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An Effective Strategy for the Preparation of α,β-Unsaturated Hydrazones and Pyrazole Derivatives. Synthetic Applications of β–Functionalized Phosphorus Compounds.

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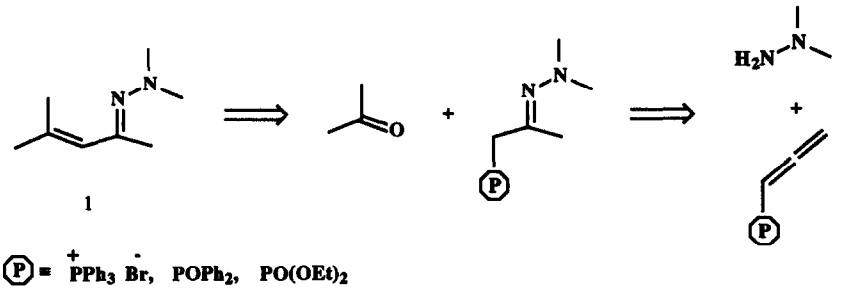
Abstract: β-Enehydrazino phosphonium salts **3** as well as β-hydrazono phosphine oxides **6** and phosphonates **7** are obtained from hydrazines, propargylphosphonium salts **2** and phosphorylated allenes **4** and **5**. β-Functionalized compounds **3**, **6** and **7** are used for the synthesis of α,β-unsaturated hydrazones **1**, pyrazoline **14** and pyrazole derivative **15**.

Hydrazones are common nitrogen derivatives of ketones and aldehydes and have received much attention in recent years because of their range of applications[1]. They form part of the structure of new azapeptides[2] and of biologically active antibiotic compounds such as cirratiomycin[3a], antrimycin[3b], azinothrycin[3c], citropeptin[3d] and megamycin[3e]. Hydrazones can be also used as a protective group of the carbonyl function[4], as formyl[5a] and acyl[5b] anion equivalents and synthetic intermediates in the preparation of heterocycles[6], nitriles[7], *gem*-difluorocompounds[8] (which play an important role in biological chemistry[9]) as well as in the asymmetric synthesis of chiral amines[10a], α-aminoaldehydes[10b] and α-aminoacids[10c]. Likewise, a very important methodology for the formation of carbon-carbon bonds has been developed in recent years using carbanions derived from hydrazones[11], which leads to very successful applications in the enantioselective synthesis of oxosulfones[12a], pheromones[12b], the potassium channel opener RP66471[12c] and of natural products such as the ionophore antibiotic indanomycin[13a], the sex pheromone serricornin[13b] and the sesquiterpene (+) eremophilinolide[13c].

In the chemistry of hydrazones the usefulness of the of α,β-unsaturated hydrazones is particularly significant as a result of their potential as starting materials in the preparation of β-hydroxy-[14] and α,β-unsaturated ketones[15] as well as of biologically active pyrazoles[16]. Likewise, unsaturated hydrazones have

recently been shown to be a versatile tool for the construction of six-membered heterocycles by means of the Diels-Alder reactivity of these substances as 1-azadienes[17]. The lack of general methods for synthesis of these compounds has probably limited their use in organic synthesis. Simple α,β-unsaturated hydrazones are mostly synthesized by the condensation reaction of carbonyl compounds with hydrazines. However, the preparation of such compounds is far from simple and especially in the case of ketones, only yields good results in very specific cases and generally leads to Michael addition[18].

In connection with our interest in the use of new β-functionalized phosphorus derivatives as synthetic intermediates in the preparation of acyclic[19] and cyclic[20] derivatives, we have recently used phosphorus compounds as homologation reagents[21] for conversion of carbonyl derivatives into α,β-unsaturated hydrazones with the introduction of two additional carbon atoms in the resulting chain. Here we aim to extend this methodology to the preparation of a wide range of unsaturated hydrazones **1** and to explore the synthetic use of phosphorylated hydrazones in the preparation of new groups of acyclic and cyclic compounds. Retrosynthetically, we envisaged obtaining hydrazones **1** by an olefination reaction of β-hydrazono phosphorus compounds (or their synthetic equivalents the tautomeric enehydrazino derivatives), obtaining both these from the addition of hydrazines to phosphorylated allenes (or the synthetic equivalent the propargylic phosphonium salts) (see scheme 1).



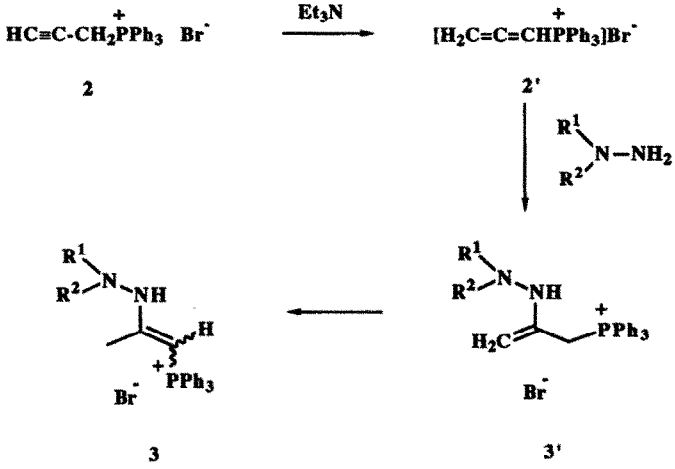
Scheme 1

RESULTS AND DISCUSSION

Preparation of β-enehydrazino phosphonium salts **3**.

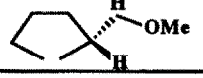
The required β-enehydrazino phosphonium salts **3** were very easily prepared in high yields through the addition of achiral and chiral hydrazines to commercially available propargyltriphenylphosphonium bromide **2** in refluxing chloroform (Scheme 2, Table 1). Compounds **3** were characterized on the basis of their spectroscopic data, which indicate that they are isolated as a mixture of the *Z*- and *E*-substituted phosphonium salts **3**, although for our purposes the separation of *Z*- and *E*-isomers is not necessary for subsequent reactions. Thus, the *^{31}P-NMR* spectrum for **3a** showed two different absorptions at δ_P 11.8 and 17.4 ppm in an approximate isomer ratio 25 / 75 as evidenced by the relative peak areas for each salt, in which the high-field chemical shift corresponds to the *Z*-isomer **3a**. Further examination of the *^1H* and *^{13}C-NMR* spectra is consistent with the enehydrazine structure of the phophonium salts. In the *^1H-NMR* spectrum of **3a**, the vinylic proton resonates at δ_H 4.61 as a well resolved doublet with coupling constant of $^2J_{PH}$ 18 Hz. and the methyl

group gives a singlet at δ_H 1.75, while the *13C-NMR* spectrum shows absorptions at δ_C 54.5 ($^1J_{PC}$ 117 Hz.) and 19.2 ppm ($^3J_{PC}$ 4.9 Hz.) assignable to the carbon bonded to phosphorus and the methyl group of the *E*-isomer[22]. Conversely, for **3a** the *Z*-isomer showed clearly different absorptions, namely a doublet at δ_H 3.58 ppm ($^2J_{PH}$ 19 Hz.) for the vinylic proton as well as a high-field signal for the methyl group at δ_H 2.07 ppm, while in the *13C-NMR* spectrum the absorption of methine carbon is shifted to higher field (δ_C 53.5) with a higher value of the phosphorus-carbon coupling constant ($^1J_{PC}$ 123 Hz.) relative to those of the *E*-isomer. Vicinal ^{13}C-^{31}P coupling constant ($^3J_{PC}$ 15.4 Hz.) showed that the methyl group and phosphorus atom in the β-enamino compound **3a** are related *trans*[22]. In this context, it is worth noting that when chiral hydrazines such as *SAMP* and *RAMP* are used, only the *E*-isomer is obtained (see Table 1).



Scheme 2

Table 1. β-Enehydrazino Phosphonium Salts **3** obtained.

Compound	R^1	R^2	Yield (%)[a]	*E/Z* ratio[b]	m.p. (°C)
3a	Me	Me	88	75 / 25	216-217(d)
3b	Me	H	91	0 / 100	134-135(d)
3c	Ph	H	70	37 / 63	189-190(d)
3d			85	100 / 0	159-160(d)
3e			79	100 / 0	159-160(d)

[a] Yield of isolated purified product. [b] *E/Z* ratio by *31P-NMR* assign.

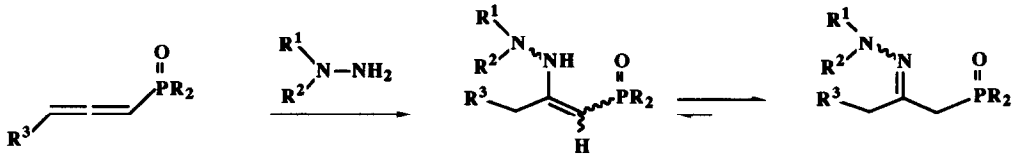
A mechanism that rationalizes the formation of **3** and that is consistent with the data is outlined in Scheme 2, in which hydrazines are caused to react with allenyltriphenylphosphonium bromide **2'** formed *"in situ"* from prop-2-ynyltriphenylphosphonium bromide and triethylamine[23]. Hydrazines undergo a nucleophilic addition

with allene and give the Michael-type adduct **3'**. This material is readily rearranged under the reaction conditions to the thermodynamically more stable isomer, the β-enehydrazino phosphonium salts **3**.

These results prompted us to extend this reaction and to explore whether stable phosphorylated allenes with hydrazines showed a similar reaction pattern leading to new β-functionalized phosphorus compounds, that could be versatile key intermediates in carbon-carbon formation processes and in the synthesis of heterocycles.

Preparation of β-hydrazono phosphine oxides **6** and phosphonates **7**.

Simple addition of achiral and chiral hydrazines to allenes derived from phosphine oxides **4** in refluxing of chloroform (*TLC* control) leads, after crystallization of the crude reaction mixture, to the formation of β-hydrazono phosphine oxides **6** in excellent yield, instead of the tautomeric enehydrazino compounds **6'** such as have been obtained in the case of phosphonium salts **3** (Scheme 3, Table 2). Compounds **6** were characterized by their spectroscopic data, which indicate that they are isolated as a mixture of the *syn* and *anti* hydrazones **6**[24,25]. Thus, the *^{31}P-NMR* spectrum of **6a** shows two absorptions at δ_P 27.8 and 29.5 ppm, in which the high-field chemical shift corresponds to the *syn*-isomer. Likewise, the *^{1}H-* and *^{13}C-NMR* spectra show well resolved doublets for the methylene proton and carbon of **6a**; the proton absorptions of the *syn* isomer is



4 R = Ph
5 R = OEt

6' R = Ph
7' R = OEt

6 R = Ph
7 R = OEt

Scheme 3

Table 2. β-Hydrazono Phosphine Oxides **6** and Phosphonates **7**.

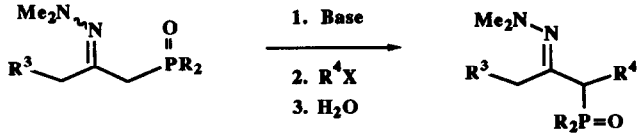
Compound	R^1	R^2	R^3	R	Yield (%)[a]	*syn/anti* ratio[b]	m.p. (°C)
6a	Me	Me	H	Ph	89	24 / 76	107-108
6b	Me	Me	Me	Ph	86	38 / 62	98-99
6c			H	Ph	90	15 / 85	91-92
6d	Me	H	H	Ph	72	46 / 54	101-102
6e	Ph	H	H	Ph	91	30 / 70	171-172
7a	Me	Me	H	OEt	92	64 / 36	oil[c]
7b	Ph	H	H	OEt	92	43 / 57	oil[c]

[a] Yield of isolated purified product. [b] *Syn/anti* ratio by *^{31}P-NMR* assign. [c] Purified by flash chromatography.

shifted to a lower field δ_H 3.73 relative to that of the *anti*-isomer δ_H 3.34, while this latter isomer shows a downfield shift absorption for the methylene carbon δ_C 41.3 relative to that observed for the *syn*-isomer δ_C 33.7 ppm. Similarly, the allene derived from phosphonate ester **5** reacts with hydrazines and gives, after short flash column chromatography, β-functionalized phosphonates **7** in very high yield.

C-Alkylation of hydrazone anions derived from phosphine oxide and phosphonates.

Carbanions derived from hydrazones are especially useful in organic synthesis[1] taking into account: the reactivity of the intermediate azaallyl anions, the control over stereochemistry of electrophilic substitution step afforded by the nitrogen substituent, and the considerable control of regiochemistry which can be reached using hydrazones.



6 R = Ph
7 R = OEt

8 R = Ph
9 R = OEt

Scheme 4

Table 3. β-Functionalized Hydrazones **8** and **9** obtained.

Compound	R^3	R^4	R	m.p.(°C)	Yield(%)[a]
8a	H	Me	Ph	118-119	72
8b	H	CH_2-CH=CH_2	Ph	124-125	80
8c	H	CH_2-$COOCH_3$	Ph	84-85	83
8d	Me	Me	Ph	oil[b]	79
9a	H	Me	OEt	oil[b]	71

[a] Yield of isolated compounds from **6** and **7**. [b] Purified by flash-chromatography.

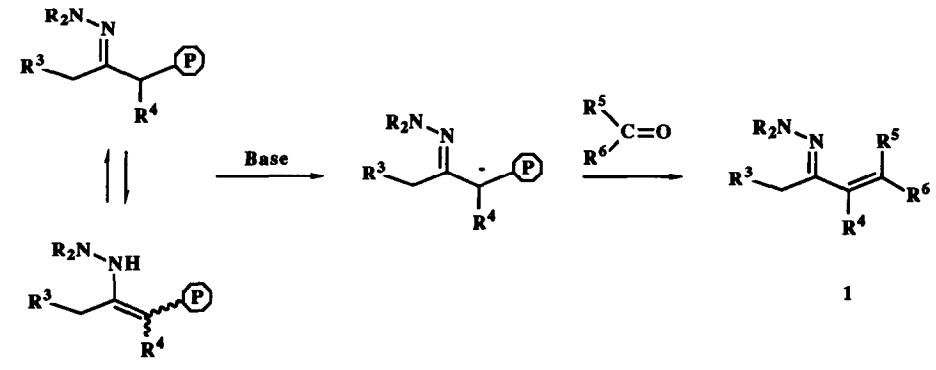
In our case, moreover, the presence of an anion stabilizing group such as phosphine oxide **6** or phosphonate **7** could control the deprotonation at the internal less-substituted carbon. Thus, when β-phosphorylated hydrazones **6** and **7** were treated with lithium diisopropylamide (*LDA*) followed by addition of alkyl halides and aqueous work-up, substituted compounds **8** and **9** were obtained (Scheme 4, Table 3).

Olefination reaction of β-functionalized phosphorus derivates **3**, **6** and **7**.

As we had proposed in Scheme 1, phosphorus compounds could be suitable to efficiently achieve the homologation of hydrazones into their vinylogous compounds. Thus, achiral and chiral phosphonium salts **3** were treated with a base followed by Wittig reaction of the phosphorane **10** with aliphatic, heteroaromatic and aromatic aldehydes (Scheme 5) leading to 1-azadienes **1** with high *E* stereoselectivity of the carbon-carbon

double bond in excellent yield (Table 4), after aqueous work-up and flash- chromatography. *n*-Buthyl lithium was the initial base chosen for the *"in situ"* generation of phosphorane **10**, although owing to the partially stabilised nature of this phosphorane, a weaker base such as potassium carbonate would suffice. The use of this base requires no special precautions and provides excellent yields (Scheme 5, Table 4). The structures of products **1** were ascertained on the basis of their spectroscopic data, which indicate that they are isolated as the *syn*- and *anti*-isomers. Vicinal ^3HH coupling constants in the range of 16-17 Hz. between the vinylic protons of **1** are consistent with the *E* configuration of the carbon-carbon double bond. Therefore, this procedure is highly stereoselective affording exclusively the *E* stereoisomer.

Wittig reaction of phosphoranes **10** generated *"in situ"* from phosphonium salts **3** and simple ketones fails, probably due to the partially stabilized character of these phosphoranes **10**. With these results in mind, we attempted to extend this methology for two carbon homologation of hydrazones, by using, instead of phosphonium salts **3**, the corresponding β-functionalized phosphines oxides **6** and phosphonates **7**. Thus, metalation of β-hydrazono phosphine oxides **6** and phosphonates **7** with methyl lithium or *LDA* followed by the addition of aldehydes and ketones led to the formation of α,β-unsaturated hydrazones **1**. While these olefination reactions by using **6** and **7** with aldehydes gave similar yields (Table 4) to that obtained in the case of phosphoranes **10**, these phosphorylated substrates **6** and **7** are especially useful for the elongation of ketones. It is noteworthy that the preparation of *C*-α-substituted hydrazones **1q**, **1r** and **1s** does not require the isolation and purification of the phosphine oxides **8a** and **8b** or the phosphonate **9a**. They can be obtained in a *"one pot"* reaction from **6** and **7** when these compounds are directly metallated in *THF* with subsequent addition of alkyl halide, a second equivalent of base, aldehydes and aqueous work-up, respectively.

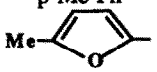


3 (P) = PPh_3 Br^-
6 (P) = $POPh_2$, R^4 = H
7 (P) = $PO(OEt)_2$, R^4 = H
8 (P) = $POPh_2$, $R^4 \neq$ H
9 (P) = $PO(OEt)_2$, $R^4 \neq$ H

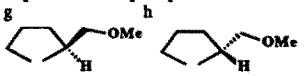
10 (P) = PPh_3
11 (P) = $POPh_2$
12 (P) = $PO(OEt)_2$

Scheme 5

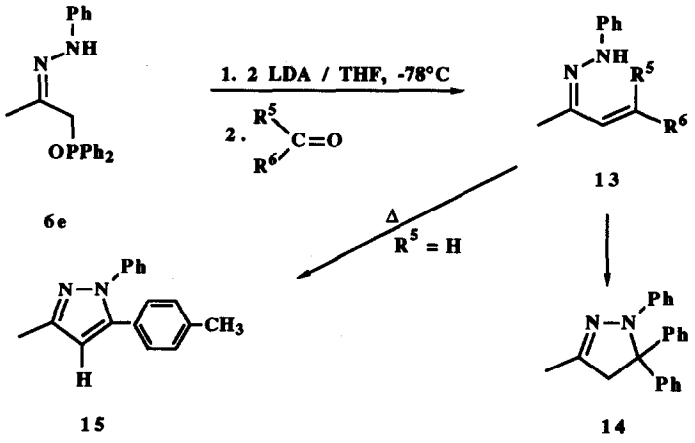
Table 4. α,β-Unsaturated Hydrazones 1 obtained.

Compound[a]	R_2	R^3	R^4	R^5	R^6	Yield.(%)		
1a	Me_2	H	H	H	p-O_2N-Ph	90[b]		
1b	Me_2	H	H	H	Me-CH=CH	84[b]		
1c	Me_2	H	H	H	Ph	82[b]		
1d	Me_2	H	H	H	p-Me-Ph	81[b]	77[c]	72[d]
1e	Me_2	H	H	H		81[b]		
1f	Me_2	H	H	H	Ph-CH_2-CH_2	91[b]		
1g	Me_2	H	H	H	$(CH_3)_2$-CH-CH_2	82[b]		
1h	g	H	H	H	p-Me-Ph	88[b]		
1i	h	H	H	H	p-Me-Ph	75[b]		
1j	Me_2	H	H	H	EtO_2C	80[b]		
1k	Me_2	Me	H	H	p-Me-Ph		85[c]	
1l	Me_2	H	H	Ph	Ph		80[c]	
1m	Me_2	H	H		- $(CH_2)_5$ -		86[c]	
1n	Me_2	H	H	Me	^{i}Bu		68[c]	
1o	g	H	H	H	Ph		93[c]	
1p	Me_2	H	H	H	p-MeO-Ph			74[d]
1q	Me_2	H	Me	H	p-Me-Ph	92[e]	66[c]	
1r	Me_2	H	CH_2=CH-CH_2-	H	p-Me-Ph	72[e]	57[c]	
1s	Me_2	H	Me	H	p-MeO-Ph		76[f]	60[d]

[a] Purified by flash-chromatography. [b] Yield of isolated compounds from phosphoranes **10**. [c] Yield of isolated compounds from phosphine oxides **6**. [d] Yield of isolated compounds from phosphonates **7**. [e] Yield of isolated compounds from **8**. [f] Yield of isolated compounds from **9**. [g] [h]



Finally, this strategy used for the preparation of α,β-unsaturated hydrazones can also be applied for five membered heterocycle formation when *N*-aryl hydrazones **6e** are used. In such substances, one or both nitrogen atoms of functionalized hydrazones can be used for the cyclisation. Acyclic α,β-unsaturated compound **13** is formed by deprotonation of both the N-H and the more substituted α-carbon of the starting *N*-phenyl hydrazone **6e** with two equivalents of a strong base like *LDA* followed by addition of *p*-tolyl aldehyde and work-up. Heating **13** at 100°C in toluene causes intramolecular Michael addition and gives pyrazole **15**. However, when diphenyl ketone reacts with the dianion from phosphorylated hydrazone **6e**, 1-azadiene **13** is not isolated and pyrazoline **14** is obtained directly instead (Scheme 6).



Scheme 6

In conclusion, β-functionalized phosphonium salts **3**, phosphine oxides **6** and phosphonates **7** described here are easily synthesized intermediates which can be used for an effective, versatile and high yielding synthesis of α,β-unsaturated hydrazones and five membered heterocycles.

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); 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: *THF* (sodium benzophenone ketyl); *DMF* (CaH_2); $CHCl_3$ (P_2O_5). All other reagents were recystallized 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 Bruker 250 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 shifs are given in ppm (δ); multiplicities are indicated by s (singlet), d (doblet), 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.

The following compounds were prepared by literature methods: 1,2-propadienyldiphenylphosphine oxide[26], 1,2-butadienyldiphenylphosphine oxide[26] and diethyl 1,2-propadienylphosphonate[26].

General Procedure for the Preparation of the β-Hydrazinoprop-1-enylphosphonium Bromides 3. A dry flask, 100-mL, 3-necked, fitted with a reflux condenser, gas inlet, dropping funnel, and magnetic stirrer, was charged 1.9 g (5

mmol) of popargyltriphenylphosphonium bromide **2**, 0.83 mL (6 mmol) of triethylamine and 30 mL of *$CHCl_3$*. A solution (5 mmol) of hydrazine and 20 mL of *$CHCl_3$* was added over 10 min. The mixture was stirred and refluxed until *TLC* indicated the disappearance of the phosphonium salt (1 day to 3 days). The mixture was diluted with 50 mL water 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 (*$CHCl_3$* / ethyl acetate).

Z- and *E*-β-dimethylhydrazino prop-1-enylphosphonium bromide (3a). 1936 mg (88 %) of **3a** as a yellow solid. Data for **3a**: mp 216-217 °C (dec.); *^1H-NMR* (250 MHz) 1.75 and 2.07 (s, 3H, *E*- and *Z*-CH_3), 2.32 and 2.72 (s, 6H, *Z*- and *E*-CH_3N), 3.58 (d, 1H, *$^2J_{PH}$* = 19 Hz, *Z*-CH), 4.61 (d, 1H, *$^2J_{PH}$* = 18 Hz, *E*-CH), 7.39-7.75 (m, 15H, arom), 9.72 and 10.01 (s, 1H, *Z*- and *E*-NH); *^{13}C-NMR* (75 MHz) 19.2 (d, *$^3J_{PC}$* = 4.9 Hz, *E*-CH_3), 22.0 (d, *$^3J_{PC}$* = 15.4 Hz, *Z*-CH_3), 45.8 and 46.0 (*E*- and *Z*-CH_3N), 53.5 (d, *$^1J_{PC}$* = 123 Hz, *Z*-CH), 54.5 (d, *$^1J_{PC}$* = 117 Hz, *E*-CH), 122.8-133.8 (C-arom), 164.2 and 164.4 (*E*- and *Z*-C-N); *^{31}P-NMR* (120 MHz) 11.8 (*Z*-isomer), 17.4 (*E*-isomer); *IR* (*KBr*) 3402, 3117, 2968, 2950, 1099; *MS* (70 eV) 360 (M^+- HBr, 5). Anal. Calcd for $C_{23}H_{26}N_2PBr$ (440.10): C, 62.71; H, 5.95 N, 6.36. Found: C, 62.52; H, 5.97; N, 6.34.

Z-β-methylhydrazino prop-1-enylphosphonium bromide (3b). 1939 mg (91 %) of **3b** as a yellow solid. Data for **3b**: mp 134-135 °C (dec.); *^1H-NMR* (250 MHz) 2.16 (s, 3H, CH_3), 3.38 (s, 3H, CH_3N), 3.51 (d, 1H, *$^2J_{PH}$* = 22.4 Hz, CH), 4.40 (s, 1H, NH), 7.39-7.63 (m, 16H, arom and NH); *^{13}C-NMR* (75 MHz) 23.3 (d, *$^3J_{PC}$* = 14.6 Hz, CH_3), 42.8 (CH_3N), 58.7 (d, *$^1J_{PC}$* = 120.7 Hz, CH), 128.4-133.8 (C-arom), 166.3 (C-N); *^{31}P-NMR* (120 MHz) 14.1; *IR* (*KBr*) 3435, 3203, 3111, 1656, 1550, 1430, 1101; *MS* (70 eV) 346 (M^+- HBr, 6). Anal. Calcd. for $C_{22}H_{24}N_2PBr$ (426.09): C, 61.96; H, 5.68; N, 6.57. Found: C, 61.72; H, 5.69; N, 6.59.

Z- and *E*-β-phenylhydrazino prop-1-enylphosphonium bromide (3c). 1708 mg (70 %) of **3c** as a yellow solid. Data for **3c**: mp 188-190 °C (dec.); *^1H-NMR* (250 MHz) 1.66 and 2.03 (s, 3H, *E*- and *Z*-CH_3), 3.90 (d, 1H, *$^2J_{PH}$* = 21.4 Hz, *Z*-CH), 4.81 (s, 1H, NH), 5.00 (d, 1H, *$^2J_{PH}$* = 14.3 Hz, *E*-CH), 5.35 (s, 1H, NH), 7.19-7.73 (m, 20H, arom); *^{13}C-NMR* (75 MHz) 21.5 (d, *$^3J_{PC}$* = 5.4 Hz, *E*-CH_3), 24.3 (d, *$^3J_{PC}$* = 14 Hz, *Z*-CH_3), 63.0 (d, *$^1J_{PC}$* = 118.4 Hz, CH), 122.5-144.4 (C-arom),165.7 (C-N); *^{31}P-NMR* (120 MHz) 15.3 (*Z*-isomer), 16.9 (*E*-isomer); *IR* (*KBr*) 3237, 3059, 1532, 1440, 1104; *MS* (70 eV) 408 (M^+- HBr, 12). Anal. Calcd for $C_{27}H_{26}N_2PBr$ (488.10): C, 66.38; H, 5.37; N, 5.74. Found: C, 66.56; H, 5.35; N, 5.72.

***E*-β-*N*-(*S*)-(-)-2-methoxymethylpyrrolidineamino prop-1-enylphosphonium bromide (3d).** 2168 mg (85 %) of **3d** as a yellow solid. Data for **3d**: mp 159-160 °C (dec.); *^1H-NMR* (250 MHz) 1.66-2.17 (m, 6H, ring CH_2), 1.75 (s, 3H, CH_3), 3.11-3.68 (m, 3H, CH_2O and CH), 3.16 (s, 3H, OCH_3), 4.84 (d, 1H, *$^2J_{PH}$* = 18.2 Hz, CH), 7.41-7.67 (m, 15H, arom), 9.68 (s, 1H, NH); *^{13}C-NMR* (75 MHz) 18.8 (d, *$^3J_{PC}$* = 5.1 Hz, CH_3), 20.7 (ring CH_2), 24.7 (ring CH_2), 52.9 (d, *$^1J_{PC}$* = 60.7 Hz, CH), 53.9 (ring CH_2), 58.3 (OCH_3), 64.1 (CH), 72.9 (CH_2O), 122.5-133.1 (C-arom), 164.5 (C-N); *^{31}P-NMR* (120 MHz) 17.5; *IR* (*KBr*) 3510, 3370, 3180, 3040, 1567, 1442; *MS* (70 eV) 430 (M^+- HBr, 3). Anal. Calcd. for $C_{27}H_{32}N_2OPBr$ (510.14): C, 63.51; H, 6.32; N, 5.49. Found: C, 63.65; H, 6.31; N, 5.47.

***E*-β-*N*-(*R*)-(+)-2-methoxymethylpyrrolidineamino prop-1-enylphosphonium bromide (3e).** 2015 mg (79 %) of **3e** as a yellow solid. Data for **3e**: mp 159-160 °C (dec.); *^1H-NMR* (250 MHz) 1.69-2.20 (m, 6H, ring CH_2), 1.80 (s, 3H, CH_3), 3.14-3.51 (m, 3H, CH_2O and CH), 3.19 (s, 3H, OCH_3), 4.87 (d, 1H, *$^2J_{PH}$* = 18.3 Hz, CH), 7.56-7.84 (m, 15H, arom), 9.79 (s, 1H, NH); *^{13}C-NMR* (75 MHz) 19.5 (d, *$^3J_{PC}$* = 5.2 Hz, CH_3), 21.4 (ring CH_2), 25.3 (ring CH_2), 52.7 (d, *$^1J_{PC}$* = 61.5 Hz, CH), 52.7 (ring CH_2), 54.6 (OCH_3), 59.0 (CH), 73.5 (CH_2O), 123.2-133.8 (C-arom), 165.2 (C-N); *^{31}P-NMR* (120 MHz) 17.6; *IR* (*KBr*) 3500, 3370, 3178, 3037, 1565, 1440; *MS* (70 eV) 431 (M^+- Br, 100). Anal. Calcd. for $C_{27}H_{32}N_2OPBr$ (510.14): C, 63.51; H, 6.32; N, 5.49. Found: C, 63.66; H, 6.30; N, 5.47.

General Procedure for the Preparation of the β-Hydrazonoalkyldiphenylphosphine oxides 6, and diethyl β-Hydrazonopropylphosphonates 7. A dry flask, 100-mL, 3-necked, fitted with a reflux condenser, gas inlet, dropping funnel, and magnetic stirrer, was charged 1.2 g (5 mmol) of allenediphenylphosphine oxide **4** (R^3 = H), or 1.27 g (5 mmol) of 1,2-butadienyldiphenylphosphine oxide **4** (R^3 = CH_3), or 0.88 g (5 mmol) of diethyl 1,2-propadienylphosphonate **5** (R^3 = H), and 30 mL of *$CHCl_3$*. A solution (5 mmol) of hydrazine and 20 mL of *$CHCl_3$* was added over 10 min. The mixture was stirred and refluxed until *TLC* indicated the disappearance of the phosphine oxide or phosphonate (1 day to 3 days). The mixture was concentrated and the crude product was purified by recrystallization (hexane / ethyl acetate).

***Syn*-and *anti*-β-*N*,*N*-dimethylhydrazonopropyldiphenylphosphine oxide (6a).** 1336 mg (89 %) of **6a** as a white solid. Data for **6a**: mp 107-108 °C; *^1H-NMR* (250 MHz) 2.08 and 2.09 (s, 3H, *anti*- and *syn*-CH_3), 2.18 and 2.22 (s, 6H, *anti*- and *syn*-CH_3N), 3.34 (d, 2H, *$^2J_{PH}$* = 14.3 Hz, *anti*-CH_2), 3.73 (d, 2H, *$^2J_{PH}$* = 14.9 Hz, *syn*-CH_2), 7.27-7.77 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 18.6 and 24.2 (*anti*- and *syn*-CH_3), 33.7 (d, *$^1J_{PC}$* = 64 Hz, *syn*-CH_2), 41.3 (d, *$^1J_{PC}$* = 64.5 Hz, *anti*-CH_2), 46.3 and 46.6 (*anti*- and *syn*-CH_3N), 127.9-133.1 (C-arom), 159.9 and 160.0 (*anti*- and *syn*-C=N); *^{31}P-NMR* (120 MHz)

27.8 and 29.5 (*syn*- and *anti*-isomers); *IR* (*KBr*) 2943, 2881, 1438, 1189; *MS* (70 eV) 300 (M^+, 6). Anal. Calcd. for $C_{17}H_{21}N_2OP$ (300.14): C, 67.97; H, 7.05; N, 9.33. Found: C, 68.14; H, 7.02; N, 9.31.

***Syn*- and *anti*-β-*N,N*-dimethylhydrazonobutyldiphenylphosphine oxide (6b).** 1351 mg (86 %) of **6b** as a white solid. Data for **6b**: mp 98-99 °C; ^{1}*H-NMR* (250 MHz) 1.02-1.14 (m, 3H, *syn*- and *anti*-CH_3), 2.15 and 2.21 (s, 6H, *syn*- and *anti*-CH_3N), 2.43-2.45 and 2.46-2.59 (m, 2H, *anti*- and *syn*-CH_2(Et)), 3.37 (d, 2H, $^2J_{PH}$ = 14.5 Hz, *syn*-CH_2), 3.71 (d, $^2J_{PH}$ = 14.9 Hz, *anti*-CH_2), 7.26-7.82 (m, 10H, arom); ^{13}*C-NMR* (75 MHz) 11.2 and 11.3 (*anti*- and *syn*-CH_3), 24.6 and 30.8 (*anti*- and *syn*-CH_2(Et)), 32.3 (d, $^1J_{PC}$ = 64.5 Hz, *syn*-CH_2), 38.2 (d, $^1J_{PC}$ = 64.8 Hz, *anti*-CH_2), 46.9 and 47.3 (*syn*- and *anti*-CH_3N), 128.3-137.8 (C-arom), 165.8 and 165.9 (*syn*- and *anti*-C=N); ^{31}*P-NMR* (120 MHz) 27.9 and 29.8 (*anti*- and *syn*-isomers); *IR* (*KBr*) 1704, 1617, 1435, 1181; *MS* (70 eV) 314 (M^+, 4). Anal. Calcd. for $C_{18}H_{23}N_2OP$ (314.16): C, 68. 76; H, 7.38; N, 8.92. Found: C, 68.57; H, 7.39; N, 8.94.

***Syn*- and *anti*-β-*N*-(*S*)-(-)-2-methoxymethylpyrrolidineimino propyldiphenylphosphine oxide (6c).** 1666 mg (90 %) of **6c** as a white solid. Data for **6c**: mp 91-92 °C; ^{1}*H-NMR* (250 MHz) 1.37-1.88 (m, 6H, ring CH_2), 1.91 and 1.92 (s, 3H, *anti*- and *syn*-CH_3), 2.85-3.21 (m, 3H, CH_2O and CH), 3.12 (s, 3H, OCH_3), 3.27 (d, 2H, $^2J_{PH}$ = 14.5 Hz, *syn*-CH_2), 3.50 (d, 2H, $^2J_{PH}$ = 14.7 Hz, *anti*-CH_2), 7.27-7.74 (m, 10H, arom); ^{13}*C-NMR* (75 MHz) 20.5 and 24.8 (*anti*- and *syn*-CH_3), 22.3 and 22.5 (ring *syn*- and *anti*-CH_2), 26.5 and 26.8 (ring *syn*- and *anti*-CH_2), 34.8 (d, $^1J_{PC}$ = 35.6 Hz, *syn*-CH_2), 41.8 (d, $^1J_{PC}$ = 35 Hz, *anti*-CH_2), 54.3 and 54.4 (ring *anti*- and *syn*-CH_2), 59.2 (*syn*- and *anti*-OCH_3), 66.1 and 66.5 (*syn*- and *anti*-CH), 74.9 and 75.4 (*syn*- and *anti*-CH_2O), 128.3-133.4 (C-arom), 156.7 and 161.4 (*anti*- and *syn*-C=N); ^{31}*P-NMR* (120 MHz) 27.4 and 29.7 (*syn*- and *anti*-isomers); *IR* (*KBr*) 1636, 1591, 1553, 1122; *MS* (70 eV) 370 (M^+, 100). Anal. Calcd. for $C_{21}H_{27}N_2O_2P$ (370.18): C, 68.07; H, 7.35; N, 7.57. Found: C, 68.26; H, 7.37; N, 7.54.

***Syn*- and *anti*-β-*N*-methylhydrazonopropyldiphenylphosphine oxide (6d).** 1030 mg (72 %) of **6d** as a white solid. Data for **6d**: mp 101-102 °C; ^{1}*H-NMR* (250 MHz) 1.54 and 1.82 (s, 3H, *anti*- and *syn*-CH_3), 2.76 and 2.90 (s, 3H, *syn*- and *anti*-CH_3N), 3.34 (d, 2H, $^2J_{PH}$ = 14 Hz, *syn*-CH_2), 3.44 (d, 2H, $^2J_{PH}$ = 14.5 Hz, *anti*-CH_2), 4.60 (s, 1H, NH), 7.26-7.81 (m, 10H, arom); ^{13}*C-NMR* (75 MHz) 15.9 and 25.3 (*anti*- and *syn*-CH_3), 34.9 (d, $^1J_{PC}$ = 64.5 Hz, *syn*-CH_2), 37.9 and 38.1 (*anti*- and *syn*-CH_3N), 41.4 (d, $^1J_{PC}$ = 66.4 Hz, *anti*-CH_2), 128.4-133.5 (C-arom), 140.0 and 141.2 (*syn*- and *anti*-C=N); ^{31}*P-NMR* (120 MHz) 29.7 and 31.2 (*anti*- and *syn*-isomers); *IR* (*KBr*) 3263, 2939, 1664, 1435, 1177; *MS* (70 eV) 286 (M^+, 32). Anal Calcd. for $C_{16}H_{19}N_2OP$ (286.12): C, 67.10; H, 6.69; N, 9.79. Found: C, 66.96; H, 6.72; N, 9.76.

***Syn*- and *anti*-β-*N*-phenylhydrazonopropyldiphenylphosphine oxide (6e).** 1584 mg (91 %) of **6e** as a white solid. Data for **6e**: mp 171-172 °C; ^{1}*H-NMR* (250 MHz) 1.58 and 1.91 (s, 3H, *anti*- and *syn*-CH_3), 3.38 (d, 2H, $^2J_{PH}$ = 14 Hz, *syn*-CH_2), 3.42 (d, 2H, $^2J_{PH}$ = 14.7 Hz, *anti*-CH_2), 6.73-7.79 (m, 15H, arom), 9.67 (s, 1H, NH); ^{13}*C-NMR* (75 MHz) 16.3 and 25.7 (*anti*- and *syn*-CH_3), 35.9 (d, $^1J_{PC}$ = 64.6 Hz, *syn*-CH_2), 41.2 (d, $^1J_{PC}$ = 66.2 Hz, *anti*-CH_2), 112.9-132.5 (C-arom), 145.2 and 146.9 (*anti*- and *syn*-C=N); ^{31}*P-NMR* (120 MHz) 30.2 and 31.7 (*syn*- and *anti*-isomers); *IR* (*KBr*) 3256, 1604, 1506, 1439, 1150; *MS* (70 eV) 348 (M^+, 100). Anal. Calcd. for $C_{21}H_{21}N_2OP$ (348.14): C, 72.38; H, 6.08; N, 8.04. Found: C, 72.54; H, 6.06; N, 8.06.

***Syn*- and *anti*-diethyl β-*N,N*-dimethylhydrazonopropylphosphonate (7a).** The crude product was purified by flash-chromatography (hexane / diethyl ether, 1 / 1) to afford 1086 mg (92 %) of **7a** as a yelow oil (R_f = 0.13, ethyl acetate). Data for **7a**: ^{1}*H-NMR* (250 MHz) 1.16-1.23 (m, 6H, *syn*- and *anti*-CH_3(Et)), 1.74 and 1.81 (s, 3H, *anti*- and *syn*-CH_3), 2.12 and 2.16 (s, 6H, *anti*- and *syn*-CH_3N), 2.53 (d, 2H, $^2J_{PH}$ = 22.3 Hz, *syn*-CH_2), 3.02 (d, 2H, $^2J_{PH}$ = 23.5 Hz, *anti*-CH_2), 3.96-4.02 (m, 4H, *syn*- and *anti*-CH_2(Et)); ^{13}*C-NMR* (75 MHz) 16.0 and 16.1 (*anti*- and *syn*-CH_3(Et)), 17.8 and 23.6 (*anti*- and *syn*-CH_3), 29.5 (d, $^1J_{PC}$ = 136 Hz, *syn*-CH_2), 36.9 (d, $^1J_{PC}$ = 134.3 Hz, *anti*-CH_2), 46.6 and 46.9 (*anti*- and *syn*-CH_3N), 61.6 and 61.7 (*anti*- and *syn*-CH_2(Et)), 159.0 and 160.2 (*anti*- and *syn*-C=N); ^{31}*P-NMR* (120 MHz) 24.1 and 25.2 (*anti*- and *syn*-isomers); *IR* 1644, 1453, 1256, 1019; *MS* (70 eV) 236 (M^+, 37). Anal. Calcd. for $C_9H_{21}N_2O_3P$ (236.13): C, 45.74; H, 8.96; N, 11.86. Found: C, 45.63; H, 8.99; N, 11.82.

***Syn*- and *anti*-diethyl β-*N*-phenylhydrazonopropylphosphonate (7b).** The crude product was purified by flash-chromatography (hexane / diethyl ether, 1 / 1) to afford 1307 mg (92 %) of **7b** as a yelow oil (R_f = 0.51, ethyl acetate). Data for **7b**: ^{1}*H-NMR* (250 MHz) 1.26-1.38 (m, 6H, *syn*- and *anti*-CH_3(Et)), 1.97 and 2.10 (s, 3H, *anti*- and *syn*-CH_3), 2.91 (d, 2H, $^2J_{PH}$ = 21.7 Hz, *syn*-CH_2), 2.93 (d, 2H, $^2J_{PH}$ = 23 Hz, *anti*-CH_2), 4.05-4.19 (m, 4H, *syn*- and *anti*-CH_2(Et)), 6.76-7.34 (m 5H, arom), 8.50 (s, 1H, NH); ^{13}*C-NMR* (75 MHz) 15.5 and 25.1 (*anti*- and *syn*-CH_3), 16.3 and 16.4 (*syn*- and *anti*-CH_3(Et)), 30.5 (d, $^1J_{PC}$ = 135.9 Hz, *syn*-CH_2), 36.7 (d, $^1J_{PC}$ = 136 Hz, *anti*-CH_2), 62.0 and 62.7 (*anti*- and *syn*-CH_2(Et)), 112.1-129.0 (C-arom); 145.6 and 146.5 (*anti*- and *syn*-C=N); ^{31}*P-NMR* (120 MHz) 24.7 and 25.8 (*anti*- and *syn*-isomers); *IR* 3281, 1608, 1498, 1241, 1028; *MS* (70 eV) 284 (M^+, 100). Anal. Calcd. for $C_{13}H_{21}N_2O_3P$ (284.13): C, 54.90; H, 7.45; N, 9.86. Found: C, 54.71; H, 7.43; N, 9.88.

General Procedure for the *C*-alkylation of β-Hydrazonoalkyldiphenylphosphine oxides 6 and diethyl β-hydrazonopropylphosphonates 7. A dry flask, 100-mL, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged 5 mmol of lithium diisopropylamide (LDA) and 45 mL of THF. The temperature was allowed to descend to -78 °C and a solution 1.5 g (5 mmol) of β-*N,N*-dimethylhydrazonopropyldiphenylphophine oxide **6a**, or 1.6 g (5 mmol) of β-*N,N*-dimethylhydrazonobutyldiphenylphophine oxide **6b**, or 1.2 g (5 mmol) of diethyl β-*N,N*-dimethylhydrazonopropylphosphonate **7a** in 40 mL of THF was then added. The mixture was allowed to stir for 1 h. A solution 5 mmol of alkyl halide in 10 mL of THF was added at -78 °C. The mixture was stirred until TLC indicated the disappearance of compounds **6a**, **6b** or **7a** (3 h to 2 days). The mixture was diluted with 50 mL water and extracted with CH_2Cl_2. The CH_2Cl_2 layers were washed with water. The organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by recrystallization from CH_2Cl_2 / hexane or by flash-chromatography (hexane / diethyl ether, 1 / 1).

α-Methyl-β-*N,N*-dimethylhydrazonopropyldiphenylphosphine oxide (8a). 1131 mg (72 %) of **8a** as white solid. Data for **8a**: mp 118-119 °C; ^1H-*NMR* (250 MHz) 1.37 (dd, 3H, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 15.9 Hz, CH_3), 2.00 (s, 3H, CH_3), 2.12 (s, 6H, CH_3N), 3.46-3.52 (m, 1H, CH), 7.26-7.86 (m, 10H, arom); ^{13}C-*NMR* (75 MHz) 11.2 (CH_3), 15.3 (CH_3), 43.9 (d, $^1J_{PC}$ = 65.7 Hz, CH), 46.5 (CH_3N), 128.1-131.6 (C-arom), 165.6 (C=N); ^{31}P-*NMR* (120 MHz) 32.2; *IR* (*KBr*) 2973, 2848, 1440, 1203; *MS* (70 eV) 314 (M^+, 9). Anal. Calcd for $C_{18}H_{23}N_2OP$ (314.16): C, 68.76; H, 7.38; N, 8.91. Found: C, 68.54; H, 7.40; N, 8.88.

α-Allyl-β-*N,N*-dimethylhydrazonopropyldiphenylphosphine oxide (8b). 1361 mg (80 %) of **8b** as white solid. Data for **8b**: mp 124-125 °C; ^1H-*NMR* (250 MHz) 2.01 (s, 3H, CH_3), 2.15 (s, 6H, CH_3N), 2.23-2.46 (m, 1H, CH_2), 2.73-2.87 (m, 1H, CH_2), 3.46-3.56 (m, 1H, CH), 4.94-5.06 (m, 2H, H_2C=), 5.56-5.69 (m, 1H, =CH), 7.26-7.91 (m, 10H, arom); ^{13}C-*NMR* (75 MHz) 15.9 (CH_3), 29.6 (CH_2), 46.6 (CH_3N), 49.3 (d, $^1J_{PC}$ = 64.5 Hz, CH), 116.9 (H_2C=), 128.1-131.7 (C-arom), 134.5 (d, $^3J_{PC}$ =14.5 Hz, =CH), 164.1 (C=N); ^{31}P-*NMR* (120 MHz) 31.3; *IR* (*KBr*) 2967, 2861, 1440, 1177; *MS* (70 eV) 340 (M^+, 2). Anal. Calcd. for $C_{20}H_{25}N_2OP$ (340.17): C, 70.55; H, 7.41; N, 8.23. Found: C, 70.28; H, 7.43; N, 8.21.

α-Methoxycarbonylmethyl-β-*N,N*-dimethylhydrazonopropyldiphenylphosphine oxide (8c). 1544 mg (83 %) of **8c** as white solid. Data for **8c**: mp 84-85 °C; ^1H-*NMR* (250 MHz) 1.98 (s, 3H, CH_3), 2.19 (s, 6H, CH_3N), 2.57-2.68 (m, 1H, CH_2), 3.04-3.49 (m, 1H, CH_2), 3.58 (s, 3H, OCH_3), 3.62-3.91 (m, 1H, CH), 7.26-7.86 (m, 10H, arom); ^{13}C-*NMR* (75 MHz) 17.0 (CH_3), 31.5 (CH_2), 46.5 (d, $^1J_{PC}$ = 64.5 Hz, CH), 46.5 (CH_3N), 51.8 (OCH_3), 127.6-132.1 (C-arom), 162.7 (C=N), 171.4 (d, $^3J_{PC}$ = 17.8 Hz, C=O); ^{31}P-*NMR* (120 MHz) 31.1; *IR* (*KBr*) 2973, 2861, 1756, 1446, 1190; *MS* (70 eV) 372 (M^+, 9). Anal. Calcd. for $C_{20}H_{25}N_2O_3P$ (372.16): C, 64.49; H, 6.77; N, 7.52. Found: C, 64.62; H, 6.75; N, 7.50.

α-Methyl-β-*N,N*-dimethylhydrazonobutyldiphenylphosphine oxide (8d). 1296 mg (79 %) of **8d** as a yelow oil (R_f = 0.51, acetone). Data for **8d**: ^1H-*NMR* (250 MHz) 0.84-1.05 (m, 3H, $CH_{3(Et)}$), 1.29-1.44 (m, 3H, CH_3), 2.26 (s, 6H, CH_3N), 2.36-2.55 (m, 2H, CH_2), 3.47-3.62 (m, 1H, CH), 7.26-7.79 (m, 10H, arom); ^{13}C-*NMR* (75 MHz) 7.3 (CH_3), 11.2 (CH_3), 26.7 (CH_2), 43.1 (d, $^1J_{PC}$ = 66 Hz, CH), 47.3 (CH_3N), 128.0-132.9 (C-arom), 169.9 (C=N); ^{31}P-*NMR* (120 MHz) 31.3; *IR* (*KBr*) 1702, 1438, 1187, 1118; *MS* (70 eV) 328 (M^+, 14). Anal. Calcd for $C_{19}H_{25}N_2OP$ (328.17): C, 69.48; H, 7.68; N, 8.53. Found: C, 69.66; H, 7.65; N, 8.51.

α-Methyl diethyl β-*N,N*-dimethylhydrazonopropylphosphonate (9a). 888 mg (71 %) of **9a** as a yelow oil (R_f = 0.49, acetone). Data for **9a**: ^1H-*NMR* (250 MHz) 1.17-1.36 (m, 9H, CH_3 and $CH_{3(Et)}$), 1.98 (s, 3H, CH_3), 2.39 (s, 6H, CH_3N), 2.83-2.94 (m, 1H, CH), 3.98-4.12 (m, 4H, CH_2); ^{13}C-*NMR* (75 MHz) 12.2 (CH_3), 15.3 (CH_3), 16.2 ($CH_{3(Et)}$), 41.4 (d, $^1J_{PC}$ = 134 Hz, CH), 46.6 (CH_3N), 61.9 (CH_2), 164.0 (C=N); ^{31}P-*NMR* (120 MHz) 28.7; *IR* 1637, 1453, 1392, 1050; *MS* (70 eV) 250 (M^+, 34). Anal. Calcd. for $C_{10}H_{23}N_2O_3P$ (250.15): C, 47.97; H, 9.27; N, 11.20. Found: C, 47.88; H, 9.24; N, 11.23.

General Procedure for the Preparation of the α,β-Unsaturated Hydrazones 1 from Functionalized Ylides 10. A dry flask, 100-mL, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged 5 mmol of β-enehydrazino phosphonium salt **3** and 0.69 g (5 mmol) of potassium carbonate (K_2CO_3) and 40 mL of *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 5 days). The mixture was diluted with 50 mL water and extracted with diethyl ether. The diethyl ether layer was washed with water. The organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash-chromatography.

***p*-Nitrophenylbuten-3-one *N,N*-dimethylhydrazone (1a).** 1049 mg (90 %) of **1a** as a red oil (R_f = 0.15, hexane). Data for **1a**: ^1H-*NMR* (250 MHz) 2.12 and 2.13 (s, 3H, *anti*- and *syn*-CH_3), 2.49 and 2.57 (s, 6H, *syn*- and *anti*-CH_3N), 6.93 (d, 1H, $^3J_{HH}$ = 16.4 Hz, =CH), 7.49-8.16 (m, 5H, arom and HC=); ^{13}C-*NMR* (75 MHz) 13.6 and 20.2 (*anti*- and *syn*-CH_3), 47.1 and 48.1 (*anti*- and *syn*-CH_3N), 123.8-147.3 (C-arom, *syn*- and *anti*-C=C), 160.0 and 160.1 (*anti*- and *syn*-C=N); *IR* 2952, 2857, 1597,

1518, 1342; *MS* (70eV) 233 (M^+, 100). Anal. Calcd. for $C_{12}H_{15}N_3O_2$ (233.12): C, 61.77; H, 6.48; N, 18.02. Found: C, 62.00; H, 6.47; N, 18.08.

2,4-Heptadien-6-one *N,N*-dimethylhydrazone (1b). 639 mg (84 %) of **1b** as a yelow oil (R_f = 0.21, hexane / diethyl ether, 10 / 1). Data for **1b**: *^{1}H-NMR* (250 MHz) 1.75 (t, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.99 (s, 3H, CH_3), 2.42 and 2.45 (s, 6H, *syn*- and *anti*-CH_3N), 5.72-6.72 (m, 4H, HC=CH-CH=CH); *^{13}C-NMR* (75 MHz) 13.3 and 20.2 (*anti*- and *syn*-CH_3), 18.4 (CH_3), 47.3 and 47.9 (*anti*- and *syn*-CH_3N), 121.4-136.9 (HC=CH-CH=CH), 161.0 and 162.1 (*syn*- and *anti*-C=N); *IR* 2967, 1446, 1269, 1104, 1025; *MS* (70 eV) 152 (M^+, 17). Anal. Calcd. for $C_9H_{16}N_2$ (152.13): C, 70.99; H, 10.60; N, 18.41. Found: C, 70.94; H, 10.56; N, 18.39.

Phenylbuten-3-one *N,N*-dimethylhydrazone (1c). 771 mg (82 %) of **1c** as a yelow oil (R_f = 0.19, hexane / diethyl ether, 10 / 1). Data for **1c**: *^{1}H-NMR* (250 MHz) 2.17 and 2.18 (s, 3H, *anti*- and *syn*-CH_3), 2.54 and 2.57 (s, 6H, *syn*- and *anti*-CH_3N), 6.88-7.47 (m, 6H, arom and HC=), 7.47 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH); *^{13}C-NMR* (75 MHz) 13.3 and 20.2 (*anti*- and *syn*-CH_3), 47.1 and 47.8 (*anti*- and *syn*-CH_3N), 120.1-136.2 (C-arom, *syn*- and *anti*-C=C), 161.0 and 162.2 (*syn*- and *anti*-C=N); *IR* 2949, 2847, 1578, 1450; *MS* (70 eV) 188 (M^+, 100). Anal Calcd. for $C_{12}H_{16}N_2$ (188.13): C, 76.54; H, 8.57; N, 14.88. Found: C, 76.72; H, 8.60; N, 14.90.

***p*-Tolylbuten-3-one *N,N*-dimethylhydrazone (1d).** 819 mg (81 %) of **1d** as a yelow oil (R_f = 0.17, hexane). Data for **1d**: *^{1}H-NMR* (250 MHz) 2.17 and 2.18 (s, 3H, *anti*- and *syn*-CH_3), 2.33 (s, 3H, CH_3-arom), 2.53 and 2.56 (s, 6H, *syn*- and *anti*-CH_3N), 6.86 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH), 6.89-7.46 (m, 5H, arom and HC=); *^{13}C-NMR* (75 MHz) 13.4 and 20.4 (*anti*- and *syn*-CH_3), 21.3 (CH_3-arom), 47.3 and 48.1 (*anti*- and *syn*-CH_3N), 119.4-139.1 (C-arom, *syn*-and *anti*-C=C), 161.4 and 162.7 (*syn*- and *anti*-C=N); *IR* 2950, 2855, 1618, 1580, 1518, 1460; *MS* (70 eV) 202 (M^+, 74). Anal Calcd. for $C_{13}H_{18}N_2$ (202.15): C, 77.17; H, 8.97; N, 13.85. Found: C, 76.91; H, 9.01; N, 13.89.

4-Methylfurfurylbuten-3-one *N,N*-dimethylhydrazone (1e). 778 mg (81 %) of **1e** as a yelow oil (R_f = 0.18, hexane / diethyl ether, 10 / 1). Data for **1e**: *^{1}H-NMR* (250 MHz) 2.08 and 2.09 (s, 3H, *anti*- and *syn*-CH_3), 2.25 and 2.30 (s, 3H, *anti*- and *syn*-CH_3-Het), 2.51 and 2.52 (s, 6H, *syn*- and *anti*-CH_3N), 7.20 (d, 1H, $^3J_{HH}$ = 16.4 Hz, =CH), 5.94-7.16 (m, 3H, =CH-CH= and HC=); *^{13}C-NMR* (75 MHz) 12.9 and 19.8 (*anti*- and *syn*-CH_3), 13.5 and 13.6 (*anti*- and *syn*-CH_3-Het), 47.1 and 47.8 (*anti*- and *syn*-CH_3N), 107.9-153.6 (C=CH-CH=C and *syn*- and *anti*-C=C), 160.8 and 161.9 (*syn*- and *anti*-C=N); *IR* 2947, 2848, 1629, 1585, 1450, 1365; *MS* (70 eV) 192 (M^+, 78). Anal. Calcd. for $C_{11}H_{16}N_2O$ (192.13): C, 68.70; H, 8.39; N, 14.58. Found: C, 68.49; H, 8.36; N, 14.54.

Phenyl-3-hexen-5-one *N,N*-dimethylhydrazone (1f). 984 mg (91 %) of **1f** as a yelow oil (R_f = 0.15, hexane). Data for **1f**: *^{1}H-NMR* (250 MHz) 2.07 (s, 3H, CH_3), 2.47 and 2.54 (s, 6H, *syn*- and *anti*-CH_3N), 2.46-2.80 (m, 4H, CH_2), 6.83 (d, 1H, $^3J_{HH}$ = 16.1 Hz, =CH), 6.20-7.30 (m, 6H, arom and HC=); *^{13}C-NMR* (75 MHz) 13.4 and 20.4 (*anti*- and *syn*-CH_3), 34.7-35.3 (CH_2), 47.3 and 47.8 (*anti*- and *syn*-CH_3N), 123.7-142.0 (C-arom, *syn*- and *anti*-C=C), 161.4 and 163.0 (*syn*- and *anti*-C=N); *IR* 2945, 2850, 1645, 1607, 1588, 1500, 1456, 1367; *MS* (70 eV) 216 (M^+, 43). Anal. Calcd. for $C_{14}H_{20}N_2$ (216.16): C, 77.72; H, 9.32; N, 12.96. Found: C, 77.97; H, 9.36; N, 12.91.

6-Methyl-3-hepten-2-one *N,N*-dimethylhydrazone (1g). 689 mg (82 %) of **1g** as a yelow oil (R_f = 0.16, hexane). Data for **1g**: *^{1}H-NMR* (250 MHz) 0.84-0.90 (m, 6H, CH_3), 1.59-1.70 (m, 1H, CH), 1.97-2.04 (m, 5H, CH_3 and CH_2), 2.45 (s, 6H, CH_3N), 6.06-6.16 (m, 1H, HC=), 6.70 (d, 1H, $^3J_{HH}$ = 16.1 Hz, =CH); *^{13}C-NMR* (75 MHz) 13.1 and 20.3 (*anti*- and *syn*-CH_3), 22.3 (CH_3), 28.2 (CH), 42.1 (CH_2), 47.1 and 47.6 (*anti*- and *syn*-CH_3N), 124.0 and 132.6 (*syn*- and *anti*-HC=), 135.9 and 138.7 (*anti*- and *syn*-=CH), 161.2 and 162.8 (*syn*- and *anti*-C=N); *IR* 2060, 2868, 1663, 1591, 1466, 1366; *MS* (70 eV) 168 (M^+, 100). Anal. Calcd. for $C_{10}H_{20}N_2$ (168.16): C, 71.36; H, 11.98; N, 16.65. Found: C, 71.58; H, 11.97; N, 16.63.

***p*-Tolylbuten-3-one *N,N*-(*S*)-(-)-2-methoxymethylpirrolidinehydrazone (1h).** 1198 mg (88 %) of **1h** as a yelow oil (R_f = 0.18, hexane). Data for **1h**: *^{1}H-NMR* (250 MHz) 1.64-2.71 (m, 6H, ring CH_2), 2.10 and 2.11 (s, 3H, *anti*-and *syn*-CH_3), 2.32 (s, 3H, CH_3-arom), 3.31-3.55 (m, 3H, CH_2O and CH), 3.36 (s, 3H, OCH_3), 6.88 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH), 6.73-7.42 (m, 5H, arom and HC=); *^{13}C-NMR* (75 MHz) 14.8 and 20.5 (*anti*- and *syn*-CH_3), 21.3 (ring CH_2), 23.0 (CH_3-arom), 27.1 (ring CH_2), 55.4 (ring CH_2), 59.2 (OCH_3), 66.8 (CH), 75.7 (CH_2O), 120.9-138.8 (C-arom, *syn*-and *anti*-C=C), 158.0 and 158.3 (*syn*- and *anti*-C=N); *IR* 2974, 2872, 1621, 1521, 1452, 1108; *MS* (70 eV) 272 (M^+, 21). Anal. Calcd. for $C_{17}H_{24}N_2O$ (272.19): C, 74.95; H, 8.89; N, 10.29. Found: C, 75.22; H, 8.86; N, 10.26.

***p*-Tolylbuten-3-one *N,N*-(*R*)-(+)-2-methoxymethylpirrolidinehydrazone (1i).** 1020 mg (75 %) of **1i** as a yelow oil (R_f = 0.20, hexane / diethyl ether, 10 / 1). Data for **1i**: *^{1}H-NMR* (250 MHz) 1.80-2.54 (m, 6H, ring CH_2), 2.10 (s, 3H, CH_3), 2.32 (s, 3H, CH_3-arom), 3.28-3.53 (m, 3H, CH_2O and CH), 3.36 (s, 3H, OCH_3), 6.88 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH), 6.81-7.36 (m, 5H, arom and HC=); *^{13}C-NMR* (75 MHz) 14.8 (CH_3), 21.3 (ring CH_2), 23.0 (CH_3-arom), 27.1 (ring CH_2), 55.3

(ring CH_2), 59.2 (OCH_3), 66.8 (CH), 75.7 (CH_2O), 126.7-137.9 (C-arom and C=C), 158.3 (C=N); *IR* 2973, 2872, 1618, 1519, 1452, 1107; *MS* (70 eV) 272 (M^+, 3). Anal. Calcd. for $C_{17}H_{24}N_2O$ (272.19): C, 74.95; H, 8.89; N, 10.29. Found: C, 75.13; H, 8.87; N, 10.27.

Ethyl-4-dimethylhydrazono-*E*-2-pentenoate (1j). 736 mg (80 %) of **1j** as a yelow oil (R_f = 0.21, hexane / diethyl ether, 10 / 1). Data for **1j**: *^{1}H-NMR* (250 MHz) 1.24 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CH_{3(Et)}$), 2.00 (s, 3H, CH_3), 2.61 (s, 6H, CH_3N), 4.16 (q, 2H, $^3J_{HH}$ = 7.1 Hz, OCH_2), 6.06 (d, 1H, $^3J_{HH}$ = 16 Hz, HC=), 7.24 (d, 1H, $^3J_{HH}$ = 16 Hz, =CH); *^{13}C-NMR* (75 MHz) 13.5 ($CH_{3(Et)}$), 13.6 (CH_3), 46.6 (CH_3N), 59.8 (OCH_2), 120.9 (HC=), 145.2 (=CH), 155.8 (C=N), 165.6 (C=O); *IR* 2960, 2868, 1723, 1637, 1473, 1262; *MS* (70 eV) 184 (M^+, 23). Anal. Calcd. for $C_9H_{16}N_2O_2$ (184.12): C, 58.66; H, 8.76; N, 15.21. Found: C, 58.78; H, 8.73; N, 15.16.

General Procedure for the Preparation of the α,β-Unsaturated Hydrazones 1 from Functionalized Phosphine Oxides 8 (6), or from phosphonates 9 (7). A dry flask, 100-mL, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged 5 mmol of methyl lithium or 5 mmol of lithium diisopropylamide (*LDA*) and 40 mL of *THF*. The temperature was allowed to descend to - 78 °C and a solution 5 mmol of compounds **6**, **7**, **8** or **9** in 40 mL of *THF* was then added. The mixture was allowed to stir at this temperature for 1 h. A solution 5 mmol of carbonyl compound (aldehydes or ketones) in 10 mL of *THF* was added at -78 °C. The mixture was stirred until *TLC* indicated the disappearance of the carbonyl compound (14 h to 3 days). The mixture was diluted with 50 mL water and extracted with CH_2Cl_2. The CH_2Cl_2 layers were washed with water. The organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash-chromatography.

***p*-Tolylpenten-3-one *N,N*-dimethylhydrazone (1k).** 919 mg (85 %) of **1k** as a yelow oil (R_f = 0.17, hexane). Data for **1k**: *^{1}H-NMR* (250 MHz) 1.14-1.21 (m, 3H, CH_3), 2.32 (s, 3H, CH_3-arom), 2.52 (s, 6H, CH_3N), 2.55-2.70 (m, 2H, CH_2), 6.72 (d, 1H, $^3J_{HH}$ = 16.6 Hz, =CH), 6.89-7.42 (m, 5H, arom and HC=); *^{13}C-NMR* (75 MHz) 12.4 (CH_3), 20.1 (CH_3-arom), 21.0 (CH_2), 47.8 (CH_3N), 118.4-141.6 (C-arom and C=C), 168.9 (C=N); *IR* 2987, 2855, 1609, 1511, 1465; *MS* (70 eV) 216 (M^+, 100). Anal. Calcd. for $C_{14}H_{20}N_2$ (216.16): C, 77.72; H, 9.32; N, 12.96. Found: C, 77.67; H, 9.33; N, 13.00.

Diphenylbuten-3-one *N,N*-dimethylhydrazone (1l). 1057 mg (80 %) of **1l** as a yelow oil (R_f = 0.20, hexane / diethyl ether, 10 / 1). Data for **1l**: *^{1}H-NMR* (250 MHz) 1.57 (s, 3H, *anti*- and *syn*-CH_3), 2.54 and 2.66 (s, 6H, *anti*- and *syn*-CH_3N), 6.78 and 6.95 (s, 1H, *anti*- and *syn*-HC=), 7.19-7.37 (m, 10H, arom); *^{13}C-NMR* (75 MHz) 18.1 and 22.4 (*anti*- and *syn*-CH_3), 47.0 and 47.9 (*syn*- and *anti*-CH_3N), 123.3-146.2 (C-arom, *syn*- and *anti*-HC=C), 160.5 and 162.4 (*syn*- and *anti*-C=N); *IR* 2947, 2843, 1603, 1493, 1445, 1350; *MS* (70 eV) 264 (M^+, 100). Anal Calcd. for $C_{18}H_{20}N_2$ (264.16): C, 81.77; H, 7.63; N, 10.60. Found: C, 81.80; H, 7.62; N, 10.58.

Cyclohexylidenpropen-2-one *N,N*-dimethylhydrazone (1m). 775 mg (86 %) of **1m** as a yelow oil (R_f = 0.15, hexane). Data for **1m**: *^{1}H-NMR* (250 MHz) 1.89 and 1.92 (s, 3H, *anti*- and *syn*-CH_3), 2.34 (s, 6H, CH_3N), 1.41-2.30 (m, 10H, ring CH_2), 5.53 and 5.83 (s, 1H, *anti*- and *syn*-HC=); *^{13}C-NMR* (75 MHz) 18.2 (CH_3), 24.1-37.7 (ring CH_2), 46.8 (CH_3N), 118.2 and 121.8 (*syn*- and *anti*-HC=), 145.7 and 147.2 (*anti*- and *syn*-=C), 160.3 and 162.4 (*syn*- and *anti*-C=N); *IR* 2955, 2857, 1618, 1512, 1446; *MS* (70 eV) 180 (M^+, 22). Anal. Calcd for $C_{11}H_{20}N_2$ (180.16): C, 73.27; H, 11.19; N, 15.54. Found: C, 73.32; H, 11.15; N, 15.52.

4,6-Dimethyl-3-hepten-2-one *N,N*-dimethylhydrazone (1n). 619 mg (68 %) of **1n** as a yelow oil (R_f = 0.18, hexane / diethyl ether, 10 / 1). Data for **1n**: *^{1}H-NMR* (250 MHz) 0.77-0.99 (m, 6H, $CH_{3(i\text{-}Bu)}$), 1.75-2.03 (m, 3H, CH_2 and CH), 2.05 and 2.09 (s, 3H, *anti*- and *syn*-CH_3), 2.48 and 2.50 (s, 6H, *syn*- and *anti*-CH_3N), 5.72 and 6.09 (s, 1H, *anti*- and *syn*-HC=); *^{13}C-NMR* (75 MHz) 18.5 (CH_3), 22.5 ($CH_{3(i\text{-}Bu)}$), 26.1 (CH), 41.8 (CH_2), 47.2 (CH_3N), 122.4 (HC=), 126.0 (=C), 162.8 (C=N); *IR* 2960, 1650, 1473, 1387; *MS* (70 eV) 182 (M^+, 19). Anal Calcd. for $C_{11}H_{22}N_2$ (182.18): C, 72.46; H, 12.17; N, 15.37. Found: C, 72.56; H, 12.13; N, 15.41.

Phenylbuten-3-one *N,N*-(*S*)-(-)-2-methoxymethylpirrolidinehydrazone (1o). 1201 mg (93 %) of **1o** as a yelow oil (R_f = 0.19, hexane). Data for **1o**: *^{1}H-NMR* (250 MHz) 1.84-2.70 (m, 6H, ring CH_2), 2.11 (s, 3H, CH_3), 3.32-3.53 (m, 3H, CH_2O and CH), 3.36 (s, 3H, OCH_3), 6.85 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH), 7.24-7.48 (m, 6H, arom and HC=); *^{13}C-NMR* (75 MHz) 14.9 (CH_3), 23.1 (ring CH_2), 27.1 (ring CH_2), 55.4 (ring CH_2), 59.2 (OCH_3), 66.8 (CH), 75.7 (CH_2O), 126.8-136.8 (C-arom and C=C), 157.8 (C=N); *IR* 2973, 2874, 1722, 1669, 1449, 1110; *MS* (70 eV) 258 (M^+, 18). Anal. Calcd. for $C_{16}H_{22}N_2O$ (258.17): C, 74.37; H, 3.59; N, 10.85. Found: C, 74.12; H, 3.60; N, 10.88.

***p*-Anisylbuten-3-one *N,N*-dimethylhydrazone (1p).** 807 mg (74 %) of **1p** as a yelow oil (R_f = 0.20, hexane / diethyl ether, 10 / 1). Data for **1p**: *^{1}H-NMR* (250 MHz) 2.00 and 2.02 (s, 3H, *anti*- and *syn*-CH_3), 2.40 and 2.41 (s, 6H, *syn*- and *anti*-CH_3N), 3.59 and 3.60 (s, 3H, *anti*- and *syn*-OCH_3), 6.65 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH), 6.67-7.31 (m, 5H, arom and HC=);

^{13}C-NMR (75 MHz) 13.3 and 20.3 (*anti-* and *syn*-CH_3), 47.3 and 48.0 (*anti-* and *syn*-CH_3N), 55.2 and 55.3 (*anti-* and *syn*-OCH_3), 114.1-143.1 (C-arom, *syn-* and *anti*-C=C), 159.8 and 162.8 (*anti-* and *syn*-C=N); *IR* 2955, 2861, 1604, 1511, 1249, 1175; *MS* (70 eV) 218 (M^+, 92). Anal. Calcd. for $C_{13}H_{18}N_2O$ (218.14): C, 71.51; H, 8.32; N, 12.84. Found: C, 71.67; H, 8.29; N, 12.80.

2-Methyl-*p*-tolylbuten-3-one *N,N*-dimethylhydrazone (1q). 994 mg (92 %) from **8** and 713 mg (66 %) from **6** of **1q** as a yelow oil (R_f = 0.18, hexane / diethyl ether, 10 / 1). Data for **1q**: *^{1}H-NMR* (250 MHz) 2.13 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.37 (s, 3H, CH_3-arom), 2.57 (s, 6H, CH_3N), 6.88 (s, 1H, =CH), 7.17 (d, 2H, $^4J_{HH}$ = 8 Hz, arom), 7.25 (d, 2H, $^4J_{HH}$ = 8 Hz, arom); *^{13}C-NMR* (75 MHz) 14.3 (CH_3), 14.7 (CH_3), 21.3 (CH_3-arom), 47.4 (CH_3N), 127.1-138.8 (C-arom and C=C), 164.2 (C=N); *IR* 2955, 2858, 1510, 1447, 1365; *MS* (70 eV) 216 (M^+, 60). Anal. Calcd. for $C_{14}H_{20}N_2$ (216.16): C, 77.72; H, 9.33; N, 12.96. Found: C, 77.79; H, 9.26; N, 12.95.

2-Allyl-*p*-tolylbuten-3-one *N,N*-dimethylhydrazone (1r). 872 mg (72 %) from **8** and 690 mg (57 %) from **6** of **1r** as a yelow oil (R_f = 0.16, hexane). Data for **1r**: *^{1}H-NMR* (250 MHz) 2.21 (s, 3H, CH_3), 2.36 (s, 3H, CH_3-arom), 2.55 (s, 6H, CH_3N), 3.38-3.41 (m, 2H, CH_2), 5.00-5.08 (m, 2H, CH_2=), 6.00-6.06 (m, 1H, =CH), 6.94 (s, 1H, =CH), 7.15-7.34 (m, 4H, arom); *^{13}C-NMR* (75 MHz) 14.6 (CH_3), 21.2 (CH_3-arom), 31.9 (CH_2), 47.4 (CH_3N), 114.9 (CH_2=), 128.9-139.3 (C-arom and C=CH), 137.4 (=CH), 162.4 (C=N); *IR* 2955, 2856, 1670, 1511, 1567; *MS* (70 eV) 242 (M^+, 28). Anal. Calcd. for $C_{16}H_{22}N_2$ (242.18): C, 79.28; H, 9.15; N, 11.56. Found: C, 79.28; H, 9.18; N, 11.54.

2-Methyl-*p*-anisylbuten-3-one *N,N*-dimethylhydrazone (1s). 882 mg (76 %) from **9** and 696 mg (60 %) from **7** of **1s** as a yelow oil (R_f = 0.20, hexane / diethyl ether, 10 / 1). Data for **1s**: *^{1}H-NMR* (250 MHz) 2.11 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.55 (s, 6H, CH_3N), 3.82 (s, 3H, OCH_3), 6.88 (s, 1H, =CH), 6.92-7.32 (m, 4H, arom); *^{13}C-NMR* (75 MHz) 14.2 (CH_3), 14.6 (CH_3), 47.4 (CH_3N), 55.3 (OCH_3), 113.6-130.7 (C-arom and C=CH), 164.1 (C=N); *IR* 2955, 2853, 1606, 1519, 1251, 1178; *MS* (70 eV) 232 (M^+, 94). Anal. Calcd. for $C_{14}H_{20}N_2O$ (232.16): C, 72.36; H, 8.68; N, 12.06. Found: C, 72.59; H, 8.66; N, 12.02.

Reaction of β-*N*-phenylhydrazonopropyldiphenylphosphine oxide 6e with *p*-tolyl aldehyde. A dry flask, 100-mL, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged 10 mmol of lithium diisopropylamide (*LDA*) and 50 mL of *THF*. The temperature was allowed to descend to - 78 °C and a solution 1.74 g (5 mmol) of phosphine oxide **6e** in 40 mL of *THF* was then added. The mixture was allowed to stir for 1 h. A solution 0.6 g (5 mmol) of *p*-tolyl aldehyde in 10 mL of *THF* was added at -78 °C. The mixture was stirred at room temperature until *TLC* indicated the disappearance of the carbonyl compound (17 h). The mixture was diluted with 50 mL water and extracted with CH_2Cl_2. The CH_2Cl_2 layers were washed with water. The organic layers were dried over $MgSO_4$, filtered, and concentrated.

***p*-Tolylbuten-3-one *N*-phenylhydrazone (13).** The crude product was purified by flash-chromatography (hexane / diethyl ether, 10 / 1) to afford 875 mg (70 %) of **13** as a yelow solid. Data for **13**: mp 165-167 °C; *^{1}H-NMR* (250 MHz) 2.08 (s, 3H, CH_3), 2.36 (s, 3H, CH_3-arom), 6.73 (d, 1H, $^3J_{HH}$ = 16.4 Hz, =CH), 6.87-7.41 (m, 10H, arom, HC= and NH); *^{13}C-NMR* (75 MHz) 10.1 (CH_3), 21.3 (CH_3-arom), 113.2-144.7 (C-arom and C=C), 144.7 (C=N); *IR* (*KBr*) 3348, 2927, 2855, 1618, 1506, 1249, 1137; *MS* (70 eV) 250 (M^+, 100). Anal. Calcd. for $C_{17}H_{18}N_2$ (250.15): C, 81.55; H, 7.25; N, 11.20. Found: C, 81.57; H, 7.27; N, 11.20.

Synthesis of 1-Phenyl-3-methyl-5-*p*-tolylpyrazole (15).
1.25 g (5 mmol) of *p*-tolylbuten-3-one *N*-phenylhydrazone **13** were heated at 100 °C in 15 mL of Toluene until *TLC* indicated the disappearance of the compound **13**. The mixture was concentrated and the crude product was purified by flash-chromatography (hexane / diethyl ether, 10 / 1) to afford 1191 mg (96 %) of **15** as a yelow oil (R_f = 0.19). Data for **15**: *^{1}H-NMR* (250 MHz) 2.34 (s, 3H, CH_3), 2.38 (s, 3H, CH_3-arom), 6.28 (s, 1H, HC=), 6.91-7.34 (m, 9H, arom); *^{13}C-NMR* (75 MHz) 13.6 (CH_3), 21.3 (CH_3-arom), 107.5 (HC=), 124.5-143.9 (C-arom and =C), 149.4 (C=N); *IR* 3026, 2921, 1598, 1499, 1368; *MS* (70 eV) 248 (M^+, 100). Anal. Calcd for $C_{17}H_{16}N_2$ (248.13): C, 82.21; H, 6.50; N, 11.29. Found: C, 82.23; H, 6.52; N, 11.25.

Reaction of β-*N*-phenylhydrazonopropyldiphenylphosphine oxide 6e with diphenyl ketone. This reaction was performed like synthesis of compound **13** with diphenyl ketone 0.91 g (5 mmol) and was refluxed for 3 days. **1,5,5-triphenyl-3-methyl-4,5-dihydropyrazole (14).** The crude product was purified by flash-chromatography (hexane) to afford 999 mg (64 %) of **14** as a white solid. An analytical sample was obtained by recrystallization from $CHCl_3$ / hexane. Data for **14**: mp 193-194 °C; *^{1}H-NMR* (250 MHz) 2.10 (s, 3H, CH_3), 3.66 (s, 2H, CH_2), 6.59-7.54 (m, 15H, arom); *^{13}C-NMR* (75 MHz) 15.8 (CH_3), 61.4 (CH_2), 114.9-128.3 (C-arom and C($Ph)_2$), 146.9 (C=N); *IR* (*KBr*) 2920, 2835, 1597, 1498, 1353; *MS* (70 eV) 312 (M^+, 100). Anal. Calcd for $C_{22}H_{20}N_2$ (312.16): C, 84.57; H, 6.46; N, 8.97. Found: C, 84.61; H, 6.44; N, 8.94.

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