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PAPER

P═C–N-Heterocycles: synthesis of biaryl-type 1,3-benzazaphospholes with ortho-substituted phenyl or 2-heteroaryl groups†

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A facile synthesis of functionally substituted 2-(hetero)aryl 1,3-benzazaphospholes *via* nickel- or palladium-catalyzed phosphonylation of N-acyl-2-bromoanilides **1a–k** with triethyl phosphite is presented. Anilidophosphonates **2a–g** with naphthoyl-, *o*-substituted phenyl, furoyl- or thenoyl groups allow direct reductive cyclization with $LiAlH_4$ to benzazaphospholes **3**. The reaction of the *o*-bromoderivative **2d** proceeds with concomitant replacement of bromine by hydrogen, whereas the electron-withdrawing pyridyl group of **2h** prevents the synthesis of **3h** by this short route. An alternative synthesis of 2-pyridylbenzazaphosphole **3h** *via* anilidophosphonates succeeded starting from Fmoc-anilinophosphonate **2k** *via* selective cleavage of the N-protecting group, reduction of the resulting phosphonoaniline to phosphinoaniline and cyclization with pyridine-2-carboxaldehyde *via* a dihydrobenzazaphosphole **8**. *N*-Substituted pyridylmethylbenzazaphosphole **9** was detected as a side product. The structure elucidation of the new compounds is based on multinuclear NMR data and X-ray crystal structure analyses of a phosphonoanilide, underlining the dominance of N–H···O═P hydrogen bonds over N–H···O═C type hydrogen bonds, of **3h** and a supramolecular associate of **3b** and its unprecedented air oxidation product **10**.

Introduction

Biaryl phosphines have proved to be valuable ligands in various homogenous transition metal catalyzed cross-coupling reactions. Substituents at phosphorus and at the *o*-positions offer versatile tuning abilities.[1] Biaryl-type ligands involving σ^2-phosphorus heterocycles have been much less investigated, in particular compounds with donor functions in the second (hetero)aryl group such as bis(phosphinines) or pyridylphosphinines.[2] However, because σ^2-phosphorus possesses π-acceptor rather than σ-donor properties such ligands exhibit distinct coordination properties and might thus be interesting extensions to classic phosphine or phosphite ligands.[3] These phosphinine chelate ligands are currently under closer investigation.[4] We are investigating strongly aromatically stabilized π-excess type σ^2-phosphorus heterocycles,[5] benzo- and pyrido-annulated 1*H*-1,3-azaphospholes.[6–8] These compounds form stable $LM^{VI}(CO)_5$ complexes (M^{VI} = Cr, Mo, W)[8–10] in the same manner as phosphinines but seem to have a lower tendency to afford coordination compounds with non-zero valent late transition metals such as Rh(I) or Pd(II) for which phosphinine complexes are known.[2,11] *o*-Functionally substituted 2-aryl-1,3-benzazaphospholes, at least formally allowing chelate complexes, should favour the coordination of mono- or divalent late transition metals and might be useful in catalysis with such metals by stabilizing hemilabile coordination of low- or zero-valent transition metal catalyst intermediates. 2-Phenyl-1,3-benzazaphosphole and 2-phenyl-1,3-azaphosphole have been known since the earliest reports of these heterocycles,[9,12] but *ortho*-functionally substituted derivatives thereof or 2-heterocyclic derivatives have not yet, to the best of our knowledge, been reported.[13] We describe here ways of synthesizing such ligands by reductive cyclocondensation. In addition, an unusual P═C oxidation product is presented.

Results and discussion

1*H*-1,3-Benzazaphospholes have been synthesized by two methods. The first consists of multistep procedures *via* 2-aminophenylphosphonic[12a] or 2-aminophenylphosphonous acid esters,[12b,14] with subsequent reduction to 2-phosphinoanilines and cyclocondensation with suitable carboxylic acid derivatives. The second method presents a two- or three-step route *via* nickel-catalyzed phosphonylation of *N*-acyl 2-bromoanilides, followed by reductive cyclization.[14,15] The second route is much shorter and more convenient, provided problems involving interference of heteroatoms or functional groups[15] can be overcome and steric hindrance is not a major issue. Therefore, we have mainly investigated the applicability of the second synthetic route to

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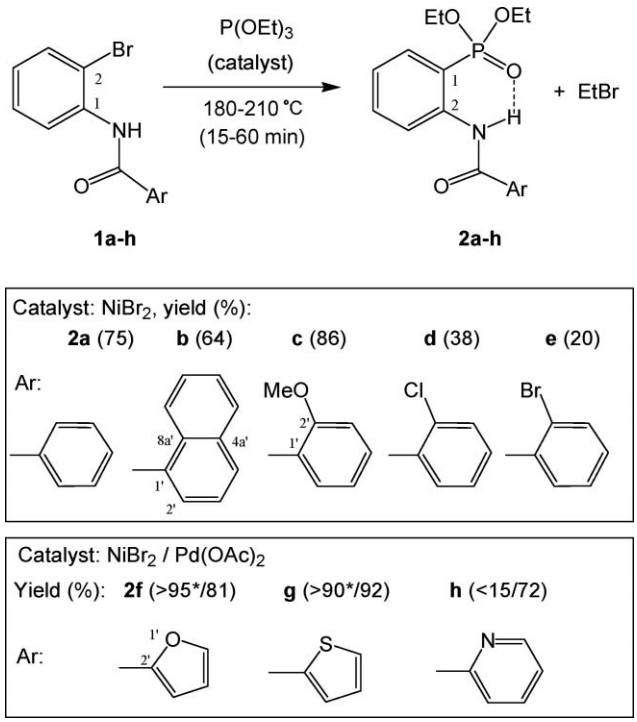
access 2-phenyl-1,3-benzazaphospholes with *o*-methoxy, *o*-chloro and *o*-bromo substituents and *O*-, *S*- and *N*-donor-functional 2-heteroaryl-1,3-benzazaphospholes. 2-Phenyl compounds **1a–3a**[14] are included for comparison as are 2-(naphth-1-yl) derivatives to distinguish possible steric effects of *ortho*-substituents from heteroatom effects.

2-Acylamido-phenylphosphonates

The synthesis started with *N*-acyl 2-bromoanilides **1a–h**, prepared from 2-bromoaniline and the corresponding acid chloride in the presence of a base. For phosphonylation, **1a–h** was heated with triethyl phosphite in the presence of anhydrous nickel bromide for 10–15 min to 180–190 °C and in some cases up to about 200 °C. Despite the high temperature this method proved successful for P–C coupling of triethyl phosphite[15] or methylphosphonite[16] with 2-bromoanilides of simple aliphatic acids and also gave high to excellent yields of **2a–c** and the heterocyclic derivatives **2e** and **2f** (Scheme 1).



Scheme 1 Phosphonylation of acyl-2-bromoanilides (**2a**,[14] * yields by NMR, others by isolation).

The P–C coupling with the *o*-chloro- and *o*-bromo-derivatives **1d** and **1e**, however, was less efficient and gave rather low yields of **2d** and particularly **2e**. Competing side reactions are the problem, *e.g.* phosphonylation of the 2-bromobenzoyl group. This was demonstrated by isolation of **1i** and **2i** (Chart 1), separated from **2e** by column chromatography. Attempts to couple triethyl phosphite with picolinic acid 2-bromoanilide **1h** in the presence of $NiBr_2$ as the catalyst failed at 190 °C and gave a highly impure product at 210 °C. It succeeded, however, using palladium acetate as the catalyst. This is more tolerant to amine donors than the nickel catalyst but needs the same high temperature (210 °C) to provide **2h** in good yield. The higher tolerance does not necessarily mean higher activity, as seen from the coupling of *o*-methoxy compound

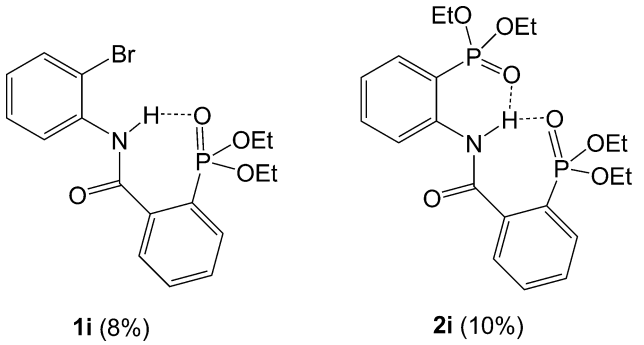


Chart 1 Compounds **1i** and **2i**.

1c with $P(OEt)_3$ to **2c**. The yield here was lower for catalysis by $Pd(OAc)_2$ than by $NiBr_2$ (70% *versus* 86% at 180 °C, 30 min). The same was observed for the conversion of **1f** to **2f**. The high yields of the electron-rich, π-excess-aromatic furyl- and thienyl-substituted *N*-acylbromoanilides **2f** and **2g** in the nickel catalyzed coupling show tolerance of the furan and thiophene donor sites to the nickel catalyst. This can be attributed to the low donor strength and basicity of the heteroatoms[17] in these π-excess type heteroaryl groups by repulsion of $p_z(\pi)$ (HOMO) and $sp^2(\sigma)$ lone electron pairs.[18] The formation of $[Ni^0\{(P(OEt_3)_4\})]$ was detected by ^{31}P NMR monitoring of the crude pale yellow reaction mixtures of **2f** and **2g**. A peak at δ = 159 ppm (*cf*. ref. 19) indicated this complex along with the product, excess triethylphosphite (broad signal shifted from 137 to *ca.* 145 ppm by ligand exchange), a small amount of *O*,*O*-diethyl ethylphosphonate (δ = 33.6 ppm) formed by classic Arbuzov reaction with ethyl bromide[20] and a small amount of triethylphosphate (δ = –0.9 ppm), caused by reduction of $NiBr_2$ and Br_2/O exchange of $(EtO)_3PBr_2$ with amide.

The coupling products are easily identified by phosphorus chemical shifts in the region δ = 18.2–20.4 ppm. Further structural proof was provided by analysis of ^1H and ^{13}C NMR data, satisfactory elemental analyses or conclusive molar peaks in HRMS. Characteristic features are the relatively large $^3J_{PH}$ coupling constants of H6 (14.3–14.8 Hz), indicating the *o*-phosphono group, and the strong downfield shifts of H3 (δ = 8.35–8.91 ppm, $^4J_{PH}$ *ca.* 6–8 Hz), which hint at strong magnetic deshielding by the C═O bond of the *o*-amide group, arranged in a "side-on" direction. This orientation is forced by stronger P═O···H–N than C═O···H–N hydrogen bonds and additionally indicated in solution by strongly downfield shifted NH proton signals (δ = 9.63–11.93 ppm) and for the solid state by the X-ray crystal structure analysis of **2g** (Fig. 1). In this compound the conjugated O═C–NH and C_6H_4 π-systems (O4,C22,C1,N *vs.* C11...C16) are nearly co-planar (interplanar angle 8°), and the torsion angle C1–N–C12–C13 –18.5(2)°, indicating the orientation of the C═O bond towards the close C–H bond in the aniline ring (O4···H13 2.31 Å), is relatively small because of support of this arrangement by the oppositely directed intramolecular P═O···H–N bridging bond. The electron-rich thiophene π-system is also effectively co-planar with the aniline ring (interplanar angle 4°). Bond lengths and angles display usual values.

Reduction by $LiAlH_4$ and cyclization to 1*H*-1,3-benzazaphospholes

Lithium alanate is known to reduce phosphonic acid diesters to primary phosphines and *N*-secondary amides to amines, both

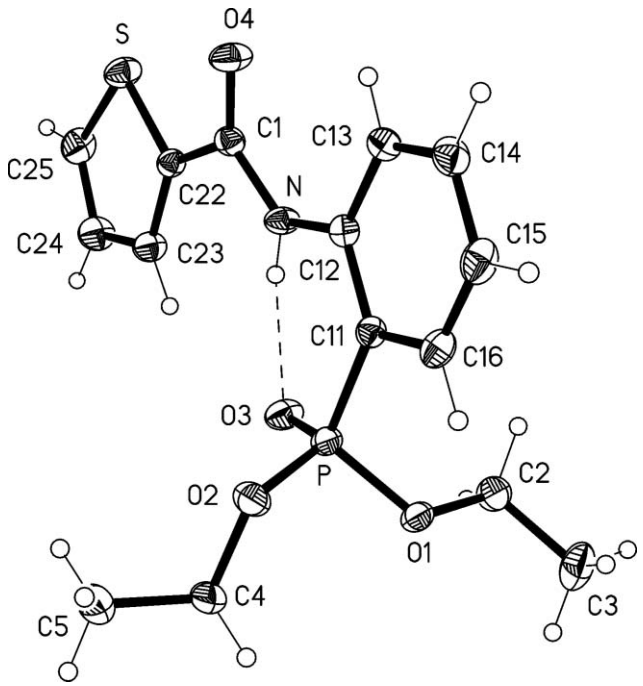
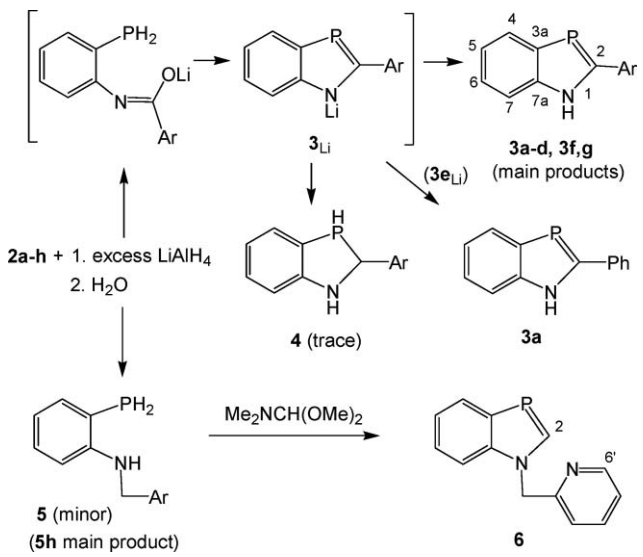


Fig. 1 Crystal structure of **2g**. Ellipsoids represent 50% probability levels. Selected bond lengths (Å) and angles (°): P–C11 1.7904(13), N–C12 1.4038(16), C1–N 1.3657(17), C1–C22 1.4800(18); P–C(11)–C(12) 123.52(10), C(11)–C(12)–N 118.38(11), N–C(1)–C(22) 113.29(11); N–H(01) 0.862(19), H···O3 1.96(2), N···O3 2.7508(15), N–H···O3 152.6(18); C(12)–N–C(1)–O(4) 5.5(2).

usually in high yields. The presence of both functions in the same molecule changes the behaviour. The reduction of **2a–d** and **2f,g** with excess $LiAlH_4$ provides the 1*H*-1,3-benzazaphospholes **3a–d** and **3f,g** as the main products (Scheme 2). Reaction monitoring of crude mixtures by NMR revealed the additional formation of small amounts of side products of type **4** and **5** in some cases. Treatment of **2e** and **2h** with excess $LiAlH_4$ led however to different results. Only traces of **3e** and **3h** were detected by ^{31}P NMR (δ = 86.4 and 81.1 ppm) and mass spectrometry in the crude products. In the case of **2e** a major part of a precursor of **3e** underwent replacement of *o*-bromine with hydrogen from excess hydride to give finally 2-phenyl-benzazaphosphole **3a**. Reduction of **2h** led mainly to primary phosphines with a strong phosphorus resonance at δ = –152.8 ppm and three weaker signals slightly upfield (δ = –153.02, –153.15, –153.45 ppm). The main signal is assigned to **5h** because prolonged heating with $Me_2NCH(OMe)_2$, known to convert primary *o*-phosphinoanilines to 2-unsubstituted 1*H*-1,3-benzazaphospholes,[6,9] led to *N*-pyridylmethyl-benzazaphosphole **6**. This could not be obtained in a pure state but was unambiguously detected by characteristic phosphorus (δ = 76.9 ppm) and proton NMR signals, *e.g.* for H2 (δ = 8.62 ppm, d, $^1J_{PH}$ = 37.5 Hz), H6′ (δ = 8.62 ppm, br d, $^3J \approx 4.7$ Hz) and NCH_2 (δ = 5.65 ppm), and also by the base peak for M^+ (*m*/*e* = 226) in the EI mass spectrum.



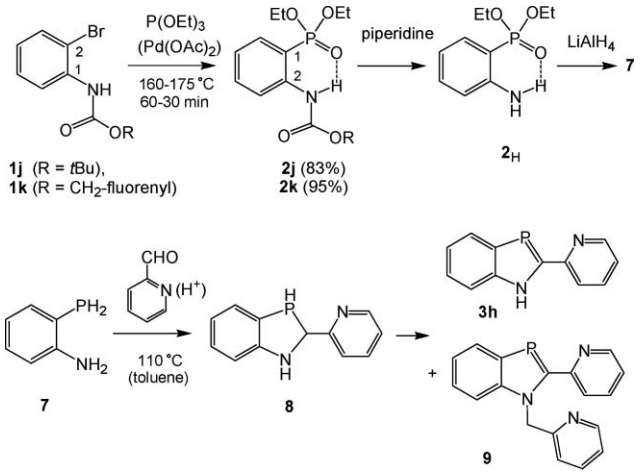
Scheme 2 Synthesis of (hetero)aryl-substituted 1,3-benzazaphospholes from *o*-phosphonoanilides.

The preferred conversion of **2a–g** to 1*H*-1,3-benzazaphospholes is attributed to a more rapid reduction of the diethylphosphono compared to the *N*-secondary amido group. This allows ring closure by nucleophilic attack of the primarily formed phosphino or phosphido group at the soft electrophilic imidate site, arising by NH-metallation. The benzazaphospholide anions $\mathbf{3}_{Li}$ produced in this way are aromatically stabilized and rather unreactive towards $LiAlH_4$, at least at room temperature. Only traces of **4** are detectable. The replacement of bromide by hydride in $\mathbf{3e}_{Li}$ is a reaction known for aryl bromides and possibly favored in the case of $\mathbf{3e}_{Li}$ by intramolecular Li···bromide interactions supporting the hydride attack. The behavior of **2h** is completely different and attributable to the electron-withdrawing –M-effect of the 2-pyridyl substituent. This activates the amide group, which is then reduced prior to or concomitantly with the phosphono group, thus preventing cyclization to $\mathbf{3h}_{Li}$ and leading mainly to **5h** and other primary phosphines. The evidence for this explanation is provided by competition experiments, performed to understand a similar behavior of *o*-amidopyridine-phosphonates.[7] While treatment of a mixture of 2-pivaloylamido-pyridine and diethyl phenylphosphonate with $LiAlH_4$ in a 1 : 1 : 1 molar ratio, insufficient for complete reduction, affords mainly *N*-neopentylpyridine, the reduction product of the amide, the opposite was observed with a mixture of pivaloylanilide and diethyl phenylphosphonate. In this case more phenylphosphine than *N*-neopentylaniline was obtained.[7]

Another aspect to be mentioned is the steric influence. Whereas reduction of **2a,e,f** with non-bulky phenyl or π-excess heteroaryl groups provides the benzazaphospholes **3a,e,f** in good yields (60–65%), the reduction of the more bulky 1-naphthyl or *ortho*-substituted phenyl compounds **2b–d** gives significantly lower yields of the heterocycles **3b–d** (32–45%), the best within this group for the +M-activated *o*-methoxy compound **3c**. This accounts for steric unfavorability of the reductive cyclization.

Phosphonylation of 2-bromophenyl carbamides and alternative synthesis of 2-pyridyl-1,3-benzazaphosphole *via* 2-phosphinoaniline

For an alternative access to **3h** we explored the phosphonylation of 2-bromophenyl carbamic acid esters, conversion to 2-phosphinoaniline and subsequent cyclocondensation with a suitable pyridine derivative (Scheme 3). Heating 1-Boc-2-bromoaniline **1j**[21] with triethyl phosphite in the presence of anhydrous nickel bromide or chloride did not lead to coupling



Scheme 3 Synthesis of 2-pyridyl-benzazaphosphole **3h**.

at 175 °C over 15 min, only traces were seen at 190 °C over 30 min and thermal decomposition occurred at 200 °C. However, high yield coupling to **2j** was achieved by use of palladium acetate as the precatalyst at 175 °C over 30 min. Removal of the Boc group under the usual acidic conditions[22] caused partial hydrolysis of the diethyl phosphonate, and direct reduction of **2j** with excess $LiAlH_4$ (molar ratio 1 : 3) in diethyl ether furnished mixtures containing 2-phosphinoaniline (**7**) ($\delta^{31}P = -153.5$ ppm), secondary phosphines ($\delta^{31}P = -90.5$ and -87.1 ppm) and a small amount of unsubstituted 1*H*-1,3-benzazaphosphole ($\delta^{31}P = 80.4$ ppm). In a 1 : 2 molar ratio of **2j** and $LiAlH_4$ additionally substantial amounts of 1-Boc-2-phosphinoaniline ($\delta^{31}P = -143.8$ ppm, cf. *N*-ethoxycarbonyl-2-phosphinoaniline[9]) were observed. Therefore, we turned to Fmoc derivatives, which allow removal of the protecting group by amines under mild anhydrous conditions. Fmoc-2-bromoaniline **1k** was synthesized from 2-bromoaniline and Fmoc-chloride in the presence of pyridine and was coupled in the presence of palladium acetate with triethyl phosphite at 160 °C/1 h, yielding **2k** in excellent yield. The Fmoc protection group was removed by excess piperidine in diethyl ether to give 2-aminophenylphosphonate $\mathbf{2_H}$ nearly quantitatively.

The reduction of compound $\mathbf{2_H}$ by $LiAlH_4$ provides **7**.[23] This is the starting material for the synthesis of benzazaphospholes *via* the original cyclocondensations with iminoester hydrochlorides, imidoyl chlorides or orthoformates.[6,9,12] Also cyclocondensation with benzaldehyde and thermal decomposition of the resulting 2-phenylbenzazaphospholine to **2a** was reported.[9] Despite the low total yield of only 10% we were interested in studying the potential of this method for the synthesis of **3h**. Whereas the aromaticity-driven dehydrogenation of indolines to indoles, the closest relatives of benzazaphospholes within the P–C diagonal relationship, requires oxidizing agents or catalysis by Pd on carbon,[24] the long known condensations of *o*-phenylenediamine or *o*-aminothiophenol with aldehydes may provide benzimidazoles[25] or benzothiazoles,[26] depending on the conditions and type of aldehyde. Excess aldehyde may take up a part of the hydrogen in the condensation with *o*-phenylenediamine resulting in *N*-alkylation, but the fate of most of the hydrogen is unclear – usually air oxidation is assumed. The advantage of the use of aldehydes in the condensations is that pyridine-2-carboxaldehyde and various other *N*-heterocyclic carbaldehydes are stable and in part easily available, whereas reactive carboxylic acid derivatives may be incompatible with the basic nitrogen. The reaction of pyridine-2-carboxaldehyde with 2-phosphinoaniline was performed under nitrogen atmosphere in a roughly 1 : 1 molar ratio (6% excess aldehyde) by reflux in toluene in the presence of catalytic amounts of *p*-toluene sulfonic acid. Reaction monitoring by NMR after 3 h gave evidence that the major part of **7** was converted and that the largest part of the primarily formed diastereoisomers of the 2-pyridylbenzazaphospholine **8** had lost hydrogen under these conditions. Only small amounts of the two diastereoisomers of **8** were detected by their characteristic ^{31}P NMR signals (δ = –64.2, –52.8 ppm, relative intensities 3 and 4% along with an unknown minor phosphorus compound (δ = 32.3 ppm) whereas **3h** and another benzazaphosphole **9** form the major signals (δ = 81.5, 88.9 ppm). Proton NMR integrals of characteristic signals (NH, NCH_2, PH_2, PH) display **3h**, **9**, **7** and **8** in a molar ratio of approximately 60 : 20 : 15 : 5. When heating was stopped after *ca.* 20 h, **8** was no longer detectable. Removal of the acidic catalyst with 5% aqueous sodium hydroxide provided **3h** along with **9** and residual *o*-phosphinoaniline. Pure **3h** was obtained by column chromatography on silica gel. The nature of **9** was derived from conclusive ^{1}H, ^{13}C NMR and HRMS data. Concerning the formation of **9** condensation of the pyridine-carboxaldehyde with the intermediate **8** in competition to **7** is assumed. The attack of the aldehyde at benzazaphospholines may become possible by aldehyde activation by the –M effect of the pyridyl group. It is still unclear whether the reaction proceeds *via* primary attack at the secondary phosphino or amino group and if a further five-membered ring is formed, which would imply generation of a possibly unstable four-membered 1,3-azaphosphetane as intermediate of the hydrogen transfer from the one to the other carbon atom. A transient compound with $\delta^{31}P = 32.3$ ppm could not be identified. Also the fate of the hydrogen formed along with **3h** is an open question. Oxidation by air is improbable under the inert conditions and by the presence of residual unconverted, highly air-sensitive primary phosphine **7**. We hope to obtain answers to these questions in further investigations to explore the potential of this reaction with a broader variety of aldehydes.

Structure and properties, nature of air oxidation product

The structure elucidation of the new 2-(hetero)aryl-benzazaphospholes, for O, S and in particular N donor-atoms potential σ^2P,X hybrid or chelate ligands, is based on conclusive multinuclear NMR and HRMS data. Additional information is available for **3h** by X-ray crystal structure analysis (Fig. 2). The compound crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with eight molecules in the unit cell, forming four pairs. The two independent molecules of each pair, linked by hydrogen bonds, differ in the interplanar angle between the benzazaphosphole and pyridine ring plane, with slightly larger angle in the upper than in the lower depicted nearly coplanar molecule (22°, 8° respectively). The torsion angles amount to N1–C2–C11–N12 18.52(15), P3–C2–C11–C16 22.73(16) *versus* N1′–C2′–C11′–N12′ 3.27(16), P3′–C2′–C11′–C16′ 2.20(17)°. The nearly coplanar arrangement in both molecules is atypical for biaryls and attributable to the two N–H···N′ hydrogen bonds (N1–H1 0.864(18), H1···N12′ 2.086(18), N1···N12′ 2.9183(15) Å, NHN′ 161.7(16)°; N1′–H1′ 0.908(18), H1′···N12

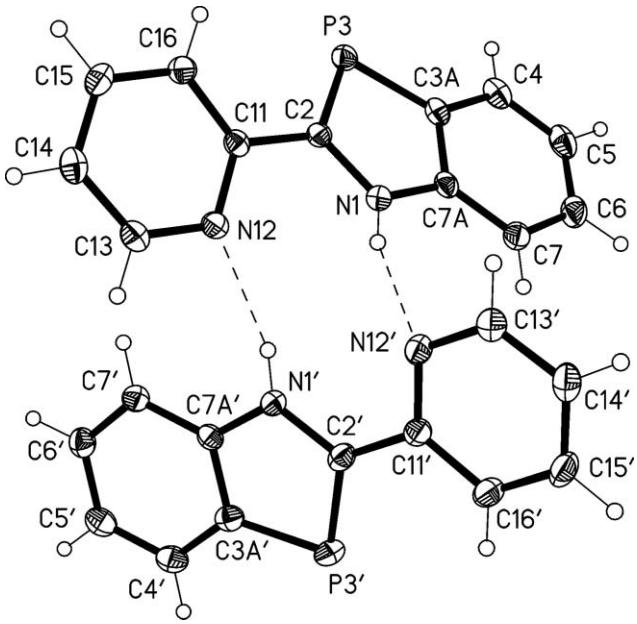


Fig. 2 Structure of **3h**. Ellipsoids represent 50% probability levels. Selected bond lengths (Å) and angles (°) of **3h**: P3–C2 1.7299(12), P3–C3A 1.7831(12), N(1)–C(2) 1.3628(15), N1–C7A 1.3732(15), C3A–C7A 1.4110(17), C2–C11 1.4685(15); C2′–P3′ 1.7376(13), P3′–C3A′ 1.7715(13), C2′–C11′ 1.4648(17); N1–C2–P3 114.36(9), C2–N1–C7A 113.76(10), C2–P3–C3A 88.42(6), N1–C2–C11 118.89(10), C11–C2–P3 126.61(9).

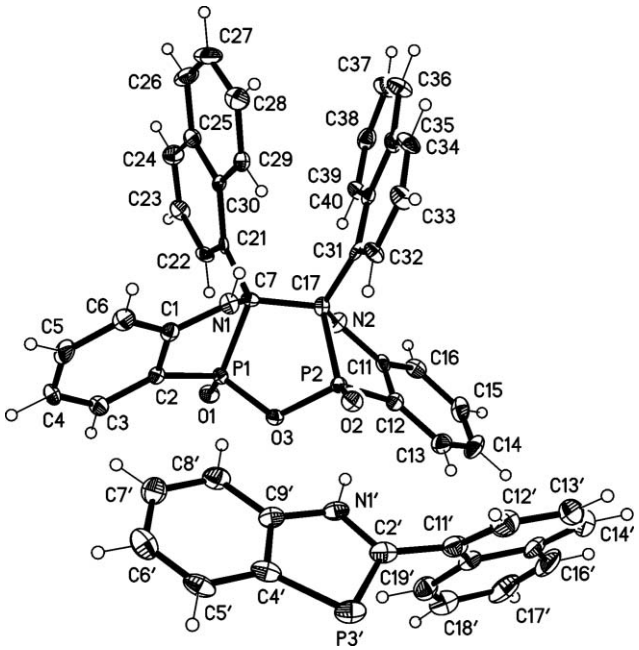
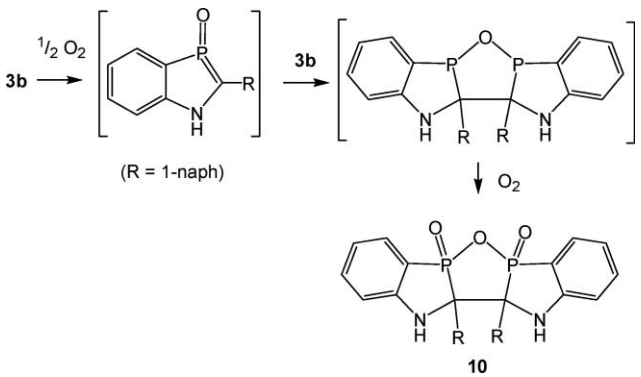


Fig. 3 Structure of **3b**, co-crystallizing with **10**. Ellipsoids represent 50% probability levels. The H atom at N2 is eclipsed. Selected bond lengths (Å) and angles (°) of **3b**: P3′–C2′ 1.737(4), P3′–C4′ 1.798(4), N1′–C2′ 1.356(5), N1′–C9′ 1.371(5), C4′–C9′ 1.405(6), C2′–C11′ 1.490(6); N1′–C2′–P3′ 113.2(3), N1′–C2′–C11′ 119.4(4), P3′–C2′–C11′ 127.4(3), C2′–P3′–C4′ 88.7(2). **10**: P1–C7 1.882(4), P1–C2 1.763(4), C7–N1 1.475(5), N1–C1 1.391(5), C1–C2 1.392(5), C7–C17 1.568(5), P1–O3 1.622(3), P1–O1 1.466(3); P1–C7–N1 96.3(2), C2–P1–C7 93.34(17); P1–C7–C17 104.1(2), C7–P1–O3 96.15(15).

2.126(18), N1′···N12 3.0006(14) Å, N′HN 161.3(15)°) between these molecules. The small deviations from planarity within the benzazaphosphole ring system (mean deviations for both molecules < 0.02 Å) are in agreement with an aromatic ring system, although the two different P–C and N–C bond lengths in the five-membered ring seem to indicate a rather weakly coupled benzene-azaphosphaallyl π-system. However, this is attributable to the particular electronic structure of cyclodelocalized 10π heterocycles composed of a benzene and a five-membered π-excess heterocyclic ring system.[5] The C–C bonds C2–C11 and C2′–C11′ are elongated compared to the C–C bonds within the aromatic rings as is also typical for biaryls in the coplanar orientation. The chemical properties of the 2-(hetero)aryl benzazaphospholes are in accordance with the existence of an aromatic system in the planar benzazaphosphole ring. The compounds do not exhibit N-basic properties by involvement of the nitrogen lone electron pair into the cyclodelocalized 10π-electron system, and they are thermally and hydrolytically stable. This allows purification by column chromatography on silica gel or, except for the N-basic pyridine derivatives **3h** and **9**, by extraction of basic impurities with dilute aqueous sulfuric acid. Solid benzazaphospholes are also quite stable to air, but in solution they are somewhat sensitive to air oxidation. Single crystals, formed during slow diffusion of air into an ethereal solution of **3b**, led to a first insight into the nature of the oxidation products. The X-ray crystal structure analysis reveals the oxidation product **10** co-crystallizing with one molecule of **3b** (Fig. 3).

The oxidised compound **10** is a P–O–P bridged and C–C coupled pentacyclic bis(benzazaphospholine-P-oxide), suggesting that a primarily formed, highly reactive benzazaphosphole P-oxide undergoes [3+2] cycloaddition with the P═C bond of a second benzazaphosphole (or P-oxide) and is then preferably further oxidized (Scheme 4). The supramolecular architecture is attributable to slow oxidation and N–H···O═P hydrogen bonds between **3b** and **10** both within the asymmetric unit [N(1′)–H(01′) 0.83(3), H(01′)···O(2) 2.02(3), N(1′)···O(2) 2.842(4) Å; N(1′)–H(01′)···O(2) 171(4)°] and over an inversion centre [N(2)–H(02) 0.82(3), H(02)···O(1)#1 2.06(3), N(2)···O(1)#1 2.850(4) Å; N(2)–H(02)··· O(1)#1 160(4)°], leading to dimers (Fig. 4). Bond lengths and angles are in the usual ranges for benzazaphospholes or dihydrobenzazaphospholes[6] except that P1–C2 is shorter in the P-oxide. The P1–O3–P2 angle (120.84(16)°) is large for a five-membered ring because of the small C–P–O angles (*ca.* 96°) and



Scheme 4 Assumed route to **10**.

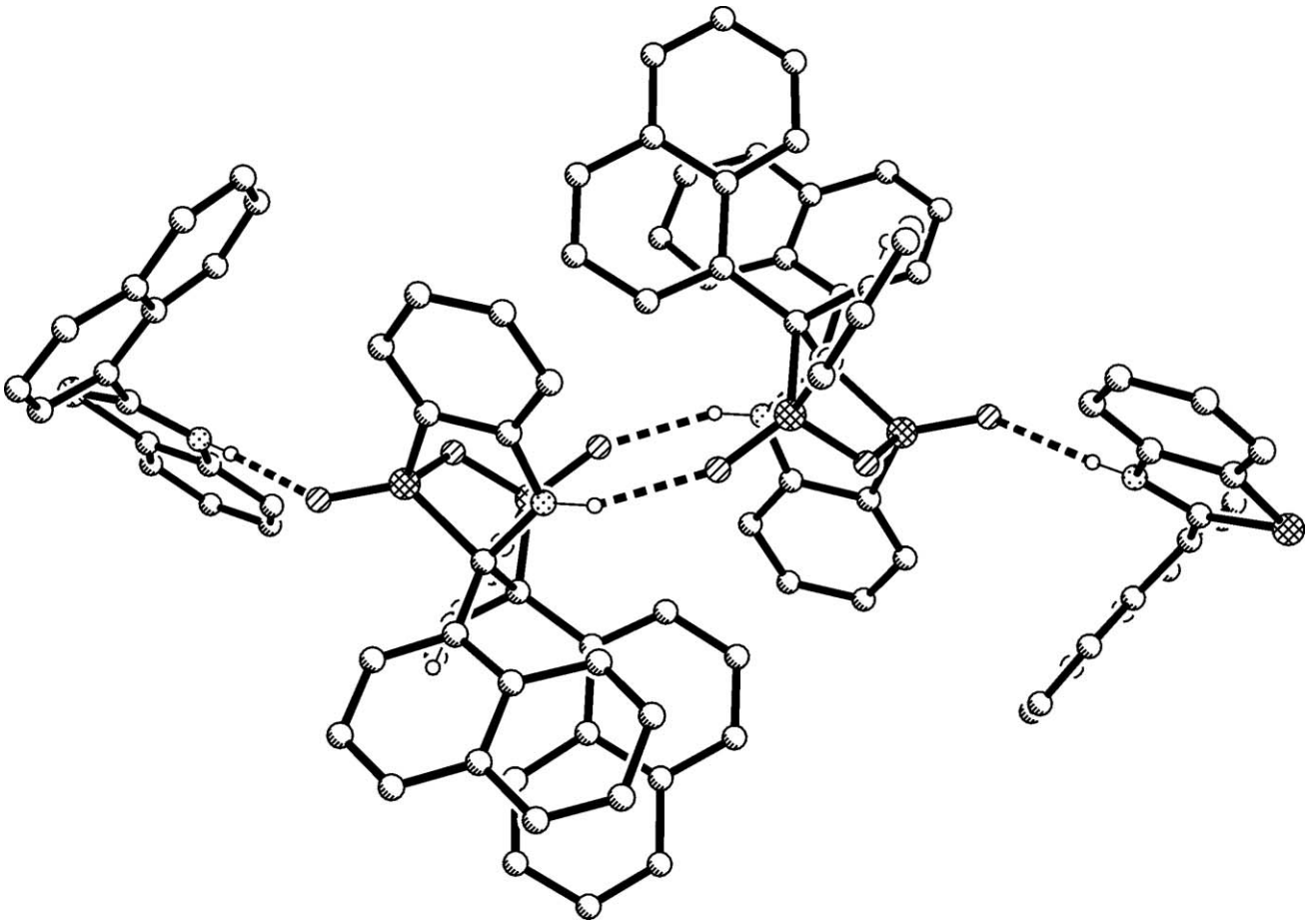


Fig. 4 Inversion symmetric dimers of **3b**···**10** in the packing (N1 not involved in hydrogen bonds).

a marked deviation from planarity. The angles O1–P1–C7 and O2–P2–C17 (127.08(16), 126.71(16)°) are appreciably widened.

Conclusions

2-Bromoanilides with naphthoyl or *o*-substituted benzoyl groups undergo nickel-catalyzed phosphonylation on heating with triethyl phosphite. The high yields of **2c** and also of **2f** and **2g** compared to **2a** demonstrate that the increase of electron density by the +M-effect of the *o*-methoxy group or by π-excess heteroaryl groups favours the coupling and overcompensates possible steric constraints (lower yield of **2b** compared to **2a**). It shows further that ether groups or the less nucleophilic oxygen of furyl or sulfur of thienyl groups, respectively, do not restrict the activity of the nickel catalysts as was observed for the pyridyl (nitrogen donor) or carbamate groups of **1h** and **1j**. The presence of chlorine and in particular bromine at the *o*-position of the benzoyl group causes low yields, at least in part because of interfering reactions, indicated by the formation of **1i** and **2i**. Reduction of the *N*-acylanilidophosphonates **1a–g** with excess $LiAlH_4$ provides benzazaphospholes as the main products, induced by primary reduction of the phosphonate group and intramolecular nucleophilic attack of phosphino or phosphido at the imidate group, formed by lithiation of the secondary amide. *o*-Bromine is concomitantly replaced by hydrogen in this reaction. Pyridyl and carbamate derivatives do not react in this way but give mixtures containing primary phosphinoanilines as main components. 2-Pyridylbenzazaphosphole **3h**, accompanied by a small amount of 1-pyridylmethyl-2-pyridylbenzazaphosphole **9**, is available by dehydrogenative cyclocondensation of 2-phosphinoaniline with pyridine-2-carboxaldehyde *via* an intermediate 2-pyridyldihydrobenzazaphosphole **8**. The new 2-donor-substituted 2-phenyl or 2-heteroaryl-1,3-benzazaphospholes extend the range of potential donor-functional σ^2P hybrid or chelate ligands by representatives stabilized by π-excess cyclodelocalization and should encourage coordination chemical and catalytic studies with these compounds. Further challenges are studies of the potential and scope of the cyclocondensation reactions with donor-functional (hetero)arylaldehydes, the mechanism and the fate of hydrogen that is formed along with **3h** under inert conditions and whether **3h** or related compounds can be catalytically hydrogenated and the products dehydrogenated.

Experimental Section

General considerations

All reactions with air- or moisture-sensitive compounds were carried out under a nitrogen atmosphere using Schlenk techniques and deoxygenated dry solvents. Reagents were used as received from commercial suppliers or dried by standard methods and recondensed or distilled before use. NMR spectra were measured

on a multinuclear FT-NMR spectrometer Bruker ARX300. ^{1}H, ^{13}C and ^{31}P chemical shifts are δ values and given in ppm relative to Me_4Si and H_3PO_4 (85%), respectively. Assignment numbers are indicated in Scheme 1 and 2. Coupling constants refer to H–H (^{1}H NMR) or P–C couplings (^{13}C NMR) unless stated otherwise. Elemental analyses were carried out with a CHNS-932 analyzer from LECO using standard conditions. HRMS measurements were performed in Göttingen using a double focusing sector-field instrument MAT 95 (Finnigan) (EI 70 eV) or a 7T Fourier transform ion cyclotron resonance mass spectrometer APEX IV (Bruker Daltonics) (ESI). PFC were used as reference substances. LR Mass spectra were measured on a single focusing sector-field mass spectrometer AMD40. Melting points were determined in sealed capillaries and are uncorrected.

General synthesis of *N*-secondary-*o*-bromoanilides

The acid chloride was added dropwise at 0 °C to a solution of the equimolar amount of 2-bromoaniline in either triethylamine (2 equivalents) and diethyl ether or in pyridine. After stirring overnight at room temperature water was added. The reaction mixture was extracted with CH_2Cl_2. The organic phase was separated and dried over Na_2SO_4. If necessary the residue was purified by column chromatography on silica, eluting with hexane–ethyl acetate (80 : 20). 2-Methoxybenzoic acid 2-bromoanilide **1c**,[27] thiophene-2-carboxylic acid 2-bromoanilide **1g**,[27] and *N*-(2-bromophenyl)carbamic acid *tert*-butylester (**1j**)[21] were prepared according to known procedures. Spectroscopic data and melting points agree with published data.

Naphthalene-1-carboxylic acid 2-bromoanilide (1b). Reaction of 1-naphthoylchloride (7.9 mL, 52.4 mmol), 2-bromoaniline (8.9 g, 51.7 mmol) and triethylamine (14.5 mL, 104.0 mmol) in diethyl ether (100 mL) afforded 15.0 g (89%) colorless solid, mp. 149 °C. ^{1}H NMR ($CDCl_3$): δ 7.05 (td, ^{3}J = 7.8, ^{4}J = 1.6 Hz, 1 H, H-4), 7.42 (td, ^{3}J = 8.5, ^{4}J = 1.3 Hz, 1 H, H-5), 7.54 (t, ^{3}J = 8.1, 7.3 Hz, 1 H, naph), 7.55–7.63 (2 superimp. t, 2 H, naph), 7.59 (superimp. dd, ^{3}J = 8.1, ^{4}J = 1.5 Hz, 1 H, H-3), 7.83 (dd, ^{3}J = 7.1, ^{4}J = 1.1 Hz, 1 H, naph), 7.91 (dd, ^{3}J = 7.5, ^{4}J = 2.0 Hz, 1 H, naph), 8.00 (d, ^{3}J = 8.3 Hz, 1 H, naph), 8.24 (br s, NH), 8.47 (d, ^{3}J = 8.5, ^{4}J = 1.4 Hz, 1 H, H-6), 8.64 ppm (d br, ^{3}J = 8.1 Hz, 1 H, H-8′). ^{13}C{^{1}H} NMR: δ 113.81 (C_q-2), 122.06 (CH-6), 124.80, 125.33, 125.38, 125.54 (CH-4, 3 CH naph), 126.71, 127.51 (2 CH naph), 128.47, 128.53 (CH-5, CH naph), 130.16 (C_q-8a′), 131.54 (CH naph), 132.37 (CH-3), 133.88, 133.96 (C_q-4a′, C_q-1′), 135.97 (C_q-1), 167.33 ppm (CO). MS (EI, 70 eV, 325 °C): *m*/*z* (%) = 327 (7) [M$^+$], 325 (7) [M$^+$], 246 (10), 156 (12), 155 (100), 101 (23), 127 (61), 86 (95). HRMS (EI): Calcd. for $C_{17}H_{12}NOBr^+$: 326.01750; found: 326.01747.

2-Chlorobenzoic acid 2-bromoanilide (1d). Reaction of 2-chlorobenzoyl chloride (4.8 mL, 37.9 mmol) with 2-bromoaniline (6.0 g, 34.9 mmol) and triethylamine (9.7 mL, 69.6 mmol) in diethyl ether (150 mL) gave 10.7 g (99%) colorless solid, mp. 108 °C. ^{1}H NMR ($CDCl_3$): δ 7.04 (td, ^{3}J = 7.9, ^{4}J = 1.6 Hz, 1 H, H-4), 7.34–7.51 (m, 4 H, H-5, H-3′, H-4′, H-5′), 7.58 (dd, ^{3}J = 8.1, ^{4}J = 1.5 Hz, 1 H, H-3), 7.80 (dd, ^{3}J = 7.3, ^{4}J = 1.8 Hz, 1 H, H-6′), 8.42 (br s, NH), 8.55 ppm (d br, ^{3}J = 8.1 Hz, 1 H, H-6). MS (EI, 70 eV, 25 °C): *m*/*z* (%) = 311 (3) [M$^+$], 309 (2) [M$^+$], 230 (18), 141 (31), 139 (100), 110 (30), 86 (50). HRMS (EI): Calcd. for $C_{13}H_9NOBrCl^+$: 309.96288; found: 309.96291.

2-Bromo-*N*-(2-bromophenyl)-benzamide (1e). Reaction of 2-bromobenzoyl chloride (10.0 mL, 76.5 mmol) with 2-bromoaniline (13.1 g, 76.2 mmol) and Et_3N (22.0 mL, 157.8 mmol) in Et_2O (300 mL) gave 22.7 g (84%) colorless solid, mp. 132 °C. ^{1}H NMR ($CDCl_3$): δ 7.04 (dt, ^{3}J = 7.8, ^{4}J = 1.6 Hz, 1 H, H-4), 7.35 (td, ^{3}J = 7.7, ^{4}J = 1.9 Hz, 1 H) and 7.38 (br t, ^{3}J = 7.8 Hz, 1 H) and 7.44 (td, ^{3}J = 7.5, ^{4}J = 1.1 Hz, 1 H) (H-5, H-5′, H-4′), 7.58 (dd, ^{3}J = 8.0, ^{4}J = 1.5 Hz, 1 H) and 7.67 (superimposed dd, ^{3}J = 7.9, ^{4}J = 1.3 Hz, 2 H) (H-3, H-6′, H-3′), 8.15 (br s, NH), 8.54 ppm (br d, ^{3}J = 8.1 Hz, 1 H, H-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 113.70 (C_q-2), 119.36 (C_q-2′), 122.08 (CH-6), 125.69 (CH-4), 127.77 (CH-5′), 128.46 (CH-5), 129.68 (CH-6′), 131.85 (CH-3′), 132.40 (CH-3), 133.75 (CH-4′), 135.48 (C_q-1), 137.53 (C_q-1′), 165.47 ppm (CO). MS (EI, 70 eV, 200 °C): *m*/*z* (%) = 357 (5) [M$^+$], 355 (10) [M$^+$], 353 (5) [M$^+$], 276 (53), 274 (54), 185 (100), 183 (89), 157 (26), 155 (25), 76 (27), 76 (20). HRMS (ESI in MeOH/H_2O, HCOONa): Calcd. for $C_{13}H_9NOBr_2$+H$^+$: 353.91237: found: 353.91234.

Furan-2-carboxylic acid 2-bromoanilide (1f). Reaction of 2-furoylchloride (2.86 mL, 29.0 mmol) with 2-bromoaniline (5.0 g, 29.1 mmol) in pyridine (30 mL) gave 6.8 g (88%) colorless solid, mp. 94–95 °C (mp. 90–91 °C[28]). ^{1}H NMR ($CDCl_3$): δ 6.58 (dd, ^{3}J = 3.6, 1.8 Hz, 1 H, H-4′), 7.00 (td, ^{3}J = 8.0, 7.4, ^{4}J = 1.6 Hz, 1 H, H-4), 7.27 (dd, ^{3}J = 3.6, ^{4}J = 0.7 Hz, 1 H, H-3′), 7.35 (tdd, ^{3}J = 8.0, 7.5, ^{4}J = 1.5, J = 0.4 Hz, 1 H, H-5), 7.57 (dd, ^{3}J = 1.7, ^{4}J = 0.9 Hz, 1 H, H-5′), 7.58 (partly superimp. dd, ^{3}J = 8.1 Hz, ^{4}J = 1.5 Hz, 1 H, H-3), 8.51 (dd, ^{3}J = 8.3, ^{4}J = 1.6 Hz, 1 H, H-6), 8.71 ppm (br s, NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 112.68 (CH-4′), 113.44 (C_q-2), 115.70 (CH-3′), 121.60 (CH-6), 125.22 (CH-4), 128.49 (CH-5), 132.34 (CH-3), 135.43 (C_q-1), 144.66 (CH-5′), 147.67 (C_q-2′), 155.92 ppm (CO). MS (EI, 70 eV, 200 °C): *m*/*z* (%) = 268 (5), 267 (40) [M$^+$], 266 (6), 265 (47) [M$^+$], 187 (9), 186 (86), 95 (100), 68 (6). Anal. calcd for $C_{11}H_8BrNO_2$ (266.09): C 49.65, H 3.03, N 5.26; found: C 49.92, H 3.12, N 5.25.

Pyridine-2-carboxylic acid 2-bromoanilide (1h). Our earlier reported synthesis[15] from 2-bromoaniline and 2-picolinic acid was modified. A mixture of 2-picolinic acid (1.0 g, 8.12 mmol), $SOCl_2$ (10 mL) and a catalytic amount of DMF (0.1 mL) was stirred at reflux temperature for 2 h. Then, excess $SOCl_2$ was removed in vacuum, and finally the residue was washed with toluene and dried in vacuum to give 1.15 g (nearly 100%) crude pyridine-2-carbonyl chloride. ^{1}H NMR (DMSO-d_6, ref. 2.50): δ 7.97 (tm, ^{3}J = 7.5, 5.3, ^{4}J = 1.0 Hz, 1 H, H-5), 8.27 (br d, ^{3}J = 7.7 Hz, 1 H, H-3), 8.40 (td, ^{3}J = 7.8, ^{4}J = 1.4 Hz, 1 H, H-4), 8.84 (br d, $^{3}J \approx 5$ Hz, 1 H, H-6); 9.29 (br s, H_2O of solvent, 4 H). A solution of the crude pyridine-2-carbonyl chloride (1.0 g, 7.06 mmol) in THF (10 mL) was added to a solution of 2-bromoaniline (1.1 g, 6.39 mmol) and Et_3N (1.8 mL, 12.9 mmol) in THF and the mixture worked up as described for **2b**. Purification by column chromatography on silica using hexane–ethyl acetate (90 : 10) provided 1.5 g (85%) colorless solid, mp. 129 °C. The spectroscopic data are in accordance with the earlier reported values.[15]

(2-Bromophenyl)carbamic acid 9*H*-fluoren-9-yl methylester (1k). Fmoc-Cl (330 mg, 1.28 mmol) was added at 0 °C to a solution of 2-bromoaniline (200 mg, 1.16 mmol) and pyridine (0.1 mL, 1.24 mmol) in CH_2Cl_2 (5 mL). Stirring was continued at room

temperature for 4 h. More CH_2Cl_2 was added, and the solution was washed with 1 M $NaHSO_3$ (2 × 10 mL) and dried over Na_2SO_4. The solvent was removed and the residue purified by chromatography on silica, eluting with hexane–diethyl ether (92 : 8) to give 420 mg (92%) of colorless solid. ^{1}H NMR ($CDCl_3$): δ 4.28 (t, ^3J = 7.1 Hz, 1 H, H-9′), 4.49 (d, ^3J = 7.1 Hz, 2 H, OCH_2), 6.95 (td, ^3J = 8.1, 7.5, ^4J = 1.5 Hz, 1 H, H-4), 7.20 (vbr s, NH), 7.27 (td, ^3J = 8.4, 7.4, ^4J = 1.1 Hz, 1 H, H-5) 7.31 (td, ^3J = 7.4, ^4J = 1.2 Hz, 2 H, H-2′), 7.39 (t, ^3J = 7.2 Hz, 2 H, H-3′), 7.49 (dd, ^3J = 8.1, ^4J = 1.4 Hz, 1 H, H-3), 7.61 (d, ^3J = 7.4 Hz, 2 H, H-1′), 7.76 (d, ^3J = 7.4 Hz, 2 H, H-4′), 8.07 ppm (vbr s, 1 H, H-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 46.95 (CH-9′), 67.39 (OCH_2), 112.89 (C_q-2), 120.03 (2 C_f), 120.58 (br, CH-6), 124.47 (CH-4), 124.97 (2 C_f), 127.08 (2 C_f), 127.77 (2 C_f), 128.36 (CH-5), 132.24 (CH-3), 135.57 (C_q-1), 141.26 (C_q, 2 C_f), 143.56 (C_q, 2 C_f), 153.03 ppm (CO); (C_f fluorenyl carbons). MS (EI, 70 eV, 345 °C): *m/z* (%) = 395 (0.4) [M$^+$], 393 (0.4) [M$^+$], 200 (0.4), 199 (0.4), 198 (0.5), 197 (0.5), 179 (21), 178 (100), 166 (6), 165 (10).

Phosphonylation of *N*-secondary 2-bromoanilides

2-(Naphthalene-1-carboxamido)phenylphosphonic acid diethyl ester (2b). A mixture of compound **1b** (1.3 g, 3.99 mmol) and anhydrous $NiCl_2$ (*ca.* 0.2 g) was heated to 155 °C in a distillation apparatus. Triethyl phosphite (1.02 mL, 5.95 mmol) was added dropwise maintaining the temperature at 155–160 °C. After the addition, heating was continued for 15 min and the temperature raised up to 200 °C. To limit the formation of ethylphosphonate, ethyl halide formed during the reaction was displaced by a slow stream of argon. The crude product was purified by column chromatography on silica, eluting with hexane–ethyl acetate (88 : 12) to give 0.97 g (63%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, ^3J = 7.0 Hz, 6 H, CH_3), 4.08 (m, 4 H, OCH_2), 7.19 (tdd, ^3J = 7.5, $^4J_{PH}$ = 3.1, ^4J = 1.0 Hz, 1 H, H-5), 7.54 (m, 3 H, aryl), 7.63 (ddd, $^3J_{PH}$ = 14.5, ^3J = 7.7, ^4J = 1.5 Hz, H-6), 7.66 (superimp. td, ^3J = 7.8, ^4J = 1.4 Hz, 1 H, naph), 7.88 (dd br, 1 H, naph), 7.91 (dd, ^3J = 7.6, $^4J \approx$ 2 Hz, 1 H, naph), 7.95 (d br, ^3J = 8.3 Hz, 1 H, naph), 8.57 (dm, $^3J \approx$ 8.0, ^4J = 1.7, J = 0.5 Hz, 1 H, H-8′), 8.91 (tm, $^3J \approx {}^4J_{PH}$ = 7.5–8.5, ^4J = 1.1 Hz, 1 H, H-3), 11.11 ppm (br s, NH). ^{13}C{^{1}H} and DEPT-135 NMR ($CDCl_3$): δ 16.10 (d, ^3J = 6.6 Hz, CH_3), 62.60 (d, ^2J = 5.3 Hz, OCH_2), 114.45 (d, ^1J = 179.8 Hz, C_q-1), 121.13 (d, ^3J = 11.3 Hz, CH-3), 123.31 (d, ^3J = 13.8 Hz, CH-5), 124.85, 125.44, 125.62, 126.29, 127.03, 128.28 (6 CH-naph), 130.48 (C_q-4a′), 131.27 (CH-naph), 132.59 (d, ^2J = 6.0 Hz, CH-6), 133.91 (C_q-8a′), 133.97 (C_q-1′), 134.04 (d, ^4J = 2.5 Hz, CH-4), 142.82 (d, ^2J = 7.2 Hz, C_q-2), 167.73 ppm (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.66 ppm. MS (EI, 70 eV, 345 °C): *m/z*(%) = 384 (6) [M$^+$], 383 (32), 279 (15), 167 (31), 155 (100), 148 (73), 127 (41). HRMS (EI): Calcd. for $C_{21}H_{22}NO_4P^+$: 384.13592; found: 384.13580.

2-(2-Methoxybenzoylamido)phenylphosphonic acid diethyl ester (2c). A mixture of compound **1c** (265 mg, 0.866 mmol), anhydrous $NiBr_2$ (30 mg) and triethyl phosphite (0.23 mL, 1.34 mmol) was heated for 30 min at 180 °C in a distillation apparatus. The crude product was purified by column chromatography on silica, eluting with hexane–ethyl acetate (60 : 40) to give 261 mg (83%) pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, ^3J = 7.1 Hz, 6 H, CH_3), 3.97–4.17 (m, 4 H, $POCH_2$), 4.04 (s, 3 H, OCH_3), 7.02 (d sh, ^3J = 8.3 Hz, 1 H, H-3′), 7.08 (td, ^3J = 7.6, ^4J = 1.0 Hz, 1 H, H-5′), 7.18 (tdd, ^3J = 7.6, 7.5, $^4J_{PH}$ = 3.2, ^4J = 1.1 Hz, 1 H, H-5), 7.48 (td, ^3J = 8.3, 7.4, ^4J = 1.9 Hz, 1 H, H-4′), 7.58 (tt, ^3J = 7.8, 7.7, $^4J + {}^5J_{PH}$ = 2.0–2.5 Hz, 1 H, H-4), 7.74 (ddd, $^3J_{PH}$ = 14.6, ^3J = 7.7, ^4J = 1.7 Hz, 1 H, H-6), 8.13 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, H-6′), 8.62 (t br, ^3J = 7.8, $^4J_{PH}$ = 7.8 Hz, 1 H, H-3), 10.98 ppm (br s, NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.89 (d, ^3J = 6.6 Hz, CH_3), 55.48 (OCH_3), 62.18 (d, ^2J = 5.2 Hz, OCH_2), 111.20 (CH-3′), 116.27 (d, ^1J = 179.5 Hz, C_q-1), 120.66 (CH-5′), 122.34 (C_q-1′), 123.05 (d, ^3J = 11.1 Hz, CH-3), 123.18 (d, ^3J = 13.7 Hz, CH-5), 131.76 (CH-4′ or -6′), 132.81 (d, ^2J = 6.6 Hz, CH-6), 132.92 (CH-6′ or -4′), 133.29 (d, ^4J = 2.5 Hz, CH-4), 141.62 (d, ^2J = 6.0 Hz, C_q-2), 157.36 (Cq-2′), 164.30 ppm (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 18.52 ppm. MS (EI, 70 eV, 280 °C): *m/z* (%) = 364 (1.5), 363 (12) [M$^+$], 229 (23), 155 (15), 135 (100), 99 (15), 77 (16). Anal. calcd. for $C_{18}H_{22}NO_5P$ (363.34): C, 59.50; H, 6.10, N, 3.85. Found: C, 59.25; H, 6.19; N, 3.86.

2-(2-Chlorobenzoylamido)phenylphosphonic acid diethyl ester (2d). A mixture of compound **1d** (6.5 g, 20.9 mmol), anhydrous $NiBr_2$ (*ca.* 0.2 g) and triethyl phosphite (3.95 mL, 23.0 mmol) was heated for 15 min at 200 °C in a distillation apparatus. The crude product was purified using column chromatography in silica, eluting with hexane–ethyl acetate (75 : 25) to give 2.9 g (38%) pale yellow oil, which formed colorless crystals on standing at room temperature, mp. 90 °C. ^{1}H NMR ($CDCl_3$): δ 1.30 (td, ^3J = 7.1, $^4J_{PH}$ = 0.3 Hz, 6 H, CH_3), 3.98–4.21 (m, 4 H, OCH_2), 7.19 (tdd, ^3J = 7.6, $^4J_{PH}$ = 3.1, ^4J = 1.0 Hz, 1 H, H-5), 7.30–7.40 (m, 2 H′-aryl), 7.42–7.46 (m, 1 H′-aryl), 7.56–7.68 (m, 3 H, H-4, H-6, H′-aryl), 8.79 (t br, ^3J = 8.2, $^4J_{PH}$ = 6.7 Hz, 1 H, H-3), 10.98 ppm (br s, NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.00 (d, ^3J = 6.6 Hz, CH_3), 62.51 (d, ^2J = 5.2 Hz, OCH_2), 114.31 (d, ^1J = 179.6 Hz, C_q-1), 120.98 (d, ^3J = 11.5 Hz, CH-3), 123.42 (d, ^3J = 13.7 Hz, CH-5), 126.92 (CH-5′), 128.77 (CH-6′), 130.40 (CH-3′), 131.15 (CH-4′), 131.18 (C_q-2′), 132.41 (d, ^2J = 5.8 Hz, CH-6), 133.92 (d, ^4J = 2.2 Hz, CH-4), 135.92 (C_q-1′), 142.20 (d, ^2J = 7.3 Hz, C_q-2), 165.20 ppm (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.51 ppm. MS (EI, 70 eV, 180 °C): *m/z* (%) = 369 (9) [M$^+$], 367 (29) [M$^+$], 232 (15), 230 (44), 141 (32), 139 (100), 110 (23). Anal. calcd. for $C_{17}H_{19}ClNO_4P$ (367.76): C 55.52, H 5.21, N 3.81; found: C 55.61, H 5.28, N 4.08.

2-(2-Bromobenzoylamido)phenylphosphonic acid diethyl ester (2e) and by-products 1i and 2i. A mixture of compound **1e** (2.0 g, 5.63 mmol), anhydrous $NiBr_2$ (0.5 g) and triethyl phosphite (1.06 mL, 6.18 mmol) was heated for 20 min at 190 °C in a distillation apparatus. The crude product mixture was separated by column chromatography on silica. 525 mg of unconverted **1e** (26%) was recovered. Elution by hexane–ethyl acetate (75 : 25) provided 450 mg (26% corr. yield) of **2e** as colorless oil, which formed colorless crystals on standing at room temperature, mp. 105–106 °C. Elution with increasing content of ethyl acetate in the mixture of hexane and ethyl acetate furnished the by-products. With hexane–ethyl acetate (60 : 40) 185 mg (10%) of **1i** was collected, with neat ethyl acetate 260 mg (12%) of **2i**, both as pale yellow viscous oils. **2e** - ^{1}H NMR ($CDCl_3$): δ 1.30 (t, ^3J = 7.1 Hz, 6 H, CH_3), 4.06, 4.17 (m, ^2J = 10.1, ^3J = 7.05 (A), 7.15 (B), $^3J_{PH}$ = 7.9 (A), 7.15 (B) Hz, 4 H, OCH_{AB}), 7.20 (tdd, ^3J = 7.5, 7.6, $^4J_{PH}$ = 3.1, ^4J = 1.0 Hz, 1 H, H-5), 7.29 (td, ^3J = 7.6, 7.8, ^4J = 1.7, 1.8 Hz, 1 H, H-4′or H-5′), 7.40 (td, ^3J = 7.5, ^4J = 1.2 Hz, 1 H, H-4′or H-5′), 7.52–7.68 (m, 4 H, H-4, H-6, H-3′, H-6′), 8.79 (t, ^3J = 8.1, $^4J_{PH}$ = 6.9 Hz, 1 H, H-3), 10.96 ppm (br s, NH). ^{13}C{^{1}H}

NMR ($CDCl_3$): δ 16.06 (d, ^3J = 6.6 Hz, CH_3), 62.57 (d, ^2J = 5.2 Hz, OCH_2), 114.24 (d, ^1J = 179.3 Hz, C_q-1), 119.68 (s, C_q-2′), 120.98 (d, ^3J = 11.4 Hz, CH-3), 123.48 (d, ^3J = 13.5 Hz, CH-5), 127.52 (s, CH-5′), 128.57 (s, CH-6′), 131.27 (s, CH-3′), 132.44 (d, ^2J = 5.9 Hz, CH-6), 133.62 (s, CH-4′), 133.99 (d, ^4J = 2.2 Hz, CH-4), 138.06 (s, C_q-1′), 142.23 (d, ^2J = 7.4 Hz, C_q-2), 166.08 ppm (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.59 ppm. MS (EI, 70 eV, 100 °C): *m/z* (%) = 413 (10) [M^+], 411 (9) [M^+], 275 (46), 273 (48), 184 (100), 182 (97). Anal. calcd. for $C_{17}H_{19}BrNO_4P$ (412.21): H 4.65, N 3.40; found: H 4.90, N 3.50.

1i. ^1H NMR ($CDCl_3$): δ 1.30 (t, ^3J = 7.0 Hz, 6 H, CH_3), 4.07–4.19 (m, 4 H, OCH_2), 7.03 (td, ^3J = 8.1, 7.5, ^4J = 1.6 Hz, 1 H, H-4), 7.38 (td, ^3J = 8.0, ^4J = 1.3 Hz, 1 H, H-5), 7.57 (dd, ^3J = 8.1, ^4J = 1.2 Hz, 1 H, H-3), 7.59 (superimp. m, ^3J = 7.5, $^4J_{PH}$ = 3.3, ^4J = 1.5 Hz, 1 H, H-4′), 7.66 (tt, ^3J = 7.8, 7.2, J_{PH} + ^4J = 3.2 Hz, 1 H, H-5′), 7.73 (t br, ^3J = 7.5, $^4J_{PH}$ = 5.1, ^4J = 1.2 Hz, 1 H, H-6′), 8.02 (ddd, $^3J_{PH}$ = 14.1, ^3J = 7.5, ^4J = 1.2 Hz, 1 H, H-3′), 8.37 (brs, NH), 8.45 ppm (d br, ^3J = 8.1 Hz, 1 H, H-6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.25 (d, ^3J = 6.2 Hz, CH_3), 62.91 (d, ^2J = 6.0 Hz, OCH_2), 114.13 (s, C_q-2), 122.56 (s, CH-6), 125.68 (s, CH-4), 125.79 (d, ^1J = 187.1 Hz, C_q-2′), 128.31 (s, CH-5), 128.88 (d, ^3J = 12.7 Hz, CH-6′), 130.04 (d, ^3J = 14.1 Hz, CH-4′), 132.43 (s, CH-3), 132.71 (d, ^4J = 2.9 Hz, CH-5′), 133.51 (d, ^2J = 8.9 Hz, CH-3′), 135.79 (s, C_q-1), 140.06 (d, ^2J = 9.8 Hz, C_q-1′), 166.85 ppm (d, ^3J = 4.4 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.29 ppm. MS (EI, 70 eV, 185 °C): *m/z* (%) = 413 (1.1) [M^+], 411 (1) [M^+], 242 (12), 241 (97), 185 (100), 167 (22). Anal. calcd. for $C_{17}H_{19}BrNO_4P$ (412.21): C 49.53, N 3.40; found: C 49.60, N 3.41.

2i. ^1H NMR ($CDCl_3$): δ 1.26 (t, ^3J = 7.1 Hz, 6 H, CH_3), 1.30 (t, ^3J = 7.1 Hz, 6 H, CH_3), 4.00–4.23 (m, 8 H, OCH_2), 7.18 (tdd, ^3J = 7.6, $^4J_{PH}$ = 3.1, ^4J = 0.9 Hz, 1 H, H-5), 7.53 (tdd, ^3J = 7.5, $^4J_{PH}$ = 3.5, ^4J = 1.7 Hz, 1 H, H-4′), 7.57–7.70 (m, 4 H, H-4, H-6, H-5′, H-6′), 8.02 (ddd, $^3J_{PH}$ = 14.0, ^3J = 7.6, ^4J = 1.1 Hz, 1 H, H-3′), 8.71 (t br, ^3J = 8.0, $^4J_{PH}$ = 6.9 Hz, 1 H, H-3), 10.72 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.21, 16.30 (2d, each ^3J = 6.7 Hz, CH_3), 62.56, 62.63 (2d, ^2J = 5.1, 4.7 Hz, OCH_2), 114.72 (d, ^1J = 179.9 Hz, C_q-1), 121.71 (d, ^3J = 11.4 Hz, CH-3), 123.53 (d, ^3J = 13.5 Hz, CH-5), 126.71 (d, ^1J = 186.7 Hz, C_q-2′), 127.20 (d, ^3J = 13.1 Hz, CH-6′), 129.67 (d, ^3J = 14.2 Hz, CH-4′), 132.49 (d, ^2J = 4.0 Hz, CH-6), 132.55 (br s, CH-4), 134.08 (s, CH-5′), 134.15 (d, ^2J = 6.7 Hz, CH-3′), 141.06 (d, ^2J = 9.6 Hz, C_q-1′), 142.42 (d, ^2J = 7.2 Hz, C_q-2), 167.33 ppm (d, ^3J = 4.5 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.51 (s), 16.96 (s) ppm. MS (EI, 70 eV, 210 °C): *m/z* (%) = 470 (1), 469 (9) [M^+], 242 (13), 241 (100), 213 (25), 185 (60), 167 (12). Anal. Calcd for $C_{21}H_{29}NO_7P_2$ (469.40): C, 53.73; H, 6.23, N, 2.98. Found: C, 53.88; H, 6.62; N, 3.14.

2-(Furan-2-carbonylamido)phenylphosphonic acid diethyl ester (2f). A mixture of compound **1f** (3.3 g, 12.4 mmol), palladium acetate (111 mg, 4.0 mol%) and triethyl phosphite (3.2 mL, 18.7 mmol) was heated at 180 °C for 1 h. Then the reaction mixture was allowed to warm to room temperature, diluted with ethyl acetate and filtered through Celite. The filtrate was concentrated and the crude product was purified by column chromatography on silica, eluting with hexane/ethyl acetate (75 : 25) to give a pale yellow oil, which formed 3.24 g (81%) colorless crystals within few hours at room temperature, m.p. 97–98 °C. ^1H NMR ($CDCl_3$): δ 1.33 (td, ^3J = 7.1, $^4J_{PH}$ = 0.4 Hz, 6 H, CH_3), 4.13 (m, 4 H, OCH_2), 6.54 (dd, ^3J = 3.4, 1.7 Hz, 1 H, H-4′), 7.16 (tdd, ^3J = 7.6, $^4J_{PH}$ = 3.1, ^4J = 1.0 Hz, 1 H, H-5), 7.27 (dd, ^3J = 3.4, ^4J = 0.7 Hz, 1 H, H-3′), 7.58 (partly superimp. t br, ^3J = *ca.* 8, 7 Hz, 1 H, H-4), 7.61 (superimp. dd, ^3J = 1.7, ^4J = 0.7 Hz, 1 H, 5′-H), 7.63 (partly superimp. ddd, $^3J_{PH}$ = 14.8, ^3J = 7.7, ^4J = 1.5 Hz, 1 H, H-6), 8.76 (t br, $^3J \approx {}^4J_{PH}$ = 7–8 Hz, 1 H, H-3), 11.39 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.17 (d, ^3J = 6.5 Hz, CH_3), 62.67 (d, ^2J = 5.2 Hz, OCH_2), 112.07 (s, CH-4′), 113.60 (d, ^1J = 179.1 Hz, C_q-1), 115.13 (s, CH-3′), 121.00 (d, ^3J = 11.8 Hz, CH-3), 123.16 (d, ^3J = 14.3 Hz, CH-5), 132.56 (d, ^2J = 5.4 Hz, CH-6), 134.05 (d, ^4J = 2.5 Hz, CH-4), 142.36 (d, ^2J = 6.6 Hz, C_q-2), 145.09 (s, CH-5′), 148.03 (s, C_q-2′), 156.66 ppm (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.81 ppm. MS (EI, 70 eV, 345 °C): *m/z* (%) = 324 (14), 323 (85) [M^+], 250 (10), 214 (11), 200 (11), 186 (67), 183 (15), 156 (13), 155 (22), 95 (100). Anal. calcd. for $C_{15}H_{18}NO_5P$ (323.28): C 55.73, H 5.61, N 4.33; found: C 56.12, H 5.80, N 4.44.

{2-[(Thiophene-2-carbonyl)amino]phenyl}phosphonic acid diethyl ester (2g). A mixture of compound **1g** (500 mg, 1.77 mmol), palladium acetate (15 mg, 3.8 mol%) and triethyl phosphite (0.45 mL, 2.62 mmol) was heated at 180 °C for 15 min. At room temperature the mixture was diluted with ethyl acetate and filtered through celite. The filtrate was concentrated, and the crude product was purified by column chromatography on silica eluting with hexane–ethyl acetate (75 : 25) to give a pale brown oil, which formed 552 mg (92%) of colorless crystals in few hours at room temperature, m.p. 94–95 °C. Crystal data are compiled in Table 1 (for selected bond lengths and angles see Fig. 1). ^1H NMR ($CDCl_3$): δ 1.34 (td, ^3J = 7.0, $^4J_{PH}$ = 0.3 Hz, 6 H, CH_3), 4.09 (m, 4 H, OCH_2), 7.13 (partly superimp. dd, ^3J = 5.0, 3.8 Hz, 1 H, H-4′), 7.15 (partly superimp. tdd, ^3J = 7.6, $^4J_{PH}$ = 3.1, ^4J = 1.0 Hz, 1 H, H-5), 7.54 (dd, ^3J = 5.0, ^4J = 1.1 Hz, 1 H, H-3′), 7.60 (superimp. ddd and br t, $^3J_{PH}$ = 14.3, ^3J = 7.7, ^4J = 1.5 Hz, 1 H, H-6; ^3J = 7–8 Hz, 1 H, H-4), 7.88 (dd, ^3J = 3.8, ^4J = 1.1 Hz, 1 H, H-5′), 8.77 (t, ^3J = 8.3, $^4J_{PH}$ *ca.* 6, ^4J = 1.1 Hz, 1 H, H-3), 11.57 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.17 (d, ^3J = 6.6 Hz, CH_3), 62.72 (d, ^2J = 5.2 Hz, OCH_2), 113.35 (d, ^1J = 179.3 Hz, C_q-1), 120.60 (d, ^3J = 11.7 Hz, CH-3), 122.98 (d, ^3J = 13.4 Hz, CH-5), 128.01 (s, CH-4′), 128.69 (s, CH-5′), 131.20 (s, CH-3′), 132.44 (d, ^2J = 5.3 Hz, CH-6), 134.19 (d, ^4J = 2.5 Hz, CH-4), 140.33 (s, C_q-2′), 142.90 (d, ^2J = 7.9 Hz, C_q-2), 160.30 ppm (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.43 ppm. MS (EI, 70 eV, 300 °C): *m/z* (%) = 340 (7), 339 (44) [M^+], 228 (6), 202 (25), 110 (100), 83 (5). Anal. calcd. for $C_{15}H_{18}NO_4PS$ (339.35): C 53.09, H 5.35, N 4.13; found: C 53.28, H 5.71, N 4.20.

2-(Pyridine-2-carbonylamido)phenylphosphonic acid diethyl ester (2h). A mixture of compound **1h** (4.6 g, 16.6 mmol), palladium acetate (140 mg, 4.0 mol%) and triethyl phosphite (4.3 mL, 25.1 mmol) was heated at 210 °C for 30 min. At room temperature the reaction mixture was diluted with ethyl acetate and filtered through celite. The filtrate was concentrated and the crude product was purified by column chromatography on silica, eluting with hexane–ethyl acetate (70 : 30) yielding 4.0 g (72%) pale yellow oil. ^1H NMR ($CDCl_3$): δ 1.34 (t, ^3J = 7.1 Hz, 6 H, CH_3), 4.09–4.28 (m, 4 H, OCH_2), 7.21 (td, ^3J = 7.6, $^4J_{PH}$ = 3.2 Hz, 1 H, H-5), 7.47 (ddd, ^3J = 7.6, 4.8, ^4J = 1.0 Hz, 1 H, H-5′), 7.61 (br t, ^3J = 8.1, 7.6 Hz, 1 H, H-4), 7.81 (ddd, $^3J_{PH}$ = 14.8, ^3J = 7.7, ^4J = 1.6 Hz, 1 H, H-6), 7.89 (td, ^3J = 7.7, ^4J = 1.6 Hz, 1 H, H-4′), 8.29 (br d, ^3J = 7.8 Hz, 1 H, H-3′), 8.72 (br d, ^3J = 4.0 Hz, 1 H, H-6′),

Table 1 Crystallographic details for **2g**, **3h** and **3b**···**10**

	2g	**3h**	**3b**···**10**
formula	$C_{15}H_{18}NO_4PS$	$C_{12}H_9N_2P$	$C_{51}H_{36}N_3O_3P_3$
M_t	339.33	212.18	831.74
T/K	133(2)	100(2)	133(2)
λ/Å	0.71073	1.54184	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a/Å	10.432(2)	8.32815(9)	12.5385(14)
b/Å	13.442(2)	11.83030(12)	11.3290(13)
c/Å	12.006(2)	20.9186(2)	28.960(3)
α/°	90	90	90
β/°	107.818(5)	90	102.099(4)
γ/°	90	90	90
V/Å^3	1602.8(5)	2060.99(4)	4022.4(8)
Z	4	8	4
ρ_{calc}/Mg m^{-3}	1.406	1.368	1.373
μ/mm^{-1}	0.318	2.061	0.198
F(000)	712	880	1728
Crystal size/mm^3	0.25 × 0.15 × 0.12	0.20 × 0.10 × 0.04	0.2 × 0.1 × 0.1
θ range/°	2.27 to 30.50	4.23 to 75.97	1.44 to 26.37
Index ranges	$-14 <= h <= 14$, $-19 <= k <= 19$, $-17 <= l <= 17$	$-10 <= h <= 10$, $-14 <= k <= 14$, $-26 <= l <= 26$	$-15 <= h <= 15$, $-14 <= k <= 14$, $-36 <= l <= 36$
Collected reflns	21470	45841	35203
Independent reflns	4879	4284	8219
R(int.)	0.071	0.027	0.139
Complete-ness/%	99.9	100	100
to θ/°	30	75	26
Absorption correction	None	Semi-empir. from equival.	None
Max. and min. transmission		1.000 and 0.724	
Data/restraints/parameters	4879/0/205	4284/0/279	8219/574/553
GOF on F^2	1.03	1.03	1.10
final R_1 [$I>2\sigma(I)$]	0.0391	0.0214	0.0875
final wR_2	0.0946	0.0561	0.1528
R_1 indices (all data)	0.0550	0.0216	0.1367
wR_2 (all data)	0.1002	0.0562	0.1655
Largest diff. peak/e Å^{-3}	0.41	0.14	0.45
Largest diff. hole/e Å^{-3}	–0.35	–0.27	–0.64

8.79 (br t, ^3J = 8.1, $^4J_{PH}$ = 6.7 Hz, 1 H, H-3), 11.93 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.73 (d, ^3J = 6.4 Hz, CH_3), 62.06 (d, ^2J = 5.5 Hz, OCH_2), 115.74 (d, ^1J = 181.7 Hz, C_q-1), 121.07 (d, ^3J = 10.8 Hz, CH-3), 122.11 (s, CH-3′), 123.02 (d, ^3J = 13.9 Hz, CH-5), 125.97 (s, CH-5′), 132.76 (d, ^2J = 6.7 Hz, CH-6), 133.30 (d, ^4J = 2.4 Hz, CH-4), 136.93 (s, CH-4′), 140.90 (d, ^2J = 5.9 Hz, C_q-2), 147.98 (s, CH-6′), 149.67 (s, C_q-2′), 162.67 ppm (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.28 ppm. MS (EI, 70 eV, 345 °C): m/z (%) = 335 (1), 334 (9) [M$^+$], 256 (8), 228 (9), 200 (27), 198 (13), 197 (100), 78 (26). HRMS (ESI in MeOH/H_2O and HCOOH): Calcd. for $C_{16}H_{19}N_2O_4P$+H$^+$: 335.11552; found: 335.11547.

***N*-(*tert*-Butoxycarbonyl)-2-aminophenylphosphonic acid diethyl ester (2j).** Triethyl phosphite (0.95 mL, 5.54 mmol) was added to a mixture of **1j** (1.0 g, 3.66 mmol) and palladium acetate (41 mg, 5 mol%) at 175 °C (bath) and heated at this temperature for 30 min. The crude product was purified by column chromatography on silica by eluting with hexane–diethyl ether (80 : 20) to give 1.0 g (83%) of pale yellow oil. ^1H NMR ($CDCl_3$): δ 1.32 (t, ^3J = 7.0 Hz, 6 H, CH_3), 1.52 (s, 9 H, CH_3), 4.00–4.22 (m, 4 H, OCH_2), 7.03 (tdd, ^3J = 7.7, 7.3, $^4J_{PH}$ = 3.1, ^4J = 1.0 Hz, 1 H, H-5), 7.49 (tt, ^3J = 7.9, 7.3, ^4J = 1.4, $^5J_{PH}$ = 0.9 Hz, 1 H, H-4), 7.55 (ddd, $^3J_{PH}$ = 14.5, ^3J = 7.8, ^4J = 1.4 Hz, 1 H, H-6), 8.35 (br t, ^3J = 7.9, $^4J_{PH}$ = 7.5 Hz, 1 H, H-3), 9.63 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.15 (d, ^3J = 6.6 Hz, CH_3), 28.29 (s, CH_3), 62.43 (d, ^2J = 5.2 Hz, OCH_2), 80.34 (s, C_qMe_3), 112.93 (d, ^1J = 180.1 Hz, C_q-1), 119.21 (d, ^3J = 11.4 Hz, CH-3), 121.62 (d, ^3J = 13.8 Hz, CH-5), 132.54 (d, ^2J = 6.1 Hz, CH-6), 133.85 (d, ^4J = 2.3 Hz, CH-4), 143.33 (d, ^2J = 7.2 Hz, C_q-2), 152.94 ppm (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.98 ppm. MS (EI, 70 eV, 20 °C): m/z (%) = 329 (15) [M$^+$], 273 (22), 256 (10), 230 (12), 229 (100), 201 (34), 173 (23), 155 (25), 120 (21), 57 (88). HRMS (EI): Calcd. for $C_{15}H_{24}NO_5P^+$: 329.1387; found: 329.1390.

An alternative phosphonylation of **1j** with diethyl phosphite (1.3 equivalent) in the presence of $Pd(PPh_3)_4$ and excess triethylamine in toluene (85 °C, 7d) provided **2j** in 38% yield. Analogous attempts with $PdCl_2/P(oTol)_3$ as the catalyst failed to give **2j**.

***N*-(9*H*-Fluoren-9-ylmethoxycarbonyl)-2-aminophenylphosphonic acid diethyl ester (2k).** A mixture of triethyl phosphite (0.05 mL, 0.29 mmol), **1k** (100 mg, 0.25 mmol) and palladium acetate (2 mg, 3.5 mol%) was heated at 160 °C for 1 h. The crude product was dissolved in a small amount of diethyl acetate, filtered through celite and purified by column chromatography on silica by eluting with hexane–diethyl ether (75 : 25) yielding 108 mg (95%) of colorless viscous oil. ^1H NMR ($CDCl_3$): δ 1.35 (t, ^3J = 7.1 Hz, 6 H, CH_3), 4.15 (m, 4 H, OCH_2), 4.31 (br t, ^3J = 7.2, 7.9 Hz, 1 H, CH-9′), 4.43 (br d, ^3J = 7.5 Hz, 2 H, OCH_2), 7.09 (tdd, ^3J = 7.5, $^4J_{PH}$ = 3.1, ^4J = 1.0 Hz, 1 H, H-5), 7.31 (td, ^3J = 7.4, ^4J = 1.2 Hz,

2 H, H-2′), 7.39 (td, ^3J = 7.5, ^4J = 0.9 Hz, 2 H, H-3′), 7.53 (br t, ^3J = 8.5, 7.3 Hz, 1 H, H-4), 7.60 (ddd, $^3J_{PH}$ = 14.5, ^3J = 7.7, ^4J = 1.6 Hz, 1 H, H-6), 7.68 (d, ^3J = 7.4, J = 0.6 Hz, 2 H, H-1′), 7.76 (d, ^3J = 7.4 Hz, 2 H, H-4′), 8.35 (br t, ^3J = 8.5, 6.5 Hz, 1 H, H-3), 10.18 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.16 (d, ^3J = 6.6 Hz, CH_3), 46.90 (CH-9′), 62.55 (d, ^2J = 5.0 Hz, OCH_2), 67.29 (OCH_2), 113.41 (d, ^1J = 180.0 Hz, C_q-1), 119.36 (d, ^3J = 11.4 Hz, CH-3), 119.88 (2 CH_f), 122.23 (d, ^3J = 13.4 Hz, CH-5), 125.24 (2 CH_f), 127.05 (2 CH_f), 127.65 (2 CH_f), 132.52 (d, ^2J = 6.1 Hz, CH-6), 133.98 (d, ^4J = 2.3 Hz, CH-4), 141.19 (C_q, 2 C_f), 142.65 (d, ^2J = 7.0 Hz, C_q-2), 143.76 (2$C_{q\text{-}f}$), 153.42 ppm (CO); (C_f fluorenyl carbon nuclei). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.05 ppm. Mass calcd. for $C_{25}H_{26}NO_5P$: 451.15; MS (EI, 70 eV, 345 °C): m/z (%) = 451 (0.3) [M^+], 274 (1), 229 (33), 201 (25), 189 (26), 181 (64), 180 (100), 166 (25).

2-Aminophenylphosphonic acid diethyl ester (2_H). Piperidine (1.65 mL, 16.7 mmol) was added to compound **2k** (500 mg, 1.11 mmol) in diethyl ether (15 mL) at 0 °C, stirred for 1 h at 0 °C and then at room temperature for 10 min. The product was then extracted with 2 M HCl into the aqueous phase and, after separation and neutralization with aqueous soda solution, re-extracted with diethyl ether. The combined ether layers were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica, eluting with hexane–ethyl acetate (55 : 45) to give 240 mg (94%) viscous oil. ^1H NMR ($CDCl_3$): δ 1.32 (t, ^3J = 7.1 Hz, 6 H, CH_3), 4.05, 4.14 (m, ^2J = 10.1, ^3J = 7.05 (A), 7.1 (B), $^3J_{PH}$ = 7.9 (A), 7.1 (B) Hz, 4 H, OCH_{AB}), 5.11 (vbr s, NH_2), 6.65 (br t, $^3J \approx$ 7.5, 7 Hz, 1 H, H-5), 6.70 (tdd, ^3J = 8.4, $^4J_{PH}$ = 3.3, ^4J = 0.8 Hz, 1 H, H-3), 7.26 (tt, ^3J = 8.3, 7.2, ^4J = 1.4 Hz, 1 H, H-4), 7.44 ppm (ddd, $^3J_{PH}$ = 14.3, ^3J = 7.7, ^4J = 1.6 Hz, 1 H, H-6). $^{13}C\{^1H\}$(DEPT) NMR ($CDCl_3$): δ 16.28 (d, ^3J = 6.7 Hz, CH_3), 62.00 (d, ^2J = 4.9 Hz, OCH_2), 108.08 (d, ^1J = 183.5 Hz, C_q-1), 116.26 (d, ^3J = 12.7 Hz, CH-3), 116.92 (d, ^3J = 13.9 Hz, CH-5), 133.21 (d, ^2J = 7.3 Hz, CH-6), 133.85 (d, ^4J = 2.4 Hz, CH-4), 151.20 ppm (d, ^2J = 8.5 Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.69 ppm. Mass calcd. for $C_{10}H_{16}NO_3P$: 229.09; MS (EI, 70 eV, 170 °C): m/z (%) = 230 (12), 229 (100) [M^+], 201 (38), 173 (57), 156 (28), 155 (92), 120 (24), 93 (17). (^1H data are in accordance with those of $\mathbf{2_H}$, synthesized by photoinduced Michaelis–Becker reaction from 2-iodoaniline and diethylphosphite in liquid ammonia.[23])

Reductive cyclization of 2-acylamidobenzenephosphonic acid esters

2-(Naphth-1-yl)-1*H*-1,3-benzazaphosphole (3b) and oxidation product 10. Compound **2b** (8.5 g, 22.1 mmol) was added drop by drop at 0 °C to $LiAlH_4$ tablets (2.5 g, 65.9 mmol) stirred in diethyl ether (250 mL). Stirring was continued at room temperature for 1 d. Then degassed water was added dropwise at 0 °C until the H_2 evolution ceased. The mixture was filtered and the insoluble residue thoroughly washed with ether. The combined solution was treated with cold degassed 10% aqueous H_2SO_4 to remove basic impurities. The ether layer was washed with water and dried over Na_2SO_4. Removal of ether in vacuum gave impure **3b** as yellow viscous oil. Attempts at purification by crystallization from various solvents failed, but purification of a one third aliquot succeeded by column chromatography on silica under argon by elution with hexane–diethyl ether (95 : 5) yielding 620 mg (32% referred to 1/3) yellow solid. ^1H NMR ($CDCl_3$): δ 7.18 (tq, ^3J = 7.1, 8.0, $^4J_{PH}$ = 2.0, ^4J = 1.0 Hz, 1 H, H-5), 7.33 (tt, ^3J = 8.0, $^5J_{PH}$ = 2.0, ^4J = 1.0 Hz, 1 H, H-6), 7.42–7.52 (m, 4 H, H-7, 3 H-naph), 7.63 (dt, ^3J = 7.1, $^4J_{PH}$ = 2.6, ^4J = 1.1 Hz, 1 H, H-2′), 7.86 (m, 2 H, H-naph), 8.09 (ddd, ^3J = 8.0, $^3J_{PH}$ = 3.5, ^4J = 0.5 Hz, 1 H, H-4), 8.18 (dd br, ^3J = 6.6, ^4J = 1.3 Hz, 1 H, H-8′), 9.26 ppm (br s, NH). $^{13}C\{^1H\}$ and DEPT-135 NMR ($CDCl_3$): δ 113.51 (CH-7), 120.48 (d, ^3J = 11.4 Hz, CH-5), 125.16 (d, ^4J = 2.6 Hz, CH-6), 125.27 (CH-naph), 125.42 (d, ^4J = 4.1 Hz, CH-3′), 126.23, 126.92 (2 CH-naph), 127.86 (d, ^3J = 8.7 Hz, CH-2′), 128.47 (CH-naph), 128.64 (d, ^2J = 20.5 Hz, CH-4), 129.25 (d, ^5J = 1.1 Hz, CH-4′), 131.13 (d, ^3J = 3.9 Hz, C_q-8a′), 133.00 (d, ^2J = 15.3 Hz, C_q-1′), 133.82 (C_q-4a′), 141.64 (d, ^1J = 43.1 Hz, C_q-3a), 142.39 (d, ^2J = 6.7 Hz, C_q-7a), 173.25 ppm (d, ^1J = 51.3 Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 84.44 ppm. MS (EI, 70 eV, 250 °C): m/z (%) = 261 (65) [M^+], 260 (19), 259 (11), 243 (8), 148 (20), 105 (21), 73 (30), 72 (36), 45 (42), 42 (100). HRMS (EI): Calcd. for $C_{17}H_{12}NP^+$: 261.0702; found: 261.0695. Storage of a sample of **3b** for crystallisation from ether/hexane over months, allowing slow diffusion of air through greased glass joints, gave crystals containing co-crystallized **3b** and its oxidation product **10**. Crystal data are compiled in Table 1 (for selected bond lengths and angles see Fig. 3).

2-(2-Methoxyphenyl)-1*H*-1,3-benzazaphosphole (3c). Compound **2c** (1.5 g, 4.13 mmol) was added dropwise at 0 °C to $LiAlH_4$ tablets (470 mg, 12.4 mmol) stirred in diethyl ether (30 mL). After stirring at room temperature for 1 d, the mixture was hydrolyzed at 0 °C and filtered; the solid residue was washed with diethyl ether, and the filtrate was dried over Na_2SO_4. Removal of ether left a pale yellow viscous oil, which in THF–hexane formed pale yellow crystals, yield 450 mg (45%). ^1H NMR ($CDCl_3$): δ 4.04 (s, 3 H, OCH_3), 7.03 (t, ^3J = 7.1 Hz, 1 H, H-5′), 7.04 (d br, ^3J = 8.4 Hz, 1 H, H-3′), 7.14 (tq, ^3J = 7.7, 7.2, $^4J_{PH}$ = 2.2, ^4J = 1.0 Hz, 1 H, H-5), 7.33 (tm, ^3J = 8.1–7.2 Hz, 2 H, H-6, H-4′), 7.60 (d br, ^3J = 8.6 Hz, 1 H, H-6′), 8.06 (ddbr, ^3J = 7.7, $^4J_{PH}$ = 3.8 Hz, 1 H, H-7), 8.20 (ddd, ^3J = 8.0, $^3J_{PH}$ = 4.2, ^4J = 1.7 Hz, 1 H, H-4), 11.0 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 56.02 (s, OCH_3), 112.08 (s, CH-3′), 113.79 (s, CH-7), 120.21 (d, ^3J = 12.1 Hz, CH-5), 121.87 (s, CH-5′), 123.10 (d, ^2J = 14.5 Hz, C_q-1′), 124.76 (d, ^4J = 2.9 Hz, CH-6), 128.36 (d, ^2J = 21.4 Hz, CH-4), 129.77 (d, ^3J = 18.3 Hz, CH-6′), 129.95 (s, CH-4′), 140.73 (d, ^1J = 40.4 Hz, C_q-3a), 142.46 (d, ^2J = 6.8 Hz, C_q-7a), 154.71 (d, ^3J = 7.9 Hz, C_q-2′), 173.36 ppm (d, ^1J = 51.2 Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.55 ppm. MS (EI, 70 eV, 345 °C): m/z (%) = 241 (100) [M^+], 167 (25), 148.0 (57), 84 (67), 57 (44). HRMS (ESI in MeOH/H_2O, HCOOH): Calcd. for $C_{14}H_{12}NOP+H^+$: 242.07293; found: 242.07304.

2-(2-Chlorophenyl)-1*H*-1,3-benzazaphosphole (3d). Compound **2d** (3.1 g, 8.43 mmol) was added dropwise at 0 °C to $LiAlH_4$ tablets (960 mg, 25.3 mmol) stirred in diethyl ether (30 mL). After stirring at room temperature for 2 d, the mixture was hydrolyzed and filtered, and the insoluble residue was thoroughly washed with diethyl ether. The filtrate was treated with cold degassed 10% aqueous H_2SO_4, washed with water and dried over Na_2SO_4. Filtration and removal of ether in vacuum gave 1.5 g (73%) crude **3d** as pale yellow viscous oil. Purification by column chromatography on silica gel under argon, eluting with hexane–diethyl ether (94 : 6), provided 670 mg (32%) pale yellow solid, mp. 57–59 °C. ^1H NMR (C_6D_6): δ 6.77 (tdd, ^3J = 7.4, J = 2.0, J = 0.9 Hz, 1 H, aryl), 6.82 (td br, ^3J = 7.4, ^4J = 1.7 Hz, 1 H, aryl), 7.03 (tm, ^3J = 7.9, 6.8, $^4J_{PH}$ = 2.1, ^4J = 1.2 Hz, 1 H,

H-5), 7.13 (superimp. tm, $^3J \approx 8.5$, 8, $^4J = 1.7$ Hz, 1 H, aryl), 7.15 (superimp. d, $^3J \approx 7.5$ Hz, 1 H, aryl), 7.21 (tt, $^3J = 8.1$, 6.8, $^5J_{PH}$ + $^4J = 2.1$ Hz, 1 H, H-6), 7.48 (dm, $^3J = 7.4$, $^4J_{PH}$ + $^4J = 3.7$ Hz, 1 H, H-7), 8.04 (ddm, $^3J = 8$–9, $^3J_{PH} = 3$–4, $^4J = 1.4$, $^5J = 0.8$ Hz, 1 H, H-4), 8.54 ppm (br s, NH). $^{13}C\{^1H\}$ and DEPT-135 NMR (C_6D_6): δ 114.73 (CH-7), 121.39 (d, $^3J = 12.0$ Hz, CH-5), 126.13 (d, $^4J = 2.9$ Hz, CH-6), 127.85 (CH-3′), 129.81 (d, $^2J = 21.0$ Hz, CH-4), 130.30 (d, $^4J = 1.7$ Hz, CH-4′), 131.23 (CH-5′), 132.52 (d, $^3J = 6.2$ Hz, C_q-2′), 132.88 (d, $^3J = 11.9$ Hz, CH-6′), 135.09 (d, $^2J = 16.6$ Hz, C_q-1′), 142.86 (d, $^1J = 42.7$ Hz, C_q-3a), 143.60 (d, $^2J = 7.2$ Hz, C_q-7a), 171.87 ppm (d, $^1J = 51.0$ Hz, C_q-2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 88.28 ppm. MS (EI, 70 eV, 220 °C): *m/z* (%) = 247 (28) [M^+ (^{37}Cl)], 246 (15), 245 (100) [M^+ (^{35}Cl)], 209 (10), 208 (11), 106 (61). HRMS (EI): Calcd. for $C_{13}H_9ClNP^+$: 245.01557; found: 245.01516.

Reduction of 2e to 2-phenyl-1*H*-1,3-benzazaphosphole (3a). Compound **2e** (4.0 g, 9.70 mmol) was added dropwise at 0 °C to $LiAlH_4$ tablets (1.1 g, 29.1 mmol) stirred in diethyl ether (30 mL). After stirring at room temperature for 1 d the mixture was hydrolyzed at 0 °C and filtered; the solid was thoroughly washed with diethyl ether. ^{31}P NMR control of a sample of the crude substance displayed a strong signal at δ 76.2, a minor signal at δ −153.2 (**5e**) and small signals at δ 86.4 (**3e**), −57.2, −50.2 (*E*/*Z*-**4e**). The mass spectrum showed small peaks for the envisaged bromophenyl-benzazaphosphole **3e** (*m/z* (%) = 295 (4), 293 (8), 291 (10), 289 (5)) and strong signals for 2-phenylbenzazaphosphole (*m/z* (%) = 211 (65); 124 (100)). The filtrate was dried over Na_2SO_4 and filtered. Removal of ether in vacuum gave a yellow viscous oil, which was purified by column chromatography on silica under argon. Elution with hexane–diethyl ether (95 : 5) gave 563 mg (20%) yellow **3a** whereas **3e** could not be isolated. ^1H NMR ($CDCl_3$): δ 7.17 (tdd, $^3J = 7.8$, 7.4, $^4J = 2.0$, $^4J = 1.0$ Hz, H-5), 7.35 (tt, $^3J = 8.2$, 7.1, ^4J + $^5J_{PH} = 2.2$ Hz, H-6), 7.38 (tm, 1 H, H-*p*), 7.44 (tm, 2 H, H-*m*), 7.60 (dm, $^3J = 8.2$, ^4J + $^4J_{PH}$ = 3.2 Hz, H-7), 7.78 (dm, 2 H, H-*o*), 8.05 (dddd, $^3J = 7.7$, $^3J_{PH} = 3.6$, $^4J = 1.7$, $^5J = 0.7$ Hz, H-4), 9.62 ppm (br s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 113.49 (CH-7), 120.55 (d, $^3J = 11.7$ Hz, C-5), 125.30 (d, $^3J = 12.0$ Hz, 2 CH-*o*), 125.31 (d, $^4J = 3.0$ Hz, C-6), 128.89 (d, $^4J = 20.8$ Hz, CH-4), 128.94 (d, $^5J = 2.8$ Hz, CH-*p*), 129.19 (2 CH-*m*), 134.94 (d, $^2J = 15.7$ Hz, C-*i*), 141.53 (d, $^1J = 41.2$ Hz, C-3a), 142.86 (d, $^2J = 6.9$ Hz, C-7a), 174.42 ppm (d, $^1J = 50.8$ Hz, C-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 76.47 ppm. MS (EI, 70 eV, 20 °C): *m/z* (%) = 211 (12) [M^+], 210 (26), 152 (100), 150 (10), 121 (45), 92 (8). These data match with those reported by Issleib *et al.*[9,12a]

2-(Furan-2-yl)-1*H*-1,3-benzazaphosphole (3f). Compound **2f** (1.0 g, 3.09 mmol) dissolved in diethyl ether and THF (10 and 5 mL) was added dropwise at 0 °C to $LiAlH_4$ tablets (352 mg, 9.27 mmol) stirred in diethyl ether (10 mL). After stirring at room temperature for 2 d, the mixture was hydrolyzed at 0 °C, the insoluble solid was filtered off and thoroughly washed with ether. ^{31}P NMR ($CDCl_3$) control of a sample of the crude product displayed signals at δ 72.9, −62.2 −66.6, −152.9 ppm, indicating *ca.* 85 mol% of **3f**, traces of two secondary phosphanes (*E*/*Z*-**4f**) and *ca.* 15 mol% of *N*-(2-furyl)-2-phosphinoaniline (**5f**). Purification of the ethereal solution by extraction of the impurities with air-free 10% sulfuric acid, washing with water and drying with Na_2SO_4 furnished pure **3f**, which crystallized from concentrated ether solution yielding 404 mg (65%) colorless crystals, mp. 80–82 °C. ^1H NMR ($CDCl_3$): δ 6.49 (ddd, $^3J = 3.4$, 1.8, $^5J_{PH} = 0.4$ Hz, 1 H, H-4′), 6.88 (ddd, $^3J = 3.5$, $^4J_{PH} = 1.5$, $^4J_{PH} = 0.7$ Hz, 1 H, H-3′), 7.13 (tdd, $^3J = 8.0$, 7.0, $^4J_{PH} = 3.2$, $^4J = 1.0$ Hz, 1 H, H-5), 7.32 (tt, $^3J = 8.2$, 7.0, ^4J + $^5J_{PH} = 2.3$ Hz, 1 H, H-6), 7.46 (dd, $^3J = 1.8$, $^4J = 0.7$ Hz, 1 H, H-5′), 7.53 (dq, $^3J = 8.2$, $^4J_{PH} = 2.0$, $^4J = 1.0$ Hz, 1 H, H-7), 8.02 (m, $^3J = 7.8$, $^3J_{PH} = 3.5$, $J = 1.3$, 0.6 Hz, 1 H, H-4), 9.47 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 107.54 (d, $^3J = 9.7$ Hz, CH-3′), 112.47 (d, $^4J = 2.0$ Hz, CH-4′), 113.38 (s, CH-7), 120.56 (d, $^3J = 12.0$ Hz, CH-5), 125.32 (d, $^4J = 2.7$ Hz, CH-6), 128.85 (d, $^2J = 21.6$ Hz, CH-4), 141.14 (d, $^1J = 41.1$ Hz, C_q-3a), 141.78 (d, $^2J = 7.2$ Hz, C_q-7a), 142.05 (d, $^4J = 5.3$ Hz, CH-5′), 149.88 (d, $^2J = 22.7$ Hz, C_q-2′), 162.24 ppm (d, $^1J = 49.0$ Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 72.85 ppm. MS (EI, 70 eV, 20 °C): *m/z* (%) = 202 (13), 201 (100) [M^+], 172 (42), 124 (21), 106 (18), 100 (43), 81 (58), 51 (16). HRMS (EI): Calcd. for $C_{11}H_8NOP^+$: 201.0344; found: 201.0335.

Detection of **5f** in the crude product mixture, ^1H NMR ($CDCl_3$): δ 3.59 (d, $^1J_{PH} = 201.0$ Hz, PH_2), 4.40 (s, NCH_2), 6.25 (dd br, $^3J = 3.2$, $^4J = 0.7$ Hz, H-3′), 6.33 (dd, $^3J = 3.2$, 1.9 Hz, H-4′), 6.66–6.74 (m, 2 H, H-4, H-6), 7.28 (br t, $^3J \approx 8$ Hz, H-5), 7.38 (dd, $^3J = 1.8$, $^4J = 0.7$ Hz, H-5′), 7.52 ppm (dd, $^3J = 7.6$, $^4J = 1.6$ Hz, H-3).

2-(Thien-2-yl)-1*H*-1,3-benzazaphosphole (3g). Compound **2g** (1.0 g, 2.95 mmol) dissolved in diethyl ether (10 mL) and THF (5 mL) was added dropwise at 0 °C to $LiAlH_4$ tablets (335 mg, 8.83 mmol) stirred in diethyl ether (10 mL). After stirring at room temperature for 2 d, the mixture was hydrolyzed at 0 °C. The insoluble solid was filtered off and thoroughly washed with ether. ^{31}P NMR ($CDCl_3$) monitoring of a sample of the crude product displayed **3g** as the main component (*ca.* 80 mol%) but also less intense signals characteristic for *E*/*Z*-dihydro-derivatives of **4g** ($\delta^{31}P$ −58.0, −47.5 ppm, δ^1H 4.26 (dt, $^1J_{PH} = 173.3$ Hz, J_{HH} small, PH), *ca.* 4.70 (dd, $^1J_{PH} \approx 186$, $^3J \approx 7$ Hz, PH)) and signals of **5g** ($\delta^{31}P$ −152.8, δ^1H 3.59 (d, $^1J_{PH} = 200.8$ Hz, PH_2), 4.59 ppm (s, NCH_2)). The filtrate was dried over Na_2SO_4, the solution separated and the solvent removed in vacuum to give 546 mg of a yellowish gummy solid. The impurities were more volatile than the product and distilled off at 10^{-5} mbar/60 °C bath temperature leaving 384 mg (60%) yellow solid. Trace impurities by **4g** and **5g** are removed by column chromatography on silica under argon, eluting with hexane–diethyl ether. ^1H NMR ($CDCl_3$): δ 7.10 (td, $^3J = 4.9$, 3.6, $^5J_{PH} = 1.5$ Hz, 1 H, H-4′), 7.16 (tdd, $^3J = 8.0$, 7.0, $^4J_{PH} = 2.2$, $^4J = 1.0$ Hz, 1 H, H-5), 7.33 (dd, $^3J = 4.9$, $^4J = 1.1$ Hz, 1 H, 3′-H), 7.35 (tt, $^3J \approx 8.3$, 7.1, $^4J \approx {}^5J_{PH} \approx 1$ Hz, H-6), 7.44 (td, $^3J = 3.6$, $^5J_{PH} = 1.6$, $^4J = 1.1$ Hz, 1 H, H-5′), 7.58 (dd, $^3J = 8.3$, $^4J \approx 1$ Hz, 1 H, H-7), 8.01 (ddd, $^3J = 7.8$, $^3J_{PH} = 3.7$, $^4J = 0.6$ Hz, 1 H, H-4), 9.24 ppm (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 113.39 (s, CH-7), 120.66 (d, $^3J = 11.9$ Hz, CH-5), 123.82 (d, $^3J = 11.2$ Hz, CH-3′), 125.45 (d, $^4J = 2.8$ Hz, CH-6), 125.70 (d, $J = 5.3$ Hz, CH-4′ or CH-5′), 128.27 (d, $J = 1.1$ Hz, CH-5′ or CH-4′), 128.76 (d, $^2J = 20.9$ Hz,CH-4), 138.40 (d, $^2J = 19.2$ Hz, C_q-1′), 141.52 (d, $^1J = 41.8$ Hz, C_q-3a), 142.47 (d, $^2J = 6.9$ Hz, C_q-7a), 167.03 (d, $^1J = 49.0$ Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 77.45 ppm. MS (EI, 70 eV, 345 °C): *m/z* (%) = 219 (4), 218 (12), 217 (100) [M^+], 106 (13). HRMS (EI): Calcd. for $C_{11}H_8NPS^+$: 217.0115; found: 217.0120.

2-(Pyrid-2-yl)-1*H*-1,3-benzazaphosphole (3h) and 2-(pyrid-2-yl)-1-(pyrid-2-yl)methyl-1,3-benzazaphosphole (9). A solution of **7**

(505 mg, 4.04 mmole), *p*-toluene sulfonic acid monohydrate (115 mg, 15%mole) and 2-pyridine carboxaldehyde (0.41 mL, 4.29 mmol) was refluxed in a Dean–Stark apparatus. Reaction monitoring after 3 h displayed ^{31}P NMR signals for benzazaphospholes **3h** and **9** (δ = 81.5, 88.9 ppm, relative intensities I_{rel} ≈ 50, 20%), unconverted 2-phosphinoaniline (δ = –153.7 ppm, I_{rel} = 17%), diastereoisomeric dihydro-benzazaphospholes **8** (δ = –64.2, –52.8 ppm, I_{rel} = 3, 4%) and an unknown product (δ = 32.3 ppm, I_{rel} = 6%). Heating was stopped after *ca.* 20 h and toluene removed in vacuum. Diethyl ether was added, the acidic catalyst removed by extraction with degassed 5% aqueous sodium hydroxide solution, and the ethereal layer dried over anhydrous sodium sulfate. Evaporation of the solvent gave an orange-yellow oil consisting of **3h**, **9** and residual **7** (I_{rel} = 67, 26, 7%). Separation by column chromatography on silica gel using hexane–diethyl ether (90 : 10) furnished 0.43 g (50%) **3h** as pale yellow crystals. Crystal data are compiled in Table 1 (for selected bond lengths and angles see Fig. 2). ^{1}H NMR ($CDCl_3$): δ = 7.18 (superimposed m, ^3J = 7.9, 7.0, $^4J_{PH}$ = 2.0, ^4J = 1.0 Hz, 1 H, H-5), 7.24 (superimposed m, ^3J = 7.4, 4.9, $^4J \approx J$ = 1 Hz, 1 H, H-5′), 7.39 (tt, ^3J = 8.3, 7.0, ^4J = 1 Hz, 1 H, H-6), 7.65 (ddd, ^3J = 8.3, $^4J_{PH} \approx$ 2, $^4J \approx$ 1 Hz, 1 H, H-7), 7.73 (td, ^3J = 7.8, 7.6, ^4J = 1.8 Hz, 1 H, H-4′), 8.09 (ddd, ^3J = 7.9, $^3J_{PH}$ = 4.2, ^4J = 1 Hz, 1 H, H-4), 8.13 (ddt, ^3J = 8.1, $^4J_{PH}$ = 2.2, $^4J \approx J$ = 1 Hz, 1 H, H-3′), 8.59 (d br, ^3J = 4.9 Hz, 1 H, H-6′), 10.99 ppm (br, 1 H, NH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 80.88 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 114.21 (s, CH-7), 120.49 (d, ^3J = 12.4 Hz, CH-5), 121.45 (d, ^3J = 13.3 Hz, CH-3′), 123.10 (d, ^5J = 2.7 Hz, CH-5), 125.98 (d, ^4J = 2.8 Hz, CH-6), 129.29 (d, ^2J = 21.2 Hz, CH-4), 137.06 (CH-4′), 142.13 (d, ^1J = 41.3 Hz, C_q-3a), 142.17 (d, ^2J = 6.8 Hz, C_q-7a), 148.68 (s, CH-6′), 152.10 (d, ^2J = 19.8 Hz, C_q-2′), 170.72 ppm (d, ^1J = 49.3 Hz, C_q-2). Anal. calcd. for $C_{12}H_9N_2P$ (212.05): H 4.28, N 13.20; found: H 4.42, N 13.12. **9**: ^{1}H NMR ($CDCl_3$): δ = 6.12 (s, NCH_2) ppm, aryl proton signals superimposed. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 88.94 ppm. HRMS (EI): Calcd. for $C_{12}H_9N_2P^+$ (212.0498), found: 212.0497.

Crystal structure analyses

Crystals of **2g**, **3h** and **3b**···**10** were mounted on glass fibres in inert oil. Data were recorded at low temperature on a Bruker SMART 1000 CCD using MoK$_\alpha$-radiation (λ = 0.71073 Å) (**2g**, **3b**···**10**) or Oxford Diffraction Xcalibur Nova diffractometer using CuK$_\alpha$-radiation (λ = 1.54184 Å) (**3h**). *Crystal data* are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares on F^2.[29] Hydrogen atoms were included using a riding model or rigid methyl groups, except for NH hydrogens, which were refined freely (for **3b**···**10** with N–H distance restraints). For **3h**, which crystallizes by chance in a chiral space group, the Flack parameter refined to 0.000(11). For **3b**···**10**, which diffracted weakly, displacement parameters were subjected to a series of restraints (DELU, SIMU).

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