][1,5,2]diazaphosphinine and 1*H*-pyrazolo[4,3-*c*][1,5,2]diazaphosphinine ring systems obtained earlier by us.[19,20] The feature of this cyclization is the difference in nucleophilicity of the two NH-groups of the ureido moiety. The decreased nucleophilicity of the NH-group at the pyrazole allows the reaction to be carried out with

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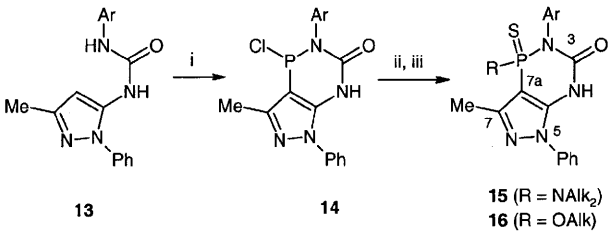
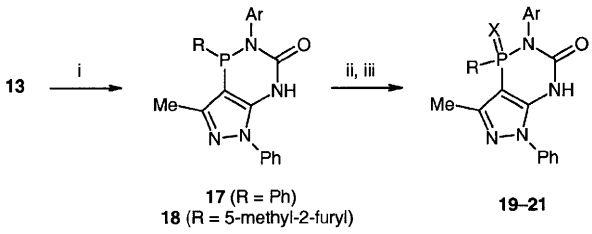


Scheme 3 *Reagents and conditions*: (i) PCl_3, pyridine, r.t., 20 h; (ii) for **15**: Alk_2NH, pyridine; for **16**: AlkOH, pyridine; (iii) S, pyridine



Scheme 4 *Reagents and conditions*: (i) for **17**: $PhPCl_2$, pyridine, r.t., 48 h; for **18**: 5-methyl-2-furyl-PBr_2, pyridine 48 h; (ii) for **19**: 30% H_2O_2, toluene; for **31** and **32**: S, pyridine

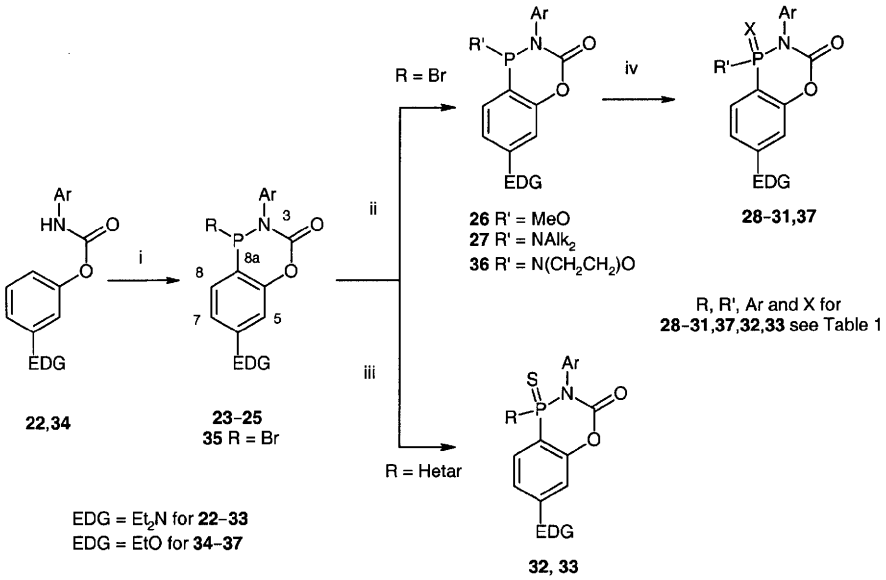
PCl_3, which we had failed to realize with urea **1**. The cyclization occurs in pyridine and is complete in 20 hours affording cyclic acid chloride **14** as a thermally unstable compound, which we cannot isolate in an analytical pure state. Fortunately, acid chloride **14** can be kept in solution so that air stable phosphorus(V) derivatives **15** and **16** can been prepared (Scheme 3, Table 2). When PBr_3 was used in place of PCl_3 target acid bromide of type **14** does not result, for the same reason as urea **1** failed to react with PCl_3.

Besides PCl_3, aryldichloro- and aryldibromophosphines undergo the reaction affording the corresponding air stable cyclic phosphines **17** and **18**, which were transformed into phosphorus(V) derivatives **19–21** (Scheme 4). It should be noted that attempts to carry out imination of **17** or **18** with arylazides were unsuccessful, which may also be due to the reactivity of the cyclic NH-moiety.

The formation of pyrazolodiazaphosphinanones was confirmed by ^1H, ^{31}P, ^{13}C NMR, and IR spectroscopy. The absence of signals corresponding to one of the NH protons of the ureido group and the pyrazole proton in the ^1H NMR spectra, along with a signal corresponding to C(7a) at 90.7 ppm ($^1J_{PC}$ = 164.7 Hz, for **16a**) in the ^{13}C NMR spectra provided evidence for the formation of the heterocycle. The presence of an endocyclic P–N bond was evident from the ^{31}P NMR spectra, which is in accordance with the spectral data for 2,5-dihydro-1*H*-pyrazolo[4,3-*c*][1,5,2]diazaphosphinine previously obtained.[19] Alternatively if pyrazolo[4,3-*c*][1,5,2]oxazaphosphinine formed bearing an endocyclic P–O bond the signals in the ^{31}P NMR spectra appear at lower field in comparison with pyrazolodiazaphosphinanones.[9b] Besides, the intensive absorption at 1685 cm^{-1} in the IR spectra proved the presence of a carbonyl moiety.

We have also applied our approach to *N*,*O*-diarylcarbamates **22** that lead to a new 2,4,1-benzoxazaphosphinan-3-one ring system – a phospha-analogue of the 2*H*-1,3-benzoxazine-2,4(3*H*)-dione system.[21] In the case of PBr_3, the reaction occurs in pyridine in the presence of Et_3N as a base, with a reaction time of 20 hours; in the case of aryldibromophosphines the reaction time was extended to 40 hours affording cyclic acid bromide **23** and cyclic phosphines **24** and **25**, respectively. The cyclic acid bromide **23** undergoes reaction with phosphorus(III) halides resulting in the formation of various phosphorus(III and V) derivatives **26–31** (Scheme 5, Table 2).

The most convincing evidence for the formation of the 2,4,1-benzoxazaphosphinan-3-one ring are the absence of the signals for the carbamate proton and one of the protons



Scheme 5 *Reagents and conditions*: (i) for **23**: PBr_3, pyridine Et_3N, 20 h; for **24** and **25**: $HetarPBr_2$, pyridine, Et_3N, 40 h; for **35**: PBr_3, pyridine, Et_3N, 4 d; (ii) for **26**: MeOH, pyridine; for **27** and **36**: Alk_2NH, pyridine; (iii) S, pyridine; (iv) for **28**, **30**, **37**: S, pyridine; for **29**: 1) Br_2, pyridine; 2) H_2O, pyridine; for **31**: $Ar'N_3$, pyridine 50 °C, 3 h

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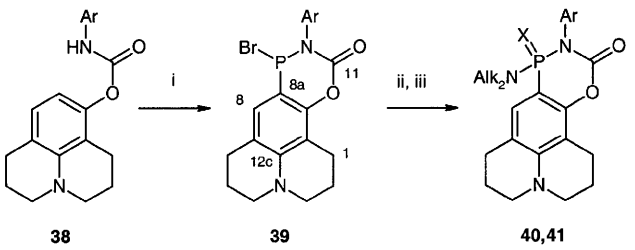


Scheme 6 *Reagents and conditions*: (i) PBr_3, pyridine Et_3N, 20 h; (ii) $O(CH_2CH_2)_2NH$, pyridine; (iii) for **40**: S, pyridine; for **41**: *p*-$NO_2C_6H_4N_3$, pyridine 50 °C, 3 h

of the phenol moiety in the ^1H NMR spectra. The ^{13}C NMR spectra established the C(8a) signal at 95.0 ppm along with a coupling constant $^1J_{PC}$ = 171.5 Hz (for **29**) and an intensive IR absorption at 1734 cm^{-1} (C=O) confirmed the 2,4,1-benzoxazaphosphinan-3-one ring structure. Besides this, the ^1H NMR spectra of phosphorus(V) derivatives exhibit distinctive features due to the spin-spin interaction of aromatic protons and the cyclic phosphorus atom. Also the signals for *ortho*-protons of the subsistent at N(2) are broad and structurally unresolved due to hindered rotation about N(2)–C(*ipso*) (Figure 3).

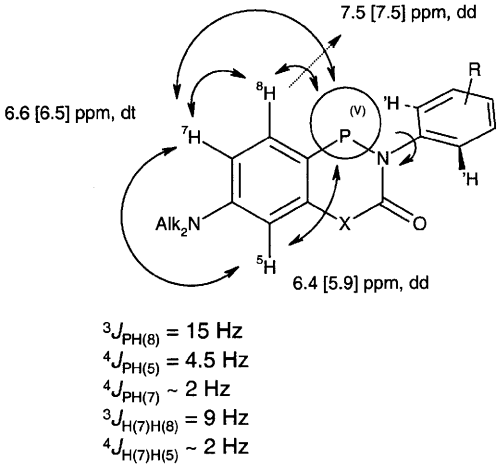
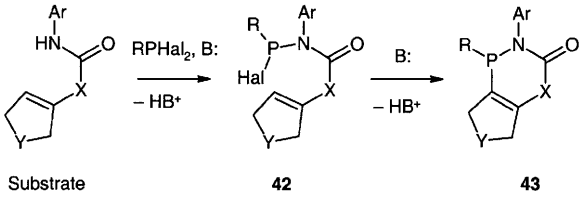


Figure 3 ^1H NMR data of the 1λ^5-2,4,1-benzoxazaphosphinan-3-ones (X = O) [1λ^5-2,4,1-benzodiazaphosphinan-3-one, (X = NH)] obtained according to H–H COSY and $^1H\{^{31}P\}$ experiments

Derivatives of other electron-rich phenols also underwent cyclization. Thus, on this basis julolidin-8-ols derivative **38** and polycyclic 2,3,6,7-tetrahydro-1*H*,5*H*,9*H*-[1,3,4]oxazaphosphinano[6,5-*f*]pyrido[3,2,1-*ij*]quinolin-11-one ring systems **39** were synthesized in the same way (Scheme 6).

In contrast to *N*-acylanilides[9a] and *N*,*N*′-diarylureas, activation of the benzene ring with one alkoxy group was sufficient for *N*,*O*-diarylcarbamates. Thus, carbamate **34** reacts with PBr_3 in pyridine in the presence of Et_3N as a base in four days affording cyclic acid bromide **35**, which was transformed to thioamide **37** in 21% overall yield (Scheme 5).

Due to the increased nucleophilicity of the reaction center of the *exo*-group in comparison with the sp^2-carbon center, the above-mentioned cyclization proceed initially through N-phosphorylated acyclic intermediates **42**, which were detected by ^{31}P NMR spectroscopy (Scheme 7, Table 1). An exception is the cyclization using urea **1**. In this case we did not detect such intermediates by ^{31}P NMR. We suggest that this reaction proceeds through several intermediates **44**–**46**, which exist in a fast dynamic equilibrium. Among them, only **46** is able to undergo further heterocyclization, as a result the equilibrium shifts towards **46** (Scheme 8).



Scheme 7

Table 1 ^{31}P NMR Data of the Reaction of Corresponding Ureas and Carbamates with Phosphorus(III) Halides

Substrate	$PHal_3$	δ for **42** (ppm)	δ for **43** (ppm)	Cyclization time (h)[a]
5	PBr_3	163	103	48
13	PCl_3	136	107	20
22	PBr_3	169	110	22
34	PBr_3	170	126	96
38	PBr_3	169	108	18

[a] Conditions: r.t., pyridine, [substrate] = [$PHal_3$] = 0.05 M.

It should be noted that investigation of non-catalytic phosphorylation of the benzene core with PBr_3 without cyclization showed that activation of the benzene ring was effective when more than two alkoxy groups were attached at an appropriate position.[6c] Heterocyclization with substrates **5** and **34** is evidence for non-catalytic C-phosphorylation of the (hetero)aromatic moiety, because in this case intermediates **42** have both an electrophilic and nucleophilic component and undergo C–P bond forming reactions but are less reactive in comparison with PPr_3 and dimethylresorcinol.

In summary, the reaction of electron-rich diarylureas and diarylcarbamates, bearing a ureido or uretano group *ortho* to the C-nucleophilic center of an aromatic or heteroaromatic moiety with 1,1-bielectrophilic phosphorus(III) halides was investigated. As a result, a flexible and convenient approach to the synthesis of various fused diaza- and oxazaphosphinanones has been elaborated. The accessibility of starting ureas and carbamates as well as 'one-pot' procedures make this method very attractive for the design and synthesis of phospha-heterocycles with a vast variety of functionalities on the final structure.

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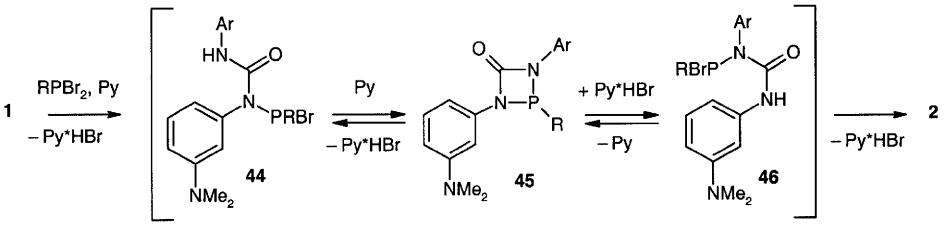


Scheme 8

Table 2 Analytical Data of Phosphorus Compounds,[e] Starting Ureas, and Carbamates

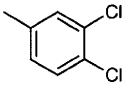
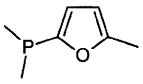
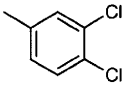
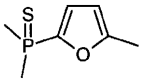
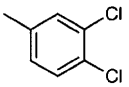
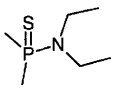
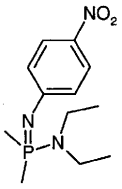
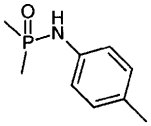
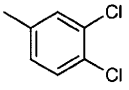
N	Phosphorus substituents	Ar	Yield, (%)[a]	Mp (°C)[b]	^{31}P NMR, δ (ppm)	^{1}H NMR, δ (ppm), *J* (Hz)
1[c]	–		73	207–209	–	2.87 [6 H, s, $N(CH_3)_2$], 6.39 (1 H, dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 2, CH), 6.7 (1 H, dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.2, CH), 6.91 (1 H, t, $^4J_{HH}$ = 1.6, CH), 7.07 (1 H, t, $^4J_{HH}$ = 8.0, CH), 7.32 (1 H, dd, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4, CH), 7.5 (1 H, d, $^3J_{HH}$ = 8.8, CH), 7.88 (1 H, d, $^3J_{HH}$ = 2.4, CH), 8.62 (1 H, s, NH), 8.9 (1 H, s, NH)
2[c]			70	210–215	11.3	2.28 (3 H, s, CH_3), 2.87 [6 H, s, $N(CH_3)_2$], 5.9 (1 H, s, CH), 6.18 (1 H, s, CH), 6.29 (1 H, d, $^3J_{PH}$ = 2.7, CH), 6.46 (1 H, d, $^3J_{HH}$ = 8.1, CH), 7.21–7.26 (2 H, m, CH), 7.42 (1 H, d, $^3J_{HH}$ = 8.1, CH), 7.48 (1 H, s, CH), 8.75 (1 H, br s, NH)
3[c]			39	266	38	2.33 (3 H, s, CH_3), 2.97 [6 H, s, $N(CH_3)_2$], 5.98 (1 H, dd, $^4J_{PH}$ = 4.5, $^4J_{HH}$ = 2.2, CH), 6.04 (1 H, br s, CH), 6.50 (1 H, dt, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = $^4J_{PH}$ = 2.2, CH), 6.99 (1 H, t, $^3J_{HH}$ = $^3J_{PH}$ = 2, CH), 7.0–7.3 (2 H, br, CH), 7.41 (1 H, d, $^3J_{HH}$ = 8.1), 7.49 (1 H, dd, $^3J_{HH}$ = 8.7, $^3J_{PH}$ = 15.0, CH)
5[c]	–	Ph	84	90–92	–	1.15 (3 H, t, $^3J_{HH}$ = 7.2, NCH_2CH_3), 3.72 (2 H, q, $^3J_{HH}$ = 7.2, NCH_2CH_3), 4.30 (4 H, s, OCH_2CH_2O), 6.18 (1 H, s, NH), 6.37 (1 H, dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 2.4, CH), 6.81 (1 H, d, $^4J_{HH}$ = 2.4, CH), 6.89 (1 H, d, $^3J_{HH}$ = 8.4, CH), 6.97 (1 H, t, $^3J_{HH}$ = 7.0, CH), 7.27 (2 H, d, $^3J_{HH}$ = 7.0, CH), 7.28 (2 H, t, $^3J_{HH}$ = 7.0, CH)
9[c]		Ph	51	170	60	0.79 [6 H, t, $^3J_{HH}$ = 6.9, $N(CH_2CH_3)_2$], 1.33 (3 H, t, $^3J_{HH}$ = 7.2, NCH_2CH_3), 3.02 [2 H, m, 8 lines, $^3J_{HH}$ = 7, $N(CH_2CH_3)_2$], 3.24 [2 H, m, 8 lines, $^3J_{HH}$ = 7, $N(CH_2CH_3)_2$], 4.01 (2 H, m, 10 lines, $^3J_{HH}$ = 7, NCH_2CH_3), 4.28 (2 H, d, $^2J_{HH}$ = 3, OCH_2CH_2O), 4.33 (2 H, d, $^2J_{HH}$ = 3, OCH_2CH_2O), 6.68 (1 H, d, $^4J_{PH}$ = 6.3, CH), 7.24 (1 H, d, $^3J_{PH}$ = 13.8, CH), 7.3–7.5 (5 H, m, CH)
10[c]		Ph	54	188	4.0	0.79 [6 H, t, $^3J_{HH}$ = 6.9, $N(CH_2CH_3)_2$], 1.38 (3 H, t, $^3J_{HH}$ = 7.2, NCH_2CH_3), 2.98 [2 H, m, 8 lines, $^3J_{HH}$ = 7, $N(CH_2CH_3)_2$], 3.18 [2 H, m, 8 lines, $^3J_{HH}$ = 7, $N(CH_2CH_3)_2$], 4.15 (2 H, m, 11 lines, $^3J_{HH}$ = 7, NCH_2CH_3), 4.27 (2 H, d, $^2J_{HH}$ = 3, OCH_2CH_2O), 4.36 (2 H, d, $^2J_{HH}$ = 3, OCH_2CH_2O), 6.50 (2 H, d, $^3J_{HH}$ = 8.4, CH), 6.76 (1 H, d, $^4J_{PH}$ = 6.3, CH), 7.10 (1 H, d, $^3J_{PH}$ = 15.3, CH), 7.12 (2 H, br m, CH), 7.34 (3 H, m, CH), 7.95 (2 H, d, $^3J_{HH}$ = 8.4, CH)
11[d]		Ph	34	138–140	67	1.20 (3 H, t, $^3J_{HH}$ = 7.2, NCH_2CH_3), 3.53 (3 H, d, $^3J_{PH}$ = 14.7, $POCH_3$), 4.00 (2 H, m, 7 lines, $^3J_{HH}$ = 7, NCH_2CH_3), 4.33 (2 H, d, $^2J_{HH}$ = 3, OCH_2CH_2O), 4.39 (2 H, d, $^2J_{HH}$ = 3, OCH_2CH_2O), 6.99 (1 H, d, $^4J_{PH}$ = 6.6, CH), 7.23 (1 H, d, $^3J_{PH}$ = 18.0, CH), 7.23 (2 H, d, $^3J_{HH}$ = 7.2, CH), 7.37–7.42 (3 H, m, CH)
12[c]		Ph	42	290–293	3.8	1.36 (3 H, t, $^3J_{HH}$ = 7.2, NCH_2CH_3), 2.22 (3 H, s, CH_3), 4.10 (2 H, m, NCH_2CH_3), 4.26 (2 H, br s, OCH_2CH_2O), 4.34 (2 H, br s, OCH_2CH_2O), 5.83 (1 H, br s, PNH), 6.39 (2 H, d, $^3J_{HH}$ = 8.2, CH), 6.78 (1 H, d, $^4J_{PH}$ = 6.3, CH), 6.92 (2 H, d, $^3J_{HH}$ = 8.2, CH), 7.14 (2 H, m, CH), 7.29 (4 H, m, CH)
13a[d]	–		84	212	–	2.21 (3 H, s, CH_3), 6.28 (1 H, s, CH), 7.25 (1 H, dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 2.4, CH), 7.4 (1 H, m, CH), 7.5 (5 H, m, CH), 7.82 (1 H, d, $^4J_{HH}$ = 2.4, CH), 8.75 (1 H, s, NH), 9.30 (1 H, s, NH)

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Table 2 Analytical Data of Phosphorus Compounds,[e] Starting Ureas, and Carbamates (continued)

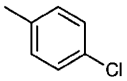
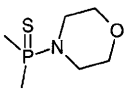
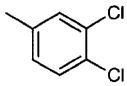
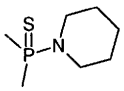
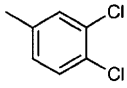
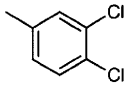
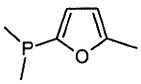
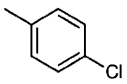
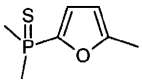
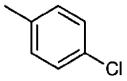
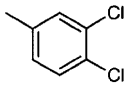
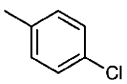
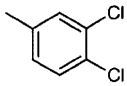
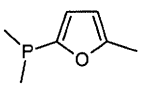
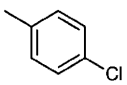
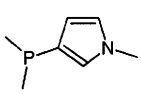
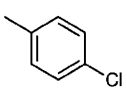
N	Phosphorus substituents	Ar	Yield, (%)[a]	Mp (°C)[b]	^{31}P NMR, δ (ppm)	^{1}H NMR, δ (ppm), *J* (Hz)
13b[c]	–	Ph	78	194–196	–	2.24 (3 H, s, CH_3), 6.24 (1 H, s, CH), 7.05 (1 H, t, $^3J_{HH}$ = 7.5, CH), 7.16 (2 H, d, $^3J_{HH}$ = 7.5, CH), 7.20 (2 H, t, $^3J_{HH}$ = 7.5, CH), 7.24 (1 H, br s, NH), 7.28 (5 H, m, CH), 7.5 (1 H, br s, NH)
13c[d]	–		86	232	–	2.19 (3 H, s, CH_3), 6.28 (1 H, s, CH), 7.30 (2 H, d, $^3J_{HH}$ = 8.7, CH), 7.42 (2 H, m, CH), 7.46 (1 H, t, CH), 7.52 (4 H, m, CH), 8.48 (1 H, s, NH), 9.13 (1 H, s, NH)
15a[d]			61	272	50	2.39 (3 H, s, CH_3), 2.96 (2 H, m, NCH_2), 3.54 (6 H, m, NCH_2, OCH_2), 7.4 (1 H, m, CH), 7.6 (4 H, m, CH), 7.66 (1 H, s, CH), 7.82 (2 H, d, $^3J_{HH}$ = 9.7, CH), 11.5 (1 H, s, NH)
15b[d]			53	222	52	1.46 (4 H, m, CH_2), 1.61 (2 H, m, CH_2), 2.45 (3 H, s, CH_3), 2.84 (2 H, m, NCH_2), 3.34 (2 H, m, NCH_2), 7.0–7.3 (2 H, br m, CH), 7.4 (4 H, m, CH), 7.52 (2 H, d, $^3J_{HH}$ = 9.7, CH), 8.5 (1 H, s, NH)
16[d]			48	279	57	2.36 (3 H, s, CH_3), 3.60 (3 H, d, $^3J_{PH}$ = 15.0, $POCH_3$), 7.30 (1 H, d, $^3J_{HH}$ = 8.5, CH), 7.50 (2 H, d, $^3J_{HH}$ = 8.5, CH), 7.55 (5 H, m, CH), 11.5 (1 H, s, NH)
18[c]		Ph	15[f]	198	2.4	2.28 (3 H, s, CH_3), 2.34 (3 H, s, CH_3), 6.0 (1 H, s, CH), 6.6 (1 H, s, CH), 7.15 (2 H, d, $^3J_{HH}$ = 6.8, CH), 7.3–7.4 (4 H, m, CH), 7.5 (4 H, m, CH), 7.75 (1 H, s, NH)
19[d]		Ph	53	264–266	13.3	1.94 (3 H, s, CH_3), 7.0 (2 H, m, CH), 7.24 (4 H, m, CH), 7.45 (2 H, dd, $^3J_{PH}$ = 15.6, $^3J_{HH}$ = 7.8, CH), 7.48–7.62 (7 H, m, CH), 11.27 (1 H, s, NH)
20[d]			45	247	48	1.96 (3 H, s, CH_3), 6.7–7.2 (2 H, br m, CH), 7.35 (2 H, m, CH), 7.5 (4 H, m, CH), 7.62 (4 H, m, CH), 7.75 (2 H, dd, $^3J_{PH}$ = 15.6, $^3J_{HH}$ = 7.8, CH), 11.42 (1 H, s, NH)
21[d]			42	232	27	2.13 (3 H, s, CH_3), 2.37 (3 H, s, CH_3), 6.20 (1 H, m, CH), 7.06 (1 H, m, CH), 7.4–7.7 (9 H, m, CH), 11.47 (1 H, s, NH)
22a[d]	–		84	108	–	1.09 (6 H, t, $^3J_{HH}$ = 7.2, CH_3CH_2N), 3.32 (4 H, q, $^3J_{HH}$ = 7.2, CH_3CH_2N), 6.38 (1 H, d, $^3J_{HH}$ = 7.3, CH), 6.45 (1 H, s, CH), 6.53 (1 H, dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.8, CH), 7.16 (1 H, t, $^3J_{HH}$ = 8.1, CH), 7.45 (1 H, dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.8, CH), 7.57 (1 H, d, $^3J_{HH}$ = 8.1, CH), 7.80 (1 H, d, $^4J_{HH}$ = 1.8, CH), 10.45 (1 H, s, NH)
22b[d]	–		85	157	–	1.08 (6 H, t, $^3J_{HH}$ = 7.2, CH_3CH$_2$N), 3.31 (4 H, q, $^3J_{HH}$ = 7.2, CH$_3$CH_2N), 6.38 (1 H, dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.6, CH), 6.43 (1 H, t, $^3J_{HH}$ = 1.6, CH), 6.52 (1 H, dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.4, CH), 7.15 (1 H, t, $^3J_{HH}$ = 8.1 CH), 7.37 (2 H, d, $^3J_{HH}$ = 9.0, CH), 7.53 (2 H, d, $^3J_{HH}$ = 9.0, CH), 10.28 (1 H, s, NH)
23[c]			70	131–133	110	1.17 (6 H, t, $^3J_{HH}$ = 7.2, CH_3CH$_2$N), 3.36 (4 H, q, $^3J_{HH}$ = 7.2, CH$_3$CH_2N), 6.42 (1 H, br s, CH), 6.56 (1 H, d, $^3J_{HH}$ = 8.1, CH), 7.31 (2 H, m, CH), 7.52 (1 H, d, $^3J_{HH}$ = 8.5, CH), 7.57 (1 H, d, $^3J_{HH}$ = 1.8, CH)
24[c]			61	120–123	8.1	1.2 (6 H, t, $^3J_{HH}$ = 7.2, CH_3CH_2N), 2.31 (3 H, s, CH_3), 3.38 (4 H, q, $^3J_{HH}$ = 7.2, CH_3CH_2N), 5.96 (1 H, br s, CH), 6.55 (2 H, m, CH), 7.17–7.27 (3 H, m, CH), 7.33 (2 H, d, $^3J_{HH}$ = 8.7, CH), 7.42 (1 H, d, $^3J_{HH}$ = 8.4, CH)
25[c]			53	171–173	19.7	1.2 (6 H, t, $^3J_{HH}$ = 7.2, CH_3CH$_2$N), 3.38 (4 H, q, $^3J_{HH}$ = 7.2, CH$_3$CH_2N), 3.61 (3 H, s, NCH_3), 6.24 (1 H, s, CH), 6.52–6.61 (3 H, m, CH), 6.72 (1 H, s, CH), 7.17 (2 H, d, $^3J_{HH}$ = 8.4, CH), 7.25 (1 H, d, $^3J_{HH}$ = 8.1, CH), 7.31 (2 H, d, $^3J_{HH}$ = 8.4, CH)

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Table 2 Analytical Data of Phosphorus Compounds,[e] Starting Ureas, and Carbamates (continued)

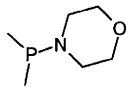
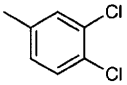
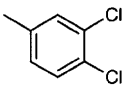
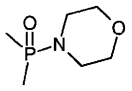
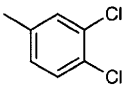
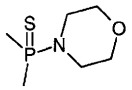
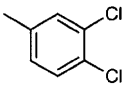
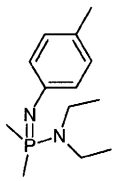
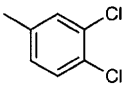
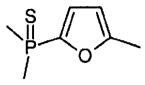
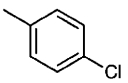
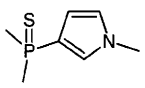
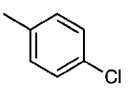
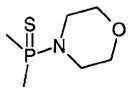
N	Phosphorus substituents	Ar	Yield, (%)[a]	Mp (°C)[b]	^{31}P NMR, δ (ppm)	^{1}H NMR, δ (ppm), *J* (Hz)
27[c]			70	159–160	77	1.2 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 2.8–3.1 (4 H, m, OCH$_2$C*H*$_2$N), 3.37 (4 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$N), 3.5 (4 H, m, OC*H*$_2$CH$_2$N), 6.39 (1 H, d, $^{4}J_{HH}$ = 1.5, CH), 6.58 (1 H, dt, $^{3}J_{HH}$ = 8.7, CH), 7.23 (2 H, m, CH), 7.45 (1 H, d, $^{4}J_{HH}$ = 1.5, CH), 7.49 (1 H, d, $^{3}J_{HH}$ = 8.4, CH)
28[c]			45	155–157	65	1.21 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 3.4 (4 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$N), 3.65 (3 H, d, $^{3}J_{PH}$ = 15.0, OCH$_3$), 6.4 (1 H, dd, $^{4}J_{PH}$ = 4.5, $^{4}J_{HH}$ = 2.2, CH), 6.62 (1 H, dt, $^{3}J_{HH}$ = 9.0, $^{4}J_{HH}$ = $^{4}J_{PH}$ = 2.2, CH), 7.23 (1 H, dm, $^{3}J_{HH}$ = 8.4, CH), 7.49 (1 H, m, CH), 7.55 (1 H, d, $^{3}J_{HH}$ = 8.4, CH), 7.62 (1 H, dd, $^{3}J_{HH}$ = 9.0, $^{3}J_{PH}$ = 15.0, CH)
29[c]			39	198	12	1.21 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 2.67 (2 H, m, OCH$_2$C*H*$_2$N), 3.14 (2 H, m, OC*H*$_2$CH$_2$N), 3.40 (4 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$N), 3.43–3.58 (4 H, m, OC*H*$_2$CH$_2$N), 6.39 (1 H, dd, $^{4}J_{PH}$ = 4.5, $^{4}J_{HH}$ = 2.2, CH), 6.61 (1 H, dt, $^{3}J_{HH}$ = 8.7, $^{4}J_{HH}$ = $^{4}J_{PH}$ = 2.2, CH), 7.37 (1 H, dd, $^{3}J_{HH}$ = 8.4, $^{4}J_{HH}$ = 2.1), 7.46 (1 H, dd, $^{3}J_{HH}$ = 8.7, $^{3}J_{PH}$ = 13.8, CH), 7.56 (1 H, d, $^{3}J_{HH}$ = 8.4), 7.61 (1 H, d, $^{4}J_{HH}$ = 2.1)
30[d]			62	220–221	60	1.12 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 2.84 (2 H, m, OCH$_2$C*H*$_2$N), 3.2 (2 H, m, OCH$_2$C*H*$_2$N), 3.34 (4 H, m, OC*H*$_2$CH$_2$N), 3.42 (4 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$N), 6.45 (1 H, d, $^{4}J_{PH}$ = 5.1, CH), 6.76 (1 H, d, $^{3}J_{HH}$ = 8.7, CH), 7.46 (1 H, dd, $^{3}J_{HH}$ = 9.0, $^{3}J_{PH}$ = 15.0, CH), 7.53 (1 H, d, $^{3}J_{HH}$ = 8.1, CH), 7.79 (1 H, d, $^{3}J_{HH}$ = 8.1, CH), 7.82 (1 H, s, CH)
31[d]			61	140–142	5.4	0.71 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 1.12 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 2.12 (3 H, s, CH$_3$), 2.92 (2 H, m, CH$_3$C*H*$_2$N), 3.19 (2 H, m, CH$_3$C*H*$_2$N), 3.41 (4 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$N), 6.41 (2 H, d, $^{3}J_{HH}$ = 7, CH), 6.49 (1 H, dd, $^{4}J_{HH}$ = 1.5, $^{4}J_{PH}$ = 4.5, CH), 6.71 (1 H, dt, $^{3}J_{HH}$ = 9.3, $^{4}J_{HH}$ = $^{4}J_{PH}$ = 1.5, CH), 6.83 (2 H, d, $^{3}J_{HH}$ = 7.2, CH), 7.26 (1 H, dd, $^{3}J_{HH}$ = 9.0, $^{4}J_{HH}$ = 2.2, CH), 7.32 (1 H, dd, $^{3}J_{HH}$ = 9.0, $^{3}J_{PH}$ = 15.0, CH), 7.52 (1 H, d, $^{4}J_{HH}$ = 2.2, CH), 7.72 (1 H, d, $^{3}J_{HH}$ = 8.7, CH)
32[c]			49	165	36	1.21 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 2.35 (3 H, s, CH$_3$), 3.41 (4 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$N), 6.05 (1 H, br s, CH), 6.43 (1 H, dd, $^{4}J_{PH}$ = 4.5 $^{4}J_{HH}$ = 2.4, CH), 6.59 (1 H, dt, $^{3}J_{HH}$ = 9.0, $^{4}J_{HH}$ = $^{4}J_{PH}$ = 2.2, CH), 6.9 (2 H, br m, CH), 7.03 (1 H, t, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 2.0, CH), 7.32 (2 H, d, $^{3}J_{HH}$ = 8.4, CH), 7.48 (1 H, dd, $^{3}J_{HH}$ = 9.0, $^{3}J_{PH}$ = 15.3, CH)
33[c]			75	170–172	45	1.2 (6 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$N), 3.38 (4 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$N), 3.63 (3 H, s, NCH$_3$), 6.17 (1 H, m, CH), 6.43 (1 H, dd, $^{4}J_{PH}$ = 4.5 $^{4}J_{HH}$ = 2.4, CH), 6.57 (1 H, dt, $^{3}J_{HH}$ = 9.0, $^{4}J_{HH}$ = $^{4}J_{PH}$ = 2.2, CH), 6.64 (1 H, m, CH), 6.98 (1 H, m, CH), 7.09 (2 H, br m, CH), 7.3 (2 H, d, $^{3}J_{HH}$ = 8.4, CH), 7.45 (1 H, dd, $^{3}J_{HH}$ = 9.0, $^{3}J_{PH}$ = 14.4, CH)
34[c]	-	Ph	80	89–91	–	1.39 (3 H, t, $^{3}J_{HH}$ = 7.2, C*H*$_3$CH$_2$O), 4.00 (2 H, q, $^{3}J_{HH}$ = 7.2, CH$_3$C*H*$_2$O), 6.74–6.78 (3 H, m, CH), 7.00 (1 H, br s, NH), 7.10 (1 H, t, $^{3}J_{HH}$ = 7.5, CH), 7.26 (1 H, t, $^{3}J_{HH}$ = 8.1, CH), 7.32 (2 H, t, $^{3}J_{HH}$ = 7.5, CH), 7.43 (2 H, d, $^{3}J_{HH}$ = 7.5, CH)
37[c]		Ph	21[f]	61–62	62	1.37 (3 H, t, $^{3}J_{HH}$ = 7, C*H*$_3$CH$_2$O), 3.10–3.28 [6 H, m, N(CH$_2$CH$_2$)$_2$O], 3.58–3.78 [2 H, m, N(C*H*$_2$CH$_2$)$_2$O], 3.95 (2 H, q, $^{3}J_{HH}$ = 7, CH$_3$C*H*$_2$O), 6.58–6.77 (2 H, m, CH), 7.24 (1 H, dd, $^{3}J_{HH}$ = 9.0, $^{3}J_{PH}$ = 15.0, CH), 7.38–7.48 (3 H, m, CH), 7.55–7.63 (2 H, br m, CH)

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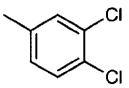
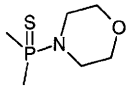
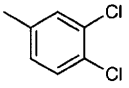
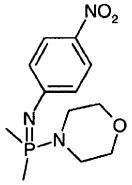
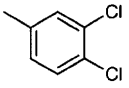
Table 2 Analytical Data of Phosphorus Compounds,[e] Starting Ureas, and Carbamates (continued)

N	Phosphorus substituents	Ar	Yield, (%)[a]	Mp (°C)[b]	^{31}P NMR, δ (ppm)	^{1}H NMR, δ (ppm), *J* (Hz)
38[d]	–		96	153–154	–	1.87 (4 H, m, CH_2), 2.5 (2 H, t, $^3J_{HH}$ = 4.5, CH_2), 6.67 (2 H, t, $^3J_{HH}$ = 4.5, CH_2), 3.10 (4 H, m, NCH_2), 6.28 (1 H, d, $^3J_{HH}$ = 8.4, CH), 6.72 (1 H, d, $^3J_{HH}$ = 8.4, CH), 7.42 (1 H, dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.8, CH), 7.58 (1 H, d, $^3J_{HH}$ = 8.4, CH), 7.79 (1 H, d, $^4J_{HH}$ = 1.8, CH), 10.4 (1 H, s, NH)
40[d]			68	215–216	60	1.88 (4 H, m, CH_2), 2.7 (4 H, m, CH_2), 2.84 (2 H, m, $N(CH_2CH_2)_2O$), 3.20–3.41 [10 H, m, NCH_2, $N(CH_2CH_2)_2O$], 7.02 (1 H, d, $^3J_{PH}$ = 15.3, CH), 7.51 (1 H, d, $^3J_{HH}$ = 8.1, CH), 7.78–7.81 (2 H, m, CH)
41[d]			83	262–267	5.5	1.84–1.95 (4 H, m, CH_2), 2.65–2.91 [6 H, m, CH_2, $N(CH_2CH_2)_2O$], 3.15–3.29 [8 H, m, NCH_2, $N(CH_2CH_2)_2O$], 3.44–3.47 [2 H, m, $N(CH_2CH_2)_2O$], 6.64 (2 H, d, $^3J_{HH}$ = 8.4, CH), 7.10 (1 H, d, $^3J_{PH}$ = 14.8, CH), 7.30 (1 H, dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 2.1, CH), 7.76 (1 H, d, $^3J_{HH}$ = 8.4, CH), 7.91 (1 H, d, $^4J_{HH}$ = 2.1, CH), 7.98 (2 H, d, $^3J_{HH}$ = 8.4, CH)

[a] Yields refer to pure isolated products.
[b] Melting points are uncorrected.
[c] $CDCl_3$.
[d] DMSO-d_6.
[e] Satisfactory microanalysis data were obtained: N ± 0.10; P ± 0.35.
[f] According to ^{31}P NMR data of reaction mixtures the real yields of the targeted products: **18** = 75%; **37** = 55%.

All procedures with compounds sensitive to hydrolysis and oxidation were carried out under an atmosphere of anhydrous argon. All solvents were purified and dried by standard methods. NMR spectra were recorded on a Varian VXR-300 spectrometer: ^{1}H and ^{13}C NMR (300 and 75.4 MHz, respectively) were carried out in $CDCl_3$ and DMSO-d_6 with TMS as an internal standard; ^{31}P NMR (121 MHz) were obtained with 85% H_3PO_4 as an external standard. H–H COSY and ^{1}H{^{31}P} spectra were obtained on a Varian Mercury-400 spectrometer. IR-spectra were recorded on Nexus-470 spectrometer on KBr discs. Mass spectra were obtained on a Hewlett-Packard HP GC/MS 5890/5972 instrument (EI, 70 eV) by GC inlet or on a MX-1321 instrument (EI, 70 eV) by direct inlet. The starting ureas and carbamates were prepared from the corresponding amines or phenols and aryl isocyanates.[22] Heteroarylbromophosphines (5-methyl-2-furyl-dibromophosphine,[7a] and *N*-methyl-3-pyrrolyl-dibromophosphine[7d]) were prepared via direct phosphorylation of the corresponding heterocycles with PBr_3. The reactions were monitored by ^{31}P NMR spectroscopy.

2-(3,4-Dichlorophenyl)-6-dimethylamino-1-(5-methyl-2-furyl)-2,4,1-benzodiazaphosphinan-3-one (2)

To a stirred solution of 5-methyl-2-furyl-dibromophosphine (1.6 g, 5.88 mmol) in anhyd pyridine (10 mL), a solution of urea **1** (1.9 g, 5.88 mmol) in anhyd pyridine (10 mL) was added. After 48 h, Et_3N (2.3 mL, 17.7 mmol) was added and the solution was stirred for 30 min. Pyridine was evaporated in vacuo and the residue was extracted with hot toluene (20 mL). After cooling to r.t., hexane (20 mL) was added, and the precipitate was filtered and crystallized from anhyd MeCN.

MS (EI): *m*/*z* (%) = 437 (7) [M^+ + 4], 436 (11) [M^+ + 3], 435 (52) [M^+ + 2], 434 (17) [M^+ + 1], 433 (78) [M^+], 352 (11) [M^+– 5-methylfuryl], 237 (10), 245 (100) [M^+ – 3,4-$Cl_2C_6H_3NCO$], 231 (24), 165 (32), 123 (25).

2-(3,4-Dichlorophenyl)-6-dimethylamino-1-(5-methyl-2-furyl)-2,4,1λ^5-benzodiazaphosphinan-3-one-1-thioxide (3)

To a stirred solution of **2** (500 mg, 1.1 mmol) in anhyd pyridine (20 mL) elemental S was added. After complete dissolution of the S, pyridine was evaporated in vacuo, and the residue was crystallized from *i*-PrOH.

^{13}C NMR [DMSO-d_6, due to hindered rotation about N(2)–C(*ipso*) the *ortho*-carbon signals of the Ar–substituent at N(2) are broad]: δ = 14.2, 40.0, 96.5 ($^1J_{PC}$ = 117.4 Hz), 97.0 ($^3J_{PC}$ = 9.9 Hz), 108.7 ($^3J_{PC}$ = 14.7 Hz), 108.8 ($^2J_{PC}$ = 9.1 Hz), 126.8 ($^3J_{PC}$ = 24.3 Hz), 131.0, 131.2, 131.5 (br), 131.7, 132.2 ($^2J_{PC}$ = 13.8 Hz), 133.1 (br), 135.6, 141.2 ($^2J_{PC}$ = 5.7 Hz), 147.3 ($^1J_{PC}$ = 139.8 Hz), 151.2, 154.4, 160.1 ($^3J_{PC}$ = 8.3 Hz).

MS (EI): *m*/z (%) = 469 (4.6) [M^+ + 4], 468 (7) [M^+ + 3], 467 (28) [M^+ + 2], 466 (12) [M^+ + 1], 465 (41) [M^+], 433 (7) [M^+ + S], 352 (100) [M^+ – S – 5-methylfuryl], 245 (20), 192 (21), 165 (88) [M^+ – S – 5-methylfuryl – 3,4-$Cl_2C_6H_3NCO$].

1-Bromo-4-ethyl-2-phenyl-7,8-dihydro[1,4]dioxino-[2,3-*g*][2,4,1]benzodiazaphosphinan-3-one (6)

To a stirred solution of **5** (500 mg, 1.59 mmol) in anhyd pyridine (30 mL), PBr_3 (0.15 mL, 1.59 mmol) and Et_3N (0.67 mL, 4.78 mmol) were added. After 48 h, the reaction mixture can be utilized for further transformations.

1-Diethylamino-4-ethyl-2-phenyl-7,8-dihydro-1λ^5-[1,4]dioxino[2,3-*g*][2,4,1]benzodiazaphosphinan-3-one-1-thioxide (9)

To a stirred solution of **6** (1.59 mmol) in anhyd pyridine, (30 mL,) Et_2NH (0.17 mL, 1.59 mmol) and elemental S (51 mg, 1.59 mmol) were added. After complete dissolution of the S, pyridine was evaporated in vacuo. The residue was triturated with H_2O and crystallized from *i*-PrOH.

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1-Diethylamino-4-ethyl-2-phenyl-7,8-dihydro-1λ^5-[1,4]dioxino[2,3-*g*][2,4,1]benzodiazaphosphinan-3-one-1-(4-nitrophenyl)imide (10)

To a stirred solution of **6** (1.59 mmol) in anhyd pyridine, (30 mL), Et_2NH (0.17 mL, 1.59 mmol) and 4-$NO_2C_6H_4N_3$ (0.261 g, 1.59 mmol) were added. The mixture was maintained at 50 °C until N_2 evolution stopped and then pyridine was evaporated in vacuo. The residue was triturated with H_2O and crystallized from *i*-PrOH.

4-Ethyl-1-methoxy-2-phenyl-7,8-dihydro-1λ^5-[1,4]dioxino[2,3-*g*][2,4,1]benzodiazaphosphinin-3-one-1-thioxide (11)

To a stirred solution of **6** (1.59 mmol) in anhyd pyridine (30 mL), anhyd MeOH (0.06 mL, 1.59 mmol) and elemental S (51 mg, 1.59 mmol) were added. After complete dissolution of the S, pyridine was evaporated in vacuo. The residue was triturated with H_2O and crystallized from a mixture of *i*-PrOH–H_2O.

^{13}C NMR (DMSO-d_6): δ = 11.9, 40.3, 52.9 ($^2J_{CP}$ = 6.4 Hz), 63.5, 64.3, 104.32 ($^3J_{CP}$ = 10.3 Hz), 108.5 ($^1J_{CP}$ = 140.1 Hz), 117.7 ($^2J_{CP}$ = 14.3 Hz), 127.5, 128.2, 129.7, 133.9, 135.4, 138.8 ($^3J_{CP}$ = 19.1 Hz), 148.2, 150.6.

MS (EI): *m*/*z* (%) = 390 (93) [M$^+$], 343 (40) [M$^+$ – CH_3 – S], 271 (36) [M$^+$ – PhNCO], 256 (29), 224 (100) [M$^+$ – PhNCO – CH_3 – S], 168 (24).

4-Ethyl-1-[(4-methylphenyl)amino]-2-phenyl-7,8-dihydro-1λ^5-[1,4]dioxino[2,3-*g*][2,4,1]benzodiaza-phosphinan-3-one-1-oxide (12)

To a stirred solution of **6** (1.59 mmol) in anhyd pyridine (30 mL), anhyd MeOH (0.06 mL, 1.59 mmol) and 4-methylphenylazide (212 mg, 1.59 mmol) were added. The mixture was maintained at 50 °C until N_2 evolution stopped, and then pyridine was evaporated in vacuo. The residue was triturated with H_2O and crystallized from *i*-PrOH.

1-Chloro-2-(3,4-dichlorophenyl)-7-methyl-5-phenylpyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one (14)

To a stirred solution of **13a** (1 g, 2.2 mmol) in anhyd pyridine (30 mL) was added PCl_3 (303 mg, 2.2 mmol). After 48 h the reaction mixture can be utilized for further transformations.

1-Dialkylamino-2-(3,4-dichlorophenyl)-7-methyl-5-phenyl-1λ^5-pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one-1-thioxide (15)

These compounds were prepared from acid chloride **14** according to the above procedure for **9**.

2-(3,4-Dichlorophenyl)-1-methoxy-7-methyl-5-phenyl-1λ^5-pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one-1-thioxide (16)

This compound was prepared from acid chloride **14** according to the above procedure for **11**.

^{13}C NMR (DMSO-d_6, due to hindered rotation about N(2)–C(*ipso*) the *ortho*-carbon signals of the Ar–substituent at N(2) are broad and overlapping): δ = 13.1, 54.3 ($^2J_{CP}$ = 6.5 Hz), 90.7 ($^1J_{CP}$ = 164.7 Hz), 125.0, 128.7, 129.3, 130.7, 131.0, 131,4, 133.1 (br), 134.6, 136.5, 141.7 ($^2J_{CP}$ = 18.5 Hz), 148.6 ($^2J_{CP}$ = 11.8 Hz), 150.2.

MS (EI): *m*/*z* (%) = 456 (6) [M$^+$ + 4], 455 (7) [M$^+$ + 3], 454 (33) [M$^+$ + 2], 453 (11) [M$^+$ + 1], 452 (49) [M$^+$], 405 (14) [M$^+$ – S – CH_3], 265 (100) [M$^+$ – 3,4-Cl_2-C_6H_3NCO], 233 (34) [M$^+$ – 3,4-Cl_2-C_6H_3NCO – S], 85 (31), 83 (41), 77 (29) [Ph$^+$].

7-Methyl-1-(5-methyl-2-furyl)-2,5-diphenylpyrazolo-[4,3-*c*][1,5,2]diazaphosphinan-3-one (18)

To a stirred solution of urea **13b** (1 g, 3.4 mmol) in anhyd pyridine (25 mL) was added 5-methyl-2-furyldibromophosphine (930 mg, 3.4 mmol). After 48 h, Et_3N (0.88 mL, 6.4 mmol) was added and the mixture was maintained at 40 °C for 30 min. Pyridine was evaporated in vacuo and the residue was extracted with hot toluene (40 mL). Toluene was evaporated in vacuo and the residue was crystallized from anhyd EtOH (it should be noted that hydrolysis of the majority of the product occurs by procedure).

MS (EI): *m*/*z* (%) = 403 (9) [M$^+$ + 1], 402 (41) [M$^+$], 283 (34) [M$^+$ – PhNCO], 262 (100), 268 (16), 122 (16), 77 (24) [Ph$^+$].

7-Methyl-1,2,5-triphenyl-1λ^5-pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one-1-oxide (19)

To a stirred solution of urea **13b** (1 g, 3.4 mmol) in anhyd pyridine (25 mL) was added $PhPCl_2$ (610 mg, 3.4 mmol). After 48 h Et_3N (0.88 mL, 6.4 mmol) was added and the mixture was maintained at 40 °C for 30 min. Pyridine was evaporated in vacuo, the residue was extracted with hot toluene (40 mL), and the extract was allowed to cool to r.t. To the stirred extract was added a 30% solution of H_2O_2 (0.4 mL). The precipitate formed was filtered and washed with *i*-PrOH (2 × 5 mL).

MS (EI): *m*/*z* (%) = 414 (38) [M$^+$], 294 (100) [M$^+$ – PhNCO], 207 (9), 118 (9), 91 (11), 77 (37) [Ph$^+$].

2-(4-Chlorophenyl)-7-methyl-1,5-diphenyl-1λ^5-pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one-1-thioxide (20)

To a stirred solution of urea **13c** (1 g, 3.1 mmol) in anhyd pyridine (25 mL) was added $PhPCl_2$ (550 mg, 3.1 mmol). After 48 h elemental S (100 mg, 3.1 mmol) was added to the stirred solution. After complete dissolution of S, pyridine was evaporated in vacuo. The residue was triturated with H_2O and crystallized from *i*-PrOH.

2-(4-Chlorophenyl)-7-methyl-1-(5-methyl-2-furyl)-5-diphenyl-1λ^5-pyrazolo[4,3-*c*][1,5,2]diazaphosphinan-3-one-1-thioxide (21)

Compound **21** was prepared from **13c** and 5-methyl-2-furyl-dibromophosphine using the above procedure for **20**.

1-Bromo-2-(3,4-dichlorophenyl)-6-diethylamino-2,4,1-benzoxazaphosphinan-3-one (23)

A

To a stirred solution of carbamate **22a** (10 g, 28.3 mmol) and Et_3N (8.6g, 85 mmol) in anhyd pyridine (100 mL), PBr_3 (7.7 g, 28.3 mmol) was added. After 24 h, the pyridine was evaporated in vacuo. To the residue, dioxane (100 mL) was added and the precipitated Et_3N·HBr formed was filtered. Dioxane was evaporated in vacuo, to the residue was added hexane (30 mL), and the solution was heated at reflux for 5 min. Hexane was decanted under an atmosphere of dry Ar and the above procedure was repeated. The orange-red crystalline precipitate formed was dried in vacuo.

B; One-Pot Transformation

To a stirred solution of urethane **22a** (1 g, 2.83 mmol) and Et_3N (860 mg, 8.5 mmol) in anhyd pyridine (25 mL) was added PBr_3 (770 mg, 2.83 mmol). After 24 h, the reaction mixture can be utilized for further transformations.

^{13}C NMR ($CDCl_3$): δ = 12.1, 44.6, 99.2, 108.5 ($^1J_{CP}$ = 14.8, 126.8 ($^3J_{CP}$ = 7.1), 129.4 ($^3J_{CP}$ = 6.1, 130.6, 130.8, 131.3, 132.6 ($^2J_{CP}$ = 3.0), 132.9, 139.8 ($^2J_{CP}$ = 17.1), 149.1 ($^2J_{CP}$ = 6.4), 152.6, 155.9.

2-(4-Chlorophenyl)-6-diethylamino-1-(5-methyl-2-furyl)-2,4,1-benzoxazaphosphinan-3-one (24)

To a stirred solution of carbamate **22b** (2 g, 6.27 mmol) and Et_3N (1.9 g, 18.82 mmol) in anhyd pyridine (25 mL) 5-methyl-2-furyl-dibromophosphine (1.7 g, 6.27 mmol) was added. After 24 h, the pyridine was evaporated in vacuo. The residue was extracted with hot toluene (50 mL). The extract was cooled to r.t., the precipitated Et_3N·HBr formed was filtered, the remaining solution was concentrated in vacuo to a volume of 30 mL, and heptane (30 mL) was add-

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ed. After the solution had cooled to r.t., the crystalline precipitate formed was filtered.

MS (EI): *m*/*z* (%) = 430 (4) [M^+ + 2], 428 (12) [M^+], 275 (21) [M^+ – 4-ClC_6H_4NCO], 260 (100) [M^+ – 4-ClC_6H_4NCO – CH_3].

2-(4-Chlorophenyl)-6-diethylamino-1-(*N*-methylpyrrol-3-yl)-2,4,1-benzoxazaphosphinan-3-one (25)
Compound **25** was prepared from **22b** and *N*-methylpyrrol-3-yl-dibromophosphine using the above procedure for **24**.

MS (EI): *m*/*z* (%) = 429 (18) [M^+ + 2], 427 (51) [M^+], 292 (18), 274 (100) [M^+ – 4ClC_6H_4NCO], 273 (66), 259 (86) [M^+ – 4-ClC_6H_4NCO – CH_3], 196 (18), 153 (65), 86 (26).

2-(3,4-Dichlorophenyl)-6-diethylamino-1-morpholin-4-yl-2,4,1-benzoxazaphosphinan-3-one (27)
To a stirred solution of acid bromide **23** (3 g, 6.5 mmol) in anhyd toluene (50 mL), morpholine (1.4 g, 16.23 mmol) was added. The reaction mixture was cooled to r.t., the precipitated $O(CH_2CH_2)_2NH$·HBr formed was filtered, the remaining solution was concentrated in vacuo to a volume of 30 mL and heptane (30 mL) was added. After cooling to r.t. the crystalline precipitate formed was filtered.

MS (EI): *m*/*z* (%) = 467 (2.6) [M^+], 381 (4) [M^+ – $O(CH_2CH_2)_2N$], 274 (18), 195 (16) [M^+ – $O(CH_2CH_2)_2N$ – 3,4-$Cl_2C_6H_3NCO$], 114 (100), 87 (26), 70 (65), 57 (25).

2-(3,4-Dichlorophenyl)-6-diethylamino-1-methoxy-1λ^5-2,4,1-benzoxazaphosphinan-3-one-1-thioxide (28)
Compound **27** was prepared in situ from **23** using the above procedure for **11**.

^{13}C NMR (DMSO-d_6): δ = 12.2, 44.1, 54.2 ($^3J_{CP}$ = 7.5 Hz), 97.5 ($^1J_{CP}$ = 149.6 Hz), 97.4 ($^3J_{CP}$ = 7.7 Hz), 109.3 ($^3J_{CP}$ = 14.1 Hz), 130.4 ($^2J_{CP}$ = 2.7 Hz), 131.0, 131.2, 131.3, 131.8, 132.1, 134.8, 149.7, 152.4, 155.7.

MS (EI): *m*/*z* (%) = 448 (4) [M^+ + 4], 447 (3.6) [M^+ + 3], 446 (16) [M^+ + 2], 445 (5.5) [M^+ + 1], 444 (25) [M^+], 257 (44) [M^+ – 3,4-$Cl_2C_6H_3NCO$], 242 (100) [M^+ – 3,4-$Cl_2C_6H_3$-NCO – CH_3].

2-(3,4-Chlorophenyl)-6-diethylamino-1-morpholin-4-yl-1λ^5-2,4,1-benzoxazaphosphinan-3-one-1-oxide (29)
To a stirred solution of **27** (1.5 g, 3.2 mmol) in anhyd pyridine, (15 mL), Br_2 (510 mg, 3.2 mmol) was added. The reaction mixture was cooled to r.t., H_2O was added (0.5 mL), and pyridine was evaporated in vacuo. The residue was triturated with H_2O and crystallized from *i*-PrOH.

^{13}C NMR (DMSO-d_6): δ = 12.7, 43.9, 44.5, 66.5, 95.0 ($^1J_{CP}$ = 171.5 Hz), 98.1 ($^3J_{CP}$ = 7.1 Hz), 109.8 ($^3J_{CP}$ = 13.8 Hz), 129.9, 130.6 ($^2J_{CP}$ = 7.8 Hz), 131.5, 131.6, 131.7, 131.8, 135.6, 149.8, 152.9, 155.7.

MS (EI): *m*/*z* (%) = 485 (15) [M^+ + 2], 483 (22) [M^+], 296 (30) [M^+ – 3,4-$Cl_2C_6H_3NCO$], 281 (100) [M^+ – 3,4-$Cl_2C_6H_3NCO$ – CH_3], 211 (24), 196 (32), 166 (14).

2-(3,4-Chlorophenyl)-6-diethylamino-1-morpholin-4-yl-1λ^5-2,4,1-benzoxazaphosphinan-3-one-1-thioxide (30)
Compound **30** was prepared in situ from **23** using the above procedure for **9**.

2-(3,4-Chlorophenyl)-1,6-bis(diethylamino)-1λ^5-2,4,1-benzoxazaphosphinan-3-one-1-(4-methylphenyl)imide (31)
Compound **42** was prepared in situ from **23** using the above procedure for **10**.

2-(4-Chlorophenyl)-6-diethylamino-1-(5-methyl-2-furyl)-2,4,1-benzoxazaphosphinan-3-one-1-thioxide (32)
Compound **32** was prepared from cyclic phosphine **24** using the above procedure for **3**.

2-(4-Chlorophenyl)-6-diethylamino-1-(*N*-methypyrrol-3-yl)-2,4,1-benzoxazaphosphinan-3-one-1-thioxide (33)
Compound **33** was prepared from cyclic phosphine **25** using the above procedure for **3**.

6-Ethoxy-1-morpholin-4-yl-2-phenyl-1λ^5-2,4,1-benzoxazaphosphinan-3-one-1-thioxide (37)
To a stirred solution of carbamate **34** (500 mg, 1.95 mmol) and Et_3N (560 mg, 5.84 mmol) in anhyd pyridine (25 mL), PBr_3 (530 mg, 1.95 mmol) was added. After 4 d, morpholine (170 mg, 1.95 mmol) and elemental S (62 mg, 1.95 mmol) were added. After complete dissolution of S, pyridine was evaporated in vacuo. The residue was triturated with H_2O and crystallized from *i*-PrOH–H_2O.

9-Bromo-10-(3,4-dichlorophenyl)-2,3,6,7-tetrahydro-1*H*,5*H*,9*H*-[1,3,4]oxazaphosphinano[6,5-*f*]pyrido-[3,2,1-*ij*]quinolin-11-one (39)
Compound **39** was prepared from carbamate **38** and PBr_3 using the above procedure **B** for **23**.

10-(3,4-Dichlorophenyl)-9-morpholin-4-yl-9λ^5-2,3,6,7-tetrahydro-1*H*,5*H*,9*H*-[1,3,4]oxazaphosphinano[6,5-*f*]pyrido[3,2,1-*ij*]quinolin-11-one-9-thioxide (40)
Compounds **40** were prepared from **39** using the above procedure for **9**.

^{13}C NMR (DMSO-d_6): δ = 20.4, 21.0, 21.2, 27.3, 45.2, 49.1, 49.7, 66.6 ($^3J_{CP}$ = 5.6 Hz), 97.3 ($^1J_{CP}$ = 171.5 Hz), 106.9 ($^3J_{CP}$ = 9.1 Hz), 119.5 ($^3J_{CP}$ = 14.4 Hz), 125.9 ($^2J_{CP}$ = 9.3 Hz), 130.5, 131.4, 131.6, 132.1, 132.3, 135.8, 147.7, 148.8 ($^2J_{CP}$ = 3.0 Hz), 149.1 ($^2J_{CP}$ = 2.8 Hz).

MS (EI): *m*/*z* (%) = 527 (4) [M^+ + 4], 526 (7) [M^+ + 3], 525 (22) [M^+ + 2], 524 (8) [M^+ + 1], 523 (35) [M^+], 405 (10) [M^+ – $O(CH_2CH_2)_2N$ – S], 336 (83) [M^+ – 3,4-$Cl_2C_6H_3NCO$], 251 (100), 218 (25), 83 (31).

10-(3,4-Dichlorophenyl)-9-morpholin-4-yl-9λ^5-2,3,6,7-tetrahydro-1*H*,5*H*,9*H*-[1,3,4]oxazaphosphinano[6,5-*f*]pyrido[3,2,1-*ij*]quinolin-11-one 9-(4-nitrophenyl)imide (41)
Compounds **41** were prepared from **39** using the above procedure for **10**.

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