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An Improved and Effective Method for the Preparation of α,β-Unsaturated Oximes and Isoxazole Derivatives.

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Abstract: β-Functionalized oximes derived from phosphine oxides **5**, phosphonates **8** and phosphonium salts **10** are easily obtained by simple addition of hydroxylamine compounds **2** to substituted allenes **3** and **6** or to propargylphosphonium salt **9**. These oximo derivatives are used for the synthesis of α,β-unsaturated oximes **1**, and isoxazole derivatives **13.**

Oxime derivatives are of significant interest not only for their synthetic value as intermediates in organic synthesis,[1] but also for their industrial applications in the areas of agrochemicals,[2a] medicinal chemistry[2b] and in the preparation of cephalosporin derivatives with potent antibacterial activity.[2c,d] Furthermore, the usefulness of the α,β-unsaturated oximes is particularly significant as a result of their activity as insecticides,[3a] vasodilators,[3b] antimicrobial agents,[3c] selective inhibitors of fatty acid activation proteins[3d] and starting materials in the synthesis of the dipeptide Radiosumin[4a] and in the preparation of a wide range of acyclic compounds, such as carbonyl derivatives,[4b] acetylenes,[4c] allylic nitro compounds,[4d] unsaturated sugars,[4e] and α-aminoacids[4f] as well as heterocycles such as pyridines,[5a,b] pyrimidines,[5c] oxazoles,[5d] pyrazoles,[5e] quinolines[5f] and azepines.[5g] In this context, it is noteworthy that recently α,β-unsaturated *O*-silyloximes have been used, for the first time, as siloxy-activated 1-azadienes in an elegant and short route to the synthesis of the antitumor antibiotic Lavendamycin,[6a] and pyridine derivatives.[6b]

Simple α,β-unsaturated oximes **1** are mostly synthesized by the condensation reaction of carbonyl compounds with hydroxylamines[1] (carbon-nitrogen double bond formation, see Scheme 1, route a). However, the preparation of such compounds is far from simple and, especially in the case of conjugated ketones, the Michael addition may occur.[7] On the other hand, a very specific example of Wittig olefination of phenanthren-9-

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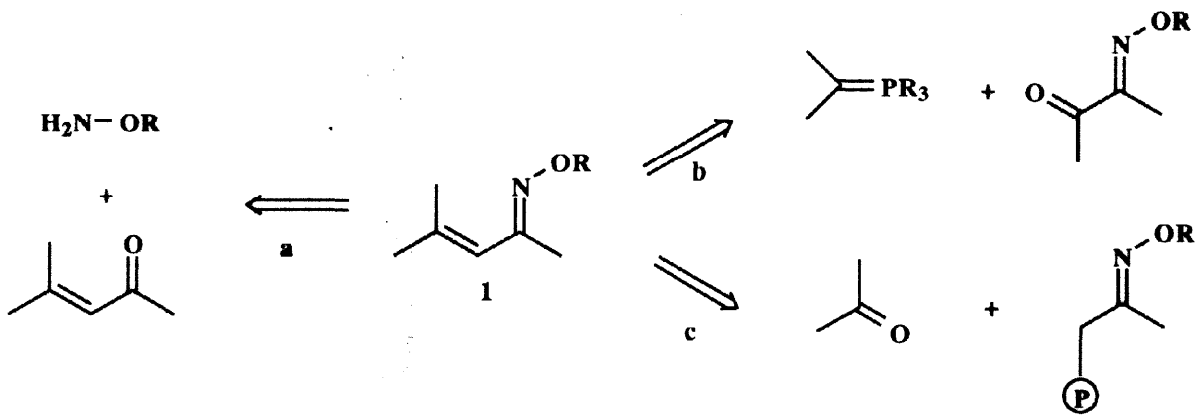
one derivatives with stabilized phosphorus ylides for the synthesis of methoxyimino phenanthren-ylidenes has been recently reported,[8] but in this reaction the carbon-carbon double bond formation involves the use of functionalized carbonyl compounds containing the oxime group, (see Scheme 1, route b). In connection with our interest in the synthesis and reactivity of 2-azadienes[9] and activated 1-azadienes,[10] we have used β-functionalized phosphonium salts, phosphine oxides and phosphonates as synthetic intermediates in the preparation of hydrazones,[10a] allylamines[11a] and aminodienes.[11b] In this context, it is noteworthy that we have recently used phosphorus compounds as homologation reagents[12] for the conversion of carbonyl derivatives into α,β-unsaturated oximes with the introduction of two additional carbon atoms in the resulting chain. Here we aim to extend this methodology to the synthesis of a wide range of α,β-unsaturated oximes **1** and to explore the synthetic use of phosphorylated oximes in the preparation of acyclic oximes and isoxazoles. In our case, we envisaged obtaining oximes **1** by an olefination reaction of β-functionalized oximes derived from phosphine oxides, phosphonium salts, and phosphonates with carbonyl compounds (carbon-carbon double bond formation, see Scheme 1, route c).



Ⓟ = $POPh_2$, $PO(OEt)_2$, $P^+Ph_3Br^-$

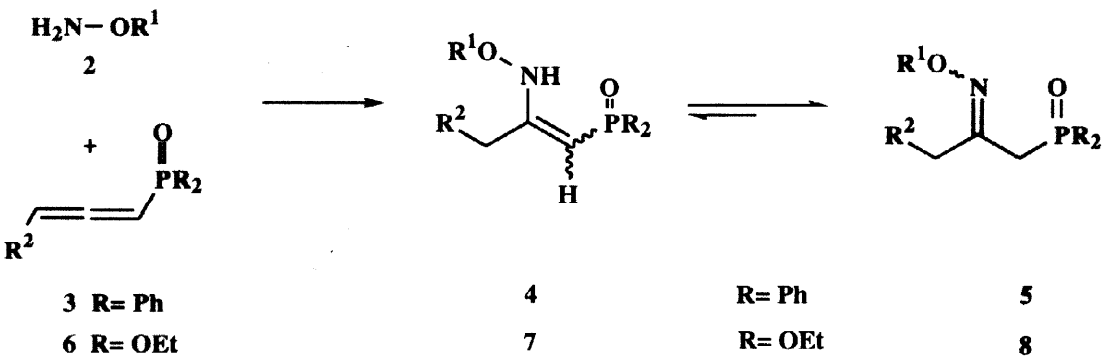
Scheme 1

RESULTS AND DISCUSSION

Synthesis of β-functionalized phosphine oxides **5**, phosphonates **8** and phosphonium salts **10**.

The preparation of phosphine oxide derivatives **5** was accomplished very easily and in very high yields by means of simple addition of hydroxylamine (**2**, R^1 = H), *O*-methyl hydroxylamine (**2**, R^1 = CH_3), and *O*-silyl hydroxylamines (**2**, R^1 = Me_3Si, $^tBuMe_2Si$) to substituted allenes **3** in chloroform (see Scheme 2, table 1). Compounds **5** were characterized on the basis of their spectroscopic data, which indicate that they are isolated as a mixture of *Z*- and *E*-oximes **5** when hydroxylamines **2** were used (see table 1). Thus, the ^{31}P-*NMR* spectrum for **5a** showed two different absorptions at δ_P 28.4 and 28.7 ppm in an approximate isomer ratio 50:50 as evidenced by the relative peak areas for each compound, in which the high-field chemical shift corresponds to the *E*-isomer **5a**. In the ^1H-*NMR* spectrum of **5a**, the methylene proton resonates at δ_H 3.59 ppm as a well resolved doublet with coupling constant of $^2J_{PH}$ 15.0 Hz, and the methyl group gives a singlet at

δ_H 1.94 ppm, while the *13C-NMR* shows absorptions at δ_C 35.3 ppm ($^1J_{PC}$ 66.7 Hz) and 13.6 ppm assignable to the carbon bonded to the phosphorus atom and the methyl group of the *E*-isomer. Conversely, the *Z*-isomer **5a** showed clearly different absorptions, namely a doublet at δ_H 3.29 ppm ($^2J_{PH}$ 14.0 Hz) for the methylene protons as well as a high-field signal for the methyl group at δ_H 1.96 ppm, while in the *13C-NMR* spectrum the methylene group resontes at δ_C 28.9 ppm ($^1J_{PC}$ 64.5 Hz) and the absorption of methyl group is shifted to a lower field (δ_C 19.5 ppm) relative to that of the *E*-isomer. This steric compression shift of about 5.9 ppm, in which the signal of the methyl group is shifted to a higher field for the *E*-isomer, is similar to that previously reported in other oximes.[13,14] The scope of this reaction for the formation of β-functionalized oximes **5** through simple addition of hydroxylamines **2** to allenes derived from phosphine oxides **3** is quite general, given that the method is applicable not only to hydroxylamine (table 1, entries 2, 3 and 4) but also to *O*-methyl (table 1, entries 5 and 6) and *O*-silyl substituted hydroxylamines (table 1, entries 4, 7, 8, 9 and 10).



Scheme 2

Table 1. β-oximophosphine oxides **4** and **5** prepared.

Entry	Compound	R^1	R^2	Yield (%)[a]	*Z/E* ratio[b]	m.p. (°C)
1	**4a**	$SiMe_2{}^tBu$	$-(C_5H_{10})-$	90	0/100	oil[c]
2	**5a**	H	H	80	50/50	190-192
3	**5b**	H	CH_3	74	0/100	150-152
4	**5c**	H	4-Me-C_6H_4	85	28/72	155-157
5	**5d**	Me	H	67	45/55	65-67
6	**5e**	Me	Me	70	67/33	88-91
7	**5f**	$SiMe_3$	H	75	60/40	157-159
8	**5g**	$SiMe_2{}^tBu$	H	84	36/64	oil[c]
9	**5h**	$SiMe_2{}^tBu$	Me	86	26/74	oil[c]
10	**5i**	$SiMe_2{}^tBu$	4-Me-C_6H_4	80	90/10	oil[c]

[a] Yield of isolated purified product. [b] *Z/E* ratio determined by ^{31}P-*NMR*. [c] Crude purified by flash chromatography.

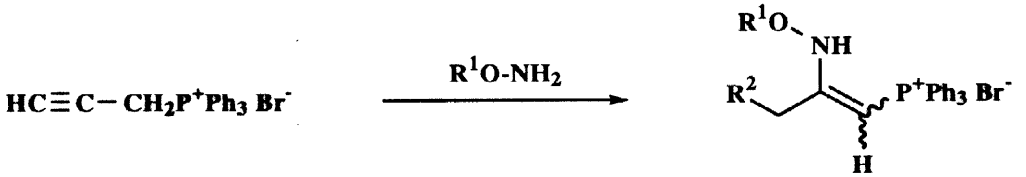
It is well known that for the construction of carbon-carbon double bonds,[15] not only phosphine oxide derivatives (Horner reaction) but also phosphonium salts (Wittig reaction) and phosphonates (Wadsworth-Emmons reaction) are very useful reagents. Therefore, taking into account our results in the preparation of β-oximo derivatives **5**, we tried to extend this reaction and to explore whether other allenes such as allenes derived from phosphonates **6** as well as the allenes derived from phosphonium salts (or their synthetic equivalent, the commercially available propargyl phosphonium salt[10a] **9**) showed a similar reaction pattern to that observed in the case of allenes **3** leading to new β-functionalized phosphorus compounds **8** and **10** in a similar way to that previously reported for hydrazines.[10a] Thus, the allene derived from phosphonate ester **6** reacted with silylated hydroxylamines (**2**, $R^1 = Me_3Si$, $^tBuMe_2Si$) and gave β-functionalized phosphonates **8** in very high yield (table 2, entries 1-5) in a similar way to that reported in the case of phosphine oxide derivatives **3**. Compounds **8** were characterized on the basis of their spectroscopic data, which indicate that they are also isolated as the *Z*- and *E*-isomer.

On the other hand, addition of trimethylsilyl hydroxylamine (**2**, $R^1 = Me_3Si$) to commercially available propargyl phosphonium bromide **9** in refluxing chloroform (*TLC* control) led to a mixture of *Z*- and *E*-functionalized enamines **10a** (see Scheme 3 and table 2, entry 6) whereas using bulky silyl hydroxylamines such *O-tert*-butyldimethylsilylhydroxylamine, *E*-β-oximo phosphonium salt **10b** (Scheme 3, table 2, entry 7) is exclusively obtained in excellent yield. Compounds **10** were characterized on the basis of their spectroscopic data. Examination of the *^1H* and *^{13}C-NMR* spectra is consistent with enamine structure of the phosphonium salt. In the *^1H-NMR* spectrum of **10a**, the vinylic proton resonates at δ_H 4.81 ppm as a well resolved doublet with coupling constant of $^2J_{PH}$ 13.2 Hz, and the methyl group gives a singlet at δ_H 1.70 ppm, while the *^{13}C-NMR* shows absorptions at δ_C 55.2 ppm ($^1J_{PC}$ 118.1 Hz) and 16.5 ppm ($^3J_{PC}$ 5.1 Hz) assignable to the carbon bonded to the phosphorus atom and the methyl group of the *E*-isomer.[10a,16] Conversely, for **10a** the *Z*-isomer showed clearly different absorptions, namely a doublet at δ_H 4.37 ppm ($^2J_{PH}$ 14.4 Hz) for the vinylic proton as well as a low-field signal for the methyl group at δ_H 1.8 ppm, while in the *^{13}C-NMR* spectrum the absorption of the methine carbon is shifted to a higher field (δ_C 54.0 ppm) with a higher value for the phosphorus-carbon coupling constant ($^1J_{PC}$ 123.8 Hz) relative to those of the *E*-isomer. Vicinal ^{13}C-^{31}P coupling constant ($^3J_{PC}$ 12.3 Hz) showed that the methyl group and the phosphorus atom in the β-enamino compound **10a** are related *trans*.[10a,16]

Table 2. β-Enamino phosphonates **8** and phosphonium salts **10** prepared.

Entry	Compound	R^1	R^2	Yield (%)[a]	*Z/E* ratio[b]	m.p. (°C)
1	**8a**	$SiMe_3$	H	55	55/45	oil[c]
2	**8b**	$SiMe_2{}^tBu$	H	65	25/75	oil[c]
3	**8c**	$SiMe_3$	Me	80	70/30	oil[c]
4	**8d**	$SiMe_2{}^tBu$	Me	68	50/50	oil[c]
5	**8e**	$SiMe_3$	4-Me-C_6H_4	70	55/45	oil[c]
6	**10a**	$SiMe_3$	H	95	55/45	190-192
7	**10b**	$SiMe_2{}^tBu$	H	90	0/100	205-207

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

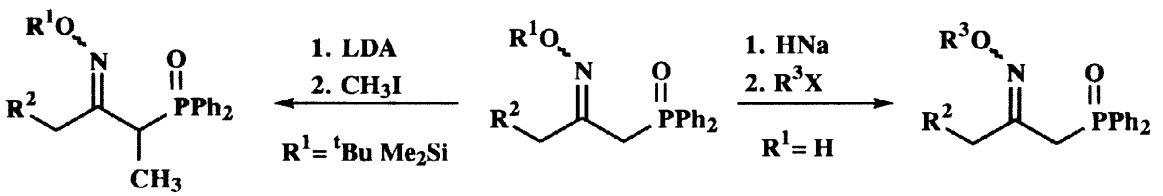


9 10

Scheme 3

O- and *C*-Alkylation of oxime anions derived from phosphine oxide **5**

Alkyl halides react with ambident oxime-anions on *O*, *N*, and *C* atoms and therefore selective alkylation of oximes is not an easy process.[1] In our case, the presence of an anion stabilizing group such as phosphine oxide could control the deprotonation at the internal less-substituted carbon. Thus, when functionalized oxime **5** was treated with lithium diisopropylamide (LDA) followed by addition of methyl iodide and aqueous work-up, *C*-methylated oxime **11** derived from phosphine oxide was obtained (Scheme 4). However, the use of natrium hydride as a base followed by addition of allyl bromide or *tert*butyldimethylsilyl chloride allows us the synthesis of *O*-substituted oximes **12** in a selective fashion. (Scheme 4).

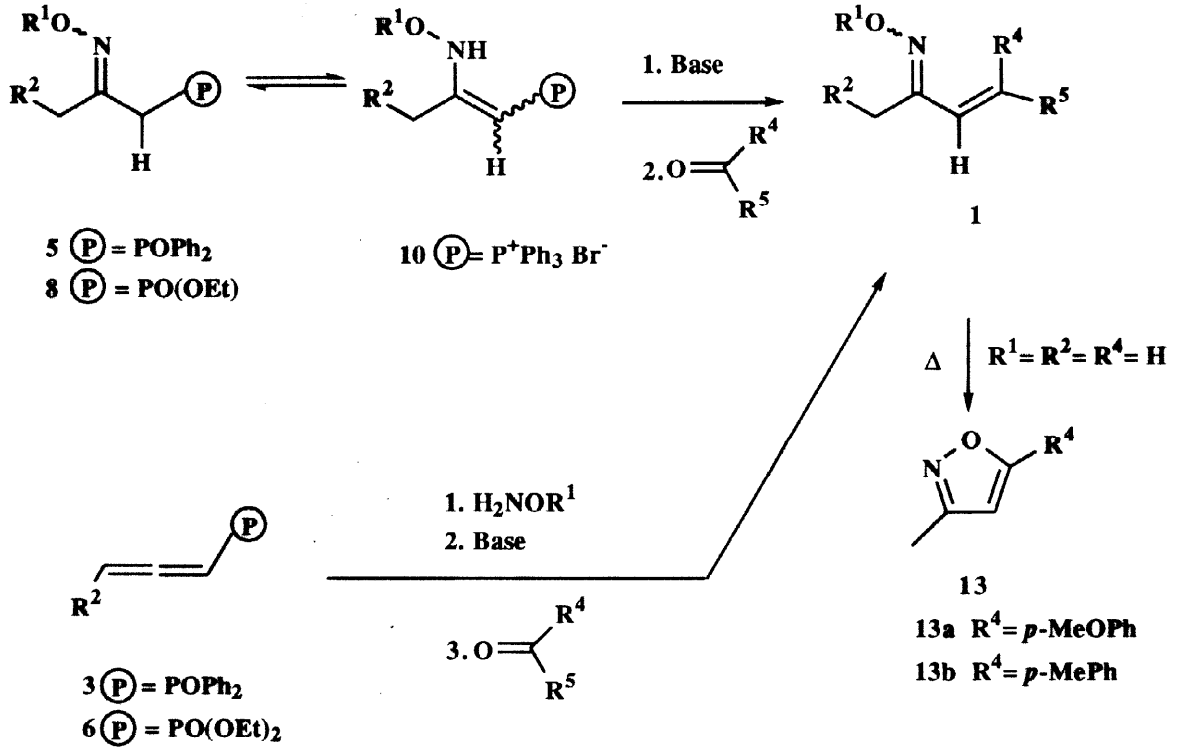


11 5 12

Scheme 4

Olefination reaction of β-functionalized phosphine oxides **5**, phosphonates **8** and phosphonium salts **10**.

β-Oximo phosphine oxides **5** could be suitable to efficiently achieve the homologation of oximes into their vinylogous compounds. Phosphine oxides **5** were treated with a base,[17] followed by addition of aromatic, heteroaromatic and aliphatic aldehydes and ketones (see Scheme 5, table 3) leading to 1-azadienes **1** with high *E*-stereoselectivity of the carbon-carbon double bond in excellent yield, after aqueous work up and flash-chromatography. The structure of compounds **1** was assigned on the basis of their spectroscopic data, which indicate that they are isolated as a mixture of *Z*- and *E*-isomers. Thus, ^{13}C-*NMR* spectrum of **1a** shows absorptions at δ_C 9.7 and 16.7 ppm for the methyl group of the *E*- and the *Z*-isomer in accordance with previous reported data.[14] Vicinal $^3J_{HH}$ coupling constants in the range of 16-17 Hz between the vinylic protons of **1** (R^4 = H) are consistent with the *E*-configuration of the carbon-carbon double bond. Therefore, this procedure is highly stereoselective affording the *E*-stereoisomer exclusively.



Scheme 5

This olefination reaction is not restricted to oximes **5**, and can be extended to oximes derived from phosphonates **8** and enamines derived from phosphonium salts **10** (Scheme 5). Methyllithium was the base chosen in the case of phosphonates **8**, whereas a weaker base such as potassium carbonate would suffice for enamines derived from phosphonium salts **10** probably owing to the partially stabilised nature of the phosphorus ylides generated . The use of this base requires no special precautions and provides excellent yields (Scheme 5, Table 3). It is noteworthy that the preparation of α,β-unsaturated oximes **1** does not require the isolation and purification of β-oximes **5**, **8** and **10**. Similar overall yields can be obtained in a "*one pot*" reaction from either allenes derived from phosphine oxides **3** and phosphonates **6** or from the commercially available propargylphosphonium bromide **9**, when these enamines **5**, **8** and **10**, after evaporation of the solvent, were directly treated with the adequate base with subsequent addition of carbonyl compounds. Finally, this route used for the preparation of α,β-unsaturated oximes can also be applied for five membered heterocycles formation when oximes **1** (R^1= H) are used. Heating **1** (R^1=R^2=R^4= H) at 110°C in toluene causes intramolecular Michael addition and gives isoxazoles **13**.

Table 3. α,β-unsaturated oximes **1** obtained.

Entry	Comp.	R^1	R^2	R^5	R^6	Yield (%)[a]	*Z/E* ratio[d]	m.p. (°C)
1	**1a**	H	H	H	$CH_3CH(CH_3)CH_2$	81	33/67	oil[e]
2	**1b**	H	H	H	3-C_5H_4N	72	0/100	124-125
3	**1c**	H	H	H	4-CH_3O-C_6H_4	79	0/100	139-140[f]
4	**1d**	H	H	C_6H_5	C_6H_5	80	56/44	oil[e]
5	**1e**	H	H		-$(CH_2)_5$-	74	0/100	oil[e]
6	**1f**	H	Me	H	$CH_3CH(CH_3)CH_2$	77	74/26	oil[e]
7	**1g**	Me	H	H	4-CH_3O-C_6H_4	75	45/55	oil[e]
8	**1h**	Me	H	H	C_6H_5-CH_2-CH_2	70	50/50	oil[e]
9	**1i**	Me	Me	H	$CH_3CH(CH_3)CH_2$	65	40/60	oil[e]
10	**1j**	Me	Me	H	2-(5-Me-furyl)	60	40/60	oil[e]
11	**1k**	$SiMe_2{}^tBu$	H	H	4-CH_3-C_6H_4	80 75[b] 78[c]	0/100	oil[e]
12	**1l**	$SiMe_2{}^tBu$	H	C_6H_5	C_6H_5	62	70/30	oil[e]
13	**1m**	$SiMe_2{}^tBu$	Me	H	C_6H_5-CH_2-CH_2	71	0/100	oil[e]
14	**1n**	$SiMe_2{}^tBu$	Me	H	4-CH_3-C_6H_4	65	0/100	oil[e]
15	**1o**	$SiMe_2{}^tBu$	Me		-$(CH_2)_5$-	60	50/50	oil[e]
16	**1p**	$SiMe_2{}^tBu$	-(C_5H_{10})-	H	4-CH_3-C_6H_4	80	40/60	oil[e]

[a] Yields of isolated compounds from phosphine oxides. [b] Yield of isolated compounds from phosphonates. [c] Yield of isolated compounds from phosphonium salt. [d] *Z/E* ratio determined by ^{31}P-*NMR*. [e] Purified by flash chromatography. [f] (*E*): 140-141[19]

In conclusion, we describe a new strategy for a simple and general method for the synthesis of a broad range of α,β-unsaturated oximes **1** and isoxazoles **13** from easily available starting materials and under mild reaction conditions. Azadienes **1** are useful compounds in organic chemistry not only for their application in organic synthesis[4-6] but also for their biological activities[3] while isoxazoles are very useful in medicinal chemistry.[18]

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 0.25 mm 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. ^1H-*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 Leco CHNS-932 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-Hydroxyenamino and/or β-Hydroximinoalkyldiphenylphosphine Oxides 4 and 5, and diethyl β-Hydroxyiminoalkylphosphonates 8. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 5 mmol of allene derivatives **3**, **6** or **9** and $CHCl_3$. (25 mL). A solution (5 mmol) of hydroxylamine or hydroxylamine hidrochloryde (in this case (6 mmol) of triethylamine was added) and $CHCl_3$ (10 mL) was added over a period of 10 min. The mixture was stirred and refluxed until *TLC* indicated the disappearance of the allene derivative (1 day to 3 days). The mixture was concentrated and the crude product was purified by recrystallization (hexane/CH_2Cl_2). In the case of hydroxylamine hydrochlorhyde the mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The CH_2Cl_2 layers were washed with water. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by recrystallization (hexane/CH_2Cl_2).

***E*-2-(*N*-^{t}butyldimethylsilyloxy)enamino-2-cyclohexylethenyldiphenylphosphine oxide (4a).** 2047 mg (90%) of **4a** as a yellow oil (*Rf* = 0.50, ethylacetate). Data for **4a**: ^1H-*NMR* (300 MHz) 0.05 (s, 6H, CH_3Si), 0.87 (s, 9H, $CH_3{}^tBu$), 1.00-1.96 (m, 12H, CH_2), 3.58 (d, $^2J_{PH}$ = 14.0 Hz, CH-P), 7.23-7.80 (m, 10H, arom); ^{13}C-*NMR* (75 MHz) -3.6 (CH_3Si), 18.2 (C-Si), 25.7 ($CH_3{}^tBu$), 25.4-30.4 (CH_2), 43.4 (CH), 83.4 (d,$^1J_{PC}$ = 108.0 Hz, CH-P), 128.2-131.8 (C-arom), 152.5 (C=N); ^{31}P-*NMR* (120 MHz) 28.6; *IR* (*KBr*) 3059, 2926, 2856, 1445, 1186; *MS* (EI) 341 (M^+-$SiMe_2{}^tBu$, 12). Anal. Calcd. for $C_{26}H_{38}NO_2PSi$: C, 68.57; H, 8.54; N, 3.15. Found: C, 68.80; H, 8.40; N, 3.20.

***Z*- and *E*-hydroxyiminopropyldiphenylphosphine oxide (5a).** 1092 mg (80%) of **5a** as a white solid. Data for **5a:** mp 190-192°C ; ^1H-*NMR* (300 MHz) 1.94 and 1.96 (s, 3H, *E*- and *Z*-CH_3), 3.29 (d, 2H,$^2J_{PH}$ = 14.0 Hz, *Z*-CH_2), 3.59 (d, $^2J_{PH}$= 14.8 Hz, *E*-CH_2), 7.26-7.48 (m, 10H, arom), 9.09 and 9.34 (s, 1H, OH); ^{13}C-*NMR* (75 MHz) 13.6 and 19.5 (*E*- and *Z*-CH_3), 28.9 (d,$^1J_{PC}$ = 64.5 Hz, *Z*-CH_2), 35.3 (d,$^1J_{PC}$ = 66.4 Hz, *E*-CH_2), 126.8-132.8 (C-arom), 145.6 and 147.4 (*E*- and *Z*-C=N); ^{31}P-*NMR* (120 MHz) 28.4 and 28.7 (*Z*- and *E*-isomers); *IR* (*KBr*) 3163, 3061, 2856, 1439,1177; *MS* (EI) 273 (M^+, 30). Anal. Calcd. for $C_{15}H_{16}NO_2P$: C, 65.93; H, 5.86; N, 5.13. Found: C, 66.02; H, 5.97; N, 5.19.

***E*-hydroxyiminobutyldiphenylphosphine oxide (5b).** 1062 mg (74%) of **5b** as a white solid. Data for **5d:** mp 150-152°C; ^1H-*NMR* (300 MHz) 1.00 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3), 2.37 (q, 2H,$^3J_{HH}$ = 7.3 Hz, CH_2), 3.59 (d, $^2J_{PH}$ = 15.0 Hz, CH_2), 7.26-7.85 (m, 10H, arom), 9.27 (s, 1H, OH); ^{13}C-*NMR* (75 MHz) 10.5 (CH_3), 28.5 (CH_2), 35.3 (d,$^1J_{PC}$ = 65.8 Hz, CH_2), 128.4-133.4 (C-arom), 153.5 (C=N); ^{31}P-*NMR* (120 MHz) 29.4; *IR* (*KBr*) 3187, 3066, 2874, 1440, 1175; *MS* (EI) 287 (M^+, 8). Anal. Calcd. for $C_{16}H_{18}NO_2P$: C, 66.87; H, 6.32; N, 4.86. Found: C, 67.02; H, 6.41; N, 4.91.

***Z*- and *E*-3-*p*-tolylhydroxyiminopropyldiphenylphosphine oxide (5c).** 1543 mg (85%) of **5c** as a white solid. Data for **5c:** mp 155-157°C; ^1H-*NMR* (300 MHz) 2.23 (s, 3H, CH_3), 3.10 (d, 2H,$^2J_{PH}$ =

13.6 Hz, Z-CH_2-P), 3.40 (d, $^2J_{PH}$ = 15.0 Hz, E-CH_2-P), 3.51 and 3.72 (s, 2H, E- and Z-CH_2), 6.97-7.76 (m, 14H, arom), 8.89 (s, 1H, OH); *^{13}C-NMR* (75 MHz) 21.0 (CH_3), 29.2 (d,$^1J_{PC}$ = 64.6 Hz, Z-CH_2), 33.8 (Z-CH_2), 34.8 (d,$^1J_{PC}$ = 67.4 Hz, Z-CH_2-P), 40.5 (E-CH_2-P), 128.4-136.1 (C-arom), 152.1 and 152.2 (E- and Z-C=N) ; *^{31}P-NMR* (120 MHz) 29.1 and 29.6 (E- and Z- isomers); *IR* (*KBr*) 3207, 1441, 1179, 1099; *MS* (EI) 363 (M^+, 9). Anal. Calcd. for $C_{22}H_{22}NO_2P$: C, 72.72; H, 6.10; N, 3.85. Found: C, 72.87; H, 6.21; N, 3.92

Z- and E-2-(*N*-methoxy)iminopropyldiphenylphosphine oxide (5d). 961 mg (67%) of **5d** as a white solid. Data for **5d**: mp 65-67°C; *^{1}H-NMR* (300 MHz) 2.04 and 2.05 (s, 3H, E- *and* Z-CH_3), 3.27 (d, $^2J_{PH}$ = 14.0 Hz, Z-CH_2), 3.51 (d, $^2J_{PH}$ = 15.2 Hz, E-CH_2), 3.51 and 3.70 (s, 3H, E- and Z-CH_3-O), 7.26-7.81 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 15.8 and 21.7 (E- and Z-CH_3), 32.6 (d, $^1J_{PC}$ = 64.1 Hz, Z-CH_2), 38.4 (d, $^1J_{PC}$ = 66.4 Hz, E-CH_2), 60.8 and 61.4 (E- and Z-CH_3-O), 128.3-131.9 (C-arom), 153.3 and 155.6 (E- and Z-C=N); *^{31}P-NMR* (120 MHz) 28.2 and 29.3 (Z- and E-isomers); *IR* (*KBr*) 3065, 2960, 2900, 1446, 1202; *MS* (EI) 287 (M^+, 8). Anal. Calcd. for $C_{16}H_{18}NO_2P$: C, 66.90; H, 6.27; N, 4.88. Found: C, 67.07; H, 6.42; N, 4.74.

Z- and E-2-(*N*-methxy)iminobutyldiphenylhosphine oxide (5e). 1053 mg (70%) of **5e** as a white solid. Data for **5e**: mp 88-91°C; *^{1}H-NMR* (300 MHz) 1.01-1.09 (m, 3H, Z- and E-CH_3), 2.39-2.43 (m, 2H, Z- and E-CH_2), 3.25 (d, $^2J_{PH}$ = 13.8 Hz, Z-CH_2-P), 3.50 (d, $^2J_{PH}$ = 14.8 Hz, E-CH_2-P), 3.48 and 3.65 (s, 3H, E- and Z-CH_3-O), 7.41-7.81 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 10.0 and 10.8 (E- and Z-CH_3), 22.6 and 28.6 (E- and Z-CH_2), 31.0 (d, $^1J_{PC}$ = 64.15 Hz, Z-CH_2-P), 36.0 (d, $^1J_{PC}$ = 66.4 Hz, E-CH_2-P), 60.7 and 61.3 (Z- and E-CH_3-O), 128.1-131.0 (C-arom), 153.3 and 155.6 (E- and Z-C=N); *^{31}P-NMR* (120 MHz) 28.1 and 29.0 (Z- and E-isomers); *IR* (*KBr*) 3066, 2940, 2814, 1438, 1193; *MS* (EI) 301 (M^+, 2). Anal. Calcd. for $C_{17}H_{20}NO_2P$: C, 67.77; H, 6.64; N, 4.65. Found: C, 67.92; H, 6.78; N, 4.76.

Z- and E-2-(*N*-trimethylsilyloxy)iminopropyldiphenylphosphine oxide (5f). 1294 mg (75%) of **5f** as a white solid. Data for **5f:** mp 157-159°C; *^{1}H-NMR* (300 MHz) 0.04 (s, 9H, E- and Z-CH_3Si), 1.93-2.07 (s, 3H, E- and Z-CH_3), 3.32 (d, $^2J_{PH}$ = 14.2 Hz, Z-CH_2-P), 3.59 (d, $^2J_{PH}$ = 15.0 Hz, E-CH_2-P), 7.61-7.81 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 15.7 and 21.2 (E- and Z-CH_3), 32.1 (d, $^1J_{PC}$ = 64.0 Hz, Z-CH_2), 38.6 (d, $^1J_{PC}$ = 66.4 Hz, E-CH_2), 128.3-131.7 (C-arom), 155.2 and 155.3 (E- and Z-C=N); *^{31}P-NMR* (120 MHz) 28.6 and 29.1 (Z- and E-isomers); *IR* (*KBr*) 3171, 3055, 2894, 1443, 1198, 815; *MS* (EI) 345 (M^+, 64). Anal. Calcd. for $C_{18}H_{24}NO_2PSi$: C, 62.61; H, 6.96; N, 4.08. Found: C, 62.92; H, 6.86; N, 4.14.

Z- and E-2-(*N*-^{t}butyldimethylsilyloxy)iminopropyldiphenylphosphine oxide (5g). 1625 mg (84%) of **5g** as a yellow oil (*Rf* = 0.56, ethylacetate). Data for **5g:** *^{1}H-NMR* (300 MHz) -0.06 and -0.04 (s, 6H, E- and Z-CH_3Si), 0.84 and 0.86 (s, 9H, E- and Z-$CH_3{}^tBu$), 1.96 and 2.01 (s, 3H, E- and Z-CH_3), 3.29 (d, $^2J_{PH}$ = 14.1 Hz, Z-CH_2), 3.59 (d, $^2J_{PH}$ = 15.2 Hz, E-CH_2), 7.42-7.75 (m, 10H, arom); *^{13}C-NMR* (75 MHz) -5.2 and -5.4 (E- and Z-CH_3Si), 15.6 and 17.7 (E- and Z-CH_3), 18.1 (C-Si), 25.8 and 25.9 (E- and Z-$CH_3{}^tBu$), (d,$^1J_{PC}$ = 65.2 Hz, Z-CH_2), 37.7 (d, $^1J_{PC}$ = 66.4 Hz, E-CH_2), 128.2-133.4 (C-arom), 152.5 and 154.8 (E- and Z-C=N); *^{31}P-NMR* (120 MHz) 28.6 and 29.0 (Z- and E-isomers); *IR* 3065, 2960, 2861, 1453, 1190, 854; *MS* (EI) 387 (M^+, 1). Anal. Calcd. for $C_{21}H_{30}NO_2PSi$: C, 65.12; H, 7.75; N, 3.62. Found: C, 65.40; H, 7.92; N, 3.50.

Z- and E-2-(*N*-^{t}butyldimethylsilyloxy)iminobutyldiphenylphosphine oxide (5h). 1724 mg (86%) of **5h** as a yellow oil (*Rf* = 0.61, ethylacetate). Data for **5h:** *^{1}H-NMR* (300 MHz) -0.01 and 0.03 (s, 6H, E- and Z-CH_3Si), 0.78 and 0.85 (s, 9H, E- and Z-$CH_3{}^tBu$), 0.80-0.99 (m, 3H, Z- and E-CH_3), 2.39-2.46 (m, 2H, Z- and E-CH_2), 3.25 (d, $^2J_{PH}$ = 15.4 Hz, E- CH_2-P), 3.53 (d, $^2J_{PH}$ = 14.3 Hz, Z-CH_2-P), 7.35-7.76 (m, 10H, arom); *^{13}C-NMR* (75 MHz) -5.2 and -3.4 (E- and Z-CH_3Si), 9.98 and 10.8 (E- and Z-CH_3), 18.2 (C-Si), 22.7 and 28.5 (E- and Z-CH_2), 25.8 and 26.0 (E- and Z-$CH_3{}^tBu$), 30.2 (d, $^1J_{PC}$ = 65.5 Hz, Z-CH_2), 36.0 (d,$^1J_{PC}$= 67.5 Hz, E-CH_2), 128.5-131.9 (C-arom), 153.1 and 160.1 (E- and Z-C=N); *^{31}P-NMR* (120 MHz) 29.8 and 30.1 (Z- and E-isomers); *IR* 3065, 2940, 2854, 1439, 1203, 841; *MS* (EI) 401 (M^+, 3). Anal. Calcd. for $C_{22}H_{32}NO_2PSi$: C, 65.84; H, 7.98; N, 3.49. Found: C, 65.70; H, 8.15; N, 3.56.

Z- and E-2-(*N*-^{t}butyldimethylsilyloxy)imino-3-*p*-tolylpropyldiphenylphosphine oxide (5i). 1908 mg (80%) of **5i** as a yellow oil (*Rf* = 0.52, ethylacetate). Data for **5i:** *^{1}H-NMR* (300 MHz) -0.02 and 0.01 (s, 6H, Z- and E-CH_3Si), 0.91 and 0.92 (s, 9H, Z- and E-$CH_3{}^tBu$), 2.17 and 2.30 (s, 3H, E- and Z-CH_3), 3.19 (d, $^2J_{PH}$ = 13.5 Hz, Z-CH_2), 3.42 (d, $^2J_{PH}$ = 14.4 Hz, E-CH_2), 3.75 and 3.91 (s, 2H, E- and Z-

CH_2), 7.05-7.78 (m, 14H, arom); *^{13}C-NMR* (75 MHz) -5.3 and -5.6 (*Z*- and *E*-CH_3Si), 18.2 (C-Si), 21.0 (*Z*- and *E*-CH_3), 25.6 and 26.0 (*E*- and *Z*-$CH_3{}^tBu$), 30.1 (d, $^2J_{PC}$ = 64.9 Hz, *Z*-CH_2-P), 34.2 (*Z*- and *E*-CH_2), 34.8 (d, $^1J_{PC}$ = 66.6 Hz, *E*-CH_2-P), 128.2-138.1 (C-arom), 156.7 (C=N); *^{31}P-NMR* (120 MHz) 28.2 and 29.2 (*Z*- and *E*-isomers); *IR* 3053, 2932, 1434, 1199, 843; *MS* (EI) 477 (M^+,1). Anal. Calcd. for $C_{13}H_{30}NO_4PSi$: C, 70.44; H, 7.55; N, 2.94. Found: C, 70.62; H, 7.40; N, 3.05.

***Z*- and *E*- 2-(*N*-trimethylsilyloxy)iminopropyldiethylfosfonate (8a).** 773 mg (55%) of **8a** as a colourless oil. Data for **8b:** *^1H-NMR* (300 MHz) 0.10-0.11 (s, 9H, CH_3Si), 1.21-1.30 (m, 6H, *Z*- and *E*-CH_3), 1.92 and 1.93 (s, 3H, *E*- and *Z*-CH_3), 2.70 (d, $^2J_{PH}$ = 21.6 Hz, *Z*-CH_2-P), 2.98 (d, $^2J_{PH}$ = 23.4 Hz, *E*- CH_2-P), 4.00-4.09 (m, 4H, *Z*- and *E*-CH_2-O); *^{13}C-NMR* (75 MHz) 1.2-1.8 (CH_3Si), 16.2-16.3 (*E*- and *Z*-CH_3), 26.8 (d, $^1J_{PC}$ = 135.2 Hz, *Z*-CH_2-P), 33.6 (d, $^1J_{PC}$ = 138.2 Hz, *E*-CH_2-P), 62.1 and 62.8(*Z*- and *E*-CH_2-O), 149.9 and 150.1 (*E*- and *Z*-C=N); *^{31}P-NMR* (120 MHz) 23.5 and 24.9 (*Z*- and *E*-isomers); *IR* 2885, 1455, 1202, 1025, 978; *MS* (EI) 281 (M^+, 11). Anal. Calcd. for $C_{10}H_{24}NO_4PSi$: C, 42.69; H, 8.60; N, 4.98. Found: C, 42.89; H, 8.72; N, 5.05.

***Z*- and *E*-2-(*N*-^{t}butyldimethylsilyloxy)iminopropyldiethylfosfonate (8b).** 1050 mg (65%) of **8b** as a yellow oil. Data for **8b:** *^1H-NMR* (300 MHz) -0.04 and 0.02 (s, 6H, *Z*- and *E*-CH_3Si), 0.79 and 0.80 (s, 9H, *Z*- and *E*-$CH_3{}^tBu$), 1.21-1.26 (m, 6H, *Z*- and *E*-CH_3), 1.87 and 1.92 (m, 3H, *E*- *and Z*- CH_3), 2.67 (d, $^2J_{PH}$ = 21.9 Hz, *Z*-CH_2-P), 2.97 (d, $^2J_{PH}$ = 23.4 Hz, *E*-CH_2-P), 3.99-4.08 (m, 4H, *Z*- and *E*-CH_2-O); *^{13}C-NMR* (75 MHz) -5.5 and -3.8 (*Z*- and *E*-CH_3Si), 15.8 and 15.9 (*E*- and *Z*-CH_3), 18.2 (C-Si), 25.5 and 25.8 (*Z*- and *E*-$CH_3{}^tBu$), 26.4 (d, $^1J_{PC}$ = 135.8 Hz, *Z*-CH_2-P), 33.5 (d, $^1J_{PC}$ = 137.2 Hz, *E*-CH_2-P), 61.9 and 62.7 (*Z*- and *E*-CH_2-O), 154.2 and 154.4 (*E*- and *Z*-C=N); *^{31}P-NMR* (120 MHz) 23.7 and 24.8 (*Z*- and *E*-isomers); *IR* 2989, 2856, 1496, 1256, 1024; *MS* (EI) 308 (M^+-CH_3, 2). Anal. Calcd. for $C_{13}H_{30}NO_4PSi$: C, 48.30; H, 9.29; N, 4.33. Found: C, 48.50; H, 9.40; N, 4.25.

***Z*- and *E*- 2-(*N*-trimethylsilyloxy)iminobutyldiethylfosfonate (8c).** 1180 mg (80%) of **8c** as a yellow oil. Data for **8c:** *^1H-NMR* (300 MHz) -0.04 and 0.02 (s, 9H, *Z*- and *E*-CH_3Si), 0.99-1.28 (m, 9H, *Z*- and *E*-CH_3), 1.69-1.73 (m, 4H, *Z*- and *E*-CH_2), 2.62 (d, 2H, $^2J_{PH}$ = 21.9 Hz, *Z*-CH_2-P), 2.96 (d, 2H, $^2J_{PH}$ = 23.7 Hz, *E*-CH_2-P), 4.00-4.13 (m, 4H, CH_2); *^{13}C-NMR* (75 MHz) 3.4 and 3.5 (CH_3Si), 16.2 and 16.3 (*E*- and *Z*-CH_3), 25.6 (d, $^1J_{PC}$ = 136.5 Hz, *Z*-CH-P), 27.7 and 27.8 (*E*- and *Z*- CH_2), 31.3 (d, $^1J_{PC}$ = 138.7 Hz, *E*-CH-P), 62.7 and 62.8 (*E*- and *Z*-CH_2-O), 152.3 and 154.5 (*E*- and *Z*-C=N); *^{31}P-NMR* (120 MHz) 23.5 and 23.9 (*Z*- and *E*-isomers); *IR* 2992, 1461, 1232, 1024, 978; *MS* (EI) 295 (M^+, 12). Anal. Calcd. for $C_{11}H_{26}NO_4PSi$: C, 44.74; H, 8.87; N, 4.74. Found: C, 44.92; H, 8.96; N, 4.81.

***Z*- and *E*-2-(*N*-^{t}butyldimethylsilyloxy)iminobutyldiethylfosfonate (8d).** 1146 mg (68%) of **8d** as a yellow oil. Data for **8d:** *^1H-NMR* (300 MHz) -0.06-(-0.04) (m, 6H, *Z*- and *E*-CH_3Si), 0.78-0.92 (m, 12H, *E*- and *Z*- CH_3 and $CH_3{}^tBu$), 1.27-1.37 (m, 6H, *Z*- and *E*-CH_3), 1.77-1.81 (m, 2H, *Z*- and *E*-CH_2), 2.69 (d, 2H, $^2J_{PH}$ = 21.6 Hz, *Z*-CH_2-P), 3.08 (d, 2H, $^2J_{PH}$ = 23.7 Hz, *E*-CH_2-P), 4.06-4.20 (m, 4H, *E*- and *Z*-CH_2); *^{13}C-NMR* (75 MHz) 3.5-3.6 (CH_3Si), 10.5 (*E*- and *Z*-CH_3), 16.2 and 16.3 (*E*- and *Z*-CH_2), 18.3 (C-Si), 25.6 (d, $^1J_{PC}$ = 135.7 Hz, *E*-CH-P), 25.6 ($CH_3{}^tBu$), 31.4 (d, $^1J_{PC}$ = 137.2 Hz, *Z*-CH_2-P), 61.8 and 62.7 (*Z*- and *E*-CH_2-O); *^{31}P-NMR* (120 MHz) 23.7 and 24.7 (*Z*- and *E*-isomers); *IR* 2985, 1441, 1236, 1025, 978; *MS* (EI) 337 (M^+, 20). Anal. Calcd. for $C_{14}H_{32}NO_4PSi$: C, 49.83; H, 9.56; N, 4.15. Found: C, 50.05; H, 9.66; N, 4.21.

***Z*- and *E*-2-(*N*-trimethylsilyloxy)imino-3-*p*-tolylpropyldiethylfosfonate (8e).** 1298 mg (70%) of **8e** as a yellow oil. Data for **8e:** *^1H-NMR* (300 MHz) 0.03 (m, 9H, CH_3Si), 1.18-1.36 (m, 6H, *Z*- and *E*-CH_3), 2.25 and 2.28 (s, 3H, *Z*- and *E*-CH_3), 2.62 (d, 2H, $^2J_{PH}$ = 21.9 Hz, *Z*-CH_2-P), 2.90 (d, 2H, $^2J_{PH}$ = 23.7 Hz, *E*-CH_2-P), 3.60 and 3.61 (s, 2H, *E*- and *Z*-CH_2), 4.05-4.14 (m, 4H, *E*- and *Z*-CH_2), 7.01-7.23 (AA'BB' system, 4H, arom); *^{13}C-NMR* (75 MHz) 1.9 (CH_3Si), 16.2 (*Z*- and *E*-CH_3), 20.9 (*Z*- and *E*-CH_3), 24.2 (d, $^1J_{PC}$ = 134.7 Hz, *E*-CH-P), 31.1 (d, $^1J_{PC}$ = 136.8 Hz, *Z*-CH_2-P), 39.9 (*Z*- and *E*-CH_2), 61.3-62.3 (*Z*- and *E*-CH_2-O), 128.1-136.4 (C-arom), 151.7 and 151.8 (*E*- and *Z*-C=N); *^{31}P-NMR* (120 MHz) 23.2 and 24.9 (*E*- *and Z*-isomers); *IR* 2980, 1445, 1202, 1024, 970; *MS* (EI) 371 (M^+, 9). Anal. Calcd. for $C_{17}H_{30}NO_4PSi$: C, 54.97; H, 8.14; N, 3.77. Found: C, 55.12; H, 8.19; N, 3.83.

General Procedure for the Preparation of the β-(*N*-alkylsiloxy)enaminoprop-1-enylphosphonium Bromides 10. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet,

and magnetic stirrer, was charged with (5 mmol) of propargyltriphenylphosphonium bromide **9** and *$CHCl_3$*. (25 mL). A solution (5 mmol) of hydroxylamine and *$CHCl_3$*. (10 mL) was added over a period of 10 min. The mixture was stirred and refluxed until *TLC* indicated the disappearance of the phosphonium salt **9** (1 day to 3 days). The mixture was concentrated and the crude product was purified by recrystallization ($CHCl_3$/ethyl acetate).

***Z*- and-*E*-2-(*N*-trimethylsilyloxy)enaminoprop-1-enylphosphonium bromide (10a).** 2186 mg (95%) of **10a** as a white solid. Data for **10a:** mp 190-192°C; *^1H-NMR* (300 MHz) -0.22 (s, 9H, *Z*- and-*E*-CH_3Si), 1.70 (s, 3H, *E*-CH_3), 1.80 (s, 3H, *Z*-CH_3), 4.37 (d, $^2J_{PH}$ = 14.4 Hz, *Z*-CH), 4.81 (d, $^2J_{PH}$ = 13.2 Hz, *E*-CH), 7.57-7.85 (m, 10H, arom), 9.42 (s, 1H, *Z*- and-*E*-NH); *^{13}C-NMR* (75 MHz) -1.0 (*Z*- and-*E*-CH_3Si), 16.5 (d, $^3J_{PC}$ = 5.1 Hz, *E*-CH_3),21.5 (d, $^3J_{PC}$= 12.3 Hz, Z-CH_2), 54.0 (d, $^1J_{PC}$ = 123.8 Hz, *Z*-CH), 55.2 (d, $^1J_{PC}$ = 118.1 Hz, *E*-CH), 128.4-135.0 (C-arom), 147.6 (*Z*- and-*E*-C=N); *^{31}P-NMR* (120 MHz) 21.8; *IR* (*KBr*) 3056, 2825, 1444, 1260, 852; *MS* (EI) 317 (M^+-Br^--$OSiMe_3$, 2). Anal. Calcd. for $C_{24}H_{29}NOPSiBr$: C, 59.27; H, 5.97; N, 2.88. Found: C, 59.52; H, 6.09; N, 2.90.

***E*-2-(*N*-^{t}butyldimethylsilyloxy)enaminoprop-1-enylphosphonium bromide (10b).** 2375 mg (90%) of 10b as a white solid. Data for 10b: mp 205-207°C; *^1H-NMR* (300 MHz) 0.00 (s, 6H, CH_3Si), 1.54 (s, 9H, $CH_3{}^tBu$), 1.97 (s, 3H, CH_3), 4.75 (d, $^2J_{PH}$ = 13.4 Hz, CH-P), 7.58-7.80 (m, 10H, arom), 9.05 (s, 1H, NH); *^{13}C-NMR* (75 MHz) 2.0 (CH_3Si), 15.6 (d, $^3J_{PC}$ = 6.5 Hz, CH_3), 18.0 (C-Si), 31.4 ($CH_3{}^tBu$), 54.5 (d, $^1J_{PC}$ = 121.8 Hz, CH), 130.0-135.0 (C-arom), 147.9 (C=N); *^{31}P-NMR* (120 MHz) 21.2; *IR* 3140, 2865, 1588, 1434, 1112; *MS* (EI) 333 (M^+-Br^--$SiMe_2{}^tBu$, 12). Anal. Calcd. for $C_{27}H_{35}NOPSiBr$: C, 61.37; H, 6.63; N, 2.65. Found: C, 61.52; H, 6.49; N, 2.70.

Synthesis of α-methyl 2-(*N*-^{t}butyldimethylsilyloxy)iminopropyldiphenylphosphine oxide 11 from 2-*O*-^{t}butyldimethylsilylhydroxyiminopropyldiphenylphosphine oxide 5g. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 5 mmol of lithium diisopropylamide (*LDA*) and *THF* (45 mL) The temperature was allowed to descend to -78°C and a solution (5 mmol) of phosphine oxide **5g** was then added. The mixture was allowed to stir for 1 h at room temperature. Then a solution (5 mmol) of alkyl halide in *THF* (10 mL) was added at -78°C. The mixture was stirred and refluxed until *TLC* indicated the disappearance of compound **5g** (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.

***Z*- and *E*-2-(*N*-^{t}butyldimethylsilyloxy)imino-1-methyl-propyldiphenylphosphine oxide (11).** 1343 mg (67%) of **11** as a yellow oil (*Rf* = 0.70, ethylacetate). Data for **11:** *^1H-NMR* (300 MHz) 0.02 and 0.06 (s, 6H, *E*- and *Z*-CH_3Si), 0.90 and 0.91 (s, 9H, *E*- and *Z*-$CH_3{}^tBu$), 1.22-1.39 (m, 3H, *E*- and *Z*-CH_3), 1.96 and 1.97 (s, 3H, *E*- and *Z*-CH_3), 4.65-4.70 (m, 1H, *E*- and *Z*-CH), 7.24-7.37 (m, 10H, arom); *^{13}C-NMR* (75 MHz) -5.0 and -4.9 (*E*- and *Z*-CH_3Si), 10.7 and 10.8 (*E*- and *Z*-CH_3), 18.2 (*E*- and *Z*-CH_3), 26.2 and 26.4 (*Z*- and *E*-$CH_3{}^tBu$), 32.4 (d,$^1J_{PC}$= 67.6 Hz, *E*-CH), 40.7 (d,$^1J_{PC}$= 67.1 Hz, *Z*-CH), 128.2-132.5 (C-arom), 158.5 and 160.5 (*E*- and *Z*-C=N); *^{31}P-NMR* (120 MHz) 28.7 and 29.2 (*Z*- and *E*-isomers); *IR* 3052, 2851, 1413, 1199, 847; *MS* (EI) 401 (M^+, 2). Anal. Calcd. for $C_{22}H_{32}NO_2PSi$: C, 65.84; H, 7.98; N, 3.49. Found: C, 66.03; H, 7.92; N, 3.50.

General Procedure for the Preparation of *O*-substituted oximes 12 from oxime 5a. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with NaH (6 mmol) and *THF* (30 mL). A solution of oxime **5a** (5 mmol) was then added. The mixture was allowed to stir for 1 h. A solution (5 mmol) of ^{t}butyldimethylsilyl chloride or allyl bromide in *THF* (10 mL) was added at room temperature. The mixture was stirred until *TLC* indicated the disappearance of the oxime (6 h to 1 day). The mixture was washed with water and extracted with *CH_2Cl_2*. The organic layers were dried over *$MgSO_4$*, filtered, and concentrated.

***E*-2-(*N*-^{t}butyldimethylsilyloxy)iminopropyldiphenylphosphine oxide (12a).** 1741 mg (90%) of **12a** as a yellow oil. Data for **12a**: same as *E*- isomer of **5g.**

***Z*- and *E*-2-(*N*-alyloxy)iminopropyldiphenylphosphine oxide (12b).** 1308 mg (80%) of **12b** as a yellow oil (*Rf* = 0.60, ethylacetate). Data for **12b:** *^1H-NMR* (300 MHz) 0.96-1.04 (m, 3H, *Z*- and *E*-CH_3), 2.27-2.46 (m, 2H, *Z*- and *E*-CH_2), 3.22 (d, 2H, $^2J_{PH}$= 14.4 Hz Z-CH_2), 3.45 (d, 2H, $^2J_{PH}$= 15.0 Hz,

E-CH_2), 4.16-4.36 (m, 2H, *Z*- and *E*-CH_2),4.92-5.22 (m, 2H, =CH_2), 5.62-5.75 (m, 1H, HC=), 7.22-7.84 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 10.2 and 11.1 (*E*- and *Z*-CH_3Si), 28.8 and 29.4 (*E*- and *Z*-CH_2), 31.2 (d, *$^1J_{CP}$*= 64.1 Hz, *Z*-CH_2), 36.2 (d,*$^1J_{PC}$*= 67.1 Hz, *E*-CH_2), 74.4 (CH_2), 117.5 (=CH_2), 128.2-135.0 (C-arom) 153.7 and 156.0 (*E*- and *Z*-C=N); *^{31}P-NMR* (120 MHz) 28.7 and 30.8 (*Z*- and *E*-isomers); *IR* 3067, 2982, 1649, 1446, 1200; *MS* (EI) 327 (M^+, 7) . Anal. Calcd. for $C_{19}H_{22}NO_2P$: C, 69.72; H, 6.73; N, 4.28 Found: C, 70.02; H, 6.83; N,4.35.

General Procedure for the Preparation of the Azadienes 1 from Functionalized Phosphine Oxides 5 or from Phosphonates 8. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 5 mmol of compound **5a** and *THF* (30 mL). The temperature was allowed to descend to-78°C and a solution of methyl lithium in *THF* was then added. The mixture was allowed to stir for 1 h. A solution (5 mmol) of carbonyl compound in *THF* (10 mL) 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 (50 mL) and extracted with CH_2Cl_2 (3 x 25 mL). 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).

***Z*- and *E*-6-methyl-3-hepten-2-one oxime (1a).** 570 mg (81%) of **1a** as a yellow oil (*Rf* = 0.40, ethylacetate/hexane, 1/3). Data for **1a:** *^{1}H-NMR* (300 MHz) 0.89-0.93 (m, 6H, CH_3), 1.67-1.73 (m, 1H, CH), 2.00 (s, 3H, *E*- and*Z*-CH_3), 2.03-2.13 (m, 2H, CH_2), 6.04-6.09 (m, 3H, *E*-CH=CH and *Z*-CH), 6.83 (d, 1H, *$^3J_{HH}$* = 16.0 Hz, *Z*- =CH); *^{13}C-NMR* (75 MHz) 9.7 and 16.7 (*E*- and *Z*-CH_3), 22.3 (CH_3), 28.3 (CH), 42.1 and 42.4 (*E*- and Z-CH_2), 135.2 and 139.3 (*E*- and *Z*- =CH), 153.1 and 156.3 (*E*- and *Z*-C=N); *IR* 3202, 2962, 2869, 1648, 1468, 1372; *MS* (EI) 141 (M^+, 31). Anal. Calcd. for $C_8H_{15}NO$: C, 68.03; H, 10.71; N, 9.92. Found: C, 67.86; H, 10.68; N, 9.95.

***E*-1-(3-pyridil)buten-3-one oxime (1b).** 580 mg (72%) of **1b** as a white solid. Data for **1b:** mp 124-125°C; *^{1}H-NMR* (300 MHz) 2.09 (s, 3H, CH_3), 6.77 (d, 1H, *$^3J_{HH}$* = 16.5 Hz, HC=), 6.89 (d, 1H, *$^3J_{HH}$* = 16.5 Hz, =CH) 7.20-7.29 (m, 1H, arom), 7.61-7.86 (m, 1H, arom), 8.44-8.50 (m, 1H, arom), 8.64-8.68 (m, 1H, arom), 10.21 (s, 1H, OH); *^{13}C-NMR* (75 MHz) 9.6 (CH_3), 119,0-149.5 (C-arom and C=C), 156.1 (C=N); *IR* (*KBr*) 3154, 3026, 2858, 1475, 1427, 1025; *MS* (EI) 162 (M^+, 27). Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.63; H, 6.22; N, 17.28. Found: C, 66.48; H, 6.24; N, 17.24.

***E*-1-(*p*-methoxyphenyl)buten-3-one oxime (1c).** 790 mg (79%) of **1c** as a white solid. Data for **1c:** mp 139-140°C; *^{1}H-NMR* (300 MHz) 2.07 (s, 3H, CH_3), 3.74 (s, 3H, CH_3-O), 6.67 (d, 1H, *$^3J_{HH}$*= 16.4 Hz, HC=), 6.76-6.83 (m, 3H, arom and =CH), 7.07 (AA'BB' system, 4H, arom), 7.68 (s, 1H, OH); *^{13}C-NMR* (75 MHz) 9.8 (CH_3), 55.3 (CH_3-O), 114.2 (HC=), 123.6 (C-arom), 128.2 (C-arom), 129.2 (C-arom), 133.0 (=CH), 156.9 (C-arom), 159.9 (C=N); *IR* (*KBr*) 3203, 3032, 1603, 1511, 1420, 1244; *MS* (EI) 191 (M^+, 41). Anal. Calcd. for $C_{11}H_{13}N_2O$: C, 69.08; H, 6.86; N, 7.33. Found: C, 68.89; H, 6.94; N, 7.35.

***Z*- and *E*-1,1-diphenylbuten-3-one oxime (1d).** 950 mg (80%) of **1d** as yellow oil (*Rf* = 0.34, ethylacetate/hexane, 1/3). Data for **1d:** *^{1}H-NMR* (300 MHz) 1.43 and 1.86 (m, 3H, *E*-and *Z*-CH_3), 6.58 (s, 1H, HC=), 7.13-7.34 (m, 11H, arom and OH); *^{13}C-NMR* (75 MHz) 14.1 and 30.9 (*E*- and *Z*-CH_3), 125.1-130.5 (C-arom), 140.2, 142.5, 146.8, 157.5 (C=N); *IR* 3082, 3062, 1601, 1496, 1447; *MS* (EI) 237 (M^+, 100). Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.97; H, 6.38; N, 5.91. Found: C, 80.74; H, 6.36; N, 5.89.

***E*-cyclohexylidenpropen-2-one oxime (1e).** 570 mg (74%) of **1e** as a yellow oil (*Rf* = 0.43, ethylacetate/hexane, 1/3). Data for **1e:** *^{1}H-NMR* (300 MHz) 1.38-2.35 (m, 10H, CH_2), 1.90 (s, 3H, CH_3), 4.67 (s, 1H, OH), 5.48 (s, 1H, =CH); *^{13}C-NMR* (75 MHz) 15.1 (CH_3), 22.1-39.2 (CH_2), 29.2 (CH_3), 118.3 (HC=), 147.7 (=C), 154.8 (C=N); *IR* 3281, 2931, 2854, 1710, 1660, 1451; *MS* (EI) 153 (M^+, 68). Anal. Calcd. for $C_9H_{15}NO$: C, 70.54; H, 9.87; N, 9.15. Found: C, 70.36; H, 9.89; N, 9.12.

***Z*- and *E*-7-methyl-4-octen-2-one oxime (1f).** 600 mg (77%) of **1f** as a yellow oil (*Rf* = 0.69, ethylacetate). Data for **1f:** *^{1}H-NMR* (300 MHz) 0.88-0.92 (m, 6H, CH_3), 1.05-1.23 (m, 3H, *E*- and *Z*-CH_3), 1.69-1.74 (m, 1H, CH), 2.02-2.12 (m, 2H, CH_2), 2.36-2.53 (m, 2H, *Z*- and *E*-CH_2), 6.01-6.03 (m, 2H, *E*-HC=CH), 6.17 (d, 1H, *$^3J_{HH}$*= 16.2 Hz, *Z*- HC=), 6.76 (d, 1H, *$^3J_{HH}$* = 16.2 Hz, *Z*-CH=); *^{13}C-NMR* (75 MHz) 10.9 and 12.1 (*E*- and *Z*-CH_3), 17.5 and 24.1 (*E*- and Z-CH_2), 22.3 (CH_3), 28.2 and 28.3 (*Z*- and *E*-CH), 42.1 and 42.5 (CH_2), 119.6 and 127.1 (*Z*- and *E*-HC=), 134.6 and 138.4 *E* -and *Z*- =CH), 156.8 and 160.7 (*E*- and *Z*-C=N); *IR* 3221, 2961, 1649, 1467; *MS* (EI) 155 (M^+, 54). Anal. Calcd. for $C_9H_{17}NO$: C, 69.62; H, 11.04; N, 9.03. Found: C, 69.46; H, 11.17; N, 9.01.

***Z*- and *E*-1-(*p*-methoxyphenyl)buten-3-one *O*-methyloxime (1g).** 769 mg (75%) of **1g** as a yellow oil (*Rf* = 0.42, ethylacetate/hexane, 1/3). Data for **1g**: *^{1}H-NMR* (300 MHz) 2.05 and 2.08 (s, 3H, *Z*- and *E*-CH_3), 3.80 and 3.91 (s, 3H, *E*- and *Z*- CH_3-O), 3.86 and 3.94 (s, 3H, *Z*- and *E*-CH_3-O), 6.65-7.84 (m, 6H, arom and HC=CH); *^{13}C-NMR* (75 MHz) 10.0 and 16.7 (*Z*- and *E*-CH_3), 55.1 and 55.4 (*E*- and *Z*-CH_3-O), 61.4 and 61.7 (*E*- and *Z*-CH_3-O), 114.2-135.7 (C-arom and HC=CH), 152.4 and 155.6 (*E*- and *Z*-C=N).; *IR* 3221, 2933, 1614, 1466, 1059; *MS* (EI) 205 (M^+, 8). Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70,24; H, 7.32; N, 6.83. Found: C, 70.53; H, 7.20; N, 7.02.

***Z*- and *E*-6-phenyl-3-hexen-2-one *O*-methyloxime (1h).** 710 mg (70%) of **1h** as a yellow oil (*Rf* = 0.90, ethylacetate). Data for **1h**: *^{1}H-NMR* (300 MHz) 1.85 and 1.92 (s, 1H, *Z*- and *E*-CH_3), 2.67-2.79 (m, 4H, CH_2), 3.81 and 3.87 (s, 3H, *Z*- and *E*-CH_3-O), 6.12-7.21 (m, 7H, arom and HC=CH); *^{13}C-NMR* (75 MHz) 10.3 (CH_3), 34.8-35.6 (CH_2), 61.8 and 62.2 (*E*- and *Z*-CH_3-O) 126.1-146.1 (C-arom and HC=CH), 155.6 (C=N); *IR* 3040, 2940, 1460, 1123, 1053; *MS* (EI) 203 (M^+, 8). Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 77.12; H, 8.56; N, 6.94.

***Z*- and *E*-7-methyl-4-octen-3-one *O*-methyloxime (1i).** 549 mg (65%) of **1i** as a yellow oil (*Rf* = 0.83, ethylacetate). Data for **1i**: *^{1}H-NMR* (300 MHz) 0.87-0.90 (m, 6H, CH_3), 0.96-1.10 (m, 3H, CH_3), 1.61-1.70 (m, 1H, CH), 1.97-2.05 (m, 2H, CH_2), 2.28-2.48 (m, 2H, CH_2), 3.79 and 3.80 (s, 3H, *E*- and *Z*-CH_3-O), 5.93-6.59 (m, 2H, HC=CH); *^{13}C-NMR* (75 MHz) 12.5 (CH_3), 22.3 (CH_3), 24.2 (CH_2), 28.2 (CH), 42.4 (CH_2), 61.2 (CH_3-O), 119.6-138.3 (C=C), 156.6 and 160.4 (*E*- and *Z*-C=N); *IR* 2954, 2821, 1656, 1480, 1066; *MS* (EI) 169 (M^+, 100). Anal. Calcd. for $C_{10}H_{19}NO$: C, 71.00; H, 11.24; N, 8.28. Found: C, 71.27; H, 11.36; N, 8.35.

***Z*- and *E*-1-[2-(5-methylfuryl)]-penten-3-one *O*-methyloxime (1j).** 579 mg (60%) of **1j** as a yellow oil (*Rf* = 0.83, ethylacetate). Data for **1j**: *^{1}H-NMR* (300 MHz) 1.05-1.20 (m, 3H, *E*- and *Z*-CH_3), 2.28 and 2.30 (s, 3H, *E*- and *Z*-CH_3), 2.41-2.51 (m, 2H, CH_2), 3.90 (s, 3H, CH_3-O), 5.97-6.33 (m, 2H, *E*- and *Z*- =CH-CH), 6.62 (d, 1H, $^3J_{HH}$ =16.6 Hz, CH=), 7.12 (d, 1H, $^3J_{HH}$ =16.5 Hz, CH=); *^{13}C-NMR* (75 MHz) 11.1 and 12.4 (*E*- and *Z*-CH_3), 13.4 and 13.5 (*Z*- and *E*-CH_3), 17.7 and 23.8 (*E*- and *Z*-CH_2), 61.3 and 61.5 (*E*- and *Z*-CH_3), 107.8-152.8 (C=CH-CH=C and HC=CH), 156.2 and 160.1 (*E*- and *Z*-C=N); *IR* 2940, 2821, 1740, 1467, 1382; *MS* (EI) 193 (M^+, 100). Anal. Calcd. for $C_{10}H_{19}NO$: C, 68.39; H, 7.77; N, 7.25. Found: C, 68.52; H, 7.83; N, 7.33.

***E*-1-*p*-tolylbuten-3-one *O*-^{t}butyldimethylsilyloxime(1k).** 1156 mg (80%) of **1k** as a yellow oil (*Rf* = 0.78, ethylacetate/hexane, 1/1). Data for **1k**: *^{1}H-NMR* (300 MHz) 0.34 (s, 6H, CH_3Si), 1.09 (s, 9H, $CH_3{}^tBu$), 2.19 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.94-7.46 (m, 6H, AA'BB' system and HC=CH); *^{13}C-NMR* (75 MHz) -5.0 (CH_3Si), 10.1 (CH_3), 18.1 (C-Si), 21.4 (CH_3), 26.3 ($CH_3{}^tBu$), 125.2-138.2 (C-arom and HC=CH), 156.3 (C=N); *IR* 3203, 2968, 1467, 1263, 1031; *MS* (EI) 289 (M^+, 2). Anal. Calcd. for $C_{17}H_{27}NOSi$: C, 70,59; H, 9.34; N, 4.84. Found: C, 70.83; H, 9.20; N, 4.95.

***Z*- and *E*-1,1-diphenylbuten-3-one *O*-^{t}butyldimethylsilyloxime (1l).** 1156 mg (62%) of **1l** as a yellow oil (*Rf* = 0.46, ethylacetate/hexane, 1/3). Data for **1l**: *^{1}H-NMR* (300 MHz) 0.17 and 0.21 (s, 6H, *Z*- and *E*-CH_3Si), 0.94 and 0.97 (s, 9H, *Z*- and *E*-$CH_3{}^tBu$), 1.49 and 1.52 (s, 3H, *E*- and *Z*-CH_3), 6.74-7.37 (m, 11H, arom and HC=); *^{13}C-NMR* (75 MHz) -5.1 (CH_3Si), 14.1 (CH_3), 18.4 (C-Si), 26.1 ($CH_3{}^tBu$), 126.0-130.3 (C-arom and C=C), 160.9 (C=N); *IR* 3073, 2940, 1460, 1263, 849; *MS* (EI) 351 (M^+, 4). Anal. Calcd. for $C_{22}H_{29}NOSi$: C, 75.21; H, 8.26; N, 3.99. Found: C, 75.52; H, 8.16; N, 4.05.

***E*-7-phenyl-4-hexen-2-one *O*-^{t}butyldimethylsilyloxime (1m).** 1179 mg (71%) of **1m** as a yellow oil (*Rf* = 0.88, ethylacetate). Data for **1m**: *^{1}H-NMR* (300 MHz) 0.20 (s, 6H, CH_3Si), 0.99 (s, 9H, $CH_3{}^tBu$), 1.05 (t, 3H,$^3J_{HH}$ = 7.5 Hz CH_3), 2.49-2.53 (m, 4H, CH_2), 2.80 (q, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2), 6.11-6.14 (m, 1H, =CH), 7.21-7.40 (m, 6H, arom and HC=); *^{13}C-NMR* (75 MHz) -5.0 (CH_3 Si), 11.4 (CH_3), 18.1 (CH_2), 18.4 (C-Si), 26.3 ($CH_3{}^tBu$), 35.1 (CH_2), 35.8 (CH_2), 126.2-141.7 (C-arom and C=C), 164.9 (C=N); *IR* 3039, 2933, 1747, 1473, 947; *MS* (EI) 317 (M^+-CH_3, 4). Anal. Calcd. for $C_{19}H_{31}NOSi$: C, 71.92; H, 9.78; N, 4.42. Found: C, 72.24; H, 9.67; N, 4.47.

***E*-1-*p*-tolylpenten-3-one *O*-^{t}butyldimethylsilyloxime (1n).** 985 mg (65%) of **1n** as a yellow oil (*Rf* = 0.84, ethylacetate/hexane, 1/1). Data for **1n**: *^{1}H-NMR* (300 MHz) 0.19 (s, 6H, CH_3Si), 0.95 (s, 9H, $CH_3{}^tBu$), 1.10 (t, 3H,$^3J_{HH}$ = 7.5 Hz, CH_3), 2.33 (s, 3H, CH_3), 2.61 (q, 2H,$^3J_{HH}$ = 7.8 Hz, CH_2), 6.73 (d,$^3J_{HH}$ = 16.5 Hz, HC=), 6.84 (d, $^3J_{HH}$ = 16.8 Hz, =CH), 7.12-7.38 (AA'BB' system, 4H, arom); *^{13}C-*

NMR (75 MHz) -5.2 (CH_3Si), 11.3 (CH_3), 18.1 (CH_2), 18.2 (C-Si), 21.3 (CH_3), 26,6 ($CH_3{}^tBu$), 124.6-138.1 (C-arom and C=C), 156.2 (C=N); *IR* 3203, 2968, 1473, 1256, 954; *MS* (EI) 303 (M^+, 5). Anal. Calcd. for $C_{18}H_{29}NOSi$: C, 71.29; H, 9.57; N, 4.62. Found: C, 71.03; H, 9.40; N, 4.67.

Z- and *E*-cyclohexylidenbuten-2-one *O*-^{t}butyldimethylsilyloxime (1o). 843 mg (60%) of **1o** as a yellow oil (*Rf* = 0.93, ethylacetate). Data for **1o**: ^{1}*H-NMR* (300 MHz) 0.19 and 0.20 (s, 6H, *E*- and *Z*-CH_3Si), 0.98 and 0.99 (s, 9H, *E*- and *Z*-$CH_3{}^tBu$), 1.04-1.14 (m, 3H, *E*- and *Z*-CH_3), 1.60-1.63 (m, 2H, *E*- and *Z*-CH_2), 2.21-2.50 (m, 10H, *E*- and *Z*-CH_2), 5.42 and 5.56 (s, 1H, *E*- and *Z*- =CH); ^{13}*C-NMR* (75 MHz) -5.15-(-5.13) (*E*- and *Z*-CH_3Si), 10.4 and 11.6 (*E*- and *Z*-CH_3), 18.4 (C-Si), 22.6-37.3 (*E*- and *Z*-CH_2), 26.1 and 26.3 (*E*- and *Z*-$CH_3{}^tBu$), 113.7 and 116.9 (*E*- and *Z*-=CH), 147.0 and 148.6 (*E*- and *Z*- =C), 162.0 and 163.5 (*E*- and *Z*-C=N); *IR* 3281, 2931, 2860, 1655, 1467; *MS* (EI) 281(M^+, 41). Anal. Calcd. for $C_{16}H_{31}NOSi$: C, 68.33; H, 11.03; N, 4.98. Found: C, 68.52; H, 11.17; N, 5.07.

Z- and *E*-3-cyclohexyl-1-*p*-tolylpropen-3-one *O*-^{t}butyldimethylsilyloxime (1p). 1428 mg (80%) of **1p** as a yellow oil (*Rf* = 0.91, ethylacetate). Data for **1p**: ^{1}*H-NMR* (300 MHz) 0.00 (s, 6H, CH_3Si), 0.74 and 0.75 (s, 9H, *Z*- and *E*-$CH_3{}^tBu$), 0.97-1.94 (m, 10H, CH_2), 2.11 and 2.13 (s, 3H, *Z*- and *E*-CH_3), 6.93-7.27 (m, 6H, arom and HC=CH); ^{13}*C-NMR* (75 MHz) -5.2 (CH_3Si), 18.0 (C-Si), 21.3 and 21.4 (*Z*- and *E*-CH_3), 26.1 and 26.3 (*Z*- and *E*-$CH_3{}^tBu$), 26.3-35.9 (CH_2), 39.8 (CH), 115.7 (HC=), 134.2 (=CH), 126.1-129.4 (C-arom), 153.2 and 156.6 (*E*- and *Z*-C=N); *IR* 3026, 2939, 1696, 1252, 951; *MS* (EI) 357(M^+, 6). Anal. Calcd. for $C_{22}H_{35}NOSi$: C, 73.95; H, 9.80; N, 3.92. Found: C, 73.72; H, 9.93; N, 4.02.

Synthesis of 1-*p*-tolylbuten-3-one *O*-trimethyloxime 1k from Functionalized Ylide 10b. A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with (5 mmol, 0.69 g) of E-2-(*N*-^{t}butyldimethylsilyloxy)enaminoprop-1-enylphosphonium bromide **10b**, (5 mmol) of potassium carbonate (K_2CO_3) and dried *DMF* (30 mL). The mixture was allowed to stir for 1 h at room temperature. Then a solution (5 mmol) of aldehyde in *DMF* (10 mL) 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 (50 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The organic layers were dried over $MgSO_4$, filtered, and concentrated. The azadiene **1k** was purified by flash-chromatography on silica gel (hexane/diethyl ether, 7/1).

General Procedure for the Preparation of Isoxazoles 13 from α,β-unsaturated oximes 1. 5 mmol of α,β-unsaturated oximes **1** were heated at 100°C in Toluene (15 mL) until *TLC* indicated the disappearance of the compound **1**. The mixture was concentrated and the crude product was purified by flash-chromatography on silica gel (hexane/diethyl ether, 10/1).

3-methyl-5-*p*-methoxyphenylisoxazol (13a). 280 mg (30%) of **13a** as a yellow solid. Data for **13a**: mp 107-109°C; ^{1}*H-NMR* (300 MHz) 2.25 (s, 3H, CH_3), 3.76 (s, 3H, CH_3-O), 6.15 (s, 1H, CH), 7.29 (AA'BB' system, 4H, arom); ^{13}*C-NMR* (75 MHz) 11.5 (CH_3), 55.4 (CH_3-O), 98.8 (CH), 114.3-132.0 (C-arom), 160.3, 160.9; *IR* (*KBr*) 1619, 1514, 1258, 836, 796; *MS* (EI) 189 (M^+, 100). Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.81; H, 5.86; N, 7.41. Found: C, 69.94; H, 5.84; N, 7.39.

3-methyl-5-*p*-tolylisoxazol (13b). 220 mg (26%) of **13b** as a yellow solid. Data for **13b**: mp 123-125°C; ^{1}*H-NMR* (300 MHz) 2.34 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 6.31 (s, 1H, CH), 7.45 (AA'BB' system, 4H, arom); ^{13}*C-NMR* (75 MHz) 11.5 (CH_3), 21.2 (CH_3), 99.5 (CH), 125.7-140.2 (C-arom), 159.8, 161.7; *IR* (*KBr*) 1624, 1509, 1267, 844; *MS* (EI) 173 (M^+, 100). Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.26; H, 6.41; N, 8.09. Found: C, 76.50; H, 6.40; N, 8.07.

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