An Efficient Synthesis of *N*-Phosphorylated Azadienes, Primary (*E*)-Allylamines, and β-Amino-Phosphane Oxides and -Phosphonates from β-Functionalized Oxime Derivatives

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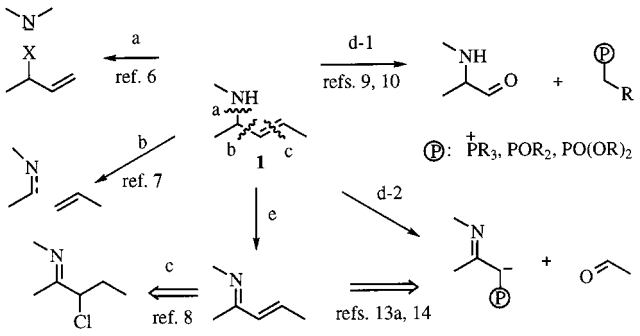
A simple and stereoselective synthesis of primary (*E*)-allylamines **1** and 1-azadienes **5**, **7** is reported. *N*-Phosphorylated azadienes **5** and **7** are obtained by addition of phosphorus chlorides **3** to unsaturated oximes **2**, while azadienes **24** are prepared by olefination reactions of functionalized enamines **20/21**. Reduction of azadienes **5**, **7**, **24** and derivatives **13/14** and **20/21** with hydrides, followed by deprotection of the resulting amines leads to the formation of primary allylamines **1** and β-aminophosphane oxides **17**, phosphonates **18**, and phosphonic acid derivatives **19**.

Allylamines represent an important class of compounds, not only because of their occurrence in natural products[1a] and in vinylogous polypeptides[1b], but also as they are key intermediates in both organic synthesis[2] and in medicinal chemistry, given their activities as chemotherapeutic agents[3a], enzyme inhibitors[3b], and as antifungals[3c][3d]. Moreover, primary allylamines are rapidly gaining interest as target compounds of synthetic organic methodologies due to their usefulness in the preparation of plasma polymers[4a], and of acyclic[4b] and cyclic compounds[4c][4d].

While there are many approaches available for allylamine preparation[1a], these are often multi-step or are specific for individual examples, and lead to mixtures of regio- and stereoisomers. Despite the growing interest in these compounds, the development of a methodology directed towards the synthesis of primary allylic amines is still an active area of research in organic chemistry[5][6][7][8][9][10]. In recent years, considerable efforts have been focussed on their preparation by means of amination reagents[6] (Scheme 1, route a), by coupling reactions with carbon−carbon bond formation[7] (Scheme 1, route b) of 1,2-dehydrogenation of α-haloimines and subsequent hydride reduction[8] (Scheme 1, route c), and by olefination reactions using phosphorus ylides[9], phosphonates[10a][10b][10c], and phosphane oxides[10d] with carbonyl compounds (Scheme 1, route d-1). However, all attempts to extend these routes to the α-substituted derivatives have failed[10d]. Similarly, although the reduction of α,β-unsaturated oximes may provide attractive starting materials for the synthesis of primary allylic amines, in most cases, reduction of these compounds unfortunately leads to many compounds, among which the allylic amine is obtained in poor to moderate yields besides aziridines[1a] (Scheme 1, route e).

Scheme 1



In connection with our interest in the preparation and use of phosphorus-nitrogenated compounds[11] as building blocks in synthetic strategies, we have used β-phosphorylated enamines as starting materials in the synthesis of heterocycles such as pyrazoles[12a], aminoquinolines[12b], pyridines[12c], pyridones[12d], and diaza-phosphanines[12e], as well as of acyclic derivatives such as oximes[13a], hydrazones[13b], functionalized enamines[13c], and aminodienes[13d]. In this context, it is noteworthy that we have recently used phosphorus compounds derived from imines and oximes as homologation reagents[14] for the conversion of carbonyl derivatives into secondary allylamines[14], as well as into α,β-unsaturated oximes[13a], with the introduction of two additional carbon atoms in the resulting chain. Here, we aim to extend this methodology to the preparation of a wide range of primary (*E*)-allylamines from functionalized *N*-phosphorylated amines, given that these compounds represent protected analogues of primary amines that can be unmasked by mild acidic cleavage, and that they are easily obtained by reduction of functionalized *N*-di-

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phenylphosphanylimines[15]. In this context, it is noteworthy that *N*-diphenylphosphanylaldimines are easily obtained from oximes[15] and have been used for the synthesis of aziridines[16a], oxazirines[16b], and amines[15][16c]. Retrosynthetically, we envisaged obtaining allylamines **1** (Scheme 1, route d) through simple addition of chlorodiphenylphosphane or diethyl chlorophosphite to unsaturated oximes **2**, followed by selective reduction of the carbon−nitrogen double bond of α,β-unsaturated imines **5** and **7**, while unsaturated oximes **2** (R^2 = H, $SiMe_3$) may be easily prepared from allenes derived from phosphane oxides **9** and phosphonates **10**[13a].

Results and Discussion

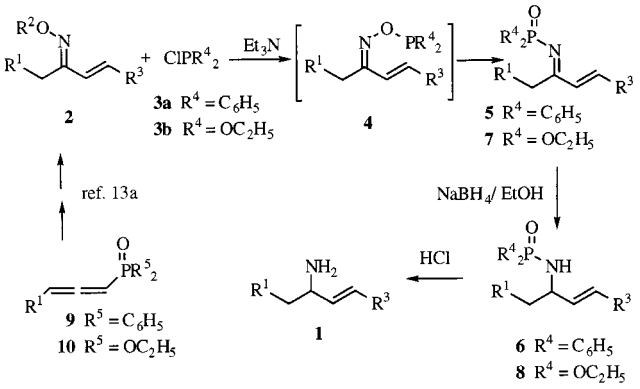
Synthesis of *N*-Phosphorylated 1-Azadienes 5, 7 and Allylamines 6, 8, and 1

The preparation of *N*-phosphorylated 1-azadienes **5** (Table 1, entries 1−3) was easily accomplished in very high yields from α,β-unsaturated oximes **2** (R^2 = H, $SiMe_3$) by reaction with chlorodiphenylphosphane **3a** (R^4 = C_6H_5), followed by free-radical rearrangement of the initially formed phosphorus(III) oxime ester **4** (Scheme 2). Compounds **5** were characterized by their spectroscopic data. The ^{31}P-NMR spectrum of **5a** showed an absorption at δ = 19.0, and further examination of the ^{1}H- and ^{13}C-NMR spectra was consistent with the azadiene structure.

The reduction of azadienes containing an aryl group in the 4-position, such as **5a**, **c**, was usually conducted with sodium tetrahydridoborate (in refluxing ethanol) and led to diphenylphosphinic amides **6** (Table 1, entries 4−6). Monitoring by TLC indicated that the reactions were often complete within 24 h. The highly electron-withdrawing diphenylphosphanyl moiety greatly augments the electrophilicity of the imine carbon atom, so that nucleophilic attack by hydride reagents is rapid. Vicinal $^3J_{HH}$ coupling constants in the range 16−17 Hz between the vinylic protons of **6** are consistent with the (*E*) configuration of the carbon−carbon double bond. Therefore, this procedure is highly selective; the configuration of the carbon−carbon double bond is retained, thereby affording exclusively the (*E*) stereoisomer. However, under these reaction conditions, the reduction of azadienes **5** bearing aliphatic substituents at the 4-position led to the formation not only of the protected allylic amines **6**, but also of the saturated amine as a side product. Consequently, in order to avoid the reduction of both the carbon−nitrogen and the carbon−carbon double bonds of compounds **5** and the formation of saturated amines, reductions of azadienes **5** were performed below −30°C. At such temperatures, the process provides allylic amines **6** in a selective fashion (Table 1, entry 5). Protected primary amines **6** can be easily unmasked by mild acidic cleavage. Treatment of the substituted amines **6** with 2 N hydrogen chloride in ethanol afforded the primary allylic amines **1** in excellent yields (Scheme 2, Table 1, entries 14, 16).

Diethyl chlorophosphite **3b** (R^4 = OC_2H_5) showed a similar reaction pattern, also leading to azadienes **7** as well as to protected **8** and primary allylamines **1**. Simple addition of **3b** to α,β-unsaturated oximes **2** led to the formation of *N*-phosphorylated 1-azadienes **7** (Scheme 2, Table 1, entries 7−9), reduction of which with sodium tetrahydridoborate at low temperature gave allylic amines **8** in a selective fashion (Table 1, entries 10−12). These primary amines **8** are easily cleaved in acidic media to afford the primary allylic amines **1** (Table 1, entries 13, 17). From a preparative point of view, it is noteworthy that the synthesis of amines **1** does not require the isolation and purification of azadienes **5** and **7**. The products can be obtained in a "one-pot" reaction from oximes **2**, when, after evaporation of the solvent, compounds **5** and **7** are directly reduced with hydrides and then the amines **6** and **8** are deprotected in acidic media (Table 1, entries 14, 16, 18, 19). These results prompted us to extend this reaction and to explore whether β-functionalized oximes **11** derived from phosphane oxides (R^5 = C_6H_5), from phosphonates **12** (R^5 = OC_2H_5), or from their precursor allenes **9** or **10** could be useful synthetic intermediates, providing an easy and efficient access to β-aminophosphane oxides and -phosphonates.

Scheme 2



Synthesis of β-Aminophosphane Oxides 15/17, Phosphonates 16/18, and Phosphonic Acid Derivatives 19

β-Aminophosphorus derivatives represent an important class of compounds, not only because they can form part of a peptide structure[17a], but also because of their biological activities as enzyme inhibitors[17b][17c][17d], as modulators of quisqualic acid/phosphoinositide[17e], as well as in the synthesis of phosphorus analogues of pantotheine[17f]. However, despite the growing interest in these compounds, there is only a relatively small number of procedures available for their synthesis[17f][18].

β-Functionalized oximes **11** and **12**, derived from phosphane oxides and phosphonates, respectively, and easily prepared by simple addition of hydroxylamines to allenes derived from phosphane oxide **9** (R^5 = C_6H_5) and phosphonates **10** (R^5 = OC_2H_5), have recently been used for the preparation of α,β-unsaturated oximes[14a]. Similarly, these β-phosphorylated oximes **11** and **12** represent starting materials for the synthesis of *N*-phosphorylated imines or enamines derived from phosphane oxides **13/13′** and iminophosphonates **14**. The preparation of phosphane oxide deriva-

Table 1. 1-Azadienes **5**, **7** and allylamines **6**, **8**, and **1** obtained

Entry	Comp.	R^1	R^3	Yield[a]	m.p. [°C]
1	**5a**	H	4-MeC_6H_4	80	100−102
2	**5b**	H	$CH_2CH(CH_3)_2$	82	oil[f]
3	**5c**	Me	4-MeC_6H_4	92	140−143
4	**6a**	H	4-MeC_6H_4	80	137−140
5	**6b**	H	$CH_2CH(CH_3)_2$	72	oil[f]
6	**6c**	Me	4-MeC_6H_4	83	145−147
7	**7a**	H	4-MeC_6H_4	92	oil[f]
8	**7b**	H	4-$MeOC_6H_4$	85	oil[f]
9	**7c**	Me	3-C_5H_4N	85	oil[f]
10	**8a**	H	4-MeC_6H_4	89	oil[f]
11	**8b**	H	4-$MeOC_6H_4$	70	oil[f]
12	**8c**	Me	3-C_5H_4N	85	oil[f]
13	**1a**	H	4-$MeOC_6H_4$	73[c] 78[e]	oil[f]
14	**1b**	H	$CH_2CH(CH_3)_2$	82[b] 69[d]	oil[f]
15	**1c**	H	$CH_2CH_2C_6H_5$	72[e]	oil[f]
16	**1d**	Me	4-MeC_6H_4	79[b] 73[d] 74[e]	oil[f]
17	**1e**	Me	3-C_5H_4N	80[c]	oil[f]
18	**1f**	Me	$CH_2CH_2C_6H_5$	67[d]	oil[f]
19	**1g**	Me	$CH_2CH(CH_3)_2$	70[d]	oil[f]

[a] Yields refer to isolated compounds. − [b] Yield of isolated compounds from allylamines **6**. − [c] Yield of isolated compounds from allylamines **8**. − [d] Yield of isolated purified product referred to "one-pot" process from azadienes **2**. − [e] Yield of isolated compounds from allylamines **25**. − [f] Oils isolated by flash chromatography.

tives **13** was accomplished very easily and in high yields by means of simple addition (TLC control) of chlorodiphenylphosphane **3a** ($R^4 = C_6H_5$) or of diethyl chlorophosphite **3b** ($R^4 = OC_2H_5$) to β-functionalized oximes **11**, derived from phosphane oxides ($R^5 = C_6H_5$), in chloroform solution (Scheme 3, Table 2). Compounds **13** were characterized on the basis of their spectroscopic data, which indicate that they are formed as a mixture of β-imino and (*Z*)-β-enamino tautomers **13/13′** when methyl oximes (**11**, $R^1 = H$) are used (Table 2, entries 1, 2), although, for our purposes, separation of the isomers was not necessary for subsequent reactions. On the other hand, only (*Z*)-β-enamines **13′** are obtained (Table 2, entries 3−6) when substituted oximes (**11**, $R^1 = CH_3$, 4-Me-C_6H_4) are used. The ^{31}P-NMR spectrum of the aforementioned mixture of **13/13′a** showed four different absorptions at δ = 23.7/28.4 and 18.6/30.0, with the former pair of signals corresponding to the imino isomer **13a**. The integrals of these signals indicated an approximate isomer ratio 33:67. In the ^{1}H-NMR spectrum of **13a**, the methylene proton resonates at δ = 3.54 as a well-resolved doublet with a coupling constant of $^2J_{PH}$ = 14.7 Hz, while the methyl group gives rise to a singlet at δ = 1.87. The ^{13}C-NMR spectrum shows absorptions at δ = 48.0 ($^1J_{PC}$ = 56.6 Hz) and at δ = 32.7, attributable to the carbon bonded to the phosphorus atom and to the methyl group of the imino isomer, respectively. On the other hand, the enamino derivative **13′a** shows distinctly different absorptions, namely a doublet at δ = 4.59 ($^2J_{PH}$ = 21 Hz) for the vinylic proton, as well as a signal for the methyl group at δ = 2.14 in the ^{1}H spectrum, while in the ^{13}C spectrum the methine carbon atom resonates at δ = 88.9 ($^1J_{PC}$ = 106.5 Hz) and the absorption of the methyl group is shifted to higher field (δ = 24.3) relative to that of the imino tautomer. The vicinal ^{13}C-^{31}P coupling constant ($^3J_{PC}$ = 15.1 Hz) shows that the methyl group and phosphorus atom in the β-enamino compound **13′a** are mutually *trans* oriented.[13b][19] Similar behaviour has been observed in the reaction of oximes derived from phosphonates **12**, not only with chlorodiphenylphosphane **3a** ($R^4 = C_6H_5$), but also with diethyl chlorophosphite **3b** ($R^3 = OC_2H_5$), leading in this case to the exclusive formation of β-imino compounds **14** (Table 2, entries 7−11).

Table 2. Phosphane oxides **13/13′** and phosphonates **14** obtained

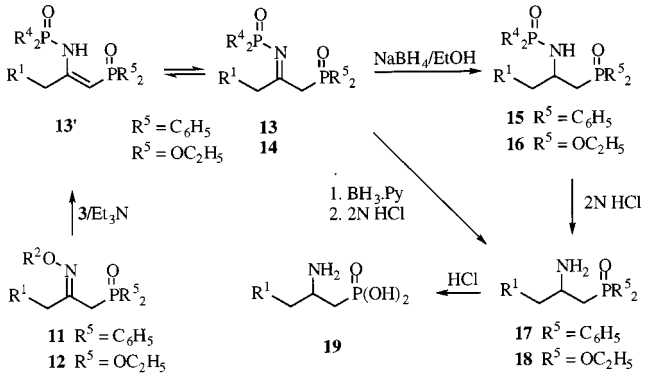
Entry	Compound	R^1	R^4	Yield (%)[a]	**13/13′** ratio[b]	m.p. [°C]
1	**13/13′a**	H	C_6H_5	75	33:67	56−58
2	**13/13′b**	H	OC_2H_5	80	20:80	oil[c]
3	**13/13′c**	Me	C_6H_5	80	0:100	66−68
4	**13/13′d**	Me	OC_2H_5	85	0:100	oil[c]
5	**13/13′e**	4-MeC_6H_4	C_6H_5	75	0:100	64−66
6	**13/13′f**	4-MeC_6H_4	OC_2H_5	80	0:100	oil[c]
7	**14a**	H	C_6H_5	75		oil[c]
8	**14b**	Me	C_6H_5	85		oil[c]
9	**14c**	Me	OC_2H_5	73		oil[c]
10	**14d**	4-MeC_6H_4	C_6H_5	80		oil[c]
11	**14e**	4-MeC_6H_4	OC_2H_5	86		oil[c]

[a] Yield of isolated purified product. − [b] **13/13′** ratio determined by ^{31}P-NMR. − [c] Oils isolated after "trap-to-trap" high-vacuum distillation (10^{-5} Torr).

Functionalized phosphane oxides **13/13′** and phosphonates **14**, prepared by addition of chloro derivatives **3** to oximes derived from phosphane oxides **11** and phosphonates **12**, as described in Scheme 3, can be used for the synthesis of amines derived from phosphane oxides and from phosphonates by reducing them with hydride reagents. Thus, treatment of the aforementioned mixtures of β-imino **13** and β-enamino phosphane oxides **13′** with sodium tetrahydridoborate in refluxing ethanol led to the formation of *N*-phosphorylated β-amino-functionalized derivatives **15** with excellent yields (Scheme 3 and Table 3, entries 1−6). Spectroscopic data were in agreement with the proposed structures. Protected amines **15** can be easily unmasked (Scheme 3) by treating them with 2 N aq. HCl, thereby affording the primary β-aminophosphane oxides **17** in excellent yields (Table 3, entries 12−14). Primary amines **17** can also be prepared by reduction of the functionalized phosphane oxides **13/13′** with neutral hydrides derived from borane and pyridine followed by the addition of HCl (Table 3, entries 12, 13).

Similarly, phosphonate esters **14** reacted with $NaBH_4$ and gave *N*-phosphorylated β-aminophosphonates **16** in very high yield (Table 3, entries 7−11). Cleavage of the phosphorus−nitrogen linkage of protected amines **16** was also performed with 2 N HCl, affording the primary β-aminophosphonates **18** (Table 3, entries 15−17). Acid hydrolysis of phosphonates **18** with 20% HCl led to the formation of β-aminoalkylphosphonic acids **19** in satisfactory yields (Table 3, entries 18−20). Once again, from a preparative point of view, it is noteworthy that the synthesis of β-aminophosphorus derivatives **17**−**19** does not require the isolation and purification of the functionalized enamines

Scheme 3



and/or imines derived from phosphane oxides **13/13′** or iminophosphonates **14**. The products can be obtained in a "one-pot" reaction from allenes **9** and **10** when, after removal of the solvent, the oxime derivatives **11** and **12** are directly treated with phosphorus chlorides **3** and then with hydride and 20% HCl (Table 3, entries 12, 16, 19).

Table 3. Phosphane oxides **15**, **17** and phosphonates **16**, **18** obtained

Entry	Comp.	R^1	R^4	Yield (%)[a]	m.p. [°C]
1	**15a**	H	C_6H_5	70	58−60
2	**15b**	H	OC_2H_5	80	oil[g]
3	**15c**	Me	C_6H_5	70	57−58
4	**15d**	Me	OC_2H_5	80	oil[g]
5	**15e**	4-MeC_6H_4	C_6H_5	75	74−76
6	**15f**	4-MeC_6H_4	OC_2H_5	79	oil[g]
7	**16a**	H	C_6H_5	70	oil[g]
8	**16b**	Me	C_6H_5	65	oil[g]
9	**16c**	Me	OC_2H_5	78	oil[g]
10	**16d**	4-MeC_6H_4	C_6H_5	72	oil[g]
11	**16e**	4-MeC_6H_4	OC_2H_5	75	oil[g]
12	**17a**	H		60[b] 60[c] 61[d] 71[e] 53[f]	oil[g]
13	**17b**	Me		67[b] 60[c] 63[d]	oil[g]
14	**17c**	4-MeC_6H_4		65[b]	oil[g]
15	**18a**	H		65[b] 73[e]	oil[g]
16	**18b**	Me		65[b] 69[e] 60[f]	oil[g]
17	**18c**	4-MeC_6H_4		68[b]	oil[g]
18	**19a**	H		60	>250
19	**19b**	Me		76 67[f]	>250
20	**19c**	4-MeC_6H_4		68	>250

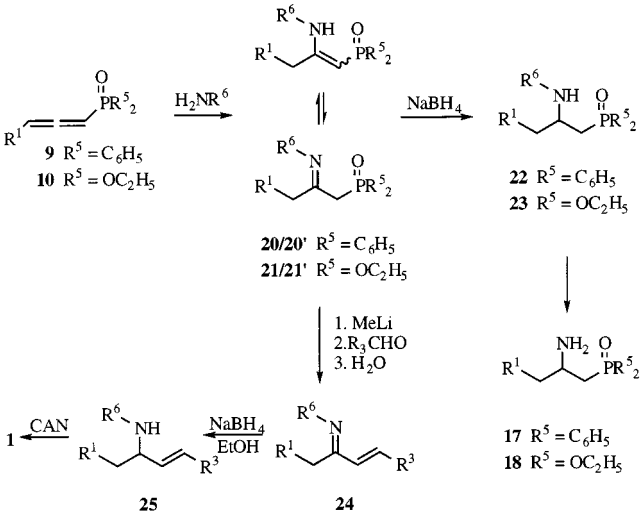
[a] Yield of isolated purified product. − [b] Yield of isolated compounds from amines **15** and **16**. − [c] Yield of isolated compounds from amines **15** using $BH_3 \cdot Py$ and HCl. − [d] Yield of isolated compounds from *N*-PMP-amines **22**. − [e] Yield of isolated compounds from amines **22** and **23**. − [f] Yield of isolated compounds from oximes **11** or **12**. − [g] Oils isolated by flash chromatography.

Synthesis of Primary Allylamines 1 and β-Aminophosphorus Derivatives 17−19 from *N*-Protected Imines and Enamines 20, 21

Primary allylamines **1** and β-aminophosphorus derivatives **17−19** can also be synthesized from functionalized *N*-protected nitrogen derivatives **20**, **21** containing easily removable groups such as *p*-methoxyphenyl (PMP) or a benzhydryl group[20]. The preparation of these *N*-PMP-enaminophosphane oxide derivatives **20** was achieved by the addition of *p*-methoxyphenylamine to allenylphosphane oxides **9** in refluxing acetonitrile. Compounds **20** were characterized by their spectroscopic data, which indicate that they are formed as a mixture of both (*Z*)- and (*E*)-enamines **20′** (minor products) and the β-iminophosphane oxides **20** (major compounds), although for our subsequent purposes, separation of the enamines and imines was not necessary. Reduction of the phosphane oxide derivatives **20/20′** with $NaBH_4$ yielded the *N*-PMP-amines **22**. The *N*-PMP protecting group of the amine was then selectively cleaved by treatment with 5 equiv. of cerium(IV) ammonium nitrate (CAN) in acetonitrile, furnishing the primary amines **17a**, **b** (Table 3, entries 12, 13). Similarly, addition of benzhydrylamine to allenes **9** and **10** gave β-enamines derived from phosphane oxide **20** and phosphonates **21**, which were formed as a mixture of the (*Z*) and (*E*) isomers. Selective removal of the benzhydrylic group was achieved by catalytic hydrogenation [$Pd(OH)_2$/C], thereby affording functionalized amines derived from phosphane oxides **17a** (Table 3, entry 12) and phosphonates **18a**, **b** (Table 3, entries 15, 16).

Finally, when β-enaminophosphane oxides **20** substituted with a *p*-methoxyphenyl (PMP) group are used, this strategy can also be used for the preparation of allylamines **1**. Thus, treatment of β-enamine **20** with methyllithium, followed by the addition of aromatic and aliphatic aldehydes, afforded *N*-PMP-azadienes **24**. Selective reduction of the imino group of α,β-unsaturated imines **24** with $NaBH_4$ gave *N*-protected allylamines **25**. The *N*-PMP protecting group of the amine was then selectively cleaved by treatment with CAN in acetonitrile, yielding primary allylic amines **1**. These allylamines **1** can also be obtained in a "one-pot" reaction from allene **9**, without the isolation and purification of enamines **20**.

Scheme 4



In conclusion, we have described a new strategy that constitutes a simple and general method for the synthesis of a broad range of allylamines **1**, 1-azadienes **5**, **7**, **24**, and β-aminophosphorus derivatives **15−19**, from easily available starting materials and under mild reaction conditions. 1-Azadienes are very versatile intermediates that find application in a wide variety of methods for the construction of

six-membered heterocycles[21], while allylamines are useful compounds in organic chemistry, not only because of their application in organic synthesis[2][3][4], but also owing to their biological activities[3].

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Experimental Section

General: Melting points were determined with a Büchi SPM-20 apparatus and are uncorrected. Analytical TLC was performed on 0.25-mm silica-gel plates (Merck). Visualization was accomplished by exposure to UV light/iodine vapour. Solvents for extraction and chromatography were technical grade and were distilled from the indicated drying agents: CH_2Cl_2 (P_2O_5), *n*-hexane and diethyl ether (sodium benzophenone ketyl), ethyl acetate (K_2CO_3). All solvents used in reactions were freshly distilled from appropriate drying agents prior to use: acetonitrile (P_2O_5), $CHCl_3$ (P_2O_5). All other reagents were recrystallized or distilled as necessary. All reactions were performed in oven− (125°C) or flame-dried glassware under dry N_2. − Column (flash) chromatography was carried out on silica gel (Merck, 70−230 mesh). − Mass spectra (EI) were obtained with a Hewlett Packard 5890 spectrometer using an ionization voltage of 70 eV. Data are reported in the form *m/z* (intensity relative to base peak = 100). − Infrared (IR) spectra were recorded with a Nicolet IRFT Magna 550 spectrometer either as neat liquids or as solids in KBr. Absorptions are reported in cm^{-1}. − ^{1}H-NMR spectra were recorded with a Varian 300 MHz spectrometer using tetramethylsilane (δ = 0.00) or chloroform (δ = 7.26) as internal references in $CDCl_3$ or D_2O solutions. ^{13}C-NMR spectra were recorded at 75 MHz with chloroform (δ = 77.0) as an internal reference in $CDCl_3$ or D_2O solutions. ^{31}P-NMR spectra were recorded at 120 MHz with 85% phosphoric acid as an external reference. Chemical shifts are given in ppm (δ). Coupling constants *J* are reported in Hertz. − Elemental analyses were determined with a Perkin-Elmer Model 240 instrument.

General Procedure for the Preparation of Imines **5** *and* **7**: A dry 100-ml 2-necked flask, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with the azadiene **2** (5 mmol), triethylamine (5 mmol), and 25 ml of benzene. The mixture was then cooled to 8°C and a solution of 5 mmol of chlorodiphenylphosphane (**3a**) or chlorodiethylphosphonate (**3b**) in 10 ml of benzene was added over a period of 5 min. The mixture was stirred until TLC indicated the disappearance of the azadiene **2** (6−12 h). The triethylamine hydrochloride formed was then filtered off, the filtrate was concentrated, and the crude product was purified by flash chromatography on silica gel.

5a: Chromatographic separation gave 1.44 g of **5a** (80%) as a yellow solid, m.p. 100−102°C. − IR (KBr): ν = 1676 cm^{-1} (C=N), 1609 (C=C), 1179 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 6.59 (d, $^3J_{HH}$ = 16.2 Hz, 1 H, =CH), 7.10−7.90 (m, 15 H, HC= and aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_3), 23.6 (d, $^3J_{PC}$ = 16.0 Hz, CH_3), 128.1−131.7 (C=C and aromatic C), 141.8 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 19.0. − MS (70 eV); *m/z* (%): 359 (10) [M^+]. − $C_{23}H_{22}NOP$ (359): calcd. C 76.86, H 6.17, N 3.90; found C 76.72, H 6.22, N 3.85.

5b: Chromatographic separation gave 1.33 g of **5b** (82%) as a yellow oil, R_f = 0.48 (ethyl acetate). − IR (NaCl): ν = 1680 cm^{-1} (C=N), 1580 (C=C), 1170 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.92 (d, $^3J_{HH}$ = 6.90 Hz, 6 H, CH_3), 1.75 (m, 1 H, CH), 2.10 (m, 2 H, CH_2), 2.53 (s, 3 H, CH_3), 6.05 (m, 1 H, =CH), 6.66 (d, 1 H, HC=), 7.36−7.94 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 22.3 (CH_3), 23.3 (CH_3), 28.2 (CH), 42.1 (CH_2), 128.2−134.0 (C=C and aromatic C), 145.6 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 18.6. − MS (70 eV); *m/z* (%): 325 (18) [M^+]. − $C_{20}H_{24}NOP$ (325): calcd. C 73.84, H 7.38, N 4.31; found C 74.02, H 7.42, N 4.35.

5c: Chromatographic separation gave 1.72 g of **5c** (92%) as a yellow solid, m.p. 140−143°C. − IR (KBr): ν = 1610 cm^{-1} (C=N), 1562 (C=C), 1179 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.29 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.97 (mc, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 7.40 (d, $^3J_{HH}$ = 16.2 Hz, 1 H, =CH), 7.16−8.00 (m, 15 H, HC= and aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 8.29 (CH_3), 21.5 (CH_3), 33.9 (CH_2), 125.1−131.9 (C=C and aromatic C), 141.8 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 18.1. − MS (70 eV); *m/z* (%): 373 (4) [M^+]. − $C_{24}H_{24}NOP$ (373): calcd. C 77.19, H 6.48, N 3.75; found C 77.32, H 6.42, N 3.82.

7a: Chromatographic separation gave 1.36 g of **7a** (92%) as a yellow oil, R_f = 0.43 (ethyl acetate). − IR (NaCl): ν = 1620 cm^{-1} (C=N), 1045 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.36 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.22 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 4.12 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 6.69 (d, $^3J_{HH}$ = 16.2 Hz, 1 H, =CH), 7.07−7.53 (m, 5 H, HC= and aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 20.9 (CH_3), 21.4 (CH_3), 62.5 (CH_2), 126.2−143.5 (C=C and aromatic C), 141.8 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 9.4. − MS (70 eV); *m/z* (%): 295 (16) [M^+]. − $C_{15}H_{22}NO_3P$ (295): calcd. C 61.01, H 7.51, N 4.74; found C 61.19, H 7.42, N 3.70.

7b: Chromatographic separation gave 1.32 g of **7b** (85%) as a yellow oil, R_f = 0.40 (ethyl acetate). − IR (NaCl): ν = 1620 cm^{-1} (C=N), 1568 (C=C), 1100 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.36 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.56 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 4.16 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 7.00 (d, $^3J_{HH}$ = 16.2 Hz, 1 H, =CH), 6.83−7.53 (m, 5 H, HC= and aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 27.3 (CH_3), 55.3 (OCH_3), 62.5 (CH_2), 113.6−143.2 (C=C and aromatic C), 143.2 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 4.1. − MS (70 eV); *m/z* (%): 311 (25) [M^+]. − $C_{15}H_{22}NO_4P$ (311): calcd. C 61.01, H 7.51, N 4.74; found C 61.19, H 7.42, N 3.70.

7c: Chromatographic separation gave 1.27 g of **7c** (85%) as a yellow oil, R_f = 0.42 (ethyl acetate). − IR (NaCl): ν = 1521 cm^{-1} (C=C), 1246 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.36 (m, 9 H, CH_3), 1.86 (c, 2 H, CH_2), 4.15 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 6.68−8.73 (m, 6 H, HC=CH and aromatic C). − ^{13}C NMR ($CDCl_3$): δ = 8.0 (CH), 16.2 (CH_3), 34.4 (CH_2), 62.6 (CH_2), 123.8−138.4 (C=C and aromatic C), 148.2 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 4.7. − MS (70 eV); *m/z* (%): 296 (3) [M^+]. − $C_{14}H_{21}NO_3P$ (296): calcd. C 56.76, H 7.09, N 9.46; found C 56.60, H 7.18, N 9.51.

General Procedure for the Preparation of Amines **6** *and* **8**: A dry 100-ml 2-necked flask, fitted with a reflux condenser, gas inlet, and magnetic stirrer, was charged with 5 mmol of imine **5** or **7**, 377 mg (10 mmol) of $NaBH_4$, and 40 ml of ethanol. The mixture was stirred under reflux until TLC indicated the disappearance of the compound **5** or **7** (1 d). The mixture was then washed with water and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel.

6a: Chromatographic separation gave 1.44 g of **6a** (80%) as a yellow solid, m.p. 137−140°C. − IR (KBr): ν = 3335 cm^{-1} (NH),

1522 (C=C), 1185 (P=O). – ^{1}H NMR ($CDCl_3$): δ = 1.28 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH_3), 2.20 (m, NH), 2.26 (s, 3 H, CH_3), 4.40 (m, 1 H, CH), 6.12 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.3 Hz, 1 H, HC=), 6.42 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, =CH), 7.02–7.58 (m, 14 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_3), 23.4 (CH_3), 68.8 (CH), 128.3–134.2 (C=C and aromatic C). – ^{31}P NMR ($CDCl_3$): δ = 22.8. – MS (70 eV); *m/z* (%): 361 (17) [M^+]. – $C_{23}H_{24}NOP$ (361): calcd. C 76.43, H 6.69, N 3.87; found C 76.32, H 6.72, N 3.80.

6b: Chromatographic separation gave 1.55 g of **6b** (72%) as a yellow oil, R_f = 0.52 (ethyl acetate). – IR (NaCl): ν = 3390 cm^{-1} (NH), 1567 (C=C), 1176 (P=O). – ^{1}H NMR ($CDCl_3$): δ = 0.87 (d, $^3J_{HH}$ = 7.2 Hz, 6 H, CH_3), 1.22 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH_3), 1.50 (m, 1 H, CH), 1.87 (m, 2 H, CH_2), 3.80 (m, 1 H, CH), 4.70 (m, NH), 6.80 (dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 6.2 Hz, 1 H, HC=), 7.42–7.94 (m, 11 H, aromatic H and =CH). – ^{13}C NMR ($CDCl_3$): δ = 22.5 (CH_3), 23.7 (CH_3), 39.9 (CH_2), 48.7 (CH), 128.3–134.8 (C=C and aromatic C). – ^{31}P NMR ($CDCl_3$): δ = 22.5. – MS (70 eV); *m/z* (%): 327 (22) [M^+]. – $C_{20}H_{26}NOP$ (327): calcd. C 73.39, H 7.95, N 4.28; found C 73.52, H 7.82, N 4.20.

6c: Chromatographic separation gave 1.56 g of **6c** (83%) as a yellow solid, m.p. 145–147°C. – IR (KBr): ν = 3207 cm^{-1} (NH), 1550 (C=C), 1199 (P=O). – ^{1}H NMR ($CDCl_3$): δ = 0.92 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3), 1.73 (m, 2 H, CH_2), 2.33 (s, 3 H, CH_3), 2.96 (m, NH), 3.72 (m, 1 H, CH), 6.05 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.9 Hz, 1 H, HC=), 6.33 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, =CH), 7.04–7.97 (m, 14 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 10.1 (CH_3), 21.2 (CH_3), 30.9 (CH_2), 55.1 (CH), 126.3–137.3 (C=C and aromatic C). – ^{31}P NMR ($CDCl_3$): δ = 22.4. – MS (70 eV); *m/z* (%): 375 (6) [M^+]. – $C_{24}H_{26}NOP$ (375): calcd. C 76.78, H 6.98, N 3.75; found C 76.92, H 6.82, N 3.80.

8a: Chromatographic separation gave 1.32 g of **8a** (89%) as a yellow oil, R_f = 0.47 (ethyl acetate). – IR (NaCl): ν = 3382 cm^{-1} (NH), 1521 (C=C), 1025 (P=O). – ^{1}H NMR ($CDCl_3$): δ = 1.28 (m, 9 H, CH_3), 1.80 (m, NH), 2.43 (s, 3 H, CH_3), 4.13 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 4.48 (m, 1 H, CH), 6.20 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.3 Hz, 1 H, HC=), 6.53 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, =CH), 7.08–7.36 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 16.1 (CH_3), 21.1 (CH_3), 23.4 (CH_3), 62.8 (CH_2), 69.0 (CH), 126.3–137.4 (C=C and aromatic C). – ^{31}P NMR ($CDCl_3$): δ = 8.1. – MS (70 eV); *m/z* (%): 297 (3) [M^+]. – $C_{15}H_{24}NO_3P$ (297): calcd. C 60.59, H 8.14, N 4.71; found C 60.69, H 8.08, N 4.77.

8b: Chromatographic separation gave 1.10 g of **8b** (70%) as a yellow oil, R_f = 0.39 (ethyl acetate). – IR (NaCl): ν = 3340 (NH) cm^{-1}, 1521 (C=C), 1146 (P=O). – ^{1}H NMR ($CDCl_3$): δ = 1.28 (m, 9 H, CH_3), 3.82 (s, 3 H, OCH_3), 4.07 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 4.40 (m, 1 H, CH), 4.60 (m, NH), 6.12 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.6 Hz, 1 H, HC=), 6.51 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, = CH), 6.84–7.40 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 23.4 (CH_3), 55.2 (OCH_3), 62.3 (CH_2), 68.8 (CH), 114.0–136.4 (C=C and aromatic C). – ^{31}P NMR ($CDCl_3$): δ = 8.1. – MS (70 eV); *m/z* (%): 313 (33) [M^+]. – $C_{15}H_{24}NO_4P$ (313): calcd. C 57.51, H 7.67, N 4.47; found C 57.64, H 7.50, N 4.37.

8c: Chromatographic separation gave 1.27 g of **8c** (85%) as a yellow oil, R_f = 0.40 (ethyl acetate). – IR (NaCl): ν = 1562 cm^{-1} (C=), 1136 (P=O). – ^{1}H NMR ($CDCl_3$): δ = 0.98 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 1.30 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.65 (mc, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 2.0 (m, NH), 3.74 (m, 1 H, CH), 4.08 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 6.18 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.6 Hz, 1 H, HC=), 6.53 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, =CH), 6.82–8.70 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 10.0 (CH_3), 16.2 (CH_3), 30.0 (CH_2), 55.2 (CH), 62.4 (CH_2), 118.2–149.6 (C=C and aromatic C). – ^{31}P NMR ($CDCl_3$): δ = 8.1. – MS (70 eV); *m/z* (%): 298 (7) [M^+]. – $C_{14}H_{23}N_2O_3P$ (313): calcd. C 56.37, H 7.72, N 9.40; found C 56.52, H 7.62, N 9.45.

General Procedure for the Preparation of Allylamines **1**: A dry 100-ml 2-necked flask, fitted with a magnetic stirrer, was charged with 5 mmol of amine **6** or **8**, and 20 ml of 2 N aq. HCl. The mixture was stirred (2–6 h) and was then basified with 2 N aq. NaOH, washed with water, and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel. Allylamines **1** could also be obtained in a "one-pot" reaction starting from azadienes **2** by following the same general procedures for generating compounds **5** and **7**, **6** and **8**, and **1**, but without isolating the intermediate products. Triethylamine hydrochloride was filtered off under nitrogen and the solvents were removed in vacuo. The allylamines **1** were purified as described above.

1a: Chromatographic separation gave 0.65 g of **1a** (73%) as a yellow oil, R_f = 0.12 (ethyl acetate). – IR (NaCl): ν = 3350 cm^{-1} (NH_2), 1528 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.23 (d, *J* = 6.3 Hz, 3 H, CH_3), 2.60 (m, NH_2), 3.15 (m, 1 H, CH), 3.79 (s, 3 H, OCH_3), 6.07 (dd, $^3J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 6.5 Hz, 1 H, HC=), 6.37 (d, $^3J_{HH}$ = 15.2 Hz, 1 H, =CH), 6.80–7.31 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 24.3 (CH_3), 43.7 (CH), 55.4 (OCH_3), 119.4–136.4 (C=C and aromatic C). – MS (70 eV); *m/z* (%): 177 (5) [M^+]. – $C_{11}H_{15}NO$ (177): calcd. C 74.57, H 8.47, N 8.24; found C 74.65, H 8.60, N 8.11.

1b: Chromatographic separation gave 0.57 g of **1b** (82%) as a yellow oil, R_f = 0.08 (ethyl acetate) – IR (NaCl): ν = 3374 cm^{-1} (NH_2), 1640 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 0.87 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH_3), 1.25 (d, $^3J_{HH}$ = 6.2 Hz, 3 H, CH_3), 1.50 (m, 3 H, CH_2 and CH), 1.85 (m, NH_2), 3.51 (m, 1 H, CH), 5.39 (dd, $^3J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 8.7 Hz, 1 H, HC=), 5.69 (m, 1 H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 10.0 (CH_3), 21.8 (CH_3), 26.4 (CH_2), 41.5 (CH), 55.5 (CH), 126.8 and 136.1 (C=C). – MS (70 eV); *m/z* (%): 141 (15) [M^+]. – $C_9H_{19}N$ (141): calcd. C 76.59, H 13.47, N 9.93; found C 76.40, H 13.52, N 10.01.

1d: Chromatographic separation gave 0.68 g of **1d** (79%) as a yellow oil, R_f = 0.03 (ethyl acetate). – IR (NaCl): ν = 3345 cm^{-1} (NH_2), 1575 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3), 1.53 (m, 2 H, CH_2), 2.33 (s, 3 H, CH_3), 3.37 (m, 1 H, CH), 3.60 (m, NH_2), 6.08 (dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, HC=), 6.43 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, =CH), 7.09–7.28 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 10.5 (CH_3), 21.1 (CH_3), 30.6 (CH_2), 55.7 (CH), 126.1–137.0 (C=C and aromatic C). – MS (70 eV); *m/z* (%): 175 (8) [M^+]. – $C_{12}H_{17}N$ (175): calcd. C 82.23, H 9.78, N 7.99; found C 82.35, H 9.83, N 8.05.

1e: Chromatographic separation gave 0.65 g of **1e** (80%) as a yellow oil, R_f = 0.02 (ethyl acetate). – IR (NaCl): ν = 3321 cm^{-1} (NH_2), 1598 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3), 1.56 (m, 2 H, CH_2), 2.60 (m, NH_2), 3.41 (m, 1 H, CH), 6.23 (dd, $^3J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, HC=), 6.47 (d, *J* = 16.2 Hz, 1 H, =CH), 7.21–8.58 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 9.3 (CH_3), 29.3 (CH_2), 54.2 (CH), 122.2–146.9 (C=C and aromatic C). – MS (70 eV); *m/z* (%): 162 (20) [M^+]. – $C_{10}H_{14}N_2$ (162): calcd. C 74.07, H 8.64, N 17.28; found C 74.25, H 8.60, N 17.31.

1f: Chromatographic separation gave 0.64 g of **1f** (67%) as a yellow oil, R_f = 0.02 (ethyl acetate). – IR (NaCl): ν = 3326 cm^{-1} (NH_2), 1640 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.15 (t, $^3J_{HH}$ = 6.3 Hz, 3 H, CH_3), 2.15 (m, 2 H, CH_2), 2.66 (m, 2 H, CH_2), 3.43 (m,

3 H, CH and CH_2), 3.20 (m, NH_2), 5.44 (m, 2 H, HC=CH), 7.13−7.67 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 30.5 (CH_2), 32.1 (CH_2), 40.8 (CH_2), 55.2 (CH), 125.7−142.3 (C=C and aromatic C). − MS (70 eV); *m/z* (%): 189 (3) [M^+]. − $C_{13}H_{19}N$ (189): calcd. C 82.54, H 10.05, N 7.41; found C 82.48, H 10.11, N 7.45.

1g: Chromatographic separation gave 0.45 g of **1g** (70%) as a yellow oil, R_f = 0.06 (ethyl acetate). − IR (NaCl): ν = 3300 cm^{-1} (NH_2), 1668 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 0.91 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH_3), 1.12 (t, $^3J_{HH}$ = 6.5 Hz, 3 H, CH_3), 1.57 (m, 3 H, CH and CH_2), 1.70 (m, NH_2), 1.84 (m, 2 H, CH_2), 3.42 (m, 1 H, CH), 5.37−5.41 (m, 2 H, HC=CH). − ^{13}C NMR ($CDCl_3$): δ = 10.0 (CH_3), 22.1 (CH_3), 22.3 (CH_2), 22.7 (CH), 41.5 (CH_2), 55.1 (CH), 127.6 and 137.9 (C=C). − MS (70 eV); *m/z* (%): 127 (12) [M^+]. − $C_8H_{17}N$ (127): calcd. C 75.59, H 13.39, N 11.02; found C 75.71, H 13.30, N 11.01.

General Procedure for the Preparation of Allylamines **1**: A solution of the allylamine **25** (5 mmol) in acetonitrile (30 ml) was cooled to 0°C and treated with a solution of CAN (8.2 g, 15 mmol) in water (70 ml) over a period of 5 min. The reaction mixture was stirred at this temperature for 1 h, then diluted with 300 ml of water and extracted with ethyl acetate (3 × 50 ml). The combined organic extracts were washed with 20% sodium sulfite solution, satd. sodium bicarbonate solution and water, and then dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel.

1a: Chromatographic separation gave 0.60 g of **1a** (68%).

1c: Chromatographic separation gave 0.64 g of **1c** (72%) as a yellow oil, R_f = 0.10 (ethyl acetate). − IR (NaCl): ν = 3396 cm^{-1} (NH_2), 1659 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 1.15 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH_3), 2.15 (m, 2 H, CH_2), 2.66 (m, 2 H, CH_2), 3.48 (m, 3 H, CH and NH_2), 5.26−5.62 (m, 2 H, HC=CH), 7.13−7.67 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 22.2 (CH_3), 34.0 (CH_2), 35.6 (CH_2), 48.8 (CH), 125.7−142.3 (C=C and aromatic C). − MS (70 eV); *m/z* (%): 175 (8) [M^+]. − $C_{12}H_{17}N$ (175): calcd. C 82.28, H 9.71, N 8.01; found C 82.14, H 9.85, N 7.91.

1d: Chromatographic separation gave 0.51 g of **1d** (59%).

General Procedure for the Preparation of Phosphane Oxides **13** *and* **13′** *and Phosphonates* **14**: A dry 100-ml 2-necked flask, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 5 mmol of the β-phosphorylated oxime **11** or **12**, triethylamine (5 mmol), and 30 ml of benzene. The mixture was cooled to 8°C and a solution of 5 mmol of chlorodiphenylphosphane **3a** or diethyl chlorophosphite **3b** in 10 ml of benzene was added over a period of 5 min. The mixture was stirred until TLC indicated the disappearance of the oxime **11** or **12** (6−12 h). Triethylamine hydrochloride was then filtered off, the filtrate was concentrated, and the crude product was either triturated with diethyl ether or distilled.

13a *and* **13′a**: The crude product was triturated with diethyl ether, giving 2.05 g of **13a/13′a** (75%) as a yellow solid, m.p. 56−58°C. − IR (KBr): ν = 3462 cm^{-1} (NH), 1612 (C=C), 1175 (P=O). − ^{1}H NMR ($CDCl_3$): **13a**: δ = 1.87 (s, 3 H, CH_3), 3.54 (d, $^2J_{PH}$ = 14.7 Hz, 2 H, CH_2), 7.21−7.91 (m, 20 H, aromatic H); **13′a**: δ = 2.14 (s, 3 H, CH_3), 4.59 (d, $^2J_{PH}$ = 21 Hz, 1 H, CH), 7.21−7.29 (m, 20 H, aromatic H), 11.00 (m, NH). − ^{13}C NMR ($CDCl_3$): **13a**: δ = 32.7 (CH_3), 48.0 (d, $^1J_{PC}$ = 56.6 Hz, C−P), 128.4−134.9 (aromatic C), 158.5 (C=N); **13′a**: δ = 24.3 (d, $^3J_{PC}$ = 15.1 Hz, CH_3), 88.9 (dd, $^1J_{PC}$ = 106.5 Hz, $^3J_{PC}$ = 7.6 Hz, C−P), 128.4−134.9 (aromatic C), 160.0 (=C−N). − ^{31}P NMR ($CDCl_3$): **13a**: δ = 23.7, 28.4; **13′a**: δ = 18.6, 30.0. − MS (70 eV); *m/z* (%): 547 (12) [M^+]. − $C_{27}H_{25}NO_2P_2$ (547): calcd. C 70.89, H 5.51, N 3.06; found C 71.03, H 5.56, N 3.02.

13b *and* **13′b**: The crude product was distilled under reduced pressure, giving 1.57 g of **13b/13′b** (80%) as a colorless oil. − IR (NaCl): ν = 3435 cm^{-1} (NH), 1582 (C=C), 1051 (P=O). − ^{1}H NMR ($CDCl_3$): **13b**: δ = 1.19 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.26 (s, 3 H, CH_3), 3.35 (d, $^2J_{PH}$ = 13.8 Hz, 2 H, CH_2), 4.01 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 7.35−7.73 (m, 10 H, aromatic H); **13′b**: δ = 1.29 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.22 (s, 3 H, CH_3), 4.06 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 4.54 (dd, $^1J_{PC}$ = 22.5 Hz, $^3J_{PC}$ = 4.5 Hz, 1 H, CH), 7.20−7.78 (m, 10 H, aromatic H), 9.5 (m, NH). − ^{13}C NMR ($CDCl_3$): **13b**: δ = 16.2 (CH_3), 32.6 (CH_3), 47.6 (d, $^1J_{PC}$ = 56.6 Hz, C−P), 62.5 (CH_2), 128.4−134.9 (aromatic C), 157.4 (C=N); **13′b**: δ = 16.0 (CH_3), 23.1 (d, $^3J_{PC}$ = 14.0 Hz, CH_3), 88.0 (dd, $^1J_{PC}$ = 107.2 Hz, $^3J_{PC}$ = 11.5 Hz, C−P), 128.1−134.8 (aromatic C), 159.0 (−C=N). − ^{31}P NMR ($CDCl_3$): **13b**: δ = 9.7, 23.3; **13′b**: δ = 0.7, 29.7. − MS (70 eV); *m/z* (%): 393 (7) [M^+]. − $C_{19}H_{25}NO_4P_2$ (393): calcd. C 58.02, H 6.41, N 3.56; found C 58.12, H 6.46, N 3.52.

13′c: The crude product was triturated with diethyl ether, giving 1.88 g of **13′c** (65%) as a yellow solid, m.p. 66−68°C. − IR (KBr): ν = 3442 cm^{-1} (NH), 1615 (C=C), 1172 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.0 (t, $^3J_{HH}$ = 7.4 Hz, 3 H, CH_3), 2.42 (mc, $^3J_{HH}$ = 7.4 Hz, 2 H, CH_2), 4.59 (dd, $^2J_{PH}$ = 21.0 Hz, $^4J_{PH}$ = 3.0 Hz, 1 H, CH), 7.21−7.83 (m, 20 H, aromatic H), 10.00 (m, NH). − ^{13}C NMR ($CDCl_3$): δ = 11.6 (CH_3), 29.0 (d, $^3J_{PC}$ = 14.9 Hz, CH_2), 86.7 (d, $^1J_{PC}$ = 115.6 Hz, $^3J_{PC}$ = 11.0 Hz, C−P), 128.4−133.8 (aromatic C), 162.2 (=C−N). − ^{31}P NMR ($CDCl_3$): δ = 18.4, 30.8. − MS (70 eV); *m/z* (%): 471 (25) [M^+]. − $C_{28}H_{27}NO_2P_2$ (547): calcd. C 71.33, H 5.77, N 2.97; found C 71.47, H 5.66, N 3.02.

13′d: The crude product was distilled under reduced pressure, giving 1.73 g of **13′d** (85%) as a colorless oil. − IR (NaCl): ν = 3429 cm^{-1} (NH), 1580 (C=C), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.10 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3), 1.19 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.57 (mc, 2 H, CH_2), 4.03 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 4.57 (dd, $^2J_{PH}$ = 21.6 Hz, $^4J_{PH}$ = 5.1 Hz, 1 H, CH), 7.35−7.77 (m, 10 H, aromatic H), 9.48 (m, NH). − ^{13}C NMR ($CDCl_3$): δ = 11.8 (CH_3), 16.1 (CH_3), 27.2 (d, $^3J_{PC}$ = 12.6 Hz, C−P), 62.5 (CH_2), 85.8 (dd, $^1J_{PC}$ = 107.2 Hz, $^3J_{PC}$ = 11.5 Hz, C−P), 128.3−133.6 (aromatic C), 163.5 (=C−N). − ^{31}P NMR ($CDCl_3$): δ = 0.5, 30.7. − MS (70 eV); *m/z* (%): 407 (2) [M^+]. − $C_{20}H_{27}NO_4P_2$ (407): calcd. C 58.97, H 6.68, N 3.44; found C 56.12, H 6.76, N 3.52.

13′e: The crude product was triturated with diethyl ether, giving 2.05 g of **13′e** (75%) as a white solid, m.p. 64−66°C. − IR (KBr): ν = 1618 cm^{-1} (=C−N), 1175 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 4.00 (s, 2 H, CH_2), 4.28 (dd, $^2J_{PH}$ = 21.0 Hz, $^4J_{PH}$ = 3.3 Hz, 1 H, CH), 6.81−7.86 (m, 24 H, aromatic H), 9.60 (m, NH). − ^{13}C NMR ($CDCl_3$): δ = 21.0 (CH_3), 41.0 (d, $^3J_{PC}$ = 16.5 Hz, CH_2), 90.5 (dd, $^1J_{PC}$ = 107.2 Hz, $^3J_{PC}$ = 11.4 Hz, C−P), 128.4−132.0 (aromatic C), 163.3 (=C−N). − ^{31}P NMR ($CDCl_3$): δ = 19.0, 30.8. − MS (70 eV); *m/z* (%): 547 (5) [M^+]. − $C_{34}H_{31}NO_2P_2$ (547): calcd. C 74.58, H 5.71, N 2.56; found C 74.69, H 5.66, N 2.61.

13′f: The crude product was distilled under reduced pressure, giving 1.93 g of **13′f** (80%) as a colorless oil. − IR (NaCl): ν = 3442 cm^{-1} (NH), 1608 (C=C), 1119 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.27 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.33 (s, 3 H, CH_3), 3.90 (s, 2 H, CH_2), 4.07 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 4.37 (dd, $^2J_{PH}$ = 21.0 Hz, $^4J_{PH}$ = 6.0 Hz, 1 H, CH), 7.05−7.60 (m, 14 H, aromatic H), 9.65 (m, NH). − ^{13}C NMR ($CDCl_3$): δ = 16.1 (CH_3), 21.0 (CH_3), 40.6 (d, $^3J_{PC}$ = 12.5 Hz, CH_2), 63.3 (CH_2), 89.3 (dd, $^1J_{PC}$ = 105.0 Hz, $^3J_{PC}$ = 11.6 Hz, C−P), 128.3−136.3 (aromatic C), 161.4

(=C−N). − ^{31}P NMR ($CDCl_3$): δ = 0.5, 30.5. − MS (70 eV); *m/z* (%): 483 (22) [M^+]. − $C_{26}H_{31}NO_4P_2$ (483): calcd. C 64.59, H 6.46, N 2.90; found C 64.65, H 6.52, N 2.96.

14a: The crude product was distilled under reduced pressure, giving 1.34 g of **14a** (75%) as a colorless oil. − IR (NaCl): ν = 1613 cm^{-1} (C=N), 1120 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.29 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.25 (s, 3 H, CH_3), 2.98 (d, $^2J_{PH}$ = 24.0 Hz, 2 H, CH_2), 4.05 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 7.23−7.86 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.1 (CH_3), 31.3 (CH_3), 43.2 (d, $^1J_{PC}$ = 126.9 Hz, C−P), 65.2 (CH_2), 127.9−135.9 (aromatic C), 161.5 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 19.9, 23.1. − MS (70 eV); *m/z* (%): 393 (10) [M^+]. − $C_{19}H_{25}NO_4P_2$ (393): calcd. C 58.02, H 6.41, N 3.56; found C 58.22, H 6.50, N 3.40.

14b: The crude product was distilled under reduced pressure, giving 1.73 g of **14b** (85%) as a yellow oil. − IR (NaCl): ν = 1620 cm^{-1} (C=N), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.27 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.74 (c, 2 H, CH_2), 2.54 (d, $^2J_{PH}$ = 22.8 Hz, 2 H, CH_2), 4.12 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 7.21−7.89 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 11.4 (CH_3), 18.8 (CH_3), 28.3 (CH_2), 42.0 (d, $^1J_{PC}$ = 127.2 Hz, C−P), 62.6 (CH_2), 127.9−132.5 (aromatic C), 156.6 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 18.4, 23.9. − MS (70 eV); *m/z* (%): 407 (33) [M^+]. − $C_{20}H_{27}NO_4P_2$ (407): calcd. C 58.97, H 6.68, N 3.44; found C 56.12, H 6.56, N 3.40.

14c: The crude product was distilled under reduced pressure, giving 1.25 g of **14c** (73%) as a yellow oil. − IR (NaCl): ν = 1618 cm^{-1} (C=N), 1175 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, CH_3), 1.26 (t, $^3J_{HH}$ = 7.02 Hz, 12 H, CH_3), 1.73 (mc, 2 H, CH_2), 2.63 (d, $^2J_{PH}$ = 21.9 Hz, 2 H, CH_2), 4.08 (m, $^3J_{PH}$ = 4.00 Hz, 8 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 8.4 (CH_3), 16.3 (CH_3), 25.6 (CH_2), 42.0 (d, $^1J_{PC}$ = 127.4 Hz, C−P), 62.0 (CH_2), 160.1 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 7.6, 23.3. − MS (70 eV); *m/z* (%): 343 (13) [M^+]. − $C_{12}H_{27}NO_6P_2$ (343): calcd. C 41.98, H 6.50, N 3.48; found C 42.12, H 6.56, N 3.40.

14d: The crude product was distilled under reduced pressure, giving 1.66 g of **14d** (80%) as a yellow oil. − IR (NaCl): ν = 1630 cm^{-1} (C=N), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.21 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.22 (s, 3 H, CH_3), 3.02 (d, $^2J_{PH}$ = 22.5 Hz, 2 H, CH_2), 3.72 (s, 2 H, CH_2), 3.93 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 6.99−7.90 (m, 14 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.3 (CH_3), 21.0 (CH_3), 42.2 (d, $^1J_{PC}$ = 127.2 Hz, C−P), 50.2 (CH_2), 62.0 (CH_2), 128.1−136.9 (aromatic C), 151.6 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 19.0, 23.6. − MS (70 eV); *m/z* (%): 483 (7) [M^+]. − $C_{26}H_{31}NO_4P_2$ (483): calcd. C 64.59, H 6.41, N 2.90; found C 64.70, H 6.36, N 2.97.

14e: The crude product was distilled under reduced pressure, giving 1.80 g of **14e** (86%) as a yellow oil. − IR (NaCl): ν = 1632 cm^{-1} (C=N), 1038 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.28 (t, $^3J_{HH}$ = 7.02 Hz, 12 H, CH_3), 2.27 (s, 3 H, CH_3), 2.87 (d, $^2J_{PH}$ = 23.7 Hz, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 4.13 (m, $^3J_{PH}$ = 4.00 Hz, 8 H, CH_2), 7.03−7.21 (m, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.1 (CH_3), 20.9 (CH_3), 41.0 (d, $^1J_{PC}$ = 126.8 Hz, C−P), 50.3 (CH_2), 62.6 (CH_2), 126.4−131.7 (aromatic C), 151.6 (C=N). − ^{31}P NMR ($CDCl_3$): δ = 9.9, 23.1. − MS (70 eV); *m/z* (%): 345 (37) [M^+]. − $C_{18}H_{31}NO_6P_2$ (345): calcd. C 51.55, H 7.45, N 3.34; found C 51.49, H 7.46, N 3.22.

General Procedure for the Preparation of Phosphane Oxides **15** *and Phosphonates* **16**: A dry 100-ml 2-necked flask, fitted with a reflux condenser, gas inlet, and magnetic stirrer, was charged with 5 mmol of the phosphane oxide **13** or **13′** or phosphonate **14**, 377 mg (10 mmol) of $NaBH_4$, and 40 ml of ethanol. The mixture was stirred under reflux until TLC indicated the disappearance of the compound **13/13′** or **14** (1 d). The mixture was then washed with water and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. The crude product was either triturated with diethyl ether or purified by flash chromatography on silica gel.

15a: The crude product was triturated with diethyl ether, giving 1.61 g of **15a** (70%) as a yellow solid, m.p. 58−60°C. − IR (KBr): ν = 3180 cm^{-1} (NH), 1179 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.31 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH_3), 2.66 (m, 2 H, CH_2), 3.50 (m, 1 H, CH), 4.20 (m, NH), 7.21−7.82 (m, 20 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 25.0 (CH_3), 38.5 (d, $^1J_{PC}$ = 63.1 Hz, C−P), 44.6 (CH), 128.6−131.8 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 22.3, 30.8. − MS (70 eV); *m/z* (%): 459 (19) [M^+]. − $C_{27}H_{27}NO_2P_2$ (459): calcd. C 70.58, H 5.92, N 3.05; found C 70.77, H 5.86, N 2.97.

15b: Chromatographic separation gave 1.58 g of **15b** (80%) as a colorless oil, R_f = 0.1 (ethyl acetate). − IR (NaCl): ν = 3429 cm^{-1} (NH), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.22 (m, 9 H, CH_3), 2.51 (m, 2 H, CH_2), 3.20 (m, NH), 3.66 (m, 1 H, CH), 3.93 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 7.36−7.77 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 24.3 (CH_3), 38.0 (dd, $^1J_{PC}$ = 68.6 Hz, $^3J_{PC}$ = 5.5 Hz, C−P), 44.8 (CH), 62.3 (CH_2), 128.4−133.3 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 7.6, 30.2. − MS (70 eV); *m/z* (%): 395 (7) [M^+]. − $C_{19}H_{27}NO_4P_2$ (395): calcd. C 57.72, H 6.88, N 3.54; found C 58.01, H 6.94, N 3.56.

15c: The crude product was triturated with diethyl ether, giving 1.66 g of **15c** (70%) as a white solid, m.p. 57−60°C. − IR (KBr): ν = 3402 cm^{-1} (NH), 1192 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.77 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 1.77 (m, 2 H, CH_2), 2.72 (m, 2 H, CH_2), 2.90 (m, NH), 3.29 (m, 1 H, CH), 7.20−7.83 (m, 20 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 30.6 (CH_2), 35.9 (d, $^1J_{PC}$ = 68.1 Hz, C−P), 50.3 (CH), 128.3−133.1 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 22.5, 31.2. − MS (70 eV); *m/z* (%): 473 (9) [M^+]. − $C_{28}H_{29}NO_2P_2$ (473): calcd. C 71.03, H 6.17, N 2.96; found C 71.23, H 6.25, N 2.97.

15d: Chromatographic separation gave 1.64 g of **15d** (80%) as a colorless oil, R_f = 0.08 (ethyl acetate). − IR (NaCl): ν = 3436 cm^{-1} (NH), 1186 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.79 (t, $^3J_{HH}$ = 6.4 Hz, 3 H, CH_3), 1.19 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.60 (m, 2 H, CH_2), 2.49 (m, 2 H, CH_2), 3.43 (m, 1 H, CH), 3.91 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 4.20 (m, NH), 7.35−7.77 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 10.2 (CH_3), 16.2 (CH_3), 29.2 (CH_2), 32.5 (d, $^1J_{PC}$ = 68.6 Hz, C−P), 50.4 (CH), 62.2 (CH_2), 128.4−134.4 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 8.1, 30.5. − MS (70 eV); *m/z* (%): 409 (26) [M^+]. − $C_{20}H_{29}NO_4P_2$ (409): calcd. C 58.68, H 7.14, N 3.42; found C 56.82, H 7.06, N 3.52.

15e: The crude product was triturated with diethyl ether, giving 2.05 g of **15e** (75%) as a yellow solid, m.p. 74−76°C. − IR (KBr): ν = 3180 cm^{-1} (NH), 1185 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 2.2 (s, 3 H, CH_3), 2.67 (m, 2 H, CH_2), 3.00 (m, 2 H, CH_2), 3.30 (m, NH), 3.52 (m, 1 H, CH), 6.80−7.72 (m, 24 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_3), 35.8 (d, $^1J_{PC}$ = 69.2 Hz, C−P), 43.1 (CH_2), 50.5 (CH), 128.2−136.0 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 25.5, 31.1. − MS (70 eV); *m/z* (%): 549 (19) [M^+]. − $C_{34}H_{33}NO_2P_2$ (549): calcd. C 74.31, H 6.05, N 2.55; found C 74.53, H 6.15, N 2.57.

15f: Chromatographic separation gave 1.92 g of **15f** (79%) as a colorless oil, R_f = 0.12 (ethyl acetate). − IR (NaCl): ν = 3415 cm^{-1} (NH), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.18 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.29 (s, 3 H, CH_3), 2.55 (m, 2 H, CH_2), 2.70 (m, NH), 2.97 (d, $^3J_{PH}$ = 6.3 Hz, 2 H, CH_2), 3.68 (m, 1 H, CH),

3.88 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 6.92−7.97 (m, 14 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.1 (CH_3), 21.0 (CH_3), 34.8 (dd, $^1J_{PC}$ = 68.3 Hz, $^3J_{PC}$ = 4.5 Hz, C−P), 42.5 (CH_2), 50.1 (CH), 62.2 (CH_2), 128.5−135.9 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 7.5, 30.5. − MS (70 eV); *m/z* (%): 485 (6) [M^+]. − $C_{26}H_{33}NO_4P_2$ (485): calcd. C 64.32, H 6.85, N 2.88; found C 64.52, H 7.02, N 2.90.

16a: Chromatographic separation gave 1.39 g of **16a** (70%) as a yellow oil, R_f = 0.09 (ethyl acetate). − IR (NaCl): ν = 3409 cm^{-1} (NH), 1024 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.28 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.82 (m, 2 H, CH_2), 1.92 (d, $^3J_{HH}$ = 9.0 Hz, 3 H, CH_3), 3.63 (m, 1 H, CH), 4.01 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 4.22 (m, NH), 7.21−7.87 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 24.2 (CH_3), 35.1 (d, $^1J_{PC}$ = 136.7 Hz, C−P), 61.7 (CH_2), 62.8 (CH), 126.5−132.6 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 22.7, 30.3. − MS (70 eV); *m/z* (%): 395 (16) [M^+]. − $C_{19}H_{27}NO_4P_2$ (395): calcd. C 57.27, H 6.88, N 3.54; found C 57.52, H 6.92, N 3.50.

16b: Chromatographic separation gave 1.32 g of **16b** (65%) as a colorless oil, R_f = 0.07 (ethyl acetate). − IR (NaCl): ν = 3327 cm^{-1} (NH), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 1.28 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.77 (m, 2 H, CH_2), 2.20 (m, 2 H, CH_2), 2.80 (m, NH), 3.61 (m, 1 H, CH), 4.10 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 7.29−7.97 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 16.1 (CH_3), 29.2 (CH_2), 31.4 (d, $^1J_{PC}$ = 135.8 Hz, C−P), 48.9 (CH), 60.6 (CH_2), 127.2−133.6 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 22.5, 29.5. − MS (70 eV); *m/z* (%): 409 (11) [M^+]. − $C_{20}H_{29}NO_4P_2$ (409): calcd. C 58.68, H 7.14, N 3.42; found C 58.51, H 7.04, N 3.36.

16c: Chromatographic separation gave 1.34 g of **16c** (78%) as a yellow oil, R_f = 0.08 (ethyl acetate). − IR (NaCl): ν = 3450 cm^{-1} (NH), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3), 1.33 (t, $^3J_{HH}$ = 7.02 Hz, 12 H, CH_3), 1.68 (m, 2 H, CH_2), 2.05 (m, 2 H, CH_2), 2.40 (m, NH), 3.30 (m, H, CH), 4.09 (m, $^3J_{PH}$ = 4.00 Hz, 8 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 16.3 (CH_3), 29.6 (CH_2), 31.8 (d, $^1J_{PC}$ = 136.7 Hz, C−P), 49.4 (CH), 61.9 (CH_2). − ^{31}P NMR ($CDCl_3$): δ = 8.2, 29.5. − MS (70 eV); *m/z* (%): 345 (21) [M^+]. − $C_{12}H_{29}NO_6P_2$ (345): calcd. C 41.74, H 8.46, N 4.06; found C 41.92, H 8.50, N 3.99.

16d: Chromatographic separation gave 1.74 g of **16d** (72%) as a colorless oil, R_f = 0.1 (ethyl acetate). − IR (NaCl): ν = 3327 cm^{-1} (NH), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.37 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 2.07 (m, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 2.83 (m, 2 H, CH_2), 3.61 (m, 1 H, CH), 3.80 (m, NH), 4.09 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2), 7.03−7.96 (m, 14 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.4 (CH_3), 21.0 (CH_3), 32.0 (d, $^1J_{PC}$ = 137.7 Hz, C−P), 43.9 (d, $^3J_{PC}$ = 16.6 Hz, CH_2), 49.5 (CH), 61.4 (CH_2), 125.7−136.0 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 22.7, 29.4. − MS (70 eV); *m/z* (%): 393 (2) [M^+]. − $C_{26}H_{32}NO_4P_2$ (393): calcd. C 64.50, H 6.66, N 2.89; found C 64.66, H 6.56, N 2.93.

16e: Chromatographic separation gave 1.57 g of **16e** (75%) as a yellow oil, R_f = 0.1 (ethyl acetate). − IR (NaCl): ν = 3380 cm^{-1} (NH), 1031 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.34 (t, $^3J_{HH}$ = 7.02 Hz, 12 H, CH_3), 1.89 (m, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 2.85 (m, 2 H, CH_2), 3.70 (m, 1 H, CH), 4.17 (m, $^3J_{PH}$ = 4.00 Hz, 8 H, CH_2), 4.60 (m, NH), 7.06−7.28 (AA′BB′ system, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 16.3 (CH_3), 21.0 (CH_3), 32.6 (d, $^1J_{PC}$ = 137.8 Hz, C−P), 43.9 (d, $^3J_{PC}$ = 16.5 Hz, CH_2), 49.5 (CH), 61.4 (CH_2), 128.2−136.0 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 7.6, 29.1. − MS (70 eV); *m/z* (%): 419 (34) [M^+]. − $C_{18}H_{33}NO_6P_2$ (419): calcd. C 51.55, H 7.45, N 3.34; found C 51.47, H 7.49, N 3.39.

General Procedure for the Preparation of Amines **17** *and* **18**: A 100-ml 2-necked flask, fitted with a magnetic stirrer, was charged with 5 mmol of the phosphane oxide **15** or the phosphonate **16**, and 20 ml of 2 N aq. HCl. The mixture was stirred (2−6 h) and was then basified with 2 N aq. NaOH, washed with water, and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel. The amines **17** and **18** could also be obtained in a "one-pot" reaction from **11** or **12** by following the same general procedures for the preparation of **13/13′**, **14**, **15** and **16**, and **17** and **18**, but without isolating the intermediate products. Triethylamine hydrochloride was filtered off under nitrogen and the solvents were removed from the filtrate in vacuo. The amines **17** and **18** were purified as described above.

17a: Chromatographic separation gave 0.78 g of **17a** (60%) as a yellow oil, R_f = 0.10 (ethyl acetate). − IR (NaCl): ν = 3362 cm^{-1} (NH_2), 1185 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.20 (d, $^3J_{HH}$ = 6.0 Hz, 3 H, CH_3), 2.42 (m, 2 H, CH_2), 3.42 (m, 1 H, CH), 4.80 (m, NH_2), 7.29−7.78 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 25.3 (d, $^3J_{PC}$ = 11.0 Hz, CH_3), 38.6 (d, $^1J_{PC}$ = 71.1 Hz, C−P), 42.8 (CH), 128.1−134.0 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 31.3. − MS (70 eV); *m/z* (%): 259 (3) [M^+]. − $C_{15}H_{18}NOP$ (259): calcd. C 69.48, H 7.06, N 5.40; found C 69.62, H 7.15, N 5.46.

17b: Chromatographic separation gave 0.91 g of **17b** (67%) as a yellow oil, R_f = 0.07 (ethyl acetate). − IR (NaCl): ν = 3388 cm^{-1} (NH_2), 1180 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3), 1.50 (m, 2 H, CH_2), 2.64 (m, 2 H, CH_2), 3.33 (m, 1 H, CH), 6.20 (m, NH_2), 7.44−7.79 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 10.0 (CH_3), 28.4 (d, $^3J_{PC}$ = 10.5 Hz, C−P), 32.0 (d, $^1J_{PC}$ = 68.6 Hz, CH_2), 49.8 (CH), 128.8−132.2 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 32.3. − MS (70 eV); *m/z* (%): 274 (14) [M^+ + 1]. − $C_{16}H_{20}NOP$ (273): calcd. C 70.31, H 7.37, N 5.12; found C 70.42, H 7.35, N 5.16.

17c: Chromatographic separation gave 1.13 g of **17c** (65%) as a yellow oil, R_f = 0.08 (ethyl acetate). − IR (NaCl): ν = 3422 cm^{-1} (NH_2), 1179 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 2.40 (m, 2 H, CH_2), 2.76 (m, 2 H, CH_2), 3.00 (m, NH_2), 3.49 (m, 1 H, CH), 7.07−7.70 (m, 14 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 21.0 (CH_3), 35.5 (d, $^1J_{PC}$ = 72.2 Hz, C−P), 44.7 (CH_2), 48.6 (CH), 128.6−136.1 (aromatic C). − ^{31}P NMR ($CDCl_3$): δ = 32.4. − MS (70 eV); *m/z* (%): 350 (12) [M^+ + 1]. − $C_{22}H_{24}NOP$ (349): calcd. C 75.63, H 6.92, N 4.01; found C 75.70, H 7.01, N 4.06.

18a: Chromatographic separation gave 0.64 g of **18a** (65%) as a yellow oil, R_f = 0.05 (ethyl acetate). − IR (NaCl): ν = 3423 cm^{-1} (NH_2), 1030 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH_3), 1.30 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.78 (m, 2 H, CH_2), 2.43 (s, NH_2), 3.14 (m, 1 H, CH), 4.08 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 16.4 (CH_3), 21.5 (d, $^3J_{PC}$ = 9.7 Hz, CH_3), 32.9 (d, $^1J_{PC}$ = 136.8 Hz, C−P), 45.7 (CH), 61.5 (CH_2). − ^{31}P NMR ($CDCl_3$): δ = 30.1. − MS (70 eV); *m/z* (%): 195 (10) [M^+]. − $C_7H_{18}NO_3P$ (195): calcd. C 43.08, H 9.23, N 7.18; found C 43.17, H 9.40, N 7.02.

18b: Chromatographic separation gave 0.68 g of **18b** (65%) as a yellow oil, R_f = 0.08 (ethyl acetate). − IR (NaCl): ν = 3398 cm^{-1} (NH_2), 1080 (P=O). − ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 1.31 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.47 (m, 2 H, CH_2), 1.85 (m, 2 H, CH_2), 2.80 (m, NH_2), 3.10 (m, 1 H, CH), 4.09 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 10.0 (CH_3), 16.3 (CH_3), 30.9 (CH_2), 32.9 (d, $^1J_{PC}$ = 138.0 Hz, C−P), 48.2 (CH), 61.5 (CH_2). − ^{31}P NMR ($CDCl_3$): δ = 30.9. − MS (70 eV); *m/z* (%): 209 (19) [M^+]. − $C_8H_{20}NO_3P$ (209): calcd. C 45.90, H 9.57, N 6.70; found C 46.03, H 9.50, N 6.74.

18c: Chromatographic separation gave 0.97 g of **18c** (65%) as a yellow oil, R_f = 0.08 (ethyl acetate). − IR (NaCl): ν = 3418 cm^{-1} (NH_2), 1070 (P=O). − ^1H NMR ($CDCl_3$): δ = 1.28 (t, $^3J_{HH}$ = 7.02 Hz, 6 H, CH_3), 1.85 (m, 2 H, CH_2), 2.25 (s, 3 H, CH_3), 2.71 (m, 2 H, CH_2), 2.80 (m, NH_2), 3.40 (m, 1 H, CH), 4.02 (m, $^3J_{PH}$ = 4.00 Hz, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 16.3 (CH_3), 20.9 (CH_3), 32.5 (d, $^1J_{PC}$ = 138.5 Hz, C−P), 43.9 (CH_2), 48.2 (CH), 61.7 (CH_2). − ^{31}P NMR ($CDCl_3$): δ = 30.6. − MS (70 eV); *m/z* (%): 285 (6) [M^+]. − $C_{14}H_{24}NO_3P$ (285): calcd. C 58.90, H 8.42, N 4.90; found C 58.98, H 8.50, N 4.86.

Alternative Procedure for the Preparation of Amines **17**: A 100-ml 2-necked flask, fitted with a reflux condenser and a magnetic stirrer, was charged with 5 mmol of the phosphane oxide **13** or **13′**, 30 ml of ethanol, and 2 ml (15 mmol) of $BH_3 \cdot Py$ complex. After 2 h, 10 ml of 30% aq. HCl was added. The mixture was stirred for 1 d, and was then made basic with aqueous Na_2CO_3 solution, washed with water, and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

17a: Chromatographic separation gave 0.78 g of **17a** (60%).

17b: Chromatographic separation gave 0.81 g of **17b** (60%).

General Procedure for the Preparation of Amines **17** *from N-PMP-Amines* **22**: A solution of the *N*-PMP-amine **22** (5 mmol) in acetonitrile (30 ml) was cooled to 0°C and then treated with a solution of CAN (8.2 g, 15 mmol) in water (70 ml) over a period of 5 min. The reaction mixture was stirred at this temperature for 1 h, then diluted with 300 ml of water, and extracted with ethyl acetate (3 × 50 ml). The combined organic extracts were washed with 20% sodium sulfite solution, satd. sodium bicarbonate solution, and water, and then dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel.

17a: Chromatographic separation gave 0.78 g of **17a** (61%).

17b: Chromatographic separation gave 0.85 g of **17b** (63%).

Hydrogenolysis of Amines **22** *and* **23**. − *Synthesis of Amines* **17** *and* **18**: To a solution of the appropriate amine **22** or **23** (5 mmol) in 25 ml of dry methanol was added 0.25 g of 20% $Pd(OH)_2/C$. The mixture was hydrogenated under 4−5 atm hydrogen and the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by filtration and the filtrate was washed with 10% citric acid (10 ml). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated to afford the pure product.

17a: Chromatographic separation gave 0.91 g of **17a** (71%).

18a: Chromatographic separation gave 0.72 g of **18a** (73%).

18b: Chromatographic separation gave 0.72 g of **18b** (69%).

General Procedure for the Preparation of Phosphonic Acids **19**: A 100-ml 2-necked flask, fitted with a reflux condenser and a magnetic stirrer, was charged with 5 mmol of the amine **18** and 15 ml of 20% aq. HCl. The mixture was refluxed for 6 h and then the solvent was removed in a rotary evaporator. The resinous residue was recrystallized from methanol/propylene oxide.

19a: Recrystallization from methanol/propylene oxide gave 0.58 g of **19a** (76%) as a white solid, m.p. > 250°C. − IR (KBr): ν = 3300 cm^{-1} (NH_2 and OH), 1180 (P=O). − ^1H NMR (D_2O): δ = 1.14 (d, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 1.88 (m, 2 H, CH_2), 3.51 (m, 1 H, CH), 4.00 (m, NH_2 and OH). − ^{13}C NMR (D_2O): δ = 14.0 (CH_3), 32.3 (d, $^1J_{PC}$ = 132.9 Hz, C−P), 44.4 (CH). − ^{31}P NMR (D_2O): δ = 20.7. − $C_3H_{10}NO_3P$ (153): calcd. C 25.90, H 7.19, N 10.07; found C 25.79, H 7.27, N 10.00.

19b: Recrystallization from methanol/propylene oxide gave 0.58 g of **19b** (76%) as a white solid, m.p. > 250°C. − IR (KBr): ν = 3388 cm^{-1} (NH_2 and OH), 1175 (P=O). − ^1H NMR (D_2O): δ = 0.94 (t, $^3J_{HH}$ = 6.9 Hz, 3 H, CH_3), 1.21 (m, 2 H, CH_2), 1.70 (m, 2 H, CH_2), 3.30 (m, 1 H, CH), 4.60 (m, NH_2 and OH). − ^{13}C NMR (D_2O): δ = 9.8 (CH_3), 28.9 (CH_2), 29.8 (d, $^1J_{PC}$ = 134.5 Hz, C−P), 38.0 (CH). − ^{31}P NMR (D_2O): δ = 22.6. − $C_4H_{12}NO_3P$ (153): calcd. C 31.37, H 7.84, N 9.15; found C 31.48, H 7.92, N 9.09.

19c: Recrystallization from methanol/propylene oxide gave 0.97 g of **19c** (68%) as a white solid, m.p. > 250°C. − IR (KBr): ν = 3388 cm^{-1} (NH_2), 1170 (P=O). − ^1H NMR (D_2O): δ = 1.90 (m, 2 H, CH_2), 2.26 (s, 3 H, CH_3), 2.96 (m, 2 H, CH_2), 3.67 (m, 1 H, CH), 6.20 (m, NH_2 and OH), 7.18 (m, 4 H, aromatic C). − ^{13}C NMR (D_2O): δ = 20.1 (CH_3), 29.8 (d, $^1J_{PC}$ = 132.9 Hz, CH_2), 38.9 (d, $^3J_{PC}$ = 11.1 Hz, CH_2), 49.6 (CH), 129.5−129.7 (aromatic C). − ^{31}P NMR (D_2O): δ = 20.0. − $C_{10}H_{16}NO_3P$ (153): calcd. C 52.40, H 6.99, N 6.11; found C 52.29, H 7.12, N 6.09.

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