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Synthesis of Secondary *E*-Allylamines and β-Aminophosphorylated Compounds from β-Functionalized Enamines Derived from Phosphonium Salts, Phosphine Oxides and Phosphonates.

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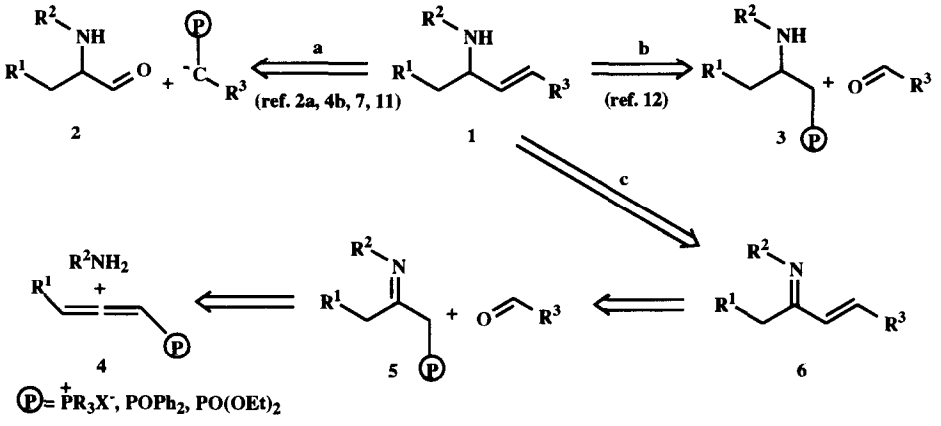
Abstract: A simple and stereoselective synthesis of secondary *E*-allylamines **1** and **20** from functionalized enamines derived from phosphine oxides **8**, phosphonium salts **11** and phosphonates **12** is reported. Phosphorus compounds **8**, **11** and **12** are obtained by amine addition to phosphorylated allenes **7**, **10** and phosphonium salts **9**. Reduction of enamines **8** and **12** with hydrides leads to the formation of β-amino phosphine oxides **13** and phosphonates **14**. Allylamines **1**, **20** and β-aminophosphorylated derivatives **13** and **14** can also be obtained in "*one pot*" reaction from allenes **7**, **10** and phosphonium salts **9** without the isolation and purification of enamines **8**, **11** and **12**.

Allylamines represent an important class of compounds not only for their occurrence as natural substances[1] and vinylogous polypeptides,[2] but also for their interest in medicinal chemistry given their activities such as chemotherapeutic agents,[3] enzyme inhibitors[4] and antifungal activities.[5] Moreover, allylamines are rapidly gaining interest as target compounds of synthetic organic methodologies due to their usefulness as a protective group[6] and in the preparation of acyclic compounds such as β-aminohydroxylamines,[7a] β[7b]-and γ-aminoacids,[7c,d] pseudopeptides,[2b] spermidine derivatives[7e] as well as of five[8a] and six[8b] membered heterocycles.

While there are many approaches available for allylamine preparation,[1a] synthetic routes to secondary allylamines are relatively few and often lead to mixtures of regio and stereoisomers. Despite the growing interest in these compounds, in recent years considerable efforts have focussed on their preparation by means of transition metal complexes,[9] amination reagents,[10] and olefination reactions by using phosphorus ylides,[2a,4b,7b,d,11a] and phosphonates[7c,11b] with carbonyl compounds **2** (route a, Scheme 1). Conversely, olefination reaction of *N*-alkyl-β-aminoethyl phosphonium salts[12a] (**3**, R^1CH_2=H) and *N*,*N*-dialkyl-β-aminoethyl phosphine oxides[12b] leads to secondary and tertiary allylamines (route b, Scheme 1). However, attempts to extend this route to the α-substituted derivatives have failed.[12b]

In connection with our interest in the preparation and in the use of phosphorus-nitrogenated compounds[13] as building blocks in synthetic strategies we have used β-functionalized enamines derived from phosphazenes, phosphonium salts, phosphine oxides and phosphonates as starting materials in the synthesis of heterocycles such as pyrazoles,[14a] pyridones,[14b] aza-[14c] and diaza-phosphirines[14d] and acyclic derivatives such as oximes,[15a] hydrazones,[15b] functionalized enamines,[15c] azadienes[15d] and aminodienes.[15e] In this context, it is noteworthy that we have recently used phosphorus compounds as homologation reagents[16] for the conversion of carbonyl derivatives into allylamines with the introduction of two additional carbon atoms in the resulting chain. Here we aim to extend this methodology[17] to the preparation of a wide range of secondary *E*-allylamines and to explore the synthetic use of β-functionalized enamines and/or imines in the preparation of β-aminophosphorylated compounds, α,β-unsaturated imines, β-hydroxyimines and β-hydroxyamines. Retrosynthetically, we envisaged obtaining allylamines **1** (route c, Scheme 1) through simple addition of amines to phosphorylated allenes **4** (or the synthetic equivalent the propargylic phosphonium salts[15b]) followed by an olefination reaction of β-imino phosphorus compounds **5** (or their synthetic equivalents the tautomeric enamine derivatives) and subsequent selective reduction of the carbon-nitrogen double bond of α,β-unsaturated imines **6**.



Scheme 1

RESULTS AND DISCUSSION

Synthesis of β-functionalized phosphine oxides **8**, phosphonium salts **11** and phosphonates **12**.

The preparation of phosphine oxide derivatives **8** was accomplished very easily and in very high yields by means of simple addition of achiral and chiral aliphatic, aromatic and functionalized amines to phosphine oxide allenes **7** in refluxing acetonitrile. Compounds **8** were characterized by their spectroscopic data, which indicate that they are isolated as a mixture of *Z*- and *E*-β-enamino compounds **8** when alkyl amines were used (see table 1), although for our purposes the separation of *Z*-and *E*-isomers is not necessary for subsequent reactions. Thus, the *^{31}P-NMR* spectrum for **8a** showed two different absorptions at δ_P 24.9 and 28.3 ppm in an approximate isomer ratio 75 : 25 as evidenced by the relative peak areas for each compound, in which the

high-field chemical shift corresponds to the *E*-isomer **8a**. Further examinations of the ^{1}H and ^{13}C-*NMR* spectra is consistent with enamine structure of the phosphine oxide. In the ^{1}H-*NMR* spectrum of **8a**, the vinylic proton resonates at δ_H 4.50 ppm as a well resolved doublet with coupling constant of $^{2}J_{PH}$=17.1 Hz, and the methyl group gives a singlet at δ_H 1.94 ppm, while the ^{13}C-*NMR* shows absorptions at δ_C 80.6 ppm ($^{1}J_{PC}$=128.0 Hz) and 22.4 ppm ($^{3}J_{PC}$=6.0 Hz) assignable to the carbon bonded to phosphorus and the methyl group of the *E*-isomer.[15b-18] Conversely, for **8a** the *Z*-isomer showed clearly different absorptions, namely a doublet at δ_H 4.00 ppm ($^{2}J_{PC}$=22.0 Hz) for the vinylic proton as well as a low-field signal for the methyl group at δ_H 2.12 ppm, while in the ^{13}C-*NMR* spectrum the absorption of methine carbon is shifted to higher field (δ_C 74.9 ppm) with a lower value of the phosphorus-carbon coupling constant ($^{1}J_{PC}$=116.0 Hz) relative to those of the *E*-isomer. Vicinal ^{13}C-^{31}P coupling constant ($^{3}J_{PC}$=15.1 Hz) showed that the methyl group and phosphorus atom in the β-enamino compound **8a** are related *trans*.[15b,18]

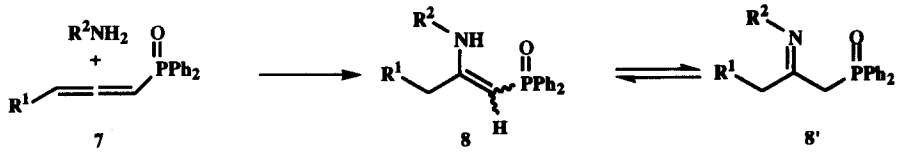
Table 1. β-Enaminophosphine Oxides **8** prepared.

Entry	Compound	R^1	R^2	Yield (%)[a]	E/ Z ratio[b]	m.p. (°C)
1	**8a**	H	^{t}Bu	89	75/25	146-148
2	**8b**	H	C_6H_5-CH_2	91	55/45	145-147
3	**8c**	H	H_2C=CH-CH_2	85	60/40	127-129
4	**8d**	H	HO-CH_2CH_2	90	80/20	124-126
5	**8e**	H	EtO_2C-CH_2	90	75/25	86-88
6	**8f**	H	4-Me-C_6H_4	88	5/10/85[c]	127-129
7	**8g**	H	C_6H_5	81	5/10/85[c]	116-118
8	**8h**	H	C_6H_5-CH-CH_3(±)	89	50/50	169-171
9	**8i**	H	C_6H_5-CH-CH_3 (*R*)	85	50/50	168-170
10	**8j**	H	C_6H_5-CH-CH_3 (*S*)	90	55/45	170-172
11	**8k**	Me	^{t}Bu	87	75/25	177-179
12	**8l**	Me	H_2C=CH-CH_2	89	55/45	106-108
13	**8m**	Me	EtO_2C-CH_2	83	75/25	118-120
14	**8n**	Me	4-Me-C_6H_4	88	10/15/75[c]	145-147
15	**8o**	Me	C_6H_5	85	6/9/85[c]	78-80

[a] Yield of isolated purified product. [b] *E*/ *Z* ratio by ^{31}P-*NMR* assign. [c] *E*-**8**/ *Z*-**8**/ **8'** by ^{31}P-*NMR* assign.

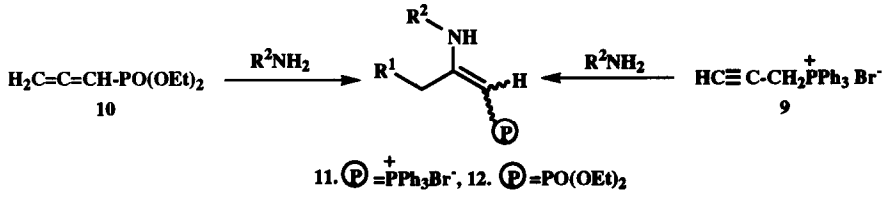
The scope of this reaction of formation of β-enamines **8** through simple addition of amines to allenes derived from phosphine oxides is quite general, given that the method is applicable not only to chiral (table 1, entries 9, 10) and achiral aliphatic amines (table 1, entries 1, 2, 8) but also to functionalized (table 1, entries 3, 4, 5, 12, 13) and aromatic amines (table 1, entries 6, 7, 14, 15). It is noteworthy that when arylamines were used, a mixture of both *Z*- and *E*-enamines **8** (minor products) and the β-iminophosphine oxides **8'** (major compounds) were obtained (table 1, entries 6, 7, 14, 15), although for our subsequent purposes the separation of the enamines and imines is not necessary. The imine **8'f**, for example, showed clearly different absorption

related to the enamine tautomers **8f**, namely a doublet at δ_H 3.57 ppm ($^2J_{PH}$=14.8 Hz) for the methylene protons as well as a high-field signal for the methyl group at 2.20, while in the *^{13}C-NMR* spectrum the absorption of methylene carbon is shifted to higher field (δ_C 45.1 ppm) with a lower value of the phosphorus-carbon coupling constant ($^1J_{PC}$=61.0 Hz) relative to those to the *E*-and *Z*-enamines **8f**.



Scheme 2

It is well known that for the construction of carbon-carbon double bonds,[19] not only phosphine oxide derivatives (Horner reaction) but also phosphonium salts (Wittig reaction) and phosphonates (Wadsworth-Emmons reaction) are very useful reagents. Therefore, taking into account our results in the preparation of β-enamino derivatives **8**, we tried to extend this reaction and to explore whether other allenes such as allenes derived from phosphonates **10** as well as the allenes derived from phosphonium salts (or their synthetic equivalent, the commercially available propargyl phosphonium salt[15b] **9**) showed a similar reaction pattern to that observed in the case of allenes **7** leading to new β-functionalized phosphorus compounds **11** and **12** in a similar way to that previously reported for hydrazines.[15b] Thus, addition of aromatic, functionalized and aliphatic chiral and achiral amines to commercially available propargyl phosphonium bromide **9** in refluxing of acetonitrile (*TLC* control) led to the exclusive formation of *E*-β-enamino phosphonium salts **11** in excellent yield (Scheme 3, Table 2, entries 1-6). Similarly, the allene derived from phosphonate ester **10** reacted with achiral and chiral amines and gave β-functionalized phosphonates **12** in very high yield (table 2, entries 7-11). Compounds **12** were characterized by their spectroscopic data, which indicate that they are isolated as the *Z*- and *E*-isomer, although as we have shown before, for our purposes the separation of both *Z*-and *E*-isomers is not necessary for subsequent reactions.



Scheme 3

Table 2. β-Enamino Phosphonium Salts **11** and phosphonates **12** prepared.

Entry	Compound	R^2	Yield (%)[a]	E/ Z ratio[b]	m.p. (°C)
1	**11a**	^tBu	89	100/0	212-214(d)
2	**11b**	C_6H_5-CH_2	91	100/0	259-260(d)
3	**11c**	H_2C=CH-CH_2	92	100/0	264-265(d)
4	**11e**	EtO_2C-CH_2	81	100/0	175-176(d)
5	**11f**	4-Me-C_6H_4	78	100/0	>285(d)
6	**11i**	C_6H_5-CH-CH_3 (*R*)	90	100/0	222-223(d)
7	**12a**	^tBu	87	65/35	oil[c]
8	**12c**	H_2C=CH-CH_2	77	60/40	oil[c]
9	**12h**	C_6H_5-CH-CH_3 (±)	85	50/50	oil[c]
10	**12i**	C_6H_5-CH-CH_3 (*R*)	83	50/50	oil[c]
11	**12j**	C_6H_5-CH-CH_3 (*S*)	80	50/50	oil[c]

[a] Yield of isolated purified product. [b] *E/ Z* ratio by ^{31}P-*NMR* assign. [c] Oils isolated after "trap to trap" high vacuum distilled (10^{-5} torr).

Reduction of β-enaminophosphine oxides **8** and phosphonates **12** with hydride reagents. Synthesis of β-amino phosphorus derivatives **13** and **14**.

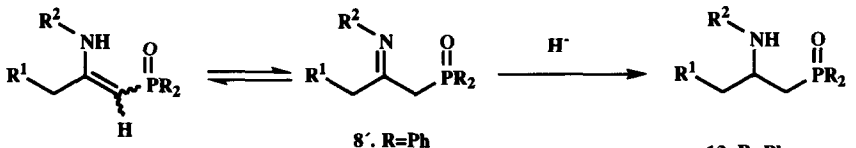
The enamine group itself is resistant to reduction by hydrides, whereas the reduction to amines often observed when sodium borohydride or other hydrides are used is due to the protonation of the enamine by the solvent (aqueous methanol). In fact, simple enamine hydrochlorides are easily and quantitatively reduced within a few minutes, whereas if the enamine is conjugated with electron-withdrawing groups, i. e. the carbonyl groups, reduction becomes more difficult and in some cases could be resistent to reduction.[20]

Functionalized enamines **8** and **12** could be useful intermediates in organic synthesis in order to provide an easy and efficient access to β-aminophosphine oxides and phosphonates by means of the reduction reaction of these enamines with hydride reagents. In this context, it is noteworthy that β-amino phosphorous derivatives represent an important class of compounds not only because they can constitute the peptide structure[21a] but also for their biological activities as enzyme inhibitors,[21b,c] modulator of the quisqualic acid/phosphoinositide coupled metabotropic excitatory amino acid receptor subtype[21d] and in the synthesis of phosphorus analoga of Pantotheine.[21e] However, despite the growing interest in these compounds, there is only a relatively small number of procedures available for the synthesis of these compounds.[21e,22]

Thus, the treatment of chiral and achiral β-enamino phosphine oxides **8** with sodium borohydride in refluxing ethanol led to the formation of β-amino functionalized derivatives **13** with excellent yields (Table 3, entries 1-9). Functional groups present in the substrate such as the phosphine oxide group and carbon-carbon double bonds (table 3, entry 3) were not reduced. Spectroscopic data were in agreement with the assigned structure. Similarly, β-enamines derived from phosphonates esters **12** reacted with $NaBH_4$ and gave β-amino phosphonates **14** in very high yield (Table 3, entries 10-14). The reduction of these secondary functionalized

enamines **8** and **12** with hydrides could have occurred through their imine forms **8'** and **12'** in a similar way to that reported for β-sulphinyl enamines.[23]

Racemic and chiral enamines (Table 3, entries 6-8 and 12-14) were also reduced with $NaBH_4$ in order to elucidate the stereoselectivity of the reaction. The reduction of functionalized compounds **8h-j** and **12h-j** derived from racemic, *R* or *S* α-methylbenzylamine with $NaBH_4$ in ethanol occurred with good yield and moderate diastereoselectivity (de = 40-49%) favouring the *R* configuration at the newly formed stereogenic center of compounds **13h-j** and **14h-j** (Table 3, entries 6-8 and 12-14). The use of modified borohydrides such as aminoborohydrides (lithium diethylamino borohydride, *LAB*[24]) increases the diastereomeric induction of the reduction giving a diastereomeric excess of 52-68%.



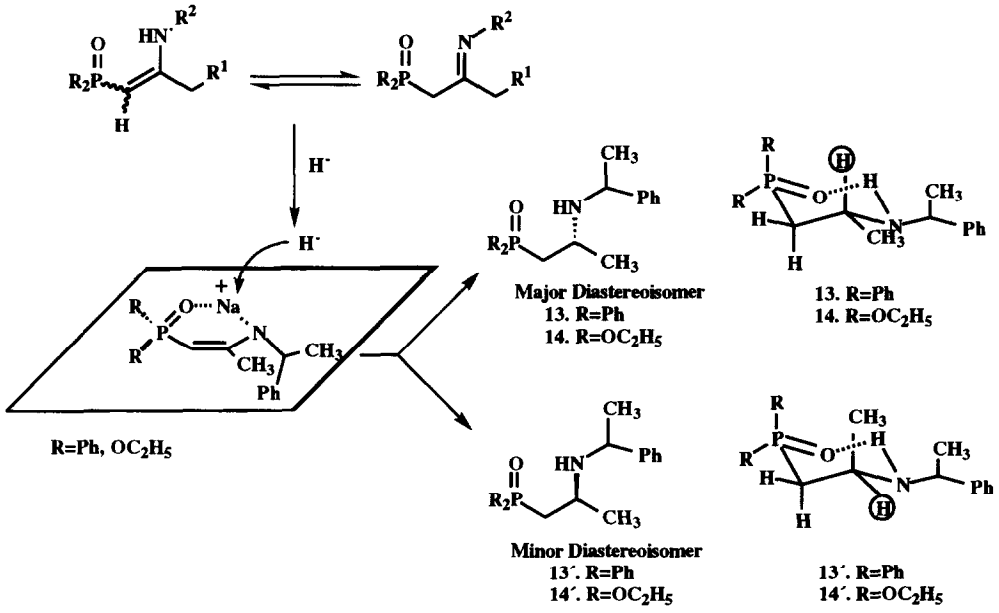
Scheme 4

Table 3. β-aminophosphine oxide **13** and phosphonates **14** obtained.

Entry	Compound	R^1	R^2	Yield (%)[a,b]	de[c,d] ($NaBH_4$)
1	**13a**	H	^tBu	87(71)	
2	**13b**	H	C_6H_5-CH_2	88	
3	**13c**	H	H_2C=CH-CH_2	84	
4	**13d**	H	HO-CH_2CH_2	87	
5	**13f**	H	4-Me-C_6H_4	81(69)	
6	**13h**	H	C_6H_5-CH-CH_3 (±)	79	41%(65%)
7	**13i**	H	C_6H_5-CH-CH_3 (*R*)	88	45%(68%)
8	**13j**	H	C_6H_5-CH-CH_3 (*S*)	87	42%
9	**13k**	Me	^tBu	89	
10	**14a**	H	^tBu	78	
11	**14c**	H	H_2C=CH-CH_2	85(71)	
12	**14h**	H	C_6H_5-CH-CH_3 (±)	79	45%(55%)
13	**14i**	H	C_6H_5-CH-CH_3 (*R*)	78	49%(65%)
14	**14j**	H	C_6H_5-CH-CH_3 (*S*)	81	40%(52%)

[a] Yield of isolated purified product. [b] Yields given in parenthesis refer to the "*one pot*" process from allenes **7** and **10**. [c] Diastereomeric excess determined by ^{31}P-*NMR*. [d] Yields given in parenthesis refer to the use of *LAB* as reducing agent.

We assigned diastereoisomers **13** and **13'** on the basis of *^{13}C-NMR*. Small phosphorus-carbon coupling constant ($^3J_{PC}$=7 Hz) is observed for the methyl group of **13h**, while a higher value of this phosphorus-carbon coupling constant ($^3J_{PC}$=12.3 Hz) is observed for the *axial* methyl group of **13'h** (see Scheme 5). These results are in good agreement with the reported data for this type of coupling constants between the phosphorus atom and *equatorial* ($^3J_{PC}$=4-8 Hz) and *axial* alkyl groups ($^3J_{PC}$=11-13 Hz)[25] and support the stereochemical assignment. The diastereomeric excess obtained was determined by *^{31}P-*, *^{1}H-NMR* and capillary *GC* analysis and suggested that the approach of the hydride (Scheme 5) to the cyclic intermediate from the upper part of the plane could favour the formation of the major diastereoisomer, whereas the approach in the direction of the underside of the plane is less favourable since it may meet the substituent of the nitrogen atom. A Felkin approach to the imine often found with ketones[26] could also explain the regioselectivity observed.



Scheme 5

From a preparative point of view it is noteworthy that the synthesis of β-amino phosphine oxides **13** and phosphonates **14** does not require the isolation and purification of functionalized enamines and/or imines **8/8'** and they can be obtained in "*one pot*" reaction from allenes **7** and **10** when compounds **8** and **12**, after evaporation of the solvent, were directly reduced with hydrides. These results prompted us to extend the synthetic usefulness as intermediates of functionalized enamines **8** and **12** and to explore whether these substrates can be used in carbon-carbon formation processes and therefore in the preparation of new families of nitrogen compounds such as 1-azadienes, allylamines and β-aminoalcohols.

Olefination reaction of β-functionalized phosphine oxides **8**, phosphonium salts **11** and phosphonates **12**.

Achiral and chiral functionalized phosphine oxides **8** were treated with methyllithium in tetrahydrofuran followed by addition of carbonyl compounds (*TLC* control) leading to α,β-unsaturated imines **6**. Subsequent treatment of the reaction mixture with an excess of hydrides (sodium borohydride or lithium diethylaminoborohydride) in ethanol-*THF* led to the corresponding allylamines **1** with good yields (Scheme 6, Table 4). Vicinal coupling constant, in the range of 14-17 Hz between the vinylic protons of amines **1** (R^4=H) is consistent with the *E*-configuration of the carbon-carbon double bond. Therefore, this procedure is highly stereoselective affording the *E* stereoisomer. Some of these azadienes **6** are very easily hydrolysed to the α,β-unsaturated ketones. However, the isolation of these compounds **6** is not necessary for the preparation of allylamines **1**.

Table 4. Allylamines **1** and **20** obtained.

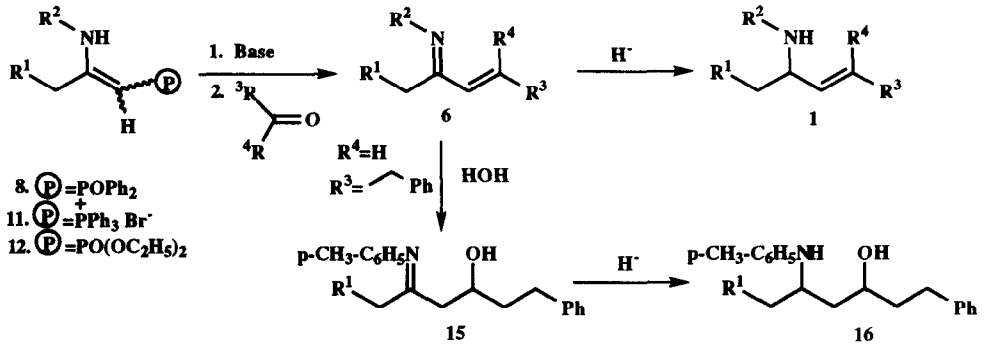
Compound	R^1	R^2	R^3	R^4	R^5	Yield (%)[a,b]		
1aa	H	^{t}Bu	4-Me-C_6H_4	H	H	74 (61)[c]	71 (60)[d]	64 (57)[e]
1ab	H	^{t}Bu	^{i}Bu	H	H	67[c]	61[d]	65[e]
1ad	H	^{t}Bu	5-Me-furyl	H	H	73[c]		
1ae	H	^{t}Bu	-$(CH_2)_5$-		H	52[c]		
1af	H	^{t}Bu	4-Cl-C_6H_4	H	H		81[d]	
1ba	H	C_6H_5-CH_2	4-Me-C_6H_4	H	H		75 (62)[d]	
1ca	H	H_2C=CH-CH_2	4-Me-C_6H_4	H	H		79[d]	
1fa	H	4-Me-C_6H_4	4-Me-C_6H_4	H	H	68 (60)[c]		
1fb	H	4-Me-C_6H_4	^{i}Bu	H	H	77 (60)[c]		
1fc	H	4-Me-C_6H_4	Ph-CH_2CH_2	H	H	72 (62)[c]		
1fd	H	4-Me-C_6H_4	5-Me-furyl	H	H	71 (60)[c]	66 (58)[d]	
1ka	Me	^{t}Bu	4-Me-C_6H_4	H	H	82 (62)[c]		
1na	Me	C_6H_5	4-Me-C_6H_4	H	H	75 (61)[c]		
20aa	H	^{t}Bu	4-Me-C_6H_4	H	Me	62 (58)[c]		
20ad	H	^{t}Bu	5-Me-furyl	H	Me	66[c]		
20fa	H	4-Me-C_6H_4	4-Me-C_6H_4	H	Me	79[c]		

[a] Yields are for isolated compounds purified by flash chomatography (7:1 Hex/Ether). [b] Yields given in parenthesis refer to the "*one pot*" process from allenes **7**, **10** and phosphonium salt **9**. [c] Yield of isolated compounds from phosphine oxides **8**. [d] Yield of isolated compounds from phosphonium salt **11**. [e] Yield of isolated compounds from phosphonates **12**.

This olefination reaction is not restricted to enamines **8**, and can be extended to the corresponding enamines derived from phosphonium salts **11** and phosphonates **12** (Scheme 6). Methyllithium was the base chosen in the case of phosphonates **12**, whereas, a weaker base such as potassium carbonate would suffice for enamines derived from phosphonium salts **11** probably owing to the partially stabilised nature of the

generated phosphorus ylides. The use of this base requires no special precautions and provides excellent yields (Scheme 6, Table 4). It is noteworthy that the preparation of allylamines does not require the isolation and purification of β-enamines **8**, **11** and **12**. Similar overall yields can be obtained in a "*one pot*" reaction from either allenes derived from phosphine oxides **7** and phosphonates **10** or from the commercially available propargylphosphonium bromide **9**, when these enamines **8**, **11** and **12**, after evaporation of the solvent, were directly treated with the adequate base with subsequent addition of carbonyl compounds, hydride and ethanol, respectively.

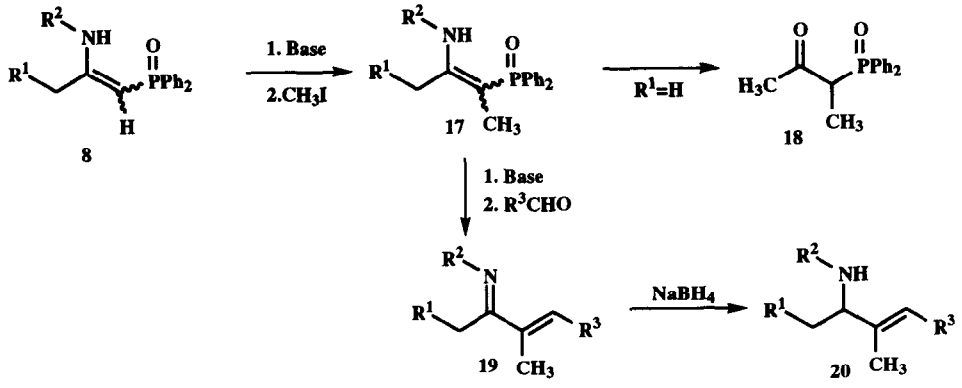
Azadienes **6**, especially when they are substituted by an alkyl group in 4-position (R^4=H, R^3=CH_2CH_2Ph) can be used not only for the preparation of allylamines **1** but also for the formation of β-hydroxyimine **15** and β-hydroxyamine **16**. Thus, Michael addition of water to α,β-unsaturated imine **6a** in refluxing of *THF* led to the formation of β-hydroxyimine **15**. Reduction of the carbon-nitrogen double bond of **15** with $NaBH_4$ afforded β-hydroxyamine **16**.



Scheme 6

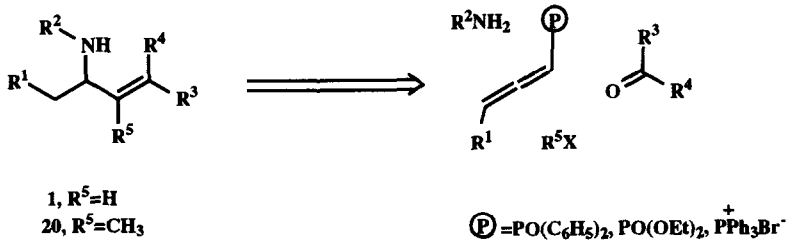
Finally, this strategy can also be used for the preparation of allylamines with an alkyl group in the position 3. It is well known that metalloenamines are especially useful in organic synthesis[27] for the carbon-carbon bond formation. In our case, moreover, the presence of a stabilizing group such as phosphine oxide in enamines **8** could control the desprotonation affording a considerable control of the regiochemistry. When β-enamino phosphine oxides **8** were treated with lithium diisopropylamide (*LDA*) or methyllithium followed by addition of methyl iodide and aqueous work-up, C-α-methylated enamine **17** was not obtained and the corresponding hydrolyzed enamine product, keto-diphenylphosphine oxide **18**, was isolated instead (Scheme 7). These results prompted us to explore whether this process could be applied to the synthesis of substituted azadienes **19** and allylamines **20** without the isolation of labile enamines **17**. Thus, treatment of β-enamino phosphine oxides **8** with methyllithium followed by addition of methyl iodide and subsequent addition of a second equivalent of base and aldehydes afforded 3-methylated azadienes **19**. The selective reduction of the imino group of α,β-unsaturated imines **19** with $NaBH_4$ gave allylamines **20** with a methyl group in 3-position. Likewise, as has been observed in the preparation of allylamines **1**, compounds **20** can also be obtained in "*one pot*" reaction from allene **7** without the isolation and purification of enamines **8** when these

compounds **8**, after the elimination of the solvent, are directly metallated in *THF* with subsequent addition of methyl iodide, a second equivalent of base, aldehydes, hydride and ethanol respectively.



Scheme 7

In conclusion, we describe a new strategy for a simple and general method of synthesis of a broad range of allylamines **1** and **20** from easily available starting materials and under mild reaction conditions (Scheme 8). Allylamines are useful compounds in organic chemistry not only for their application in organic synthesis[6-8] but also for their biological activities[3-5] and given that they are a structural unit appearing in many natural products[1] and vinylogous polypeptides.[2] Moreover, functionalized enamines **8** and **12** can also be used for the preparation of β-amino phosphine oxides **13** and phosphonates **14**.



Scheme 8

ACKNOWLEDGEMENTS

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EXPERIMENTAL SECTION

General. Melting points were determined with a Buchi SPM-20 apparatus and are uncorrected. Analytical *TLC* was performed on 0.25mm silica gel plates (Merck). Visualization was accomplished by *UV* light and iodine. Solvents for extraction

and chromatography were technical grade and 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 before use: acetonitrile (P_2O_5);$CHCl_3$ (P_2O_5). All other reagents were recrystallized or distilled as necessary. Column (flash) chromatography was carried out on silica gel (Merck, 70-230 mesh). Mass spectra were obtained on a Hewlett Packard 5890 spectrometer. Infrared spectra were taken on a Nicolet IRFT Magna 550 spectrometer. *^{1}H-NMR* spectra were recorded on a Varian 300 MHz spectrometer using tetramethylsilane (0.00 ppm) or chloroform (7.26 ppm) as an internal reference in $CDCl_3$ solutions. *^{13}C-NMR* spectra were recorded at 75 MHz with chloroform (77.0 ppm) as an internal reference in $CDCl_3$ solutions. *^{31}P-NMR* spectra were recorded at 120 MHz with 85% phosphoric acid as an external reference. Elemental analyses were performed in a Perkin Elmer Model 240 instrument. Chemical shifts are given in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), dd (double-doublet), t (triplet) q (quadruplet) or m (multiplet). Coupling constants, *J*, are reported in hertz. Infrared spectra *(IR)* were obtained as neat liquids, or as solids in *KBr*. Peaks are reported in cm^{-1}. Mass spectra *(EI)* were obtained with a ionization voltage of 70 eV. Data are reported in the form m/z (intensity relative to base = 100). All reactions were performed in oven (125 °C) or flame-dried glassware under an inert atmosphere of dry N_2.

General Procedure for the Preparation of the β-Enamino- and/or β-Iminophosphine Oxides 8. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 1.2 g (5 mmol) of allenediphenylphosphine oxide 7 (R^3=H), or 1.27 g (5 mmol) of 1,2-butadienyldiphenilphosphine oxide 7 (R^3=CH_3), and 25 mL of acetonitrile. A solution (5 mmol) of amine and 10 mL of acetonitrile was added over 10 min. The mixture was stirred and refluxed until *TLC* indicated the disappearance of the phosphine oxide 7 (1 day to 3 days). The mixture was concentrated and the crude product was purified by recrystallization (hexane / CH_2Cl_2).

***Z*-and *E*-β-*N*-^{t}Butylaminoprop-1-enyldiphenylphosphine oxide (8a).** 1392 mg (89 %) of **8a** as a white solid. Data for **8a**: mp 146-147 °C; *^{1}H-NMR* (300 MHz) 1.23 and 1.35 (s, 9H, *E*- and *Z*-CH_3), 1.94 and 2.12 (s, 3H, *E*- and *Z*-CH_3), 4.00 (d, 1H, $^2J_{PH}$= 22.0 Hz, *Z*-CH), 4.10 (s, 1H, NH), 4.50 (d, 1H, $^2J_{PH}$= 17.1 Hz, *E*-CH), 7.32-7.91 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 22.4 (d, $^3J_{PC}$= 7.0 Hz, *E*-CH_3), 23.3 (d, $^3J_{PC}$= 15.1 Hz, *Z*-CH_3), 28.8 and 31.2 (*E*- and *Z*-CH_3 ^{t}Bu), 51.3 (*E*- and *Z*-C-N), 74.9 (d, $^1J_{PC}$= 116.0 Hz, *Z*-CH), 80.6 (d,$^1J_{PC}$= 128.0 Hz, *E*-CH), 128.2-138.3 (C-arom), 156.8 and 162.8 (*E*- and *Z*-=C-N); *^{31}P-NMR* (120 MHz) 24.9 (*E*-isomer), 28.3 (*Z*-isomer); *IR* (*KBr*) 3267, 3078, 1548, 1170 cm^{-1}; *MS* (EI) 313 (M^+, 38). Anal. Calcd for $C_{19}H_{24}NOP$: C, 72.82; H, 7.72; N, 4.47. Found: C, 73.01; H, 7.62; N, 4.51.

***Z*-and *E*-β-*N*-Benzylaminoprop-1-enyldiphenylphosphine oxide (8b).** 1878 mg (91 %) of **8b** as a white solid. Data for **8b**: mp 145-146 °C; *^{1}H-NMR* (300 MHz) 1.95 and 2.06 (s, 3H, *E*- and *Z*-CH_3), 3.75 (s, 1H, NH), 4.05 (d, 1H, $^2J_{PH}$= 22.6 Hz, *Z*-CH), 4.21 (d, 2H, $^3J_{HH}$= 5.0 Hz, *Z*-CH_2), 4.31 (d, 2H, $^3J_{HH}$= 6.5 Hz, *E*-CH_2), 4.40 (d, 1H, $^2J_{PH}$= 17.5 Hz, *E*-CH), 4.65 (s, 1H, NH), 7.19-7.76 (m, 15H, arom); *^{13}C-NMR* (75 MHz) 19.3 (d, $^3J_{PC}$= 5.5 Hz, *E*-CH_3), 20.4 (d, $^3J_{PC}$= 15.1 Hz, *Z*-CH_3), 46.5 and 47.5 (*E*- and *Z*-CH_2-N), 75.7 (d,$^1J_{PC}$= 115.1 Hz, *Z*-CH), 79.0 (d,$^1J_{PC}$= 129.0 Hz, *E*-CH), 126.5-137.8 (C-arom), 159.2 and 162.5 (*E*- and *Z*-=C-N); *^{31}P-NMR* (120 MHz) 24.9 (*E*-isomer), 29.9 (*Z*-isomer); *IR* (*KBr*) 3399, 3250, 1552, 1160 cm^{-1}; *MS* (EI) 347 (M^+, 40). Anal. Calcd for $C_{22}H_{22}NOP$: C, 76.06; H, 6.38; N, 4.03. Found: C, 76.01; H, 7.66; N, 4.50.

***Z*-and *E*-β-*N*-Allylaminoprop-1-enyldiphenylphosphine oxide (8c).** 1262 mg (85 %) of **8c** as a white solid. Data for **8c**: mp 124-125 °C; *^{1}H-NMR* (300 MHz) 1.99 and 2.04 (s, 3H, *E*- and *Z*-CH_3), 3.76 (m, 2H, *E*- and *Z*-CH_2-N), 3.99 (d, 1H, $^2J_{PH}$= 22.7 Hz, *Z*-CH), 4.37 (d, 1H, $^2J_{PH}$= 17.6 Hz, *E*-CH), 4.46 (s, 1H, NH), 5.04-5.29 (m, 2H, *E*- and *Z*-CH_2=), 5.79 (m, 1H, *E*- and *Z*-CH=), 7.40-7.81 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 20.4 (d, $^3J_{PC}$= 6.9 Hz, *E*-CH_3), 21.3 (d, $^3J_{PC}$= 14.5 Hz, *Z*-CH_3), 45.4 and 45.9 (*E*- and *Z*-CH_2-N), 74.9 (d,$^1J_{PC}$= 115.5 Hz, *Z*-CH), 78.6 (d,$^1J_{PC}$= 128.5 Hz, *E*-CH), 115.3 and 116.9 (C=), 128.1-138.1 (C-arom), 159.1 and 162.5 (*E*- and *Z*-=C-N); *^{31}P-NMR* (120 MHz) 25.1 (*E*-isomer), 29.9 (*Z*-isomer); *IR* (*KBr*) 3237, 3059, 1561, 1168 cm^{-1}; *MS* (EI) 297 (M^+, 51). Anal. Calcd for $C_{18}H_{20}NOP$: C, 72.70; H, 6.78; N, 4.71. Found: C, 72.21; H, 7.69; N, 4.46.

***Z*-and *E*-β-*N*-2-Hydroxyethylaminoprop-1-enyldiphenylphosphine oxide (8d).** 1354 mg (90 %) of **8d** as a white solid. Data for **8d**: mp 128-129 °C; *^{1}H-NMR* (300 MHz) 1.87 and 1.93 (s, 3H, *E*- and *Z*-CH_3), 3.12-3.21 (m, 2H, *E*- and *Z*-CH_2-N), 3.60-3.81 (m, 2H, *E*- and *Z*-CH_2-O), 4.03 (d, 1H, $^2J_{PH}$= 22.8 Hz, *Z*-CH), 4.71 (s, 1H, OH), 4.18 (d, 1H, $^2J_{PH}$= 18.3 Hz, *E*-CH), 6.43 (s, 1H, NH), 7.41-7.77 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 20.3 (d, $^3J_{PC}$= 6.0 Hz, *E*-CH_3), 21.9 (d, $^3J_{PC}$= 14.6 Hz, *Z*-CH_3), 45.9 and 46.5 (*E*- and *Z*-CH_2-N), 59.7 and 61.4 (*E*- and *Z*-CH_2-O), 74.7 (d,$^1J_{PC}$= 115.9 Hz, *Z*-CH), 75.1 (d,$^1J_{PC}$= 131.4 Hz, *E*-CH), 128.3-137.3 (C-arom), 160.7 (*E*- and *Z*-=C-N); *^{31}P-NMR* (120 MHz) 26.8 (*E*-isomer), 30.2 (*Z*-isomer); *IR* (*KBr*) 3249, 3059, 1551, 1157 cm^{-1}. Anal. Calcd for $C_{17}H_{20}NO_2P$: C, 67.77; H, 6.64; N, 4.65. Found: C, 67.79; H, 6.69; N, 4.66.

***Z*-and *E*-β-*N*-Etoxycarbonylmethylaminoprop-1-enyldiphenilphosphine oxide (8e).** 1543 mg (90 %) of **8e** as a white solid. Data for **8e**: mp 86-88 °C; *^{1}H-NMR* (300 MHz) 1.25 (t, 3H, $^3J_{HH}$= 7.1 Hz, *E*- and *Z*-CH_3), 1.95 and 2.05 (s, 3H, *E*- and *Z*-CH_3), 3.78 and 3.84 (d, 2H, $^3J_{HH}$= 6.5 Hz, *E*- and *Z*-CH_2-N), 4.03-4.93 (m, 3H, *E*- and *Z*-CH_2-O and *E*- and *Z*-CH), 4.92 (s, 1H, NH), 7.17-7.99 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 14.1 (CH_3), 20.1 (d, $^3J_{PC}$= 5.3 Hz, *E*-CH_3), 21.3 (d, $^3J_{PC}$= 15.5 Hz, *Z*-CH_3), 44.9 and 45.1 (*E*- and *Z*-CH_2-N), 60.8 and 61.4 (*E*- and *Z*-CH_2-O), 77.2 (d,$^1J_{PC}$= 113.5 Hz, *Z*-CH), 79.9 (d,$^1J_{PC}$= 127.3 Hz, *E*-CH), 128.1-137.7 (C-arom), 158.7 and 161.3 (*E*- and *Z*-=C-N), 170.4 (C=O); *^{31}P-NMR* (120 MHz) 24.9 (*E*-isomer), 30.2 (*Z*-isomer); *IR* (*KBr*) 3230, 3039, 1747, 1567, 1190 cm^{-1}; *MS* (EI) 343 (M^+, 9). Anal. Calcd for $C_{19}H_{22}NO_3P$: C, 66.47; H, 6.41; N, 4.08. Found: C, 66.51; H, 6.39; N, 4.06.

β-*N*-*p*-Tolyliminopropyldiphenylphosphine oxide (8'f) and *Z*- and *E*-β-*N*-Tolylaminopro-1-enyldiphenylphosphine oxide (8f). 1527 mg (88 %) of **8'f/8f** as a white solid. Data for **8'f/8f**: mp 127-129 °C; ^{1}*H-NMR* (300 MHz) **8'f**: 2.21 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.60 (d, 2H, $^2J_{PH}$= 14.8 Hz, CH_2), 6.24-7.84 (m, 14H, arom). **8f**: 1.94 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.60 (s, 1H, NH), 4.25 (d, 1H, $^2J_{PH}$= 22.0 Hz, *Z*-CH), 5.00 (d, 1H, $^2J_{PH}$= 17.5 Hz, *E*-CH), 6.24-7.84 (m, 14H, arom); ^{13}*C-NMR* (75 MHz) **8'f**: 20.6 (CH_3), 21.6 (CH_3), 45.1 (d,$^1J_{PC}$= 61.1 Hz, CH_2-P), 115.2-133.1 (C-arom), 164.8 (C=N). **8f**: 20.6 and 21.4 (CH_3), 22.3 (d, $^3J_{PC}$= 15.1 Hz, *Z*-CH_3), 25.2 (d, $^3J_{PC}$= 5.1 Hz, *Z*-CH_3), 76.2 (d,$^1J_{PC}$= 113.8 Hz, *Z*-CH), 81.2 (d,$^1J_{PC}$= 130.0 Hz, *E*-CH), 115.2-133.1 (C-arom), 159.8 (=C-N); ^{31}*P-NMR* (120 MHz) **8'f**: 29.1, **8f**: 26.2 (*E*-isomer), 29.4 (*Z*-isomer); *IR* (*KBr*) 3190, 3052, 1512, 1177 cm^{-1}; *MS* (EI) 347 (M^+, 95). Anal. Calcd for $C_{22}H_{22}NOP$: C, 76.06; H, 6.38; N, 4.03. Found: C, 76.01; H, 7.66; N, 4.50.

β-*N*-Phenyliminopropyldiphenylphosphine oxide (8'g) and *Z*- and *E*-β-*N*-Phenylaminopro-1-enyldiphenylphosphine oxide (8g). 1349 mg (81 %) of **8'g/8g** as a white solid. Data for **8'g/8g**: mp 116-118 °C; ^{1}*H-NMR* (300 MHz) **8'g**: 1.91 (s, 3H, CH_3), 3.54 (d, 2H, $^2J_{PH}$= 14.6 Hz, CH_2), 6.24-7.84 (m, 15H, arom). **8g**: 2.05 and 2.29 (s, 3H, *E*- and *Z*-CH_3), 3.60 (s, 1H, NH), 4.23 (d, 1H, $^2J_{PH}$= 22.1 Hz, *Z*-CH), 5.00 (d, 1H, $^2J_{PH}$= 17.4 Hz, *E*-CH), 6.24-7.84 (m, 14H, arom); ^{13}*C-NMR* (75 MHz) **8'g**: 21.5 (CH_3), 44.8 (d,$^1J_{PC}$= 61.8 Hz, CH_2-P), 118.2-132.1 (C-arom), 164.8 (C=N). **8g**: 22.3 (d, $^3J_{PC}$= 15.1 Hz, *Z*-CH_3), 25.2 (d, $^3J_{PC}$= 5.1 Hz, *Z*-CH_3), 76.2 (d,$^1J_{PC}$= 113.8 Hz, *Z*-CH), 115.2-133.1 (C-arom), 150.2 (=C-N); ^{31}*P-NMR* (120 MHz) **8'g**: 29.1, **8g**: 26.2 (*E*-isomer), 29.5 (*Z*-isomer); *IR* (*KBr*) 3455, 3062, 1440, 1217 cm^{-1}; *MS* (EI) 333 (M^+, 30). Anal. Calcd for $C_{21}H_{20}NOP$: C, 75.67; H, 6.00; N, 4.20. Found: C, 75.71; H, 6.56; N, 4.23.

***Z*-and *E*-β-*N*-(±)-, (*R*)-, and (*S*)-Methylbenzylaminoprop-1-enyldiphenylphosphine oxide (8h/8i/8j).** 1506 mg (89 %) of **8h/8i/8j** as a white solid. Data for **8h/8i/8j**: mp 169-170 °C; ^{1}*H-NMR* (300 MHz) 1.36 and 1.41 (d, 3H, $^3J_{HH}$= 6.7 Hz, *E*- and *Z*-CH_3), 1.98 and 2.25 (s, 3H, *E*- and *Z*-CH_3), 3.95 (d, 1H, $^2J_{PH}$= 23.0 Hz, *Z*-CH), 4.11 (d, 1H, $^2J_{PH}$= 17.5 Hz, *E*-CH), 4.15 (s, 1H, NH), 4.49 (m, 1H, CH-N), 7.12-7.70 (m, 15H, arom); ^{13}*C-NMR* (75 MHz) 20.1 (d, $^3J_{PC}$= 5.2 Hz, *E*-CH_3), 21.7 (d, $^3J_{PC}$= 14.8 Hz, *Z*-CH_3), 23.6 and 24.9 (CH_3), 53.0 and 59.2 (*E*- and *Z*-CH-N), 76.2 (d,$^1J_{PC}$= 111.0 Hz, *Z*-CH), 81.2 (d,$^1J_{PC}$= 128.5 Hz, *E*-CH), 125.3-145.7 (C-arom), 157.5 and 161.9 (*E*- and *Z*-=C-N); ^{31}*P-NMR* (120 MHz) 23.9 (*E*-isomer), 29.5 (*Z*-isomer); *IR* (*KBr*) 3251, 3055, 1545, 1143 cm^{-1}; *MS* (EI) 361 (M^+, 27). Anal. Calcd for $C_{23}H_{24}NOP$: C, 76.45; H, 6.65; N, 3.88. Found: C, 76.41; H, 6.66; N, 3.90.

***Z*-and *E*-β-*N*-^{t}Butylaminobut-1-enyldiphenylphosphine oxide (8k).** 1422 mg (87 %) of **8k** as a white solid. Data for **8k**: mp 177-178 °C; ^{1}*H-NMR* (300 MHz) 0.94 (t, 3H, $^3J_{HH}$= 7.2 Hz, CH_3), 1.25 and 1.37 (s, 9H, *E*- and *Z*-CH_3), 2.38 (m, 2H, *E*- and *Z*-CH_2), 4.00 (s, 1H, NH), 4.02 (d, 1H, $^2J_{PH}$= 22.0 Hz, *Z*-CH), 4.49 (d, 1H, $^2J_{PH}$= 18.9 Hz, *E*-CH), 7.27-7.79 (m, 10H, arom); ^{13}*C-NMR* (75 MHz) 13.1 (CH_3), 27.8 (d, $^3J_{PC}$= 14.5 Hz, *Z*-CH_2), 28.6 (d, $^3J_{PC}$= 7.1 Hz, *E*-CH_2), 28.8 and 31.3 (*E*- and *Z*-CH_3 ^{t}Bu), 51.1 and 51.9 (*E*- and *Z*-C-N), 76.5 (d,$^1J_{PC}$= 114.7 Hz, *Z*-CH), 80.2 (d,$^1J_{PC}$= 128.9 Hz, *E*-CH), 128.1-138.5 (C-arom), 162.2 (*E*- and *Z*-=C-N); ^{31}*P-NMR* (120 MHz) 23.7(*E*-isomer), 28.3 (*Z*-isomer); *IR* (*KBr*) 3270, 3078, 1549, 1164 cm^{-1}; *MS* (EI) 327 (M^+, 27). Anal. Calcd for $C_{20}H_{26}NOP$: C, 73.39; H, 7.95; N, 4.28. Found: C, 73.41; H, 7.92; N, 4.31.

***Z*-and *E*-β-*N*-Allylaminobut-1-enyldiphenylphosphine oxide (8l).** 1422 mg (87 %) of **8l** as a white solid. Data for **8l**: mp 106-107 °C; ^{1}*H-NMR* (300 MHz) 0.98 and 1.15 (t, 3H, $^3J_{HH}$= 7.4 Hz, *E*- and *Z*-CH_3), 2.25-2.48 (m, 2H, *E*- and *Z*-CH_2), 3.69 (m, 2H, CH_2-N), 4.01 (d, 1H, $^2J_{PH}$= 22.0 Hz, *Z*-CH), 4.31 (d, 1H, $^2J_{PH}$= 17.7 Hz, *E*-CH),4.44 (s, 1H, NH), 5.02-5.28 (m, 2H, *E*- and *Z*-CH_2=), 5.80 (m, 1H, *E*- and *Z*-CH=), 7.26-7.81 (m, 10H, arom); ^{13}*C-NMR* (75 MHz) 12.5 and 12.9 (CH_3), 26.5 (d, $^3J_{PC}$= 13.9 Hz, *Z*-CH_2), 27.1 (d, $^3J_{PC}$= 5.5 Hz, *E*-CH_2), 44.9 and 45.7 (*E*- and *Z*-CH_2-N), 73.1 (d,$^1J_{PC}$= 116.2 Hz, *Z*-CH), 78.2 (d,$^1J_{PC}$= 128.0 Hz, *E*-CH), 115.4 and 116.7 (C=C), 128.1-138.4 (C-arom), 164.3 and 167.8 (*E*- and *Z*-=C-N); ^{31}*P-NMR* (120 MHz) 24.4 (*E*-isomer), 30.4 (*Z*-isomer); *IR* (*KBr*) 3223, 3058, 1541, 1163 cm^{-1}; *MS* (EI) 311 (M^+, 37). Anal. Calcd for $C_{19}H_{22}NOP$: C, 73.31; H, 7.07; N, 4.50. Found: C, 73.36; H, 7.02; N, 4.51.

***Z*-and *E*-β-*N*-Etoxycarbonylmethylaminobut-1-enyldiphenylphosphine oxide (8m).** 1499 mg (84 %) of **8m** as a white solid. Data for **8m**: mp 118-120 °C; ^{1}*H-NMR* (300 MHz) 1.24 (m, 3H, *E*- and *Z*-CH_3), 1.28 (m, 3H, *E*- and *Z*-CH_3), 2.22-2.52 (m, 2H, *E*- and *Z*-CH_2), 3.79 and 3.87 (d, 2H, $^3J_{HH}$= 6.2 Hz, *E*- and *Z*-CH_2-N), 4.11-4.29 (m, 3H, *E*- and *Z*-CH_2-O and *E*- and *Z*-CH), 4.86 (s, 1H, NH), 7.41-7.80 (m, 10H, arom); ^{13}*C-NMR* (75 MHz) 12.6 (CH_3), 14.1 (CH_3), 26.5 (d, $^3J_{PC}$= 10.1 Hz, *Z*-CH_2), 26.6 (d, $^3J_{PC}$= 5.5 Hz, *E*-CH_2), 44.8 (*E*- and *Z*-CH_2-N), 61.1 and 61.6 (*E*- and *Z*-CH_2-O), 75.3 (d,$^1J_{PC}$= 114.8 Hz, *Z*-CH), 80.1 (d,$^1J_{PC}$= 127.2 Hz, *E*-CH), 128.1-137.4 (C-arom), 163.3 and 166.5 (*E*- and *Z*-=C-N), 169.7 and 170.4 (C=O); ^{31}*P-NMR* (120 MHz) 24.0 (*E*-isomer), 30.8 (*Z*-isomer); *IR* (*KBr*) 3241, 3052, 1748, 1547, 1197 cm^{-1}; *MS* (EI) 357 (M^+, 43). Anal. Calcd for $C_{20}H_{24}NO_3P$: C, 67.22; H, 6.72; N, 3.92. Found: C, 67.21; H, 6.69; N, 3.96.

β-*N*-*p*-Tolyliminobutyldiphenylphosphine oxide (8'n) and *Z*- and *E*-β-*N*-Tolylaminobut-1-enyldiphenylphosphine oxide (8n). 1527 mg (88 %) of **8'n/8n** as a white solid. Data for **8'n/8n**: mp 145-147 °C; ^{1}*H-NMR* (300 MHz) **8'n**: 0.81 (t, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 2.19 (s, 3H, CH_3), 2.59 (q, 2H, $^3J_{HH}$= 6.6 Hz, CH_2), 3.53 (d, 2H, $^2J_{PH}$= 15.0 Hz, CH_2-P), 6.24-7.84 (m, 14H, arom). **8n**: 0.98 (m, 3H, *E*- and *Z*-CH_3), 2.22 (s, 3H, CH_3), 2.25-2.31 (m, *E*- and *Z*-CH_2), 3.40 (s, 1H, NH), 4.24 (d, 1H, $^2J_{PH}$= 21.9 Hz, *Z*-CH), 4.85 (d, 1H, $^2J_{PH}$= 17.7 Hz, *E*-CH), 6.24-7.84 (m, 14H, arom); ^{13}*C-NMR* (75 MHz) **8'n**: 11.6 (CH_3), 20.7 (CH_3), 26.9 (CH_2), 46.7 (d,$^1J_{PC}$= 59.1 Hz, CH_2-P), 115.2-136.6 (C-arom), 169.6 (C=N). **8n**: 12.6 (CH_3), 22.3 (CH_3), 26.9 (CH_2), 76.6 (d,$^1J_{PC}$= 113.6 Hz, *Z*-CH), 81.2 (d,$^1J_{PC}$= 130.0 Hz, *E*-CH), 115.2-133.1 (C-arom), 165.8 (=C-N); ^{31}*P-NMR* (120 MHz) **8'n**:

29.2, **8n**: 26.0 (*E*-isomer), 29.7 (*Z*-isomer); *IR (KBr)* 3180, 3032, 1509, 1159 cm^{-1}; *MS* (EI) 361 (M^+, 85). Anal. Calcd for $C_{23}H_{24}NOP$: C, 76.46; H, 6.65; N, 3.88. Found: C, 76.42; H, 6.66; N, 3.93.

β-*N*-Phenyliminobutyldiphenylphosphine oxide (8'o) and *Z*- and *E* -β-*N*-Phenylaminobut-1-enyldiphenylphosphine oxide (8o). 1474 mg (85 %) of **8'o/8o** as a white solid. Data for **8'o/8o**: mp 78-80 °C; ^{1}*H-NMR* (300 MHz) **8'o**: 0.96 (t, 3H, $^3J_{HH}$= 7.1 Hz, CH_3), 2.67 (q, 2H, $^3J_{HH}$= 7.1 Hz, CH_3), 3.37 (d, 2H, $^2J_{PH}$= 15.0 Hz, CH_2), 6.29-7.91 (m, 15H, arom). **8o**: 1.03 and 1.02 (t, 3H, $^3J_{HH}$= 7.2 Hz, *E*- and *Z*-CH_3), 2.29-2.44 (m, 2H, CH_2), 4.33-4.87 (m, 2H, NH and *E*- and *Z*-CH), 6.29-7.91 (m, 15H, arom); ^{13}*C-NMR* (75 MHz) **8'o**: 7.8 (CH_3), 27.4 (CH_2), 46.7 (d, $^1J_{PC}$= 57.5 Hz, CH_2-P), 116.2-132.1 (C-arom), 170.3(C=N). **8o**: 10.2 and 11.5 (CH_3), 27.4 (CH_2), 78.2 (d, $^1J_{PC}$= 113.3 Hz, *Z*-CH), 81.2 (d, $^1J_{PC}$= 130.0 Hz, *E*-CH), 116.2-132.1 (C-arom), 162.0 (=C-N); ^{31}*P-NMR* (120 MHz) **8'o**: 29.3, **8o**: 26.1 (*E*-isomer), 29.6 (*Z*-isomer); *IR (KBr)* 3190, 3052, 1512, 1177 cm^{-1}; *MS* (EI) 347 (M^+, 17). Anal. Calcd for $C_{22}H_{22}NOP$: C, 76.07; H, 6.34; N, 4.03. Found: C, 76.04; H, 6.36; N, 4.05.

General Procedure for the Preparation of the β-Aminoprop-1-enylphosphonium Bromides 11. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 1.9 g (5 mmol) of propargyltriphenylphosphonium bromide **9** (R^3=H), and 25 mL of acetonitrile. A solution (5 mmol) of amine and 10 mL of acetonitrile was added over 10 min. The mixture was stirred and refluxed until *TLC* indicated the disappearance of phosphonium salt (1 day to 3 days). The mixture was concentrated and the crude product was triturated with diethyl ether.

***E*-β-*N*-^{t}Butylamino prop-1-enylphosphonium bromide (11a).** 2020 mg (89 %) of **11a** as a white solid. Data for **11a**: mp 212-214 °C; ^{1}*H-NMR* (300 MHz) 1.50 (s, 9H, CH_3), 2.20 (s, 3H, CH_3), 3.84 (d, 1H, $^2J_{PH}$= 13.7 Hz, CH), 7.31-7.84 (m, 15H, arom), 8.00 (s, 1H, NH); ^{13}*C-NMR* (75 MHz) 24.0 (d, $^3J_{PC}$= 5.2 Hz, CH_3), 28.5 (CH_3), 52.8 (C-N), 56.7 (d, $^1J_{PC}$= 120.9 Hz, CH), 122.6-134.3 (C-arom), 163.7 (=C-N); ^{31}*P-NMR* (120 MHz) 16.2; *IR (KBr)* 3423, 3225, 1545, 1440, 1102 cm^{-1}; *MS* (EI) 454 (M^+-HBr, 8). Anal. Calcd for $C_{25}H_{29}NPBr$: C, 66.08; H, 6.40; N, 3.08. Found: C, 66.11; H, 6.49; N, 3.06.

***E*-β-*N*-Benzylamino prop-1-enylphosphonium bromide (11b).** 2220 mg (91 %) of **11b** as a white solid. Data for **11b**: mp 259-260 °C; ^{1}*H-NMR* (300 MHz) 1.81 (s, 3H, CH_3), 3.57 (d, 1H, $^2J_{PH}$=13.8 Hz, CH), 4.45 (d, 2H, $^3J_{HH}$= 5.6 Hz, CH_2), 7.16-7.65 (m, 20H, arom), 9.30 (s, 1H, NH); ^{13}*C-NMR* (75 MHz) 21.7 (d, $^3J_{PC}$= 5.2 Hz, CH_3), 47.1 (CH_2N), 57.3 (d, $^1J_{PC}$= 121.9 Hz, CH), 122.3-136.9 (C-arom), 164.9 (=C-N); ^{31}*P-NMR* (120 MHz) 15.9; *IR (KBr)* 3169, 3019, 1571, 1439 cm^{-1}; *MS* (EI) 488 (M^+-HBr, 100). Anal. Calcd for $C_{28}H_{27}NPBr$: C, 68.85; H, 5.53; N, 2.88. Found: C, 68.91; H, 5.49; N, 2.86.

***E*-β-*N*-Allylamino prop-1-enylphosphonium bromide (11c).** 2014 mg (92 %) of **11c** as a white solid. Data for **11c**: mp 264-265° C; ^{1}*H-NMR* (300 MHz) 1.82 (s, 3H, CH_3), 3.67 (d, 1H, $^2J_{PH}$= 14.6 Hz, CH), 3.85 (d, 2H, $^3J_{HH}$= 6.7 Hz, CH_2-N), 5.14 (m, 2H, $=CH_2$), 5.82 (m, 1H, =CH), 7.26-7.71 (m, 15H, arom), 8.80 (d, 1H, $^3J_{HH}$= 6.7 Hz, NH); ^{13}*C-NMR* (75 MHz) 22.0 (d, $^3J_{PC}$= 5.2 Hz, CH_3), 46.1 (CH_2N), 55.5 (d, $^1J_{PC}$= 121.9 Hz, CH), 117.1-133.9 (C-arom and C=C), 165.2 (=C-N); ^{31}*P-NMR* (120 MHz) 16.7; *IR (KBr)* 3440, 3182, 1561, 1436 cm^{-1}; *MS* (EI) 438 (M^+-HBr, 8). Anal. Calcd for $C_{28}H_{27}NPBr$: C, 65.75; H, 5.71; N, 3.18. Found: C, 65.81; H, 5.69; N, 3.16.

***E*-β-*N*-Etoxycarbonylmethylaminoprop-1-enylphosphonium bromide (11e)** . 1960 mg (81 %) of **11e** as a white solid. Data for **11e**: mp 175-176 °C; ^{1}*H-NMR* (300 MHz) 1.17 (t, 3H, $^3J_{HH}$= 7.1 Hz, CH_3), 1.87 (s, 3H, CH_3), 3.57 (d, 1H, $^2J_{PH}$= 13.7 Hz, CH), 4.11 (q, 2H, $^3J_{HH}$= 7.1 Hz, CH_2-O), 7.52-7.70 (m, 15H, arom), 9.10 (s, 1H, NH); ^{13}*C-NMR* (75 MHz) 14.1 (CH_3), 22.0 (d, $^3J_{PC}$= 5.2 Hz, CH_3), 44.9 (CH_2-N), 57.3 (d, $^1J_{PC}$= 121.8 Hz, CH), 61.2 (CH_2-O), 122.1-134.1 (C-arom), 165.7 (=C-N), 168.3 (C=O); ^{31}*P-NMR* (120 MHz) 16.9; *IR (KBr)* 3174, 3023, 1752, 1551, 1437 cm^{-1}; *MS* (EI) 484 (M^+-HBr, 2). Anal. Calcd for $C_{25}H_{27}NO_2PBr$: C, 61.98; H, 5.58; N, 2.89. Found: C, 61.87; H, 5.59; N, 2.86.

***E*-β-*N*-*p*-Tolylaminoprop-1-enylphosphonium bromide (11f).** 1903 mg (78 %) of **11f** as a white solid. Data for **11f**: mp 279-280 °C; ^{1}*H-NMR* (300 MHz) 2.04 (s, 3H, CH_3), 2.27(s, 3H, CH_3), 4.55 (d, 1H, $^2J_{PH}$= 13.8 Hz, CH), 7.13-7.71 (m, 20H, arom), 10.40 (s, 1H, NH); ^{13}*C-NMR* (75 MHz) 21.1 (CH_3), 22.4 (CH_3), 57.8 (d, $^1J_{PC}$= 118.8 Hz, CH), 122.1-135.8 (C-arom), 164.6 (=C-N); ^{31}*P-NMR* (120 MHz) 17.4; *IR (KBr)* 3449, 2976, 1531, 1106 cm^{-1}; *MS* (EI) 488 (M^+-Br, 23). Anal. Calcd for $C_{28}H_{27}NPBr$: C, 68.85; H, 5.53; N, 2.88. Found: C, 68.81; H, 5.59; N, 2.86.

***E*-β-*N*-(*R*)-(+)-Methylbenzylaminoprop-1-enylphosphonium bromide (11i).** 2259 mg (91 %) of **11i** as a white solid. Data for **11i**: mp 222-223 °C; ^{1}*H-NMR* (300 MHz) 1.72 (d, 3H, $^3J_{HH}$= 6.8 Hz, CH_3), 1.90 (s, 3H, CH_3), 3.47 (d, 1H, $^2J_{PH}$= 14.0 Hz, CH), 4.51 (q, 1H, $^3J_{HH}$= 6.8 Hz, CH), 7.14-7.66 (m, 20H, arom), 9.15 (s, 1H, NH); ^{13}*C-NMR* (75 MHz) 21.8 (d, $^3J_{PC}$= 5.0 Hz, CH_3), 23.6 (CH_3), 55.1 (CH-N), 58.2 (d, $^1J_{PC}$= 121.8 Hz, CH), 122.5-143.5 (C-arom), 164.8 (=C-N); ^{31}*P-NMR* (120 MHz) 15.9; *IR (KBr)* 3431, 3199, 1542, 1110 cm^{-1}; *MS* (EI) 502 (M^+-HBr, 3). Anal. Calcd for $C_{29}H_{29}NPBr$: C, 69.32; H, 5.78; N, 2.78. Found: C, 69.37; H, 5.79; N, 2.76.

General Procedure for the Preparation of Functionalized Phosphonates 12. A dry flask, 100-ml, 2-necked, fitted with a reflux condenser, gas inlet, and magnetic stirrer, was charged with 0.88 g (5 mmol) of diethyl 1,2-propadienylphosphonate **10** and 5-7 molar excess of the amine. The mixture was stirred and refluxed until *GC-FID* chromatogram of the reaction mixture showed complete disappearance of diethyl 1,2-propadienylphosphonate **10** (2 days to 4 days). The resulting crude product was distilled at reduced pressure.

Z-and *E*-Diethyl β-*N*-^{t}butylaminoprop-1-enylphosphonate (12a). 1083 mg (87 %) of **12a** as a yellow oil(R_f=0.08, ethyl acetate). Data for **12a**: *^{1}H-NMR* (300 MHz) 1.21 (m, 6H, CH_3), 1.23 and 1.25 (s, 9H, *E*- and *Z*-CH_3), 1.98 and 2.01 (s, 3H, *E*- and *Z*-CH_3), 3.39 (d, 1H, $^2J_{PH}$= 13.9 Hz, *Z*-CH), 3.88 (d, 1H, $^2J_{PH}$= 12.1 Hz, *E*-CH), 3.91 (m, 4H, CH_2), 4.00 (s, 1H, NH); *^{13}C-NMR* (75 MHz) 16.1 (CH_3), 21.3 (d, $^3J_{PC}$= 5.2 Hz, *E*-CH_3), 22.9 (d, $^3J_{PC}$= 21.1 Hz, *Z*-CH_3), 28.4 and 30.9 (*E*- and *Z*-CH_3 ^{t}Bu), 51.1 (*E*- and *Z*-C-N), 60.4 (*E*- and *Z*-CH_2), 72.5 (d, $^1J_{PC}$= 191.0 Hz, *Z*-CH), 74.5 (d, $^1J_{PC}$= 213.8 Hz, *E*-CH), 156.5 and 163.7 (*E*- and *Z*-=C-N); *^{31}P-NMR* (120 MHz) 20.4 (*E*-isomer), 27.9 (*Z*-isomer); *IR (KBr)* 3460, 2986, 1615, 1249, 1028 cm^{-1}; *MS* (EI) 249 (M^+, 60). Anal. Calcd for $C_{11}H_{24}NO_3P$: C, 53.02; H, 9.64; N, 5.62. Found: C, 53.01; H, 9.62; N, 5.57.

Z-and *E*-Diethyl β-*N*-allylaminoprop-1-enylphosphonate (12c). 897 mg (77 %) of **12c** as a yellow oil(R_f=0.1, ethyl acetate). Data for **12c**: *^{1}H-NMR* (300 MHz) 1.17 (m, 6H, CH_3), 1.81 and 2.03 (s, 3H, *E*- and *Z*-CH_3), 3.42 (d, 1H, $^2J_{PH}$= 13.5 Hz, *Z*-CH), 3.51 and 3.59 (m, 2H, CH_2-N), 3.68 (d, 1H, $^2J_{PH}$= 10.4 Hz, *E*-CH), 3.85 (m, 4H, CH_2-O), 5.10 (m, 2H, CH_2=), 5.69 (m, 1H, CH=), 7.30 (s, 1H, NH); *^{13}C-NMR* (75 MHz) 15.9 (CH_3), 18.1 (d, $^3J_{PC}$= 4.2 Hz, *E*-CH_3), 20.4 (d, $^3J_{PC}$= 21.0 Hz, *Z*-CH_3), 44.8 and 45.2 (*E*- and *Z*-CH_2-N), 60.2 (*E*- and *Z*-CH_2-O), 70.1 (d, $^1J_{PC}$= 198.7 Hz, *Z*-CH), 70.3 (d, $^1J_{PC}$= 213.1 Hz, *E*-CH), 114.7 and 115.6 (*E*- and *Z*-CH_2=), 133.3 and 135.1 (*E*- and *Z*-CH=), 159.4 and 162.9 (*E*- and *Z*-=C-N); *^{31}P-NMR* (120 MHz) 19.9 (*E*-isomer), 26.9 (*Z*-isomer); *IR (KBr)* 3287, 2985, 1604, 1206 cm^{-1}; *MS* (EI) 233 (M^+, 60). Anal. Calcd for $C_{10}H_{20}NO_3P$: C, 51.50; H, 8.58; N,6.00. Found: C, 53.52; H, 8.62; N, 5.97.

Z-and *E*-Diethyl β-*N*- (±)-, (*R*)-, and (*S*)-methylbenzylaminoprop-1-enylphosphonate (12h/12i/12j). 1173 mg (79 %) of **12h/12i/12j** as a yellow oil (R_f=0.15, ethyl acetate). Data for **12h/12i/12j**: *^{1}H-NMR* (300 MHz) 1.07 and 1.20 (t, 6H, $^3J_{HH}$= 6.2 Hz, *E*- and *Z*-CH_3), 1.32 and 1.33 (d, 3H, $^3J_{HH}$= 6.6 Hz, *E*- and *Z*-CH_3), 1.73 and 2.15 (s, 3H, *E*- and *Z*-CH_3), 3.48 (d, 1H, $^2J_{PH}$= 13.5 Hz, *Z*-CH-P), 3.61 (d, 1H, $^2J_{PH}$= 9.9 Hz, *E*-CH-P), 3.63 (m, 1H, CH-N), 3.86 (m, 4H, CH_2-O), 7.12-7.77 (m, 6H, arom and NH); *^{13}C-NMR* (75 MHz) 15.1 and 15.3 (CH_3), 18.4 (d, $^3J_{PC}$= 4.8 Hz, *E*-CH_3), 20.4 (d, $^3J_{PC}$= 21.8 Hz, *Z*-CH_3), 22.6 and 24.6 (CH_3), 50.1 and 51.8 (*E*- and *Z*-CH-N), 59.3 and 59.6 (*E*- and *Z*-CH_2-O), 71.1 (d, $^1J_{PC}$= 192.0 Hz, *Z*-CH-P), 72.5 (d, $^1J_{PC}$= 213.9 Hz, *E*-CH-P), 124.3-142.9 (C-arom), 157.4 and 161.8 (*E*- and *Z*-=C-N); *^{31}P-NMR* (120 MHz) 19.8 (*E*-isomer), 26.6 (*Z*-isomer); *IR (KBr)* 3274, 2982, 1605, 1210, 1032 cm^{-1}; *MS* (EI) 297 (M^+, 27). Anal. Calcd for $C_{15}H_{24}NO_3P$: C, 60.60; H, 8.08; N, 4.71. Found: C, 60.62; H, 8.05; N, 4.73.

General Procedure for the Preparation of the 2-Aminophosphine Oxides 13 and Phosphonates 14. A dry flask, 100-ml, 2-necked, fitted with a reflux condenser, gas inlet, and magnetic stirrer, was charged with 3 mmol of β-enamine phosphine oxide **8/8'** or β-enamine phosphonate **12**, 228 mg (6 mmol) of *$NaBH_4$* and 30 mL of ethanol. The mixture was stirred and refluxed until *TLC* indicated the disappearance of the compound **8/8'** or **12** (1 day). The mixture was washed with water and extracted with *CH_2Cl_2*. The combined organic layers were dried over *$MgSO_4$*, filtered, and concentrated. The crude product was purified by flash-chromatography on silica gel (diethyl ether).

2-*N*-^{t}Butylaminopropyldiphenylphosphine Oxide (13a). 822 mg (87 %) of **13a** as a yellow oil (R_f=0.1, ethyl acetate). Data for **13a**: *^{1}H-NMR* (300 MHz) 0.96 (s, 9H, CH3), 1.18 (d, 3H, $^3J_{HH}$= 6.3 Hz, CH_3), 2.25-2.53 (m, 3H, CH_2-P and NH), 3.20 (m, 1H, CH-N), 7.41-7.74 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 26.1 (d, $^3J_{PC}$= 7.0 Hz, CH_3), 29.7 (CH_3), 39.7 (d, $^1J_{PC}$= 68.8 Hz, CH_2-P), 43.2 (CH-N), 51.1 (C-N), 128.1-134.5 (C-arom); *^{31}P-NMR* (120 MHz) 30.2; *IR (film)* 3416, 2966, 1437, 1119 cm^{-1}; *MS* (EI) 315 (M^+-15, 15). Anal. Calcd for $C_{19}H_{26}NOP$: C, 72.38; H, 8.31; N, 4.44. Found: C, 72.31; H, 8.34; N, 4.49.

2-*N*-Benzylaminopropyldiphenylphosphine Oxide (13b). 921 mg (88 %) of **13b** as a yellow oil (R_f=0.08, ethyl acetate). Data for **13b**: *^{1}H-NMR* (300 MHz) 1.17 (d, 3H, $^3J_{HH}$= 6.1 Hz, CH_3), 2.27-2.61 (m, 3H, CH_2-P and NH), 3.11 (m, 1H, CH-N), 3.60-3.79 (dd, 2H, $^3J_{HH}$= 13.3 Hz, CH_2-N), 7.16-7.75 (m, 15H, arom); *^{13}C-NMR* (75 MHz) 22.2 (d, $^3J_{PC}$= 10.0 Hz, CH_3), 39.9 (d, $^1J_{PC}$= 70.7 Hz, CH_2-P), 47.7 (CH-N), 50.8 (CH_2-N), 126.7-139.9 (C-arom); *^{31}P-NMR* (120 MHz) 31.5; *IR (film)* 3420, 3059, 1499, 1183 cm^{-1}; *MS* (EI) 349 (M^+, 2). Anal. Calcd for $C_{22}H_{24}NOP$: C, 75.62; H, 6.92; N, 4.01. Found: C, 75.61; H, 6.94; N, 3.99.

2-*N*-Allylaminopropyldiphenylphosphine Oxide (13c). 754 mg (84 %) of **13c** as a yellow oil (R_f=0.08, ethyl acetate). Data for **13c**: *^{1}H-NMR* (300 MHz) 1.03 (d, 3H, $^3J_{HH}$= 5.3 Hz, CH_3), 2.17-2.51 (m, 2H, CH_2-P), 2.65 (s, 1H, NH), 3.03 (m, 3H, CH-N and CH_2-N), 4.91 (m, 2H, CH_2=), 5.65 (m, 1H, CH=), 7.27-7.68 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 22.1 (d, $^3J_{PC}$= 9.9 Hz, CH_3), 36.6 (d, $^1J_{PC}$= 69.9 Hz, CH_2-P), 47.8 and 49.1 (CH_2-N and CH-N), 115.6-136.3 (C-arom and C=C); *^{31}P-NMR* (120 MHz) 31.1; *IR (film)* 3431, 2975, 1438, 1186 cm^{-1}; *MS* (EI) 299 (M^+, 3). Anal. Calcd for $C_{18}H_{22}NOP$: C, 72.22; H, 7.41; N, 4.68. Found: C, 72.21; H, 7.44; N, 4.69.

2-*N*-2-Hydroxyethylaminopropyldiphenylphosphine Oxide (13d). 791 mg (87 %) of **13d** as a yellow oil (R_f=0.08, ethyl acetate). Data for **13d**: *^{1}H-NMR* (300 MHz) 1.11 (d, 3H, $^3J_{HH}$= 6.2 Hz, CH_3), 2.21-2.73 (m, 4H, CH_2-P and CH_2-N), 3.09 (m, 1H, CH-N), 3.43-3.61 (m, 4H, CH_2-O, NH and OH), 7.26-7.73 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 22.3 (d, $^3J_{PC}$= 10.2 Hz, CH_3), 36.5 (d, $^1J_{PC}$= 70.4 Hz, CH_2-P), 47.9 and 48.5 (CH_2-N and CH-N), 128.6-134.1 (C-arom); *^{31}P-NMR* (120 MHz) 32.8; *IR (film)* 3335, 2972, 1441, 1172 cm^{-1}; *MS* (EI) 303 (M^+, 3). Anal. Calcd for $C_{17}H_{22}NO_2P$: C, 67.31; H, 7.31; N, 4.62. Found: C, 67.33; H, 7.34; N, 4.59.

2-*N*-*p*-Tolylaminopropyldiphenylphosphine Oxide (13f). 848 mg (81 %) of **13f** as a yellow oil (R_f=0.3, ethyl acetate). Data for **13f**: *^{1}H-NMR* (300 MHz) 1.06 (d, 3H, $^3J_{HH}$= 6.4 Hz, CH_3), 2.21 (s, 3H, CH_3), 2.27-2.77 (m, 2H, CH_2-P), 3.20 (s, 1H, NH), 3.84 (m, 1H, CH-N), 6.33-6.91 (m, 4H, AA'BB' system), 7.38-7.81 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 20.4 (CH_3), 22.6 (d, $^3J_{PC}$= 5.0 Hz, CH_3), 36.2 (d, $^1J_{PC}$= 68.0 Hz, CH_2-P), 45.1 (CH-N), 113.9-143.9 (C-arom); *^{31}P-NMR* (120 MHz) 30.2; *IR (film)* 3309, 2920, 1538, 1439, 1182 cm^{-1}; *MS* (EI) 349 (M^+, 22). Anal. Calcd for $C_{17}H_{22}NO_2P$: C, 67.31; H, 7.31; N, 4.62. Found: C, 67.33; H, 7.34; N, 4.59.

2-*N*-^{t}Butylaminobutyldiphenylphosphine Oxide (13k). 878 mg (89 %) of **13k** as a yellow oil (R_f=0.07, ethyl acetate). Data for **13k**: *^{1}H-NMR* (300 MHz) 0.74 (t, 3H, $^3J_{HH}$= 7.3 Hz, CH_3), 0.85 (s, 9H, CH_3), 1.40-1.50 (m, 2H, CH_2-P), 2.30 (m, 2H, CH_2), 2.98 (m, 1H, CH-N), 4.10 (s, 1H, NH), 7.27-7.70 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 9.8 (CH_3), 29.8 (CH_3), 30.8 (d, $^3J_{PC}$= 6.9 Hz, CH_2), 36.7 (d, $^1J_{PC}$= 68.7 Hz, CH_2-P), 48.8 (CH-N), 50.8 (C-N), 127.9-136.7 (C-arom); *^{31}P-NMR* (120 MHz) 31.4; *IR (film)* 3335, 2967, 1438, 1120 cm^{-1}; *MS* (EI) 329 (M^+-15, 30). Anal. Calcd for $C_{20}H_{28}NOP$: C, 72.92; H, 8.57; N, 4.25. Found: C, 72.95; H, 8.54; N, 4.29.

(*R*)- and (*S*)-2-*N*-(±)-, (*R*)-, and (*S*)-Methylbenzylaminopropyldiphenylphosphine Oxide (13h/13i/13j). 860 mg (79 %) of **13h/13i/13j** (as a mixture of two diastereoisomers) as a yellow oil (R_f=0.09, ethyl acetate). Data for **13h/13i/13j**: *^{1}H-NMR* (300 MHz) 1.06 (d, 3H, $^3J_{HH}$= 6.3 Hz, CH_3), 1.18 (d, 3H, $^3J_{HH}$= 6.4 Hz, CH_3), 2.16-2.54 (m, 3H, CH_2-P and NH), 3.03 (m, 1H, CH-N), 3.73 (m, 1H, Ph-CH-N), 7.09-7.74 (m, 15H, arom); *^{13}C-NMR* (75 MHz): 22.9 (d, $^3J_{PC}$= 7.0 Hz, CH_3), 24.6 (CH_3), 36.1 (d, $^1J_{PC}$= 69.6 Hz, CH_2-P), 46.6 (CH-N), 55.4 (Ph-CH-N), 126.4-146.0 (C-arom); *^{31}P-NMR* (120 MHz) 30.5. Data for **13'h/13'i/13'j**: *^{1}H-NMR* (300 MHz) 1.06 (d, 3H, $^3J_{HH}$= 6.3 Hz, CH_3), 1.28 (d, 3H, $^3J_{HH}$= 6.5 Hz, CH_3), 2.16-2.54 (m, 3H, CH_2-P and NH), 2.70 (m, 1H, CH-N), 3.73 (m, 1H, Ph-CH-N), 7.09-7.74 (m, 15H, arom); *^{13}C-NMR* (75 MHz) 21.4 (d, $^3J_{PC}$= 12.3 Hz, CH_3), 23.8 (CH_3), 36.9 (d, $^1J_{PC}$= 70.3 Hz, CH_2-P), 45.5 (CH-N), 54.9 (Ph-CH-N), 126.4-146.0 (C-arom); *^{31}P-NMR* (120 MHz) 31.9 ; *IR (film)* 3442, 2968, 1592, 1439, 1183 cm^{-1}; *MS* (EI) 363 (M^+, 0.5). Anal. Calcd for $C_{23}H_{26}NOP$: C, 76.02; H, 7.22; N, 3.85. Found: C, 76.00; H, 7.24; N, 3.89.

Diethyl 2-*N*-^{t}Butylaminopropylphosphonate (14a). 587 mg (78 %) of **14a** as a yellow oil (R_f=0.1, ethyl acetate). Data for **14a**: *^{1}H-NMR* (300 MHz) 1.00 (s, 9H, CH_3), 1.11 (d, 3H, $^3J_{HH}$= 6.3 Hz, CH_3), 1.22 (t, 6H, $^3J_{HH}$= 7.0 Hz, CH_3), 1.61-1.89 (m, 3H, CH_2-P and NH), 3.09 (m, 1H, CH-N), 3.98 and 4.01 (q, 4H, $^3J_{HH}$= 7.0 Hz, CH_2-O); *^{13}C-NMR* (75 MHz) 16.3 (CH_3), 25.3 (d, $^3J_{PC}$=8.5 Hz, CH_3), 29.7 (CH_3), 36.2 (d, $^1J_{PC}$= 134.0 Hz, CH_2-P), 43.1 (CH-N), 51.1 (C-N), 61.1 and 61.2 (C-O); *^{31}P-NMR* (120 MHz) 29.9; *IR (film)* 3466, 2971, 1232, 1033 cm^{-1}; *MS* (EI) 251 (M^+, 100). Anal. Calcd for $C_{11}H_{26}NO_3P$: C, 52.57; H, 10.42; N, 5.57. Found: C, 52.61; H, 10.44; N, 5.59.

Diethyl 2-*N*-Allylaminopropylphosphonate (14c). 599 mg (85 %) of **14c** as a yellow oil (R_f=0.1, ethyl acetate). Data for **14c**: *^{1}H-NMR* (300 MHz) 1.11 (d, 3H, $^3J_{HH}$= 6.2 Hz, CH_3), 1.24 (t, 6H, $^3J_{HH}$= 7.1 Hz, CH_3), 1.63-1.97 (m, 3H, CH_2-P and NH), 2.97-3.25 (m, 3H, CH-N and CH_2-N), 3.98 and 4.00 (q, 4H, $^3J_{HH}$= 7.0 Hz, CH_2-O), 4.98-5.13 (m, 2H, CH_2=), 5.73-5.88 (m, 1H, CH=); *^{13}C-NMR* (75 MHz) 16.0 (CH_3), 21.4 (d, $^3J_{PC}$= 10.9 Hz, CH_3), 32.9 (d, $^1J_{PC}$= 137.7 Hz, CH_2-P), 47.6 (CH-N), 49.1 (CH_2-N), 60.9 and 61.1 (C-O), 115.2 and 136.4 (C=C); *^{31}P-NMR* (120 MHz) 30.6; *IR (film)* 3470, 2979, 12139, 1025 cm^{-1}; *MS* (EI) 235 (M^+, 95). Anal. Calcd for $C_{10}H_{22}NO_3P$: C, 51.05; H, 9.42; N, 5.95. Found: C, 52.01; H, 9.44; N, 5.98.

(*R*)- and (*S*)-Diethyl 2-*N*-(±)-, (*R*)-, and (*S*)-Methylbenzylaminopropylphosphonate (14h/14i/14j). 682 mg (76 %) of **14h/14i/14j** (as a mixture of two diastereoisomers) as a yellow oil (R_f=0.07, ethyl acetate). Data for **14h/14i/14j**: *^{1}H-NMR* (300 MHz) 1.09-1.36 (m, 12H, CH_3), 1.72-1.98 (m, 2H, CH_2-P), 2.79 (s, 1H, NH), 2.92 (m, 1H, CH-N), 3.86 (q, 1H, $^3J_{HH}$= 6.5 Hz, Ph-CH-N), 4.51 (m, 4H, CH_2-O), 7.20-7.32 (m, 5H, arom); *^{13}C-NMR* (75 MHz) 16.5 (CH_3), 22.7 (d, $^3J_{PC}$= 7.0 Hz, CH_3), 24.4 (CH_3), 32.3 (d, $^1J_{PC}$= 136.5 Hz, CH_2-P), 45.3 (CH-N), 55.4 (Ph-CH-N), 61.6 (C-O), 126.6-145.6 (C-arom); *^{31}P-NMR* (120 MHz) 30.5. Data for **14'h/14'i/14'j**: *^{1}H-NMR* (300 MHz) 1.08-1.36 (m, 12H, CH_3), 1.62-1.96 (m, 2H, CH_2-P), 2.80 (m, 3H, NH and CH-N), 3.87 (q, 1H, $^3J_{HH}$= 6.9 Hz, Ph-CH-N), 4.51 (m, 4H, CH_2-O), 7.20-7.32 (m, 5H, arom); *^{13}C-NMR* (75 MHz) 16.4 (CH_3), 21.2 (d, $^3J_{PC}$= 15.2 Hz, CH_3), 24.8 (CH_3), 33.6 (d, $^1J_{PC}$= 137.5 Hz, CH_2-P), 45.2 (CH-N), 54.9 (Ph-CH-N), 61.6 (C-O), 126.6-145.6 (C-arom); *^{31}P-NMR* (120 MHz) 30.4 ; *IR (film)* 3466, 3306, 2981, 1242, 1029 cm^{-1}; *MS* (EI) 299 (M^+, 2). Anal. Calcd for $C_{15}H_{26}NO_3P$: C, 60.19; H, 8.75; N, 4.68. Found: C, 60.20; H, 8.74; N, 4.69.

General Procedure for the Preparation of the Azadienes 6 and Allylamines 1 from Functionalized Phosphine Oxides 8 or from Phosphonates 12. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 8 mmol of compounds **8** or **12** and 30 mL of *THF*. The temperature was allowed to descend to 0 °C (compound **8**) or -78°C (compound **12**) and a solution of methyl lithium of *THF* was then added. The mixture was allowed to stir for 1 h. A solution 5 mmol of carbonyl compound in 10 mL of *THF* was added at this temperature. The mixture was stirred until *TLC* indicated the disappearance of the carbonyl compound (12 h to 3 days). The mixture was washed with water and extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash-chromatography on silica gel (hexane/diethyl ether, 7/1). Allylamines **1** can also be obtained: 5 mmol of β-enaminophosphorylated compounds **8** or **12** in 30 ml of *THF* was metallated with methyl lithium at 0 °C (compound **8**) or -78°C (compound **12**). Then a solution 5 mmol of aldehyde in 10 mL of *THF* was added. The mixture was stirred (1 day to 3 days), treated with 228 mg (6 mmol) of $NaBH_4$, 10 mL of ethanol, and heated at 70°C for 24 hours. The allylamine **1** was purified as descrived above for the azadiene **6**.

1-*p*-Tolyl-2-methyl-4-*p*-tolyl-1,3-azabutadiene (6fa). 934 mg (75 %) of **6fa** as a yellow oil (R_f=0.7, ethyl acetate). Data for **6fa**: *^{1}H-NMR* (300 MHz) 1.99 (s, 3H, CH_3-C=N), 2.27 and 2.30 (s, 3H, CH_3), 6.59-7.38 (m, 10H, arom and =CH); *^{13}C-NMR* (75 MHz) 15.7 (CH_3-C=N), 20.7 and 21.4 (CH_3), 119.6-120.4 (C=C), 127.2-148.5 (C-arom), 166.1 (C=N); *IR (film)* 3028, 2921, 1609, 1505 cm^{-1}; *MS* (EI) 249 (M^+, 100). Anal. Calcd for $C_{18}H_{19}N$: C, 86.75; H, 7.63; N, 5.62. Found: C, 86.77; H, 7.66; N, 5.61.

1-*p*-Tolyl-2-methyl-6-phenyl-1-aza-1,3-hexadiene (6fc). 973 mg (74 %) of **6fc** as a yellow oil (R_f=0.4, hexane/ethyl acetate, 2/1). Data for **6fc**: *^{1}H-NMR* (300 MHz) 2.11 (s, 3H, CH_3-C=N), 2.29 (s, 3H, CH_3), 2.68-2.83 (m, 4H, -CH_2-), 6.16 (d, 1H, $^3J_{HH}$= 16.0 Hz, CH=), 6.53-7.04 (m, 4H, AA'BB' system), 6.86 (dt, 1H, $^3J_{HH}$= 16.0 Hz, $^3J_{HH}$= 6.7 Hz, =CH-), 7.21-7.38 (m, 5H, arom); *^{13}C-NMR* (75 MHz) 20.4 and 30.8 (CH_3), 32.7 and 34.2 (-CH_2-), 113.8-145.0 (C-arom and C=C), 147.2 (C=N); *IR (film)* 2927, 1624, 1555 cm^{-1}; *MS* (EI) 263 (M^+, 1). Anal. Calcd for $C_{19}H_{21}N$: C, 86.69; H, 7.98; N, 5.32. Found: C, 86.67; H, 7.91; N, 5.34.

1-Methyl-3-*p*-tolyl-*N*-^{t}butyl-allylamine (1aa). 803 mg (74 %) of **1aa** as a yellow oil (R_f=0.15, ethyl acetate). Data for **1aa**: *^{1}H-NMR* (300 MHz) 1.05 (s, 9H, CH_3), 1.24 (d, 3H, $^3J_{HH}$= 6.5 Hz, CH_3), 2.24 (s, 3H, CH_3), 3.51 (m, 1H, CH-N), 6.04 (dd, 1H, $^3J_{HH}$= 15.9 Hz, $^3J_{HH}$= 7.5 Hz, CH=), 6.30 (d, 1H, $^3J_{HH}$= 15.9 Hz, CH=), 7.01-7.19 (m, 4H, AA'BB' system); *^{13}C-NMR* (75 MHz) 21.1 (CH_3), 24.2 (CH_3), 30.2 (^{t}Bu-CH_3), 50.8 and 51.2 (C-N), 126.1-136.7 (C-arom and C=C); *IR (film)* 2980, 2920, 1519 cm^{-1}; *MS* (EI) 217 (M^+, 33). Anal. Calcd for $C_{15}H_{23}N$: C, 82.95; H, 10.60; N, 6.45. Found: C, 82.91; H, 10.69; N, 6.46.

1-Methyl-3-isobutyl-*N*-^{t}butyl-allylamine (1ab). 613 mg (67 %) of **1ab** as a yellow oil (R_f=0.10, ethyl acetate). Data for **1ab**: *^{1}H-NMR* (300 MHz) 0.85 (d, 6H, $^3J_{HH}$= 6.6 Hz, CH_3), 1.10 (s, 9H, CH_3), 1.12 (d, 3H, $^3J_{HH}$= 5.0 Hz, CH_3), 1.57 (m, 1H, CH-CH_3), 1.84 (t, 2H, $^3J_{HH}$= 5.9 Hz, CH_2), 2.10 (s, 1H, NH), 3.42 (m, 1H, CH-N), 5.37-5.40 (m, 2H, HC=CH); *^{13}C-NMR* (75 MHz) 22.3 (^{i}Pr-CH_3), 24.7 (CH_3), 28.4 (CH_2), 29.9 (^{t}Bu-CH_3), 41.6 (CH), 50.6 and 51.6 (C-N), 127.6 and 137.9 (C=C); *IR (film)* 3360, 2959, 1465, 1067 cm^{-1}; *MS* (EI) 183 (M^+, 3). Anal. Calcd for $C_{14}H_{20}N$: C, 78.69; H, 13.67; N, 7.65. Found: C, 78.71; H, 13.69; N, 7.61.

1-Methyl-3-((2-methyl)-5-furyl)-*N*-^{t}butyl-allylamine (1ad). 714 mg (69 %) of **1ad** as a yellow oil (R_f=0.08, ethyl acetate). Data for **1ad**: *^{1}H-NMR* (300 MHz) 1.04 (s, 9H, CH_3), 1.13 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 1.28 (s, 1H, NH), 2.21 (s, 3H, CH_3), 3.43 (m, 1H, CH-N), 5.85-6.17 (m, 4H, arom and CH=); *^{13}C-NMR* (75 MHz) 13.5 (CH_3), 24.5 (CH_3), 30.0 (^{t}Bu-CH_3), 50.0 and 51.1 (C-N), 107.0 and 107.7 (C=C), 116.6-151.4 (c-arom); *IR (film)* 3403, 2966, 1535,1262 cm^{-1}; *MS* (EI) 207 (M^+, 67). Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.36; H, 10.19; N, 6.79.

1-Methyl-3-cyclohexyliden-*N*-^{t}butyl-allylamine (1ae). 507 mg (52 %) of **1ae** as a yellow oil (R_f=0.15, ethyl acetate). Data for **1ae**: *^{1}H-NMR* (300 MHz) 0.98 (d, 3H, $^3J_{HH}$= 6.1 Hz, CH_3), 1.02 (s, 9H, CH_3), 1.02-1.94 (m, 10H, -CH_2-), 2.77 (q, 1H, $^3J_{HH}$= 6.1 Hz, CH-N), 5.38 (s, 1H, CH=); *^{13}C-NMR* (75 MHz) 22.4-28.2 (CH_2), 24.4 (CH_3), 30.9 (^{t}Bu-CH_3), 50.8 and 55.0 (C-N), 124.3-135.6 (C=C); *IR (film)* 3407, 2959, 2927,1449 cm^{-1}; *MS* (EI) 195 (M^+-15, 10). Anal. Calcd for $C_{13}H_{25}N$: C, 80.01; H, 12.85; N, 7.18. Found: C, 80.06; H, 12.89; N, 7.16.

1-Methyl-3-*p*-tollyl-*N*-*p*-tolyl-allylamine (1fa). 853 mg (68 %) of **1fa** as a yellow oil (R_f=0.42, ethyl acetate). Data for **1fa**: *^{1}H-NMR* (300 MHz) 1.45 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 2.31 and 2.40 (s, 3H, CH_3), 3.60 (s, 1H, NH), 4.25 (m, 1H, CH-N), 6.24 (dd, 1H, $^3J_{HH}$= 16.0 Hz, $^3J_{HH}$= 5.8 Hz, CH=), 6.61 (d, 1H, $^3J_{HH}$= 16.0 Hz, CH=), 6.64-7.53 (m, 8H, arom); *^{13}C-NMR* (75 MHz) 20.5, 21.3 and 22.2 (CH_3), 51.2 (C-N), 124.9-145.3 (C-arom and C=C); *IR (film)* 3395, 2925, 1622, 1521 cm^{-1}; *MS* (EI) 251 (M^+, 31). Anal. Calcd for $C_{14}H_{20}N$: C, 86.08; H, 8.37; N, 5.58. Found: C, 86.10; H, 8.39; N, 5.51.

1-Methyl-3-isobutyl-*N*-*p*-tolyl-allylamine (1fb). 835 mg (77 %) of **1fb** as a yellow oil (R_f=0.21, ethyl acetate). Data for **1fb**: *^{1}H-NMR* (300 MHz) 0.85 and 0.88 (d, 6H, $^3J_{HH}$= 6.5 Hz, CH_3), 1.28 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 1.61 (m, 1H, CH-CH_3), 1.90 (t, 2H, $^3J_{HH}$= 5.8 Hz, CH_2), 2.23 (s, 3H, CH_3), 3.47 (s, 1H, NH), 3.92 (m, 1H, CH-N), 5.40 (dd, 1H, $^3J_{HH}$= 15.9 Hz, $^3J_{HH}$= 5.9 Hz, CH=), 5.58 (dt, 1H, $^3J_{HH}$= 15.9 Hz, $^3J_{HH}$= 5.8 Hz, CH=), 6.52-6.91 (m, 4H, AA'BB' system); *^{13}C-NMR* (75 MHz) 20.3 (CH_3), 22.3 (^{i}Pr-CH_3), 25.1 (CH_3), 28.4 (CH_2), 41.6 (CH), 50.9 (C-N), 113.4-134.6 (C-arom and C=C); *IR (film)* 3360, 2969, 1499, 1077 cm^{-1}; *MS* (EI) 217 (M^+, 38). Anal. Calcd for $C_{14}H_{20}N$: C, 82.95; H, 10.60; N, 6.45. Found: C, 82.91; H, 10.59; N, 6.66.

1-Methyl-3-ethylphenyl-*N*-*p*-tolyl-allylamine (1fc). 954 mg (72 %) of **1fc** as a yellow oil (R_f=0.75, ethyl acetate). Data for **1fc**: *^{1}H-NMR* (300 MHz) 1.29 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 2.29 (s, 3H, CH_3), 2.39 and 2.72 (m, 4H, CH_2), 3.49 (s, 1H, NH), 3.95 (m, 1H, CH-N), 5.45 (dd, 1H, $^3J_{HH}$= 14.9 Hz, $^3J_{HH}$= 5.9 Hz, CH=), 5.67 (m, 1H, CH=), 6.56-7.04 (m, 4H, AA'BB' system), 7.17-7.36 (m, 5H, arom); *^{13}C-NMR* (75 MHz) 20.5 (CH_3-Ph), 25.9 (CH_3), 34.2 (CH_2), 35.9 (CH_2), 50.9 (CH-N), 113.6-145.2 (C-arom and C=C); *IR (film)* 3407, 2934, 1624, 1525 cm^{-1}; *MS* (EI) 265 (M^+, 70). Anal. Calcd for $C_{19}H_{23}N$: C, 86.05; H, 8.68; N, 5.28. Found: C, 86.01; H, 8.69; N, 5.26.

1-Methyl-3-((2-methyl)-5-furyl)-*N*-*p*-tolyl-allylamine (1fd). 795 mg (66%) of **1fd** as a yellow oil (R_f=0.85, ethyl acetate). Data for **1fd**: *^{1}H-NMR* (300 MHz) 1.43 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 2.32 and 2.37 (s, 6H, CH_3-Ph and CH_3-fur), 3.49 (s, 1H, NH), 4.17 (m, 1H, CH-N), 6.01-6.14 (m, 2H, fur), 6.21 (dd, 1H, $^3J_{HH}$= 15.8 Hz, $^3J_{HH}$= 5.4 Hz, CH=), 6.41 (d, 1H, $^3J_{HH}$=1 5.8 Hz, CH=), 6.56-7.07 (m, 4H, AA'BB' system); *^{13}C-NMR* (75 MHz) 13.9 (CH_3-fur), 20.6 (CH_3-Ph), 22.2 (CH_3), 50.9 (CH-N),

107.6-151.7 (C-arom and C=C); *IR (film)* 3405, 2973, 2927, 1618, 1521 cm^{-1}; *MS* (EI) 241 (M^+, 23). Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.93; N, 5.80. Found: C, 79.61; H, 7.89; N, 7.94.

1-Ethyl-3-*p*-tolyl-*N*-^{t}butyl-allylamine (1ka). 947 mg (82 %) of **1ka** as a yellow oil (R_f=0.17, ethyl acetate). Data for **1ka**: *^{1}H-NMR* (300 MHz) 0.92 (t, 3H, $^3J_{HH}$= 7.4 Hz, CH_3), 1.15 (s, 3H, CH_3), 1.52 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 3.26 (m, 1H, CH-N), 4.50 (s, 1H, NH), 6.02 (dd, 1H, $^3J_{HH}$= 15.9 Hz, $^3J_{HH}$= 8.1 Hz, CH=), 6.38 (d, 1H, $^3J_{HH}$= 15.9 Hz, CH=), 7.11-7.30 (m, 4H, AA'BB' system); *^{13}C-NMR* (75 MHz) 10.8 (CH_3), 21.1 (CH_3), 30.2 (^{t}Bu-CH_3), 30.9 (CH_2), 50.9 (C-N), 57.4 (CH-N), 126.1-136.3 (C-arom and C=C); *IR (film)* 2962, 2924, 1515 cm^{-1}; *MS* (EI) 231 (M^+, 2). Anal. Calcd for $C_{16}H_{25}N$: C, 83.11; H, 10.82; N, 6.06. Found: C, 83.12; H, 10.85; N, 6.03.

1-Ethyl-3-*p*-tolyl-*N*-phenyl-allylamine (1na). 941 mg (75 %) of **1na** as a yellow oil (R_f=0.35, ethyl acetate). Data for **1na**: *^{1}H-NMR* (300 MHz) 1.10 (t, 3H, $^3J_{HH}$= 6.5 Hz, CH_3), 1.77 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 3.71 (s, 1H, NH), 3.95 (m, 1H, CH-N), 6.15 (dd, 1H, $^3J_{HH}$= 15.9 Hz, $^3J_{HH}$= 6.5 Hz, CH=), 6.63 (d, 1H, $^3J_{HH}$= 15.9 Hz, CH=), 6.71-7.36 (m, 9H, arom); *^{13}C-NMR* (75 MHz) 10.7 (CH_3), 21.3 (CH_3), 29.2 (CH_2), 57.3 (C-N), 113.5.9-147.9 (C-arom and C=C); *IR (film)* 2966, 1595, 1501 cm^{-1}; *MS* (EI) 251 (M^+, 17). Anal. Calcd for $C_{14}H_{20}N$: C, 86.08; H, 8.37; N, 5.58. Found: C, 86.12; H, 8.35; N, 5.51.

General Procedure for the Preparation of the Azadienes 6 and Allylamines 1 from Functionalized Ylides 11. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 5 mmol of β-enamine phosphonium salt **11**, 0.69 g (5 mmol) of potassium carbonate (*K_2CO_3*) and 30 mL of dried *DMF*. The mixture was allowed to stir for 1 h at room temperature. Then a solution 5 mmol of aldehyde in 10 mL of *DMF* was added at room temperature. The mixture was stirred until *TLC* indicated the disappearance of the aldehyde (1 day to 3 days). The mixture was washed with water and extracted with *CH_2Cl_2*. The organic layers were dried over *$MgSO_4$*, filtered, and concentrated. The azadiene **6** was purified by flash-chromatography on silica gel (hexane/diethyl ether, 7/1). Allylamines **1** can also be obtained: A solution 5 mmol of β-enamine phosphonium salt **11** and 0.69 g (5 mmol) of potassium carbonate (*K_2CO_3*) in 30 ml of *DMF* was stirred for 1 h at room temperature. Then a solution 5 mmol of aldehyde in 10 mL of *DMF* was added. The mixture was stirred (1 day to 3 days), treated with 228 mg (6 mmol) of *$NaBH_4$*, 10 mL of ethanol, and heated at 70°C for 24 hours. The allylamine **1** was purified as descrived above for the azadiene **6**.

1-*p*-Tolyl-2-methyl-4-((2-methyl)-5-furyl)-1,3-azabutadiene (6fd). 860 mg (72%) of **6fd** as a yellow oil (R_f=0.8, ethyl acetate). Data for **6fd**: *^{1}H-NMR* (300 MHz) 1.99 (s, 3H, CH_3-C=N), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.00-6.39 (m, 2H, fur), 6.53 (d, 1H, $^3J_{HH}$= 16.0 Hz, CH=), 6.76 (d, 1H, $^3J_{HH}$= 16.0 Hz, CH=), 6.86-7.27 (m, 4H, AA'BB' system); *^{13}C-NMR* (75 MHz) 13.8 (CH_3-fur), 20.9 (CH_3-Ph), 23.3 (CH_3), 108.4-154.0 (C-arom and C=C), 167.7 (C=N); *IR (film)* 3115, 2921, 1598, 1268 cm^{-1}; *MS* (EI) 239 (M^+, 65). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.85. Found: C, 80.31; H, 7.09; N, 5.86.

1-Methyl-3-*p*-chlorophenyl-*N*-^{t}butyl-allylamine (1af). 960 mg (781%) of **1af** as a yellow oil (R_f=0.12, ethyl acetate). Data for **1af**: *^{1}H-NMR* (300 MHz) 1.08 (s, 9H, CH_3), 1.17 (d, 3H, $^3J_{HH}$= 6.5 Hz, CH_3), 1.60 (s, 1H, NH), 3.52 (m, 1H, CH-N), 6.10 (dd, 1H, $^3J_{HH}$= 15.0 Hz, $^3J_{HH}$= 7.5 Hz, CH=), 6.35 (d, 1H, $^3J_{HH}$= 15.0 Hz, CH=), 7.21 (m, 4H, arom); *^{13}C-NMR* (75 MHz) 24.3 (CH_3), 30.1 (^{t}Bu-CH_3), 50.6 and 51.3 (C-N), 126.6-140.6 (C-arom and C=C); *IR (film)* 3350, 2959, 1494, 1085 cm^{-1}; *MS* (EI) 237 (M^+, 11). Anal. Calcd for $C_{14}H_{20}NCl$: C, 70.88; H, 8.40; N, 5.91. Found: C, 70.91; H, 8.39; N, 5.96.

1-Methyl- 3-*p*-tolyl-*N*-benzyl-allylamine (1ba). 941 mg (75 %) of **1ba** as a yellow oil (R_f=0.2, ethyl acetate). Data for **1ba**: *^{1}H-NMR* (300 MHz) 1.08 (d, 3H, $^3J_{HH}$= 6.2 Hz, CH_3), 1.45 (s, 1H, NH), 2.23 (s, 3H, CH_3), 3.35 (m, 1H, CH-N), 3.67 (m, 2H, CH_2-N), 5.95 (dd, 1H, $^3J_{HH}$= 16.0 Hz, $^3J_{HH}$= 5.9 Hz, CH=), 6.34 (d, 1H, $^3J_{HH}$= 16.0 Hz, CH=), 7.00-7.22 (m, 9H, arom); *^{13}C-NMR* (75 MHz) 20.8 (CH_3), 21.8 (CH_3), 50.9 (CH_2-N), 55.1 (CH-N), 125.9-138.9 (C-arom and C=C); *IR (film)* 3026, 2959, 1522, 1454 cm^{-1}; *MS* (EI) 251 (M^+, 48). Anal. Calcd for $C_{18}H_{21}N$: C, 86.06; H, 8.37; N, 5.58. Found: C, 86.01; H, 8.39; N, 5.61.

1-Methyl-3-*p*-tolyl-*N*-allyl-allylamine (1ca). 794 mg (79 %) of **1ca** as a yellow oil (R_f=0.12, ethyl acetate). Data for **1ca**: *^{1}H-NMR* (300 MHz) 1.26 (d, 3H, $^3J_{HH}$= 6.3 Hz, CH_3), 2.11 (s, 1H, NH), 2.34 (s, 3H, CH_3), 3.22-3.42 (m, 3H, CH_2-N and CH-N), 5.15 (m, 2H, $=CH_2$), 5.94 (m, 1H, =CH), 6.01 (dd, 1H, $^3J_{HH}$= 15.9 Hz, $^3J_{HH}$= 7.9 Hz, CH=), 6.44 (d, 1H, $^3J_{HH}$= 15.9 Hz, CH=), 7.09-7.30 (m, 4H, AA'BB' system); *^{13}C-NMR* (75 MHz) 21.3 (CH_3), 22.0 (CH_3), 49.9 (CH_2-N), 55.6 (CH-N), 115.9-137.1 (C-arom and C=C); *IR (film)* 3315, 3021, 2973, 1515, 969 cm^{-1}; *MS* (EI) 201 (M^+, 24). Anal. Calcd for $C_{14}H_{19}N$: C, 83.58; H, 9.45; N, 6.96. Found: C, 83.51; H, 9.39; N, 7.01.

General Procedure for the Preparation of the Azadienes 19 and Allylamines 20. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 5 mmol of compounds **8** and 30 mL of *THF*. The temperature was allowed to descend to 0 °C and a solution of methyl lithium of *THF* was then added. The mixture was allowed to stir for 1 h at this temperature. A solution 5 mmol of alkyl halide in 5 mL of *THF* was added. The mixture was stirred until *TLC* indicated the disappearance of the compound **8** (1 day to 2 days), at which point the mixture was metallated at 0 °C, and a solution 5 mmol of aldehyde was added. The mixture was stirred until disappearance of the carbonyl compound (*TLC* control), washed with water and extracted with *CH_2Cl_2*. The organic layers were dried over *$MgSO_4$*, filtered, and concentrated. The crude product was purified by flash-chromatography on silica gel (hexane/diethyl ether, 7/1). Allylamines **20** can also be obtained: 5 mmol of enamine **8** in 30 mL of *THF* was metallated with methyl lithium at 0°C. Then a solution 5 mmol of alkyl halide in 5 mL of *THF* was added. The mixture was stirred (1 day to 2 days). The mixture was metallated with methyl lithium at 0°C, then a solution 5 mmol of

aldehyde in 10 mL of *THF* was added, stirred until disappearance of the carbonyl compound, treated with 228 mg (6 mmol) of $NaBH_4$, 10 mL of ethanol, and heated at 70°C for 24 hours. The allylamine **20** was purified as described above for the azadiene **19**.

1-*p*-tolyl-2,3-dimethyl-4-*p*-tolyl-1,3-azabutadiene (19fa). 947 mg (72%) of **19fa** as a yellow oil (R_f=0.8, ethyl acetate). Data for **19fa**: *^{1}H-NMR* (300 MHz) 2.08 (s, 3H, CH_3-C=N), 2.24, 2.40 and 2.46 (s, 3H, CH_3), 6.59-7.37 (m, 8H, arom), 7.51 (s, 1H, =CH); *^{13}C-NMR* (75 MHz) 13.0 (CH_3), 20.5, 21.4 and 25.7 (CH_3), 112.6-115.2 (C=C), 127.4-139.9 (C-arom), 147.5 (C=N); *IR (film)* 3066, 2973, 1511 cm^{-1}; *MS* (EI) 263 (M^+, 72). Anal. Calcd for $C_{19}H_{21}N$: C, 86.69; H, 7.98; N, 5.32. Found: C, 86.71; H, 7.91; N, 5.34.

1,2-Dimethyl-3-*p*-tolyl-*N*-^{t}butyl-allylamine (20aa). 832 mg (72 %) of **20aa** as a yellow oil (R_f=0.15, ethyl acetate). Data for **20aa**: *^{1}H-NMR* (300 MHz) 1.13 (s, 9H, CH_3), 1.20 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 1.87 (s, 3H, CH_3), 2.56 (s, 3H, CH_3-Ph), 3.54 (q, 1H, $^3J_{HH}$= 6.6 Hz, CH-N), 4.50 (s, 1H, NH), 6.48 (s, 1H, CH=), 7.11-7.29 (m, 4H, AA'BB' system); *^{13}C-NMR* (75 MHz) 13.5 (CH_3), 21.1 (CH_3-Ph), 23.4 (CH_3), 29.9 (^{t}Bu-CH_3), 56.4 (C-N), 64.9 (CH-N), 124.3-143.3 (C-arom and C=C); *IR (film)* 3366, 2973, 1511 cm^{-1}; *MS* (EI) 231 (M^+, 17). Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05. Found: C, 83.01; H, 10.91; N, 6.06.

1,2-Dimethyl-3-((2-methyl)-5-furyl)-*N*-^{t}butyl-allylamine (20ad). 729 mg (66 %) of **20ad** as a yellow oil (R_f=0.15, ethyl acetate). Data for **20ad**: *^{1}H-NMR* (300 MHz) 1.07 (s, 9H, CH_3), 1.14 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 1.92 (s, 3H, CH_3), 2.29 (s, 3H, CH_3-fur), 3.46 (q, 1H, $^3J_{HH}$= 6.6 Hz, CH-N), 4.52 (s, 1H, NH), 5.97-6.27 (m, 3H, H arom. and olefinic); *^{13}C-NMR* (75 MHz) 13.6 (CH_3), 14.2 (CH_3), 23.5 (CH_3), 29.8 (^{t}Bu-CH_3), 55.9 (C-N), 56.9 (CH-N), 107.2-152.3 (C-arom and C=C); *IR (film)* 3336, 2963, 1539 cm^{-1}; *MS* (EI) 221 (M^+, 67). Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.93; H, 10.51; N, 6.36.

1,2-Dimethyl-3-*p*-tolyl-*N*-*p*-tolyl-allylamine (20fa). 980 mg (74 %) of **20fa** as a yellow oil (R_f=0.7, ethyl acetate). Data for **20fa**: *^{1}H-NMR* (300 MHz) 1.30 (d, 3H, $^3J_{HH}$= 6.6 Hz, CH_3), 1.76 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.60 (s, 1H, NH), 3.85 (q, 1H, $^3J_{HH}$= 6.6 Hz, CH-N), 6.41 (s, 1H, CH=), 6.46-7.15 (m, 8H, arom); *^{13}C-NMR* (75 MHz) 13.7 (CH_3), 20.3 (CH_3), 21.0 (CH_3), 21.7 (CH_3), 57.0 (CH-N), 124.3-145.2 (C-arom and C=C); *IR (film)* 3366, 2973, 1511 cm^{-1}; *MS* (EI) 265 (M^+, 12). Anal. Calcd for $C_{19}H_{23}N$: C, 85.99; H, 8.73; N, 5.28. Found: C, 86.01; H, 8.71; N, 5.24.

Reaction of 1-*p*-Tolyl-2-methyl-6-phenyl-1-aza-1,3-hexadiene 6fc with water. Synthesis of 1-Methyl-3-hydroxy-5-phenyl-*N*-*p*-tolyl-pentinimine 15. 530 mg (2 mmol) of 1-*p*-tolyl-2-methyl-6-phenyl-1-aza-1,3-hexadiene **6fc**, 5 mL of water and 30 mL of *THF* was stirred at room temperature until *GC-FID* chromatogram of the reaction mixture showed complete disappearance of 1-*p*-tolyl-2-methyl-6-phenyl-1-aza-1,3-hexadiene **6fc** (2 days). The mixture was washed with water and extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash-chromatography on silica gel (hexane/diethyl ether, 7/1) to afford 360 mg (64 %) of **15** as a yellow oil (R_f=0.3, ethyl acetate). Data for **15**: *^{1}H-NMR* (300 MHz) 1.77 (m, 2H, CH_2-CHO), 1.98 (s, 3H, CH_3-C=N), 2.15 (s, 3H, CH_3), 2.51-2.69 (m, 4H, -CH_2-), 3.40 (s, 1H, OH), 3.70 (m, 1H, CH-O), 6.39-6.90 (m, 4H, AA'BB' system), 7.07-7.21 (m, 5H, arom); *^{13}C-NMR* (75 MHz) 20.2 and 30.6 (CH_3), 32.4, 36.5 and 47.5 (CH_2), 49.5 (CH-O), 113.5-141.5 (C-arom), 144.6 (C=N); *IR (film)* 3397, 2924, 1712, 1516 cm^{-1}; *MS* (EI) 281 (M^+, 89). Anal. Calcd for $C_{19}H_{23}NO$: C, 81.14; H, 8.18; N, 4.98. Found: C, 81.11; H, 8.19; N, 4.96.

Reduction of 1-Methyl-3-hydroxy-5-phenyl-*N*-*p*-tolyl-pentinimine 15 with $NaBH_4$. Synthesis of 1-phenyl-5-*p*-tolylamino-3-hexanol 16. 281 mg (1 mmol) of 1-methyl-3-hydroxy-5-phenyl-*N*-*p*-tolyl-pentinimine **15**, 57 mg (1.5 mmol) of $NaBH_4$ and 30 mL of ethanol is refluxing 24 h. The mixture was washed with water and extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash-chromatography on silica gel (hexane/diethyl ether, 7/1) to afford 258 mg (91 %) of **16** (as a mixture of two diastereoisomers) as a yellow oil (R_f=0.2, ethyl acetate). Data for **16**: *^{1}H-NMR* (300 MHz) 1.13 (d, 3H, $^3J_{HH}$= 6.1 Hz, CH_3), 1.42-1.82 (m, 4H, -CH_2-), 2.16 (s, 3H, CH_3), 2.61 (m, 2H, -CH_2-), 3.20 (s, 2H, NH and OH), 3.45-3.54 (m, 1H, CH-N), 3.80 (m, 1H, CH-O), 6.88-7.22 (m, 9H, arom); *^{13}C-NMR* (75 MHz) 20.3 (CH_3, 2 diast.), 23.9 (CH_3, 2 diast.), 31.9 and 32.3 (CH_2, 2 diast.), 37.0 (CH_2, 2 diast.), 42.9 and 43.3 (CH_2, 2 diast.), 50.4 and 54.3 (CH-N, 2 diast.), 65.1 and 68.2 (CH-O, 2 diast.), 113.5-141.7 (C-arom); *IR (film)* 3375, 2925, 1622, 1521 cm^{-1}; *MS* (EI) 283 (M^+, 65). Anal. Calcd for $C_{19}H_{25}NO$: C, 80.56; H, 8.83; N, 4.94. Found: C, 80.51; H, 8.79; N, 4.96.

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