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3-Amino- and 3-acylamido-2-phosphonopyridines: synthesis by Pd-catalyzed P–C coupling, structure and conversion to pyrido[*b*]-anellated P═C–N heterocycles

Mohamed Shaker S. Adam [a], Olaf Kühl [a], Markus K. Kindermann [a], Joachim W. Heinicke [a,*], Peter G. Jones [b]

[a] *Institut für Biochemie, Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Strasse 4, 17489 Greifswald, Germany*
[b] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany*

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ABSTRACT

Palladium catalyzed cross-coupling of 3-amino- and 3-acylamido-2-bromopyridines **1a**–**f** with triethyl phosphite allowed the synthesis of 3-amino- and 3-acylamido pyridine-2-phosphonic acid diethyl esters **2a**–**f**, whereas nickel catalysts, although providing access to related anilido-2-phosphonates, proved inactive. Reduction of the aminophosphonate **2a** with $LiAlH_4$ afforded 3-amino-2-phosphinopyridine (**3a**), which was cyclocondensed with dimethylformamide dimethyl acetal (DMFA) via phosphaalkene intermediates **4a** to the novel pyrido[*b*]-anellated 1,3-azaphosphole **5a**. Reaction of amidophosphonates **2b**–**f** with $LiAlH_4$ did not result in the expected reductive cyclization, as shown by closely related anilido-2-phosphonates, but led to product mixtures containing *N*-secondary 3-amino-2-phosphinopyridines **3b**–**f** as the main or major component. The conversion of **3b**,**d**,**e** with DMFA to **5b**,**d**,**e** provides first examples of *N*-substituted pyrido[*b*]-anellated azaphospholes. Structures were confirmed by multinuclear NMR and X-ray crystallography (for **2c**, **3b**).

1. Introduction

Amino-substituted phosphonic acid derivatives are of interest with respect to their biological properties[1] but are also useful building blocks for the synthesis of amino-functional phosphines, *P,N*-heterocycles or hybrid ligands. This was shown by investigations of phosphonoanilines and their conversion to 2-phosphinoanilines and *P,N*-heterocycles, which in turn were found useful as ligands in Pd-catalyzed arylamination or Ni-catalyzed ethylene oligomerization.[2] Introduction of nitrogen into the arene ring would change the influence of anellation[3] on the azaphosphole ring, thus allowing ligand tuning and access to further coordination modes. 2-Pyridyl phosphines are known to form four-membered hemilabile P∩N chelate complexes, which are of importance in transition metal coordination chemistry and catalysis.[4] Pyrido-anellated azaphospholes with the same structural motif, pyridine nitrogen and phosphorus bound at the same carbon atom, have so far not been studied, whereas pyrido[*a*]-anellated azaphospholes with bridging nitrogen atom are known.[5] This prompted us to extend our studies of anellated azaphospholes[2,5–7] to related novel pyrido[*b*]-anellated 1,3-azaphospholes.

We report here the synthesis and structure of 3-amino- and 3-amido pyridine-2-phosphonates, which to the best of our knowledge were so far unknown, and their behaviour towards reduction with $LiAlH_4$. We also report the first representatives of azaphospholo[4,5-*b*]pyridines.

2. Results and discussion

2.1. Synthesis of 3-amino- and 3-amido-pyridine-2-phosphonates

The most convenient syntheses of pyridylphosphines are P–C coupling reactions of chloro- or alkoxyphosphines with metallated pyridines. Alternatively, 2-bromopyridines are also sufficiently reactive for conversion with alkali metal phosphides.[4] However, the presence of NH-groups has severely restricted the use of these methods. Attempts at triple lithiation of 3-amino-2-bromopyridine, applicable to P–C coupling of 2-bromoaniline,[6b] or double lithiation of 3-pivalamido-2-bromopyridine and subsequent coupling with excess $ClP(NMe_2)_2$ or $ClP(O)(OEt)_2$, did not lead to defined products. Therefore, couplings of 3-amino- and 3-amido-2-halopyridines with diethyl phosphite in the presence of a strong base and with triethyl phosphite were tested. Despite the considerably increased reactivity of 2-bromopyridines towards nucleophiles compared to bromobenzenes, the usual Michaelis–Becker or Michaelis–Arbuzov-reactions[8] could not be achieved with 3-amino-2-bromopyridine up to 220 °C in the absence of a catalyst. Palladium and in some cases nickel or copper catalysts are known to allow efficient coupling of diethyl or triethyl phosphite with

* Corresponding author. Tel.: +49 3834 864337.
E-mail address: heinicke@uni-greifswald.de (J.W. Heinicke).

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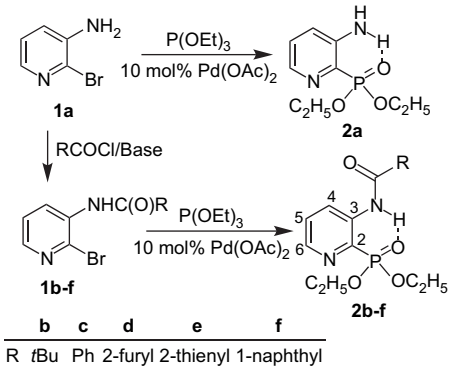
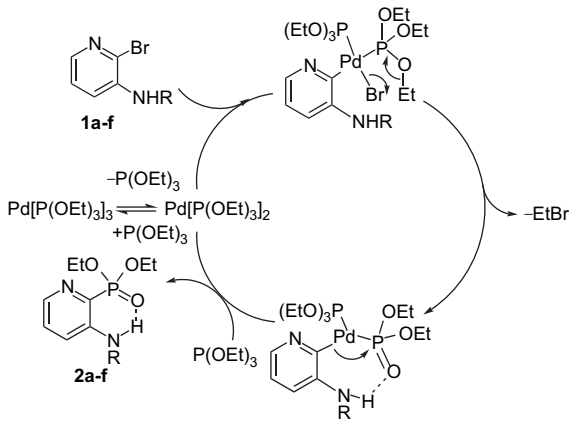
a variety of halobenzenes and even nitrogen-containing heterocycles[9,10] and were used by us in couplings of 2-amino- and 2-amidobromobenzenes.[2a,6] While fair to good yields were achieved in the palladium catalyzed coupling of 2-bromo-*N*-methylaniline with diethyl phosphite,[2a] attempts to couple 3-amino-2-bromopyridine with diethyl phosphite in the presence of $Pd(OAc)_2$ or $Pd_2(dba)_3$ (5 mol %) and triisopropylphosphine or triphenylphosphine (10 mol %) failed (in THF or toluene at 65–120 °C and reaction times up to 48 h). Attempts to couple 3-amino- or 3-amido-2-bromopyridines with triethyl phosphite in the presence of anhydrous nickel bromide were also unsuccessful, although acylamido bromobenzene couples in the presence of electron-withdrawing CF_3 groups under the same conditions (20 min, 200 °C).[6] It is therefore assumed that the catalysts are deactivated by the amino group or the combination of amino group and pyridine nitrogen. Use of palladium catalysts, which are more tolerant of functional groups, finally allowed coupling of 3-amino- and 3-amido-2-bromopyridines **1a**–**f** with triethyl phosphite (Scheme 1). The yields are rather low to moderate (very low for the chloro analogues of **1a**,**b**) and could not significantly be improved by addition of a more basic auxiliary phosphine such as tricyclohexylphosphine.



Scheme 1. Synthesis of 3-amino- and 3-amido-pyridine-2-phosphonates **2a**–**f**.

The reaction is likely to proceed via formation of the active catalyst involving phosphite coordination to palladium, oxidative addition of the bromopyridine at the palladium centre, nucleophilic substitution of bromide at an ethyl group of the coordinated phosphite with elimination of ethylbromide and subsequent reductive elimination of the product **2** and concomitant coordination of another phosphite ligand to palladium to reform the catalytic species. We assume that the catalytic cycle contains intermediate $Pd(0)[P(OEt)_3]_2$, which is stabilised in the presence of unconsumed or excess $P(OEt)_3$ as $Pd(0)[P(OEt)_3]_3$.[11] A tentative reaction mechanism is depicted in Scheme 2.



Scheme 2. Tentative P–C coupling mechanism.

Table 1
Yields of **2a**–**f** for various molar ratios of **1a**–**f** to $P(OEt)_3$ and catalyst load[a]

2	R	Yield[a] %			
		1.0 $P(OEt)_3$	1.2 $P(OEt)_3$	1.2 $P(OEt)_3$[b]	1.4 $P(OEt)_3$
a	H	15	26	20	22
b	*tert*-Butyl	26	38	33	36
c	Phenyl	20	29	25	25
d	Furyl	18	26	20	25
e	Thienyl	21	33	25	28
f	Naphthyl	16	22	17	20

[a] Unless indicated otherwise 10 mol % $PdCl_2$ or $Pd(OAc)_2$ was used; yields are identical within experimental error; work-up is more convenient in case of $PdCl_2$.
[b] 5 mol % catalyst.

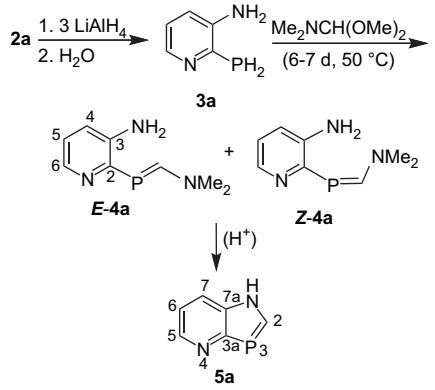
Conditions for the synthesis of **2a** were varied with regard to temperature (120–180 °C) and catalyst loading (2.5–10 mol %) showing that neat triethyl phosphite (1.2 equiv), heating at 160 °C and 10 mol % catalyst was the optimum in the low-yield couplings of **1a** and $P(OEt)_3$. Further optimization was not carried out. In a series of related bromoanilines, the yields of coupling products increased strongly in the case of *N*-secondary precursors,[2a] and the above conditions were therefore chosen also in the coupling reactions with *N*-acyl-substituted 2-bromopyridines **1b**–**f**. The rise in yield was rather low and limited to few examples, but the comparison of the yields of **2a**–**f** (*tert*-butyl>thienyl>phenyl>furyl≈hydrogen>naphthyl) (Table 1) shows still a clear influence of the substituent R and that this is mainly electronic in nature. Thus, a *tert*-butyl group with the greatest +I-effect within the series results in the highest yield. Likewise yields are higher with the electron-rich five-membered thienyl ring than with phenyl or naphthyl groups.

The amount of phosphite is crucial because it is not only required (consumed) as coupling component, but is also involved in the catalyst stabilization. Use of 1.2 equiv of phosphite, representing exactly the stoichiometric amount for a 10% catalyst load and coordination of two ligands at palladium, increased the yield by about one third compared to exactly equimolar amounts. As the $P(OEt)_3$ is added at the beginning, there is at first a factual excess, which diminishes with the progress of the reaction and may cause early catalyst decomposition in using a 1:1 molar ratio. If 1.4 equiv of phosphite were used, the yields decreased slightly, probably by favouring formation of $[Pd\{P(OEt)_3\}_3]$ at the expense of $[Pd\{P(OEt)_3\}_2]$, which is required for the oxidative addition step.

2.2. Reduction of 3-amino- and 3-amido-pyridine-2-phosphonates and synthesis of PCN heterocycles

Reduction of 3-aminopyridine-2-phosphonic acid ester **2a** with $LiAlH_4$ provided 3-amino-2-phosphinopyridine (**3a**) in moderate yield, only slightly contaminated by two other phosphines. Because of the high air sensitivity, no attempts were made at purification by chromatography. The crude product was used directly in the reaction with dimethylformamide dimethyl acetal (DMFA). Reaction control by ^1H and ^{31}P NMR indicated primary formation of a major amount of the *trans*-phosphaalkene *E*-**4a** and minor amount of the *cis*-isomer *Z*-**4a** and slow condensation to the pyridoazaphosphole **5a** (after 3 days at 50 °C, 3.5:1:1.5 molar ratio by CH-2 integration). The signals of the latter increase with the reaction time, the others decrease. Although the intermediates **4** are not fully characterized, unambiguous structure information is gained by characteristic P=CH phosphorus and proton signals. The phosphorus resonances of both intermediates, *Z*- and *E*-**4a** (δ ^{31}P 46.3, 57.1), appear strongly upfield from those of other types of phosphaalkenes, which typically absorb at δ=200–350 ppm.[12] This feature indicates the conjugation of the nitrogen lone pair to the P=C π-bond. In the heterocycle **5a** (δ ^{31}P 75.6) the effect is rendered somewhat smaller

by more effective delocalization of π-density into the electron-withdrawing pyridine ring. Even more indicative are the P=CH proton signals, which are strongly downfield shifted and display large and characteristic two-bond $^{31}P-^{1}H$ coupling constants. $^{2}J_{PH}$ is particularly large if the proton is in cis-position to the phosphorus lone pair (*Z*-**4a**, δ ^{1}H 10.05, $^{2}J_{PH}$=58.7 Hz; **5a**, δ ^{1}H 7.87, $^{2}J_{PH}$=36.9 Hz). In the opposite configuration it is considerably smaller but the value is still twice that of the other aryl protons (in $CDCl_3$ *E*-**4a** δ ^{1}H 10.68, $^{2}J_{PH}$=14.0 Hz). The intermediates **4a** are slowly converted to the heterocycle **5a**. Small amounts of acid catalyze the cyclocondensation (Scheme 3). Compound **5a** was separated from the mixture in good yield after prolonged heating by high-vacuum distillation as an air-sensitive white solid.



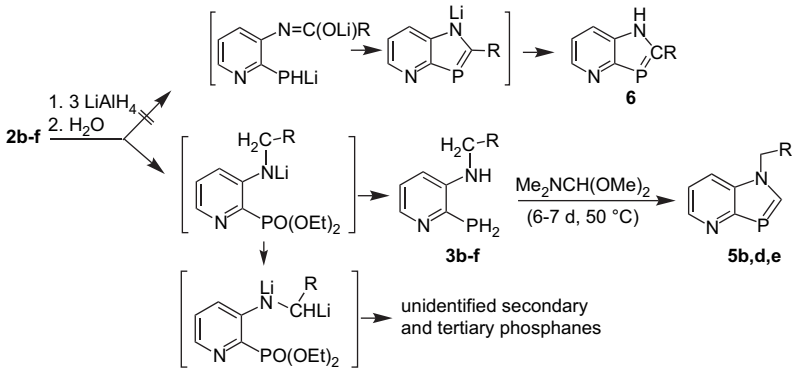
Scheme 3. Reduction of **2a** with $LiAlH_4$ and cyclization of **3a** to pyridoazaphosphole **5a**.

The reduction of the 3-amido-pyridine-2-phosphonates **2b–f** with $LiAlH_4$ (and subsequent hydrolysis) was expected to furnish pyridoazaphospholes **6** with the substituent R in 2-position by reductive cyclization, the main reaction of the closely related 2-acylamidophenyl phosphonic acid diethyl esters.[6] The experiments led, however, to mixtures, containing primary 2-phosphino-3-organomethylamino-pyridines **3** as the main (**3b**,**d**,**e**) or a major constituent (**3c**) while pyridoazaphospholes could not even be detected as trace signals in the crude mixtures, indicating that reductive cyclization is completely suppressed (Scheme 4). To understand this particular reactivity, mixtures of $PhP(O)(OEt)_2$ and $RNHC(O)^{t}Bu$ with R=phenyl and R=2-pyridyl were reduced in diethyl ether with $LiAlH_4$ in a 1:1:1 molar ratio (15 h, room temperature), which is insufficient for complete reduction. Thus, the preferred reduction site becomes evident. Whereas phenyl phosphonic acid ester is reduced faster than pivaloylanilide (R=Ph), as shown by the higher amount of phenylphosphine compared to *N*-neopentylaniline (molar ratio 2:1–2.4:1 by ^{1}H NMR integration of PH_2 and NCH_2 signals), the opposite is true for the mixture obtained with pivaloyl-2-pyridylamide (R=pyridyl), which displays phenylphosphine and *N*-neopentyl-2-aminopyridine in a molar ratio of 1:3. The faster reduction of pivaloyl pyridylamide compared to pivaloylanilide is attributed to the −M effect of the pyridyl group and will also lead to preferred reduction of the amido groups of **2b–f**. This prevents the reductive cyclization, which requires primary formation of 2-phosphino- or 2-phosphido imidates. The resulting *N*-secondary lithium pyridylamides are then reduced at the phosphono group to give **3b–f** after aqueous work-up (Scheme 4). The identity of the by-products was not studied in detail, but phosphorus resonances of the reaction mixtures in the region of δ −71 to −50 and −25 to −4 ppm hint at secondary and tertiary phosphines.[12] These might be formed by lithiation of the amidomethyl group and nucleophilic attack of CLi at the phosphono group, known from intramolecular carbanionic rearrangements of arylphosphates,[13] and subsequent reduction of P(V) to P(III) species. The potential of the *N*-secondary 2-phosphino pyridylamines as starting materials for the synthesis of *N*-substituted pyridoazaphospholes **5b**,**d**,**e** was demonstrated by reaction of crude **3b**,**d**,**e** with DMFA (Scheme 4). The use of crude **3b**,**d**,**e** did not lead to optimal results and pure products, but provides initial information on the new type **5** of pyrido[*b*]-anellated P=C–N heterocycles.

2.3. Structure elucidation and conformation control by hydrogen bonds

The structure elucidation is based on characteristic ^{31}P and fully assigned, conclusive proton and ^{13}C NMR data, elemental analysis or molecular ions in HRMS, and crystal structure analyses of **2c** and **3b**. The solution NMR spectra of the 3-amidopyridine derivatives display strongly downfield shifted resonances (Δδ 2.0–2.4 ppm) for the protons H-4 in *o*-position to the amido group (^{1}H NMR **1b–f** δ 8.70–8.97, **2b–f** δ 9.04–9.39 ppm) compared to the corresponding pyridylamines (**2a** δ 7.02 ppm) while the impact on the *p*-protons H-6, similarly influenced by the +M-effect of the acylamido group, is much lower (Δδ ca. 0.4 ppm). The major contribution is thus due to the magnetic anisotropy influence of the C=O double bond in the *Z*-configuration, where oxygen is directed towards the pyridine ring. The large downfield NH proton shifts of the *o*-phosphono amides **2b–f** (δ 11.0–11.9 ppm in $CDCl_3$) compared to the *o*-bromo amides **1b–f** (δ 8.0–8.7 ppm in $CDCl_3$) give evidence that the *o*-amidopyridine phosphonates form significantly stronger P=O···H–N than C=O···H–N hydrogen bonds; the former are also favoured by the possibility of intramolecular hydrogen bonds. The preferred solution structures are thus similar to the structure determined for **2c** in the crystal.

The X-ray crystal structure analysis of **2c** (Fig. 1) reveals four molecules in the monoclinic unit cell, space group $P2_1/c$. The bond



Scheme 4. Reduction of **2b–f** with $LiAlH_4$ and cyclization of **3b–f** to pyridoazaphosphole **5b**,**d**,**e**.

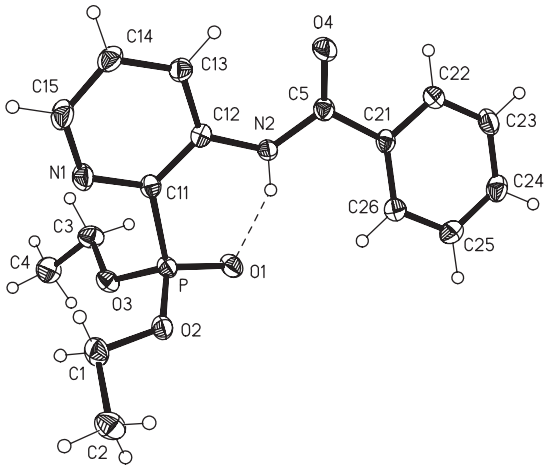


Figure 1. Molecular structure of **2c** in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): P–O1 1.4759(9), P–O2 1.5595(9), P–C11 1.8086(13), C12–N2 1.4031(15), N2–C5 1.3664(16), C5–O4 1.2170(15); O1–P–O2 111.01(6), O(2)–P–O(3) 102.25(5), C5–N2–C12 127.74(11), O4–C5–N2 123.86(12), O4–C5–C21 121.17(11), N2–C5–C21 114.97(11), N1–C11–P 113.23(9), C12–C11–P 123.99(9), C13–C12–C11 117.68(11). 3.1762(18) Å, N2–H···N1 146.5(16)°.

lengths and angles lie in the normal ranges. The O and C atoms at phosphorus form a distorted tetrahedron with the O2–P–O3 angle smaller than the O–P=O angles. The pyridine ring is somewhat distorted with a rather small angle C13–C12–C11. The phosphono group forms a six-membered ring with an intramolecular P=O···H–N hydrogen bond (H02···O1 1.926(16), N2···O1 2.7217(14) Å, angle 151.3(14)°). The geometry at C11 and, to a lesser extent, C12, is irregular; the phosphorus is angled towards the pyridine-N atom (N1–C11–P 113.23(9)°, cf. C12–C11–P 123.99(9)°), while N2 is slightly bent towards O1 (C13–C12–N2 123.22(11), C11–C12–N2 119.09(11)°). The distance of H13 to O4 is 2.22 Å. The π-systems of the amido group and pyridine ring are nearly coplanar (interplanar angle 3.1°) allowing stabilization by extended delocalization while the benzene π-plane is somewhat rotated with respect to the amide plane (interplanar angle 22.6°). The packing is rather featureless, with just two weak C–H···O interactions from ethyl hydrogens.

3-Neopentylamino-2-phosphinopyridine (**3b**) also formed single crystals with four molecules (Fig. 2) in the tetragonal unit cell, space group $P4_1$. In the packing (Fig. 3) the molecules interact via the 4_1 screw axis by N2–H···N1 hydrogen bonds (H01···N1 2.42(2), N2···N1 3.176 Å).

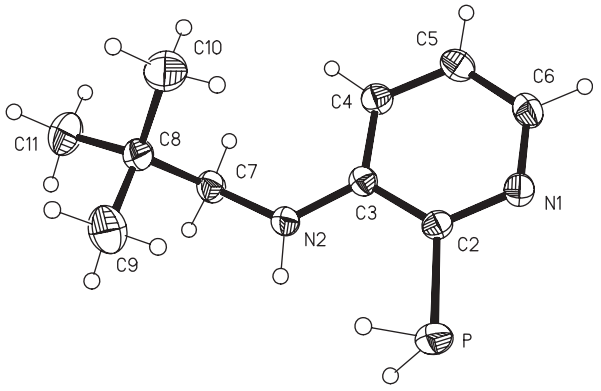


Figure 2. Molecular structure of **3b** in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): P–C(2) 1.8299(15), C(2)–C(3) 1.4199(19), N(1)–C(2) 1.3429(19), N(2)–C(3) 1.3673(18), N(2)–C(7) 1.4512(18); C(3)–C(2)–P 123.84(10), N(2)–C(3)–C(4) 123.44(13); C(3)–N(2)–C(7)–C(8) −104.08(17).

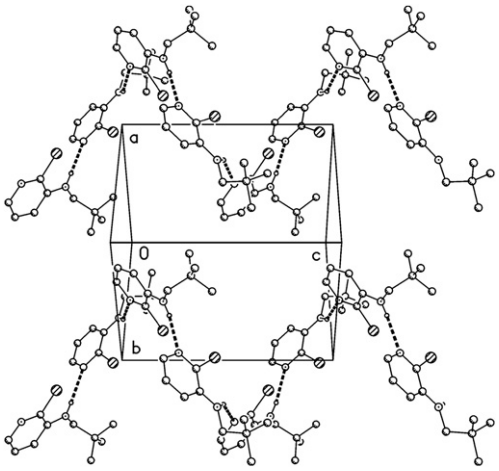


Figure 3. Packing of **3b** in the crystal.

Neighbouring strands, not shown in Figure 3, are connected by C5–H5···Cent interactions (Cent=centroid of pyridyl ring) with H5···Cent 2.64 Å, angle 138°. The phosphorus is slightly angled towards N1 (N1–C2–P 113.09(10)°) and nitrogen N2 slightly towards phosphorus. The torsion angle C2–C3–N2–C7 (2.0(2)°) indicates a nearly planar structure and sp^2-hybridization of nitrogen (cf. C3–N2–C7 126.27(12)°), allowing mesomeric interactions between the nitrogen lone electron pair and the pyridine π-system.

3. Conclusions

A route to novel 3-amino- and 3-acylamidopyridine-2-phosphonates by palladium-catalyzed cross-coupling of 3-amino- and 3-acylamido-functional 2-bromopyridines was demonstrated. Optimization is still necessary to improve yields. Reduction of 3-aminopyridine-2-phosphonic acid esters with $LiAlH_4$ leads to 3-amino-2-phosphinopyridine, which allows cyclocondensation with *N*,*N*-dimethylformamide dimethyl acetal to novel pyrido[*b*]-anellated 1*H*-1,3-azaphospholes. Reductive cyclization of 3-acylamidopyridine-2-phosphonates with $LiAlH_4$, in analogy to the synthesis of benzazaphospholes from acylanilido-2-phosphonates, is, however, not possible. The crucial step is the relative reduction rate of phosphono and amido groups. Reductive cyclization requires primary reduction of the phosphono group, but the electron-withdrawing pyridyl group activates the C=O bond of the amide and thus causes preferred reduction at this site. Subsequent reduction of the phosphono group leads to *N*-secondary 3-amino-2-phosphinopyridines, in some cases the main product, but more or less abundant side reactions prevent this being a suitable route to these compounds. By use of enriched samples, it could be, however, shown that these compounds are suitable starting materials for the synthesis of *N*-substituted pyrido[*b*]-anellated 1,3-azaphospholes.

4. Experimental

4.1. General

All manipulations were performed under dry argon, using Schlenk techniques and freshly distilled ketyl-dried solvents. 3-Amido-2-bromopyridines were prepared in analogy to 2-amido-3-bromopyridines.[14] 3-Amino-2-bromopyridine (**1a**) and other chemicals were used as purchased. NMR spectra were recorded at 25 °C on multinuclear FT-NMR spectrometers ARX 300 (Bruker) or Avance II 300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Chemical shifts δ are given in parts per million, shift references are tetramethylsilane for ^{1}H and ^{13}C and H_3PO_4 (85%) for ^{31}P. Coupling

constants, unless indicated otherwise, refer to J_{HH} in ^1H and J_{PC} in ^{13}C NMR data. Assignment numbers follow the nomenclature and/or use position abbreviations (*i*, *o*, *m*, *p* for aryl and α, β, etc. for alkyl groups); examples for numbering pyridine derivatives and heterocycles are given in schemes. IR spectra were measured on a FTIR-spectrometer System 2000 (Perkin–Elmer) and EI mass spectra on a single-focusing mass spectrometer AMD40 (Intectra). HRMS data were recorded on MAT95 (Finnigan) with EI (70 eV, PFK as reference substances) or on a 7T Fourier transform ion cyclotron resonance mass spectrometer APEX IV (Bruker Daltonics) with ESI ($[M+H]^+$ in MeOH/NH_4OAc or Me/H_2O/formic acid) at the University of Göttingen. Elemental analyses were carried out with a CHNS-932 analyzer from LECO using standard conditions. Melting points were determined in a capillary and are uncorrected.

4.1.1. *N-(2-Bromopyrid-3-yl)trimethylacetamide (**1b**)*

Pivaloylchloride (2.55 mL, 20.8 mmol) was added dropwise to a solution of **1a** (3.0 g, 17.34 mmol) and triethylamine (2.90 mL, 20.8 mmol) in THF (20 mL) and Et_2O (20 mL) at 0 °C. The mixture was stirred at room temperature overnight and digested with water and concd aqueous $NaHCO_3$ solution. The ether extracts were dried over $MgSO_4$. Removal of solvent in vacuum gave 3.72 g (83%) of NMR spectroscopically pure **1b**, mp 47 °C. ^1H NMR ($CDCl_3$, ppm): δ 1.36 (s, 9H, CMe_3), 7.27 (dd, ^3J=8.2, 4.6 Hz, 1H, 5-H), 8.04 (br s, 1H, NH), 8.08 (dd, ^3J=4.6 Hz, ^4J=1.8 Hz, 1H, 6-H), 8.70 (dd, ^3J=8.1 Hz, ^4J=1.8 Hz, 1H, 4-H). MS (EI 70 eV, 210 °C): *m*/*z* (%)=259 (0.9), 258 (5) [M^+ (^{81}Br)], 257 (0.9), 256 (5) [M^+ (^{79}Br)], 177 (31), 174 (12), 172 (12), 93 (10), 57 (100), 41 (20). Anal. Calcd for $C_{10}H_{13}BrN_2O$ (257.13): C, 46.71; H, 5.10; N, 10.89. Found: C, 46.92; H, 4.82; N, 10.90.

4.1.2. *N-(2-Bromopyrid-3-yl)benzamide (**1c**)*

Benzoylchloride (2.15 mL, 18.5 mmol) was added dropwise to a solution of **1a** (3.20 g, 18.5 mmol) in pyridine (20 mL) at −10 °C. The reaction mixture was stirred at room temperature overnight, washed with water several times and the product was extracted by ethyl acetate. After drying with anhydrous $MgSO_4$ and removal of the solvent in vacuum the residue was purified by column chromatography on silica gel using ethyl acetate/*n*-hexane (5:95%). The yield was 3.82 g (74%), mp 95 °C. ^1H NMR ($CDCl_3$, ppm): δ 7.34 (dd, ^3J=8.1, 4.6 Hz, 1H, 5-H), 7.55 (tm, $^3J\approx7$ Hz, 2H, *m*′-H), 7.63 (tm, $^3J\approx7$ Hz, 1H, *p*′-H), 7.94 (dm, $^3J\approx7$ Hz, $^4J\approx2$ Hz, 2H, *o*′-H), 8.14 (dd, ^3J=4.6 Hz, ^4J=1.8 Hz, 1H, 6-H), 8.50 (br s, 1H, NH), 8.88 (dd, ^3J=8.1 Hz, ^4J=1.8 Hz, 1H, 4-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 123.72 (CH-4 or CH-5), 127.11 (2CH-*o*′), 128.60 (CH-5 or CH-4), 129.10 (2CH-*m*′), 132.65 (CH-*p*′), 133.40, 133.74, 133.83 (C_q-*i*′, C_q-2, C_q-3), 144.59 (CH-6), 165.56 (s, CO). IR (KBr pellet): ν_{CO}=1653 cm^{-1}. MS (EI 70 eV, 260 °C): *m*/*z* (%)=279 (0.3), 278 (3) [M^+ (^{81}Br)], 277 (0.3), 276 (3) [M^+ (^{79}Br)], 197 (40), 105 (100), 77 (58), 51 (14). Anal. Calcd for $C_{12}H_9BrN_2O$ (277.12): C, 52.01; H, 3.27; N, 10.11. Found: C, 51.88; H, 3.34; N, 9.88.

4.1.3. *N-(2-Bromopyrid-3-yl)furan-2-carboxamide (**1d**)*

2-Furoylchloride (2.00 mL, 20.3 mmol) was converted with **1a** (3.50 g, 20.2 mmol) in pyridine (20 mL) and worked up as described for **1c**. Purification on silica gel using ethyl acetate/*n*-hexane (10:90%) yielded 3.75 g (69%) **1d**, mp 108 °C. ^1H NMR ($CDCl_3$, ppm): δ 6.61 (dd, ^3J=3.5 Hz, ^4J=1.7 Hz, 1H, 4′-H), 7.30 (superimposed dd, ^3J=3.5 Hz, ^4J=0.7 Hz, 1H, 3′-H), 7.32 (superimposed dd, ^3J=8.2, 4.8 Hz, 1H, 5-H), 7.60 (dd, ^3J=1.7 Hz, ^4J=0.7 Hz, 1H, 5′-H), 8.13 (dd, ^3J=4.7 Hz, ^4J=1.8 Hz, 1H, 6-H), 8.82 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 1H, 4-H), 8.73 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 112.89 (CH-4′), 116.34 (CH-3′), 123.65, 128.45 (CH-5, CH-4), 133.18, 133.41 (C_q-2, C_q-3), 144.59, 145.10 (CH-6, CH-5′), 147.07 (C_q-2′), 156.17 (s, CO). IR (KBr pellet): ν_{CO}=1680 cm^{-1}. MS (EI 70 eV, 270 °C): *m*/*z* (%)=268 (5) [M^+ (^{81}Br)], 266 (5) [M^+ (^{79}Br)], 187 (100), 95 (97). Anal. Calcd for $C_{10}H_7BrN_2O_2$ (267.08): C, 44.97; H, 2.64; N, 10.49. Found: C, 45.43; H, 2.83; N, 10.30.

4.1.4. *N-(2-Bromopyrid-3-yl)thiophene-2-carboxamide (**1e**)*

Thiophene-2-carbonyl chloride (1.86 mL, 17.4 mmol) was converted with **1a** (3.00 g, 17.34 mmol) in pyridine (18 mL) and worked up as described for **1c**. Purification on silica gel using ethyl acetate/*n*-hexane (10:90%) gave 3.35 g (68%) of **1e**, mp 126 °C. ^1H NMR ($CDCl_3$, ppm): δ 7.19 (dd, ^3J=5.0, 3.8 Hz, 1H, 4′-H), 7.32 (dd, ^3J=8.2, 4.6 Hz, 1H, 5-H), 7.63 (dd, ^3J=5.0 Hz, ^4J=1.1 Hz, 1H, 3′-H), 7.71 (dd, ^3J=3.8 Hz, ^4J=1.1 Hz, 1H, 5′-H), 8.13 (dd, ^3J=4.6 Hz, ^4J=1.8 Hz, 1H, 6-H), 8.35 (br s, 1H, NH), 8.79 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 1H, 4-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 123.73, 128.14, 128.50, 129.09, 131.96 (CH-5, CH-4, CH-4′, CH-5′, CH-3′), 133.14, 133.49 (C_q-2, C_q-3), 138.32 (C_q-2′), 144.57 (CH-6), 159.88 (s, CO). IR (KBr pellet): ν_{CO}=1671 cm^{-1}. $C_{10}H_7BrN_2OS$ (283.15), HRMS (ESI) calcd for $[M+1]^+$: 282.95352, found: 282.95368.

4.1.5. *N-(2-Bromopyrid-3-yl)-1-naphthalene-carboxamide (**1f**)*

1-Naphthoylchloride (3.33 mL, 22.1 mmol) was converted with **1a** (3.82 g, 22.1 mmol) in pyridine (23 mL) and worked up as described for **1c**. Purification on silica gel using ethyl acetate/*n*-hexane (10:90%) gave 4.50 g (62%) **1f**, mp 142 °C. ^1H NMR ($CDCl_3$, ppm): δ 7.39 (dd, ^3J=8.1, 4.6 Hz, 1H, 5-H), 7.53–7.67 (m, 3H, naph-H), 7.85 (dd, ^3J=7.1 Hz, ^4J=1.2 Hz, 1H, naph-H), 7.94 (dd, ^3J=7.5 Hz, ^4J=2 Hz, 1H, naph-H), 8.04 (br d, ^3J=8.3 Hz, 1H, naph-H), 8.18 (dd, ^3J=4.6 Hz, ^4J=1.8 Hz, 1H, 6-H), 8.30 (br s, 1H, NH), 8.46 (dm, $^3J\approx7$ Hz, ^4J= 1.3 Hz, 1H, naph-H), 8.97 (dd, ^3J=8.2 Hz, ^4J=1.7 Hz, 1H, 4-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 123.68, 124.77, 125.08, 125.59, 126.84, 127.72, 128.58, 128.89 (8CH), 130.06 (C_q-1′), 132.03 (CH-4′), 133.18, 133.42, 133.86, 133.89 (C_q-8a′, C_q-4a′, C_q-2, C_q-3), 144.82 (CH-6), 167.60 (CO). IR (KBr pellet): ν_{CO}=1660 (s), 1675 (m) cm^{-1}. $C_{16}H_{11}BrN_2O$ (327.18), HRMS (ESI) calcd for $[M+1]^+$: 327.01275, found: 327.01276.

4.1.6. *3-Amino-2-pyridine phosphonic acid diethylester (**2a**)*

Triethyl phosphite (4.8 mL, 27.7 mmol) was added dropwise to a mixture of solid **1a** (4.0 g, 23.1 mmol) and palladium acetate (0.52 g, 2.3 mmol, 10 mol %) heated at 160 °C in a distillation apparatus while a slow stream of nitrogen or argon removed the ethylbromide formed in the reaction. Heating was continued for 15 min at 160 °C. The resulting yellow oil was purified by distillation at 10^{-5} mbar/100 °C (bath temperature) in repeated experiments by column chromatography using silica gel and ethyl acetate/*n*-hexane (25:75%) yielding 1.4 g (26%) of yellow oil. ^1H NMR ($CDCl_3$, ppm): δ 1.34 (t, ^3J=7.1 Hz, 6H, CH_3), 4.14, 4.21 (m, $^2J_{AB}$=10.1 Hz, ^3J=7.1 Hz, $^3J_{PH}$=7.9 Hz, 4H, OCH_2), 5.54 (br s, 2H, NH), 7.02 (dt, ^3J=8.5 Hz, $^4J_{PH}$=7.6 Hz, ^4J=1.3 Hz, 1H, 4-H), 7.15 (ddd, ^3J=8.5, 4.3 Hz, $^5J_{PH}$=2.1 Hz, 1H, 5-H), 8.09 (dd, ^3J=4.3 Hz, ^4J=1.2 Hz, 1H, 6-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 16.01 (d, ^3J=6.4 Hz, CH_3), 62.56 (d, ^2J=5.7 Hz, OCH_2), 123.23 (d, ^3J=11.0 Hz, CH-4), 126.81 (d, ^4J=3.5 Hz, CH-5), 129.94 (d, ^1J=225.9 Hz, C_q-2), 139.10 (d, ^3J=21.5 Hz, CH-6), 148.95 (d, ^2J=25.8 Hz, C_q-3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 14.44. MS (EI 70 eV, 130 °C): *m*/*z* (%)=231 (9), 230 (62) [M^+], 201 (28), 186 (48), 127 (62), 99 (100). Anal. Calcd for $C_9H_{15}N_2O_3P$ (230.20): C, 46.96; H, 6.57. Found: C, 46.75; H, 7.02.

4.1.7. *3-Pivaloylamido-pyridine-2-phosphonic acid diethylester (**2b**)*

Triethyl phosphite (4.3 mL, 24.8 mmol), **1b** (5.4 g, 21.0 mmol) and palladium acetate (0.47 g, 2.1 mmol) were heated for 15 min at 160 °C in a slow stream of argon (see **2a**), and the resulting yellow oil was purified by distillation at 10^{-6} mbar/110 °C (bath temperature) and subsequently by column chromatography using silica gel and ethyl acetate/*n*-hexane (10:90%), yield 2.5 g (38%). ^1H NMR ($CDCl_3$, ppm): δ 1.35 (s, 9H, CMe_3), 1.35 (t, ^3J=7.2 Hz, 6H, CH_3), 4.18, 4.26 (m, $^2J_{AB}$=10.0 Hz, ^3J=7.1 Hz, $^3J_{PH}$=8.0 Hz, 4H, OCH_2), 7.41 (ddd, ^3J=8.8, 4.5 Hz, $^4J_{PH}$=2.0 Hz, 1H, 5-H), 8.44 (br d, ^3J=4.5 Hz, 1H, 6-H), 9.04 (td, ^3J=8.7 Hz, $^4J_{PH}$=7.6 Hz, ^4J=1.4 Hz, 1H, 4-H), 11.01 (br s, 1H, NH).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 16.10 (d, ^3J=6.1 Hz, CH_3), 27.28 (s, C*Me*$_3$), 40.24 (s, *C*Me$_3$), 63.55 (d, ^2J=5.9 Hz, OCH_2), 126.73 (d, ^4J=3.9 Hz, CH-5), 127.55 (d, ^3J=9.5 Hz, CH-4), 136.08 (d, ^1J=220.1 Hz, C_q-2), 141.68 (d, ^2J=24.1 Hz, C_q-3), 144.15 (d, ^3J=21.3 Hz, CH-6), 178.51 (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 12.05. Anal. Calcd for $C_{14}H_{23}N_2O_4P$ (314.32): C, 53.50; H, 7.38; N, 8.91. Found: C, 53.73; H, 6.90; N, 8.83. MS (EI 70 eV, 25 °C): *m*/*z* (%)=315 (0.2), 314 (4) [M^+], 258 (11), 257 (100), 229 (22), 201 (39), 57 (10).

4.1.8. 3-Benzoylamido-2-pyridine phosphonic acid diethylester (**2c**)

Triethyl phosphite (4.1 mL, 23.6 mmol), **1c** (5.5 g, 19.9 mmol) and palladium acetate (0.45 g, 2.0 mmol, 10 mol %) were heated for 15 min in a slow stream of argon (see **2a**). The resulting brown oil was purified by column chromatography using silica gel and ethyl acetate/*n*-hexane (15:85%) to yield 1.9 g (29%) of white crystalline solid, mp 65 °C. Single crystals were grown by slow evaporation of an ethereal solution, for crystal data see Table 2. ^1H NMR ($CDCl_3$, ppm): δ 1.36 (td, ^3J=7.1 Hz, $^4J_{PH}$=0.5 Hz, 6H, CH_3), 4.20, 4.29 (m, $^2J_{AB}$=10.0 Hz, ^3J=7.1 Hz, $^3J_{PH}$=7.8 Hz, 4H, OCH_2), 7.48 (ddd, ^3J=8.7, 4.5 Hz, $^5J_{PH}$=1.9 Hz, 1H, 5-H), 7.50–7.60 (m, 3H, *m*′-H, *p*′-H), 8.13 (dm, $^3J\approx$8 Hz, $^4J\approx$2 Hz, 2H, *o*′-H), 8.50 (dm, ^3J=4.4 Hz, ^4J=1.4 Hz, $^4J_{PH}\approx$0.8 Hz, 1H, 6-H), 9.26 (td, ^3J=8.7 Hz, $^4J_{PH}$=7.5 Hz, ^4J=1.4 Hz, 1H, 4-H), 11.92 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 16.07 (d, ^3J=6.4 Hz, CH_3), 63.72 (d, ^2J=6.0 Hz, OCH_2), 126.91 (d, ^4J=3.7 Hz, CH-5), 127.43 (s, 2CH-*o*′), 127.49 (d, ^2J=8.5 Hz, CH-4), 128.68 (s, 2CH-*m*′), 132.09 (s, CH-*p*′), 133.80 (s, C_q-*i*′), 136.17 (d, ^1J=219.1 Hz, C_q-2), 141.67 (d, ^2J=24.0 Hz, C_q-3), 144.43 (d, ^3J=21.2 Hz, CH-6), 165.93 (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 12.1. $C_{16}H_{19}N_2O_4P$, HRMS (ESI in MeOH+NH_4OAc) calcd for $[M+H]^+$: 335.11552, found: 335.11557.

Table 2
Crystal data and structure refinement

Identification code	**2c**	**3b**
Empirical formula	$C_{16}H_{19}N_2O_4P$	$C_{10}H_{17}N_2P$
Formula weight	334.30	196.23
Temperature	133(2) K	133(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$	$P4_1$
Unit cell dimensions	a=10.6093(18) Å α=90°	a=9.6108(11) Å α=90°
	b=12.119(2) Å β=110.531(5)°	b=9.6108(11) Å β=90°
	c=13.328(2) Å γ=90°	c=12.229(2) Å γ=90°
Volume	1604.7(5) Å^3	1129.5(3) Å^3
Z	4	4
Density (calcd)	1.384 Mg/m^3	1.154 Mg/m^3
Absorption coefficient	0.193 mm^{-1}	0.204 mm^{-1}
F(000)	704	424
Crystal size	0.35×0.20×0.10 mm^3	0.4×0.3×0.1 mm^3
Theta range for data collection	2.05–30.50°	2.12–30.51°
Index ranges	$-15\le h\le 15$, $-17\le k\le 17$, $-19\le l\le 19$	$-13\le h\le 13$, $-13\le k\le 13$, $-17\le l\le 17$
Reflections collected	22,163	15,938
Independent reflections	4887 [R(int)=0.0617]	3456 [R(int)=0.0287]
Completeness to theta=30.00°	99.9%	100.0%
Absorption correction	None	Semi-empirical from equivalents
Max. and min. transmission		0.9799 and 0.8546
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4887/0/214	3456/3/130
Goodness-of-fit on F^2	1.027	1.058
Final R indices [$I>2\sigma(I)$]	$R1$=0.0407, $wR2$=0.0963	$R1$=0.0372, $wR2$=0.0898
R indices (all data)	$R1$=0.0616, $wR2$=0.1043	$R1$=0.0452, $wR2$=0.0947
Absolute structure parameter		0.00(8)
Largest diff. peak and hole	0.390 and −0.316 e Å^{-3}	0.333 and −0.125 e Å^{-3}

4.1.9. 3-(2-Furoyl)amido-pyridine-2-phosphonic acid diethylester (**2d**)

Triethyl phosphite (3.48 mL, 20.1 mmol), **1d** (4.5 g, 16.8 mmol) and palladium acetate (0.38 g, 1.7 mmol, 10 mol %) were heated for 15 min at 160 °C in a slow stream of argon (see **2a**), and the resulting brown oil was purified by column chromatography using silica gel and ethyl acetate/*n*-hexane (20:80%) yielding 1.4 g (26%) of pale yellow solid, mp 48 °C. ^1H NMR ($CDCl_3$, ppm): δ 1.36 (td, ^3J=7.1 Hz, $^4J_{PH}$=0.5 Hz, 6H, CH_3), 4.20, 4.28 (m, $^2J_{AB}$=10.1 Hz, ^3J=7.1 Hz, $^3J_{PH}$=7.7 Hz, 4H, OCH_2), 6.55 (dd, ^3J=3.6 Hz, ^4J=1.7 Hz, 1H, 4′-H), 7.30 (dd, ^3J=3.6 Hz, ^4J=0.7 Hz, 1H, 3′-H), 7.46 (ddd, ^3J=8.8, 4.5 Hz, $^4J_{PH}$=2.0 Hz, 1H, 5-H), 7.63 (dd, ^3J=1.7 Hz, ^4J=0.7 Hz, 1H, 5′-H), 8.49 (dm, ^3J=4.5 Hz, ^4J=1.4 Hz, $^4J_{PH}\approx$0.7 Hz, 1H, 6-H), 9.16 (td, ^3J=8.8 Hz, $^4J_{PH}$=7.6 Hz, ^4J=1.4 Hz, 1H, 4-H), 11.77 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 16.23 (d, ^3J=6.2 Hz, CH_3), 63.82 (d, ^2J=5.5 Hz, OCH_2), 112.22 (CH-4′), 115.76 (CH-3′), 127.02 (d, ^4J=3.8 Hz, CH-5), 127.69 (d, ^2J=10.1 Hz, CH-4), 136.45 (d, ^1J=226 Hz, C_q-2), 141.11 (d, ^2J ca. 24 Hz, C_q-3), 144.70 (d, ^3J=21.2 Hz, CH-6), 145.56 (CH-5′), 147.63 (C_q-2′), 157.21 (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 12.0. IR (KBr pellet): ν=1684 (CO), 1308 (PO), 1028 (vs) cm^{-1}. Anal. Calcd for $C_{14}H_{17}N_2O_5P$ (324.27): C, 51.86; H, 5.28; N, 8.64. Found: C, 49.46 (incomplete combustion); H, 5.05; N, 8.47.

4.1.10. 3-(2-Thenoyl)amido-pyridine-2-phosphonic acid diethylester (**2e**)

Triethyl phosphite (3.6 mL, 20.8 mmol), **1e** (5.0 g, 17.7 mmol) and palladium acetate (0.39 g, 1.74 mmol, 10 mol %) were heated for about 15 min at 160 °C in a slow stream of argon (see **2a**), and the resulting yellow oil was purified by column chromatography using silica gel and ethyl acetate/*n*-hexane (20:80%) yielding 2.0 g (33%) of white solid, mp 64 °C. ^1H NMR ($CDCl_3$, ppm): δ 1.36 (td, ^3J=7.1 Hz, $^4J_{PH}$=0.5 Hz, 6H, CH_3), 4.20, 4.28 (m, $^2J_{AB}$=10.1 Hz, ^3J=7.1 Hz, $^3J_{PH}$=7.7 Hz, 4H, OCH_2), 7.14 (dd, ^3J=5.0, 3.8 Hz, 1H, 4′-H), 7.46 (ddd, ^3J=8.8, 4.5 Hz, $^5J_{PH}$=2.0 Hz, 1H, 5-H), 7.58 (dd, ^3J=5.1 Hz, ^4J=1.1 Hz, 1H, 3′-H), 7.91 (dd, ^3J=3.8 Hz, ^4J=1.1 Hz, 1H, 5′-H), 8.48 (ddd, ^3J=4.5 Hz, ^4J=1.4 Hz, $^4J_{PH}$=0.7 Hz, 1H, 6-H), 9.14 (td, ^3J=8.7 Hz, $^4J_{PH}$=7.5 Hz, ^4J=1.4 Hz, 1H, 4-H), 11.86 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 16.20 (d, ^3J=6.0 Hz, CH_3), 63.87 (d, ^2J=6.4 Hz, OCH_2), 127.09 (d, ^4J=3.2 Hz, CH-5), 127.31 (d, ^3J=9.4 Hz, CH-4), 128.16, 129.27, 131.75 (CH-4′, CH-5′, CH-3′), 135.94 (d, ^1J=218.8 Hz, C_q-2), 139.68 (C_q-2′), 141.60 (d, ^2J=24.1 Hz, C_q-3), 144.53 (d, ^3J=21.1 Hz, CH-6), 160.86 (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 12.28. MS (EI 70 eV, 280 °C): *m*/*z* (%)=341 (8), 340 (41) [M^+], 325 (3), 232 (18), 231 (13), 204 (19), 203 (100), 143 (12), 110 (82). Anal. Calcd for $C_{14}H_{17}N_2O_4PS$ (340.33): C, 49.41; H, 5.03; N, 8.23. Found: C, 49.46; H, 5.05; N, 8.17.

4.1.11. 3-(1-Naphthoyl)amido-pyridine-2-phosphonic acid diethylester (**2f**)

Triethyl phosphite (0.32 mL, 1.84 mmol), **1f** (0.5 g, 1.53 mmol) and palladium acetate (0.15 g, 0.67 mmol, 44 mol %) were heated for 15 min at 160 °C in a slow stream of argon (see **2a**). The resulting brown oil was purified by column chromatography using silica gel and ethyl acetate/*n*-hexane (20:80%) yielding 0.13 g (22%) of white crystalline solid, mp 81 °C. ^1H NMR ($CDCl_3$, ppm): δ 1.34 (td, ^3J=7.1 Hz, $^4J_{PH}$=0.6 Hz, 6H, CH_3), 4.18, 4.26 (m, $^2J_{AB}$=10.0 Hz, ^3J=7.1 Hz, $^3J_{PH}$=7.8 Hz, 4H, OCH_2), 7.57 (m, 4H, 5-H, 3naph-H), 7.90 (dd, ^3J=7.1 Hz, ^4J=1.9 Hz, 1H, naph-H), 7.95 (dd, ^3J=7.2 Hz, ^4J=1.1 Hz, 1H, naph-H), 7.99 (br d, ^3J=8.3 Hz, 1H, naph-H), 8.55 (partly superimposed dm, $^3J\approx$4.5 Hz, ^4J=1.4 Hz, $^4J_{PH}\approx$1 Hz, 1H, 6-H), 8.57 (partly superimposed dd, $^3J\approx$8 Hz, ^4J=1.3 Hz, 1H, naph-H),

9.39 (td, ^3J=8.7 Hz, $^4J_{PH}$=7.6 Hz, ^4J=1.4 Hz, 1H, 4-H), 11.58 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 16.20 (d, ^3J=6.0 Hz, CH_3), 63.95 (d, ^2J=6.0 Hz, OCH_2), 124.92, 125.50. 125.92, 126.48 (CH-3′, CH-8′, CH-6′, CH7′), 127.22 (d, ^4J=3.7 Hz, CH-5), 127.31 (CH-5′), 128.16 (d, ^3J=9.3 Hz, CH-4), 128.45 (CH-2′), 130.51 (C_q-1′), 131.86 (CH-4′), 133.13 (C_q-8a′), 133.99 (C_q-4a′), 136.10 (d, ^1J=202 Hz, C_q-2), 141.89 (d, ^2J=22.7 Hz, C_q-3), 144.50 (d, ^3J=20.8 Hz, CH-6), 168.38 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 11.3. $C_{20}H_{21}N_2O_4P$ (384.37), MS (EI 70 eV, 185 °C): *m*/*z* (%)=384 (7) [M^+], 248 (15), 247 (71), 156 (11), 155 (100), 127 (60). HRMS (ESI in MeOH+NH_4OAc) calcd for $[M+H]^+$: 385.13117, found: 385.13125.

4.1.12. 3-Amino-2-phosphinopyridine (**3a**)

A solution of **2a** (0.90 g, 3.91 mmol) in diethyl ether (20 mL) was added dropwise with stirring at 0 °C to $LiAlH_4$ pellets (0.45 g, 11.9 mmol) in diethyl ether (10 mL). After 2 days at room temperature degassed water was added dropwise until the evolution of hydrogen ceased. Solids were filtered off and washed with ether, the filtrate was dried with Na_2SO_4, and the solvent was removed in vacuum (ca. 1 Torr) affording 0.25 g (50%) colourless oily liquid **3a**. ^1H NMR ($CDCl_3$, ppm): δ 2.69 (br s, 2H, NH_2), 3.45 (d, $^1J_{PH}$=200.2 Hz, 2H, PH_2), 5.86 (ddd, ^3J=8.1 Hz, $^4J_{PH}$=3.3 Hz, ^4J=1.4 Hz, 1H, 4-H), 6.25 (dd, ^3J=8.1 Hz, ^3J=4.6 Hz, 1H, 5-H), 7.77 (dd, ^3J=4.6 Hz, ^4J=1.3 Hz, 1H, 6-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 121.07 (s, CH-4), 124.12 (s, CH-5), 140.84 (d, ^3J=11.7 Hz, CH-6), 145.82 (d, ^2J=10.8 Hz, C_q-3), 139.87 (d, ^1J=9.2 Hz, C_q-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ −144.29. MS (EI, 25 °C): *m*/*z* (%)=127 (4), 126 (100) [M^+], 125 (9), 124 (6), 94 (19), 79 (12). HRMS (EI) calcd for $C_5H_7N_2P$: 126.03469, found: 126.0347. (The ^{31}P NMR spectrum indicated small impurities at δ −123.2, −63.3 ppm.)

4.1.13. 3-Neopentylamino-2-phosphino-pyridine (**3b**)

Reduction of **2b** (0.80 g, 2.55 mmol) in diethyl ether (10 mL) by $LiAlH_4$ pellets (0.29 g, 7.64 mmol) in diethyl ether (10 mL) and work-up as described for **3a** furnished 0.21 g pale yellow viscous oil. NMR control showed strongly impure **3b**, content slightly less than 50 mol%. Single crystals of pure **3b** were grown from diethyl ether by slow concentration (diffusion of ether through a rubber septum). For crystal data of **3b** see Table 2. ^1H NMR ($CDCl_3$, ppm): δ 1.04 (s, 9H, CMe_3), 2.93 (s, ^3J=5.7 Hz, 2H, NCH_2), 3.86 (d, $^1J_{PH}$=200.6 Hz, 2H, PH_2), 3.98 (br s, NH), 6.86 (dd, ^3J=8.5 Hz, $^4J_{PH}$=2.8 Hz, ^4J=1.3 Hz, 1H, 4-H), 7.09 (dd, ^3J=8.4, 4.6 Hz, 1H, 5-H), 7.97 (dd, ^3J=4.6 Hz, ^4J=1.0 Hz, 1H, 6-H). $^{13}C\{^1H\}$ (DEPT) NMR ($CDCl_3$, ppm): δ 27.64 (s, CMe_3), 31.91 (s, CMe_3), 55.30 (s, 7-C, NCH_2), 115.61 (s, CH-4), 124.31 (s, CH-5), 138.46 (d, ^3J=13.0 Hz, CH-6), 139.87 (d, ^1J=9.2 Hz, C_q-1, low intensity, uncertain), 147.99 (d, ^2J=9.4 Hz, C_q-3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ −146.2. $C_{10}H_{17}N_2P$ (196.11), MS (EI 70 eV, 25 °C): *m*/*z* (%)=197 (2), 196 (35) [M^+], 195 (8), 167 (26), 139 (100) [M^+−57], 106 (37), 57 (22). HRMS (ESI in MeOH+NH_4OAc) calcd for $[M+H]^+$ $C_{10}H_{17}N_2P$: 197.12021, found: 197.12033. ^{31}P NMR impurity signals: δ −62.7 (medium), −25.4 (small).

4.1.14. Detection of 3-benzylamino-2-phosphino-pyridine (**3c**) in a mixture of products

Reduction of **2c** (1.42 g, 2.25 mmol) in diethyl ether (30 mL) by $LiAlH_4$ pellets (0.48 g, 12.74 mmol) in diethyl ether (20 mL) and work-up as described for **3a** afforded 0.57 g of pale yellow oil. NMR control of the crude product showed intense phosphorus signals at δ −144.7, −62.9 (br), −60.7 (br), −55.5, −21.1, −4.8 (br) and proton signals among others for NCH_2, PH and multiplets in the NCH region. This indicates formation of a mixture containing primary 3-benzylaminopyridylphosphine **3c** (detected also by HRMS), secondary and tertiary phosphines. No attempts were made to separate the multi-component mixture. MS (EI 70 eV, 120 °C): *m*/*z* (%)=244 (2.4), 242 (1.4), 216 (7.6), 215 (7.1), 213 (8.1), 184 (34) [**3c**$^+$−PH]. HRMS (EI) calcd for **3c**, $C_{12}H_{13}N_2P$: 216.08163, found: 216.0808.

4.1.15. 3-(1-Furyl)methylamino-2-phosphino-pyridine (**3d**)

Reduction of **2d** (1.08 g, 3.33 mmol) in diethyl ether (30 mL) by $LiAlH_4$ pellets (0.38 g, 9.99 mmol) in diethyl ether (20 mL) and work-up as described for **3a** gave 0.53 g yellow oil. NMR control of the crude product showed the most intense phosphorus signal at δ −144.26, minor signals at δ −71.0, −62.6 (br), −49.6, −22.5 and trace signals at −86.7, −15.0. The proton signals of the main component and HRMS confirm its identity as **3d**. ^1H NMR ($CDCl_3$, ppm): δ 3.89 (d, ^1J=202.2 Hz, PH_2), 4.34 (s, NCH_2), 4.38 (br s, NH), 6.25 (dd, ^3J=3.2 Hz, ^4J=0.6 Hz, 3′-H), 6.33 (dd, ^3J=3.2 Hz, ^4J=1.8 Hz, 4′-H), 6.96 (ddd, ^3J=8.3 Hz, $^4J_{PH}$=2.9 Hz, ^4J=1.4 Hz, 4-H), 7.10 (ddd, ^3J=8.3, 4.7 Hz, $^4J_{PH}$=0.6 Hz, 5-H), 7.99 (dd, ^3J=4.5 Hz, ^4J=1.4 Hz, 6-H); 5′-H uncertain. MS (EI 70 eV, 100 °C): *m*/*z* (%)=206 (5), 203 (11), 202 (26), 174 (20), 173 (9) [M^+-PH_2], 95 (17), 81 (100). HRMS (EI) calcd for **3d**, $C_{10}H_{11}N_2OP$: 206.0609, found: 206.0606.

4.1.16. 3-(2-Thienyl)methylamino-2-phosphino-pyridine (**3e**)

Reduction of **2e** (1.20 g, 3.53 mmol) in diethyl ether (30 mL) by $LiAlH_4$ pellets (0.40 g, 10.54 mmol) in diethyl ether (20 mL) and work-up as described for **3a** furnished 0.50 g of pale yellow viscous liquid containing **3e** as main component. ^1H NMR ($CDCl_3$, ppm): δ 3.84 (d, $^1J_{PH}$=202.3 Hz, 2H, PH_2), 4.47 (br s, NH), 4.51 (d, ^3J=5.4 Hz, 2H, NCH_2), 6.83 (superimposed m, $^3J\approx$8 Hz, 4-H), 6.92 (dd, ^3J=5, 4 Hz, 4′-H), 7.03 (dd, ^3J=8.4, 4.4 Hz, 5-H), 7.17 (dd, ^3J=4 Hz, ^4J=1 Hz, 3′-H), 7.98 (dd, ^3J=4.6 Hz, ^4J=1.2 Hz, 1H, 6-H), 8.02 (dd, ^3J=5 Hz, ^4J=1 Hz, 5′-H). ^{31}P NMR ($CDCl_3$, ppm): δ −146.22. MS (EI 70 eV, 150 °C): *m*/*z* (%)=280 (7) [$C_{12}H_{13}N_2O_2PS^+$], 248 (9), 222 (5) [M^+ **3e**], 221 (7), 220 (5) [$C_{10}H_9N_2PS^+$], 219 (22), 97 (100). Further evidence for **3e** is provided by formation of **5e** from the crude product and DMFA. (Hints as to the nature of the side products: $C_{12}H_{13}N_2O_2PS$ is consistent with 2-thienyl-3-ethoxy-3-oxo-2,3-dihydro-1,3-azaphospholo[4,5-*b*]pyridine that might have formed after amide reduction by intramolecular attack of NCHLi at the $PO(OEt)_2$ group; $C_{10}H_9N_2PS$ might be its reduction product, *P*-secondary 2-thienyl-2,3-dihydro-1,3-azaphospholo[4,5-*b*]pyridine, occurring as a diastereoisomeric mixture.)

4.1.17. 1H-1,3-Azaphospholo[4,5-b]pyridine (**5a**)

A mixture of **3a** (0.19 g, 1.51 mmol) and dimethylformamide dimethyl acetal (DMFA) (0.22 mL, 1.66 mmol) was heated for 5 days at 50 °C. Volatiles were removed in vacuum and the product was separated by distillation at 10^{-5} mbar/45–50 °C bath temperature using a microdistillation device to yield 0.13 g (63%) of highly air-sensitive white solid. ^1H NMR ($CDCl_3$, ppm): δ 7.28 (solvent superimposed ddd, ^3J=4.5 Hz, $^5J_{PH}$=1.5 Hz, 1H, 6-H), 7.93 (d, ^3J=8.6 Hz, 1H, 7-H), 8.66 (dd, ^3J=4.5 Hz, $^4J_{PH}$=1.4 Hz, 1H, 5-H), 8.83 (dd, $^3J_{PH}$=36.8 Hz, $^3J_{HCNH}$=4.7 Hz, 1H, 2-H), 9.57 (br s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 117.45, 118.58 (2s, CH-6, CH-7), 143.1 (d, low intensity, CH-5), 163.53 (d, ^1J=55.1 Hz, CH-2), C_q-7a and C_q-3a in noise. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 81.68. MS (EI 70 eV, 100 °C): *m*/*z* (%)=137 (9), 136 (100) [M^+], 135 (4), 109 (46), 108 (11), 82 (48), 81 (20), 68 (16). HRMS (ESI in MeOH/H_2O/HCOOH) calcd for $C_6H_5N_2P$ 136.0911: $[M+H]^+$ 137.02631, found: 137.02636.

4.1.18. 1-Neopentyl-1,3-azaphospholo[4,5-b]pyridine (**5b**)

A mixture of crude **3b** (0.20 g, content of **3b** ca. 0.5 mmol) and DMFA (0.15 mL, 1.1 mmol) was heated for 7 days at 50 °C and separated at 10^{-5} Torr using a microdistillation device. Compound **5b** (0.10 g) was collected at 79–81 °C bath temperature as colourless oil, contaminated by small amounts of phosphorus compounds with δ ^{31}P −51.1, −25.3, 42.6, 43.4, content of **5b** 63 mol% (by ^1H NMR integration of aryl protons), yield of **5b** relative to **3b** was about 60%. ^1H NMR ($CDCl_3$, ppm): δ 1.02 (s, 9H, CMe_3), 4.10 (s, 2H, NCH_2), 7.26 (ddd, ^3J=8.7, 4.4 Hz, $^5J_{PH}$=1.5 Hz, 1H, 6-H), 7.88 (br d, ^3J=8.7 Hz, 1H, 7-H), 8.61 (d, $^2J_{PH}$=37.2 Hz, 1H, 2-H), 8.63 (d, ^3J=4.4 Hz, $^4J_{PH}$=1.4 Hz, 1H, 5-H). $^{13}C\{^1H\}$ (DEPT) NMR ($CDCl_3$, ppm):

δ 28.26 (s, CMe_3), 61.39 (d, ^3J=2.7 Hz, NCH_2), 67.99 (s, C_qMe_3), 118.14 (d, ^4J=1.8 Hz, CH-6), 120.24 (s, CH-7), 136.58 (low intensity d, ^1J=71 Hz, C_q-3a, uncertain), 144.26 (d, ^3J=15.1 Hz, CH-5), 165.08 (d, ^1J=53.8 Hz, CH-2), 165.78 (d, J=26.5 Hz, C_q-7a or 3a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 71.79. MS (EI 70 eV, 120 °C): m/z (%)=207 (10), 206 (92) [M^+], 165 (30), 148 (100) [$M^+-C_4H_8$], 57 (30). HRMS (EI): calcd for $C_{11}H_{15}N_2P$: 206.0973, found: 206.0974.

*4.1.19. 1-(2′-Furyl)methyl-1,3-azaphospholo[4,5-b]-pyridine (**5d**)*

A mixture of crude **3d** (0.45 g) and DMFA (0.35 mL, 2.63 mmol) was heated for 7 days at 50 °C and separated using a micro-distillation device. At 10^{-5} Torr/79–84 °C bath temperature 0.31 g of pale yellow oil was collected, consisting of **5d**, 3-(2′-furyl)methylamino-pyridine and 3-(2′-furoyl)amido-pyridine, molar ratio 10:25:5 (by ^1H NMR integration of selected aryl protons). Compound **5d**: ^1H NMR ($CDCl_3$, ppm): δ 5.42 (s, 2H, NCH_2), 6.35 (dd, ^3J=3.3 Hz, ^3J=1.8 Hz, 1H, 4′-H), 7.28 (superimposed m, 2H, ^3J=8.6, 4.5 Hz, ^4J=1.5 Hz, 6-H, 5′-H), 7.96 (br d, ^3J=8.6 Hz, 1H, 7-H), 8.1 (superimposed, 3′-H, uncertain), 8.66 (dd, ^3J=4.5 Hz, ^4J=1.5 Hz, 1H, 5-H), 8.69 (d, $^2J_{PH}$=36.7 Hz, 1H, 2-H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 76.56. HRMS: calcd for $C_{11}H_9N_2OP$ 216.0453: [M+H] 217.05264; found (ESI in MeOH, NH_4Oac): 217.05253. Side products: 3-(2′-furyl)methylamino-pyridine, ^1H NMR ($CDCl_3$, ppm): δ 3.49 (br s, NH), 4.34 (s, 2H, NCH_2), 6.25 (dd, ^3J=3.2 Hz, ^4J=0.6 Hz, 3′-H), 6.33 (dd, ^3J=3.2, 1.9 Hz, 4′-H), 6.95 (ddd, ^3J=8.3 Hz, ^4J=2.9, 1.4 Hz, 4-H), 7.10 (ddd, ^3J=8.3, 4.7 Hz, ^5J=0.5 Hz, 5-H), 7.37 (dd, ^3J=1.8 Hz, ^4J=0.7 Hz, 5′-H), 8.00 (dd, ^3J=4.7 Hz, ^4J=1.3 Hz, 6-H), 8.10 (br d, ^4J=2.8 Hz, 2-H). 3-(2′-Furoyl)amido-pyridine, ^1H NMR ($CDCl_3$, ppm): δ 6.59 (dd, ^3J=3.5, 1.8 Hz, 4′-H), 7.34 (superimposed br dd, ^3J=8.6, 4.9 Hz, 5-H), 7.38 (superimposed dd, $^3J\approx$2.7 Hz, $^4J\approx$0.7 Hz, 3′-H), 7.55 (dd, ^3J=1.7 Hz, ^4J=0.8 Hz, 5′-H), 8.30 (ddd, ^3J=8.3 Hz, ^4J=2.6, 1.5 Hz, 4-H), 8.40 (dd, ^3J=4.7 Hz, ^4J=1.5 Hz, 6-H), 8.70 (br d, ^4J=2.5 Hz, 2-H).

*4.1.20. 1-(2′-Thienyl)methyl-1,3-azaphospholo[4,5-b]pyridine (**5e**)*

A mixture of crude **3e** (0.42 g) and DMFA (0.21 mL, 1.89 mmol) was heated for 7 days at 50 °C, and 0.19 g of a pale yellow oil was separated by distillation at 10^{-5} mbar/79–84 °C bath temperature. NMR spectra indicated strongly contaminated **5e**, content 45 mol % by ^1H NMR integration of aryl protons. ^1H NMR ($CDCl_3$, ppm): δ 5.64 (s, 2H, NCH_2), 6.90–7.25 (m, 2′-H, 3′-H, 5′-H), 7.29 (solvent superimposed ddd, ^3J=8.6, 4.5 Hz, ^4J=1.4 Hz, 1H, 6-H), 7.95 (d, ^3J=8.6 Hz, 1H, 7-H), 8.66 (superimposed dd, $^3J\approx$4.0 Hz, ^4J=1.2 Hz, 1H, 5-H), 8.74 (d, $^2J_{PH}$=36.5 Hz, 1H, 2-H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 76.97. HRMS calcd for $C_{11}H_9N_2PS$ 232.25: [M+H] 233.02968, found (ESI in MeOH, NH_4OAc): 233.02980.

5. Crystal structure analysis

Data collection. Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Data were collected with monochromated Mo Kα radiation.

Structure refinement. The structures were refined anisotropically on F^2 using the program SHELXL-97 (Prof. G.M. Sheldrick, University of Göttingen, Germany).[15] *Hydrogen atom treatment*. NH free, PH free but with distance restraints, methyls as idealised rigid groups, others riding. For compound **3b**, the Flack parameter refined to 0.00(8).

For selected bond lengths and angles of **2c** and **3b** see Figures 1 and 2. The crystallographic data are listed in Table 2. Complete crystallographic data for **2c** and **3b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 687134 and CCDC 687135. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int. code) +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk].

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.06.010.

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