Tetrahedron 64 (2008) 6724–6732

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Carbon–phosphorus bond formation and transformation in the reaction of 1,2-diaza-1,3-butadienes with alkyl phenylphosphonites

Orazio A. Attanasi [a,*], Graziano Baccolini [b], Carla Boga [b], Lucia De Crescentini [a,*], Paolino Filippone [a], Fabio Mantellini [a]

[a] Istituto di Chimica Organica, Università degli Studi di Urbino 'Carlo Bo', Via I Maggetti 24, 61029 Urbino, Italy
[b] Dipartimento di Chimica Organica 'A. Mangini', Università degli Studi di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

ARTICLE INFO

Article history:
Received 18 February 2008
Received in revised form 10 April 2008
Accepted 1 May 2008
Available online 3 May 2008

Keywords:
1,2-Diaza-1,3-butadienes
Diazaphospholes
Ylides
Hydrazones
Phospha-Michael addition

ABSTRACT

The reaction of 1,2-diaza-1,3-butadienes with dialkyl phenylphosphonites under solvent-free conditions proceeds via zwitterionic intermediate and gives, by precipitation, the stable ylidic α-phosphanylidene-hydrazones that, in turn, can be transformed into the corresponding 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes. The latter compounds are converted by hydrolytic cleavage in methanol–water (95:5) into *E*-hydrazonophosphonates that are useful for the preparation of the corresponding β-ketophosphonates and 4-[alkoxy(phenyl)phosphoryl]-1,2-diaza-1,3-butadienes. These peculiar 1,2-diaza-1,3-butadienes, bearing an alkoxy(phenyl)phosphoryl group on the carbon atom in position 4 are also able to add different nucleophiles, such as methanol or thiourea, giving 2-[alkoxy(phenyl)phosphoryl]-2-methoxyhydrazones and 5-phosphinate-substituted thiazol-4-ones, respectively.

1. Introduction

Since the 1960s, investigations regarding 1,2-diaza-1,3-butadienes have drastically increased, showing the usefulness of these compounds in organic chemistry.[1,2] Our group has a 30-year experience in this field. In particular, we have studied the reactivity of these substrates, both in solution and solid phase,[3] toward a large variety of nucleophiles.[1] The 1,4-conjugate addition (Michael-type) of the latter on the terminal carbon atom of the heterodiene system and the subsequent internal ring closure of the 1,4-adduct hydrazonic intermediates form polyfunctionalized five- or six-membered heterocycles, such as pyrroles,[3a,4] thiazoles,[5] thiazolinones,[3a,c] pyrazoles,[3a,6] thiadiazoles,[7] selenadiazoles,[7] indoles,[8,4b,c] imidazoles,[9] 1,2,4-triazines,[1c] pyrazines,[10] and pyridazines.[11]

On the other hand, the phospha-Michael (P-Michael) addition, i.e., the addition of a phosphorus nucleophile to an appropriate acceptor, is probably one of the most versatile tools for the formation of the P–C bond.[12] This occurrence is important because it offers an entry to many diversely functionalised derivatives. In addition, natural products containing a P–C bond exhibit important biological activity.[13]

In the past years, all these considerations suggested us to examine the reaction between 1,2-diaza-1,3-butadienes and triphenyl-[14a] or trialkyl-phosphines[14b] to obtain pyrazoles or 4-phosphoranylidene-4,5-dihydropyrazol-5-ones. More recently, we have investigated the reaction of the same 1,2-diaza-1,3-butadienes with trialkyl phosphites that represented a facile access to new 1,2,3-diazaphospholes, if the reaction was carried out under a nitrogen atmosphere, or to *E*-hydrazonophosphonates, in the presence of atmospheric moisture.[15]

With the aim to study the behavior of other trivalent phosphorus nucleophiles towards 1,2-diaza-1,3-butadiene systems and considering the different electron-donating effects of the phenyl group with respect to the alkoxy one, in this paper we consider the reaction of these compounds with dimethyl or diethyl phenylphosphonites. It turned out to be very interesting because, in some cases, the 1,4-addition products directly precipitate from the reaction medium, permitting us to define the mechanistic aspects of the reaction.

On the other hand, with the same reaction pathway, we can obtain 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes, also in the presence of air. Furthermore, the procedure here described represents an easy alternative route to the synthesis of 1,2,3-diazaphospholes. In fact, the classical method for their preparation implicates the PCl_3 condensation of the alkylketone hydrazones[16] while 2,4,5-triphenyl-1,2,3-diazaphosphole is best prepared from the respective 1,2-diaza-1,3-butadiene and a fused benzothiadiphosphole as the phosphorus donating reagent.[17]

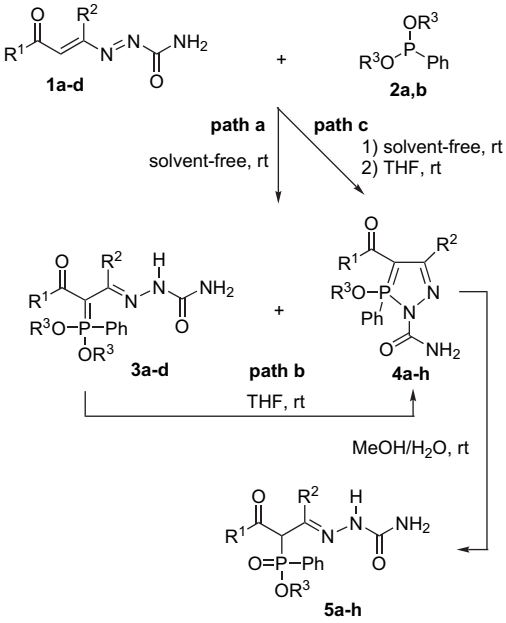
* Corresponding authors. Fax: +39 0722303441.
E-mail addresses: orazio.attanasi@uniurb.it (O.A. Attanasi), lucia.decrescentini@uniurb.it (L. De Crescentini).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.05.007

Here, we also report the hydrolytic cleavage of 1,2,3-diazaphospholes to give the corresponding *E*-hydrazonophosphonates that can be conveniently used for the preparation of interesting β-ketophosphonates and 4-[alkoxy(phenyl)phosphoryl]-1,2-diaza-1,3-butadienes. Besides, we have tested the ability of these particular 1,2-diaza-1,3-butadienes to add some nucleophiles such as methanol and thiourea to give 2-[alkoxy(phenyl)phosphoryl]-2-methoxyhydrazones and 5-phosphinate-substituted thiazol-4-ones, respectively.

2. Results and discussion

1-Aminocarbonyl-1,2-diaza-1,3-butadiene-4-carboxylates **1a**,**b** easily reacted with dimethyl or diethyl phenylphosphonites **2a**,**b** in the presence of atmospheric moisture and in solvent-free conditions in 0.5 h to give a mixture of α-phosphanylidene-hydrazones **3a**–**d** and 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a**,**b**,**e**,**f** (Scheme 1, path a, Table 1). Products **3** directly precipitated from the reaction medium, while the corresponding **4a**,**b**,**e**,**f** were obtained by chromatographic purification of the mother liquor. If the same reaction was carried out starting from **1c**,**d** with **2a**,**b**, the isolation of hydrazones **3** was not possible, either by precipitation or by chromatographic methods.



Scheme 1.

The ylidic nature of compounds **3a**–**d** is clearly supported by ^{13}C chemical shifts of the P–C signals (55.3–56.6 ppm) and by their P–C coupling constants (167–168 Hz), which are in good agreement with the values found in the literature.[15,18]

The possibility to obtain in some cases intermediates **3** simply by precipitation and subsequent filtration can suggest that the presence of a phenyl group directly bound to the phosphorus atom enhances their stability.

The isolation and the characterization of the intermediates **3a**–**d** have represented the key to determine the exact mechanism for the formation of the 1,2,3-diazaphospholes **4**. The nucleophilic 1,4-addition of the phosphorus at the terminal carbon atom of the heterodiene system induces the formation of a zwitterionic intermediate (**I**) that exists in equilibrium with its ylidic form **3**, derived from the 1,4-shift of a proton. 1,2,3-Diazaphospholes **4** are obtained by means of an intramolecular attack of the NH hydrazonic nitrogen of **3** at the phosphorus atom, with loss of an alcohol molecule (Scheme 2).

Ylidic intermediates **3a**–**d** can be easily converted into the corresponding 1,2,3-diazaphospholes **4a**,**b**,**e**,**f** in tetrahydrofuran at room temperature (Scheme 1, path b, Table 1). This represents further support for the described mechanism.

3-Phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a**–**h** can also be obtained in a one-pot procedure. In fact, 1-aminocarbonyl-1,2-diaza-1,3-butadiene-4-carboxylates **1a**,**b**,**d** and 1-aminocarbonyl-1-2-diaza-1,3-butadiene-4-carboxamide **1c** easily reacted with dimethyl or diethyl phenylphosphonites **2a**,**b** in solvent-free conditions and in the presence of atmospheric moisture. After completion of the reaction, revealed by the disappearance of the red color of 1,2-diaza-1,3-butadiene, THF was directly added to the reaction medium giving 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a**–**h** in very good yields (Scheme 1, path c, Table 1). Probably, the presence of a phenyl moiety bound to the phosphorus atom confers a particular stability to compounds **4a**–**h**, which, if stored for one year at 4 °C, showed no decomposition nor any loss in purity.

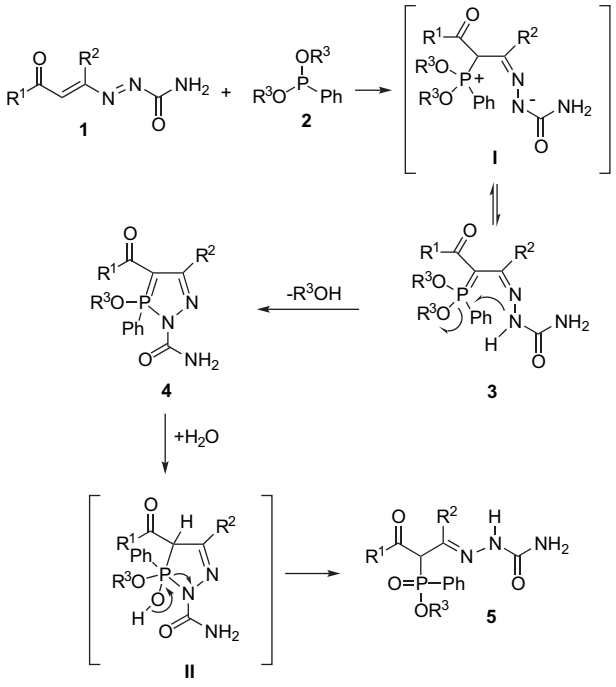
The treatment of 1,2,3-diazaphospholes **4a**–**h** with THF–water (95:5) produced the corresponding *E*-hydrazonophosphonates **5a**–**h** in 6.0–10.0 h, in good yields (Scheme 1, Table 1). Their formation is due to the hydrolytic ring opening of diazaphosphole that occurs with the cleavage of the P–N bond of the intermediate **II** (Scheme 2). The *E*-configuration of the C=N was assigned by means of NOE experiments.[15]

These hydrazonic derivatives featured an interesting synthetic utility for a series of chemical transformations. In fact, when compounds **5a**,**b**,**d**,**f**,**g**, chosen as examples, were treated with 4 equiv of Amberlyst 15H in a mixture of acetone–water (9:1), they were converted into β-ketophosphonates **6a**–**e** in 3.0–5.0 h with good yields (59–72%) (Scheme 3, Table 2), by means of the hydrolytic cleavage of the C=N hydrazonic bond.[19]

Table 1
Yields and reaction times of α-phosphanylidene-hydrazones **3a**–**d**, 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a**–**h**, and *E*-hydrazonophosphonates **5a**–**h**

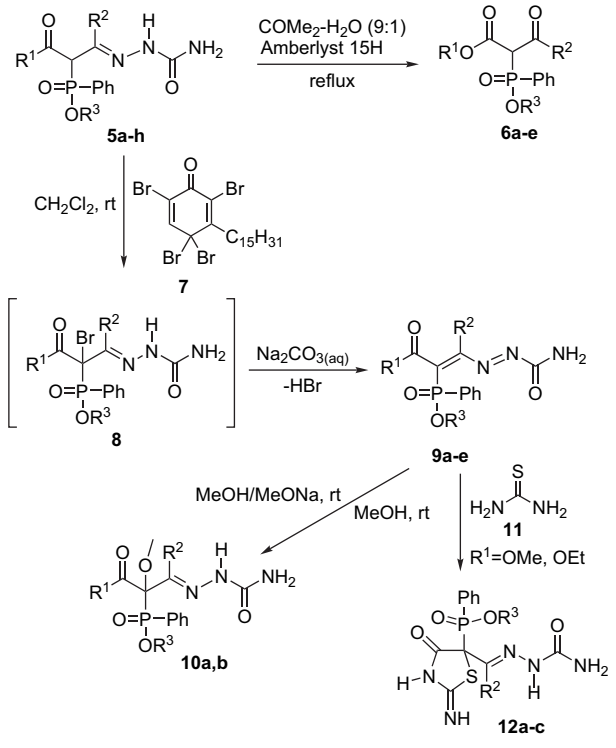
1	R^1	R^2	2	R^3	3	Yield[a] (%)	4	Yield[a] (%)	Yield[b] (%)	Yield[c] (%)	Time[d] (h)	5	Yield[e] (%)	Time[f] (h)
1a	OMe	Me	**2a**	Me	**3a**	45	**4a**	45	65	77	1.0	**5a**	79	9.0
1b	OEt	Me	**2a**	Me	**3b**	47	**4b**	47	68	78	2.0	**5b**	81	10.0
1c	NMe_2	Me	**2a**	Me			**4c**			84	1.0	**5c**	74	8.0
1d	OMe	Et	**2a**	Me			**4d**			87	2.0	**5d**	62	6.0
1a	OMe	Me	**2b**	Et	**3c**	52	**4e**	22	63	78	2.0	**5e**	65	8.0
1b	OEt	Me	**2b**	Et	**3d**	51	**4f**	26	68	69	2.0	**5f**	63	10.0
1c	NMe_2	Me	**2b**	Et			**4g**			88	1.0	**5g**	73	6.0
1d	OMe	Et	**2b**	Et			**4h**			93	2.0	**5h**	60	6.0

[a] Yield of pure isolated products, referred to the path a of Scheme 1, based on starting compounds **1a**,**b**.
[b] Yield of pure isolated products, referred to the path b of Scheme 1, based on starting compounds **3a**–**d**.
[c] Yield of pure isolated products referred to the path c of Scheme 1, based on starting compounds **1a**–**d**.
[d] Time for the formation of compounds **4a**–**h**.
[e] Yield of pure isolated products **5a**–**h**, based on starting compounds **4a**–**h**.
[f] Time of disappearance of the starting compounds **4a**–**h**.



Scheme 2.

β-Ketophosphonates owe their importance to the fact that they are valuable intermediates in organic synthesis, i.e., the Horner–Wadsworth–Emmons condensation, used for the preparation of α,β-unsaturated carbonyl compounds.[20] The classical methods for their preparation are the Arbuzov reaction[21] and the acylation of alkylphosphonate anions,[22] but both these synthetic approaches present some restrictions, due to the difficult nucleophilic substitution or poor nucleophilic power of the phosphorus reagents. In the past years, one of us described the synthesis of β-ketophosphonates starting from β-ketophosphonate-hydrazones, using paraformaldehyde and acetone in the presence of boron trifluoride, that occurred in 48 h with 47–62% yields.[23] The methodology described here for their preparation represents an improvement with respect to the previously reported procedures.



Scheme 3.

E-Hydrazonophosphonates **5a**–**f**, chosen as examples, can also be conveniently used for the preparation of 4-[alkoxy-(phenyl)phosphoryl]-1,2-diaza-1,3-butadienes **9a**–**e**. In fact, when they were treated with 2,4,4,6-tetrabromo-3-*n*-pentadecyl-2,5-cyclohexadienone **7** (TBPCO), they furnished the non-isolable 4-bromo-hydrazonophosphonate intermediates **8** that, in turn, were converted into pertinent azoalkenes **9a**–**e**, by treatment with an aqueous saturated solution of sodium carbonate to induce a dehydrobromination (Scheme 3, Table 2).[24]

TBPCO, a brominating agent easily synthesized starting from 3-*n*-pentadecylphenol,[25] proved to be more effective than other commonly used reagents for such a reaction, like phenyltrimethylammonium tribromide (PTAB) or *N*-bromosuccinimide (NBS), furnishing higher overall yields (42–56%) of the final compounds **9a**–**e**. These latter compounds are peculiar 1,2-diaza-1,3-butadienes, bearing an [alkoxy(phenyl)phosphoryl] group on the carbon atom in position 4 and they maintain the ability to add different nucleophiles.

In fact, compounds **9b**,**e** reacted with methanol in the presence of sodium methoxide to give 2-[alkoxy(phenyl)phosphoryl]-2-methoxyhydrazones **10a**,**b**,[26] by 1,4-addition of methanol to the heterodiene system (Michael-type) (Scheme 3, Table 2). Compounds **9a**,**c**,**d**, treated with thiourea **11** in methanol, furnished 5-phosphinate-substituted thiazol-4-ones **12a**–**c** (Scheme 3, Table 2).[3c,27] The mechanism for the formation of compounds **12** implicates SH nucleophilic attack of the thioloimido form to the terminal carbon atom of the azoene system and subsequent ring closure to the thiazolinone ring due to an intramolecular NH nucleophilic attack at the ester group bound to the same terminal carbon atom.

3. Conclusions

In conclusion, this work contributes to the chemistry of phosphorus derivatives from both synthetic and mechanistic points of view. The synthetic importance of the reaction between 1,2-diaza-1,3-butadienes and dialkyl phenylphosphonites is due to the development of simple and environmentally friendly procedures for the preparation of 1,2,3-diazaphospholes and *E*-hydrazonophosphonates, not easily accessible by other methods. Moreover, the latter compounds have been demonstrated to be useful starting materials to obtain β-ketophosphonates and unknown 4-[alkoxy(phenyl)phosphoryl]-1,2-diaza-1,3-butadienes that, in turn, can be used for the preparation of 2-[alkoxy(phenyl)phosphoryl]-2-methoxyhydrazones and 5-phosphinate-substituted thiazol-4-ones. Furthermore, the isolation of α-phosphanylidene-hydrazone intermediates by the reaction of 1,2-diaza-1,3-butadienes and dialkyl phenylphosphonites permitted us to throw light on mechanistic aspects involved in the formation of 1,2,3-diazaphospholes.

4. Experimental

4.1. General

Methyl or ethyl 2-chloroacetoacetate, methyl 2-chloro-3-oxopentanoate, semicarbazide hydrochloride, sodium acetate, dimethyl or diethyl phenylphosphonite, Amberlyst 15H, sodium methoxide, and thiourea were commercial materials and were used without further purification. Solvents were purchased and used without further purification with the exception of THF, which was distilled over sodium hydroxide. Melting points were determined on open capillary tubes. FTIR spectra were obtained as Nujol mulls.

Table 2
Yields and reaction times of β-ketophosphonates **6a–e**, 4-[alkoxy(phenyl)phosphoryl]-1,2-diaza-1,3-butadienes **9a–e**, 2-[alkoxy(phenyl)phosphoryl]-2-methoxyhydrazones **10a,b**, and 5-phosphinate-substituted thiazol-4-ones **12a–c**

5	6	Yield[a] (%)	Time (h)	9	Yield[a] (%)	10	Yield[b] (%)	Time (h)	12	Yield[b] (%)	Time (h)
5a	**6a**	66	3.0	**9a**	43				**12a**	61	2.0
5b	**6b**	72	4.5	**9b**	48	**10a**	65	0.5			
5d	**6c**	58	5.0	**9c**	42				**12b**	60	1.0
5e				**9d**	56				**12c**	63	1.5
5f	**6d**	66	4.0	**9e**	41	**10b**	78	1.0			
5g	**6e**	59	4.0								

[a] Yield of pure isolated products based on compounds **5**.
[b] Yield of pure isolated products based on compounds **9**.

Mass spectra EI were recorded at an ionizing voltage of 70 eV. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded at 400, 100.32, 161.9 MHz, respectively. All NMR spectra were recorded in $CDCl_3$ or in DMSO-d_6, as specified below. Chemical shifts (δ_H) are reported in parts per million (ppm), relative to TMS as internal standard. All coupling constants (J) values are given in hertz. Chemical shifts (δ_C) are reported in parts per million (ppm), relative to $CDCl_3$ or DMSO-d_6 as internal standard in a broad band decoupled mode; the multiplicities were obtained using 135° and 90° DEPT experiments to aid in assignment. Chemical shifts (δ_P) are reported in parts per million (ppm), relative to external standard 85% H_3PO_4. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. All the NH, NH_2, and OH exchanged with D_2O. Precoated silica gel plates (0.25 mm) were employed for analytical thin layer chromatography and silica gel 35–70 μ for column chromatography. All new compounds shown satisfactory elemental analysis (C±0.35; H±0.30; N±0.30). The nomenclature was generated using ACD/IUPAC Name (version 3.50, 5 Apr. 1998), Advanced Chemistry Development Inc., Toronto, ON (Canada).

4.2. General procedure for the synthesis of α-phosphanylidene-hydrazones 3a–d and of 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes 4a,b,e,f (path a)

1,2-Diaza-1,3-butadienes **1a**,**b** (1 mmol) as a mixture of *E*/*Z* isomers[24] and dialkyl phenylphosphonites **2a**,**b** (4 mmol) were magnetically stirred for 0.5 h, until the red color of the starting product disappeared. The α-phosphanylidene-hydrazones **3a–d** directly precipitate from the reaction medium as white solid. The mother liquor was then chromatographed on silica gel column (elution mixture: ethyl acetate–cyclohexane) to give 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a**,**b**,**e**,**f**. Further purification of these latter compounds can be obtained by crystallization from diethyl ether–light petroleum (bp 40–60 °C).

4.3. General procedure for the synthesis of 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes 4a,b,e,f starting from α-phosphanylidene-hydrazones 3a–d (path b)

α-Phosphanylidene-hydrazones **3a–d** (1 mmol) were dissolved in tetrahydrofuran (10 mL) and magnetically stirred for 2.0 h, until the disappearance of the starting compound **3**. 3-Phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a**,**b**,**e**,**f** were obtained by chromatography on silica gel column (elution mixture: ethyl acetate–cyclohexane) and by subsequent crystallization from diethyl ether–light petroleum (bp 40–60 °C).

4.4. General procedure for the one-pot synthesis of 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes 4a–h (path c)

1,2-Diaza-1,3-butadienes **1a–d** (1 mmol) as a mixture of *E*/*Z* isomers[24] and dialkyl phenylphosphonites **2a**,**b** (4 mmol) were magnetically stirred for 0.5 h, until the red color of the reaction mixture disappeared. At this moment, a TLC check revealed the presence of α-phosphanylidene-hydrazones **3** and 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes **4**. In order to completely convert **3** into the relevant products **4**, THF (10 mL) was added to the reaction medium, that was magnetically stirred for an additional time of 1.0–2.0 h. 3-Phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a–h** were obtained by chromatography on silica gel column (elution mixture: ethyl acetate–cyclohexane). Further purification of compounds **4** can be obtained by crystallization from diethyl ether–light petroleum (bp 40–60 °C).

*4.4.1. Methyl 3-[2-(aminocarbonyl)hydrazono]-2-(1,1-dimethoxy-1-phenyl-λ^5-phosphanylidene)butanoate (**3a**)*

White powder; mp 91–95 °C; IR (Nujol) ν_{max} 3445, 3314, 3192, 1686, 1634 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.00 (s, 3H, CH_3), 3.39 (s, 3H, CO_2CH_3), 3.70 (d, 6H, $^3J_{HP}$=12.4 Hz, $2OCH_3$), 5.67 (br s, 2H, NH_2), 7.48–7.71 (m, 5H, CH_{arom}), 8.56 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.7 (d, $^3J_{CP}$=6.8 Hz, CH_3), 49.2 (s, CH_3), 54.1 (d, $^2J_{CP}$=5.6 Hz, CH_3), 55.3 (d, $^1J_{CP}$=167.0 Hz, C), 127.9 (d, $^1J_{CP}$=189.6 Hz, C), 128.7 (d, $^2J_{CP}$=14.4 Hz, CH), 131.1 (d, $^3J_{CP}$=10.6 Hz, CH), 132.6 (s, CH), 148.2 (d, $^2J_{CP}$=7.6 Hz, C), 157.2 (s, C), 168.3 (d, $^2J_{CP}$=18.2 Hz, C); MS *m*/*z* 341 (1) [M$^+$], 309 (33), 266 (100). Anal. Calcd for $C_{14}H_{20}N_3O_5P$: C, 49.27; H, 5.91; N, 12.31. Found: C, 49.39; H, 5.67; N, 11.29.

*4.4.2. Ethyl 3-[2-(aminocarbonyl)hydrazono]-2-(1,1-dimethoxy-1-phenyl-λ^5-phosphanylidene)butanoate (**3b**)*

White powder; mp 90–95 °C; IR (Nujol) ν_{max} 3474, 3380, 3303, 3187, 1682, 1639, 1630 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.95 (t, 3H, J=7.2 Hz, $CO_2CH_2CH_3$), 2.01 (s, 3H, CH_3), 3.70 (d, 6H, $^3J_{HP}$=12.0 Hz, $2OCH_3$), 3.83 (q, 2H, J=7.2 Hz, $CO_2CH_2CH_3$), 5.70 (br s, 2H, NH_2), 7.50–7.72 (m, 5H, CH_{arom}), 8.54 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.4 (s, CH_3), 18.7 (d, $^3J_{CP}$=6.8 Hz, CH_3), 54.1 (d, $^2J_{CP}$=5.8 Hz, CH_3), 55.5 (d, $^1J_{CP}$=168.0 Hz, C), 57.6 (s, CH_2), 128.0 (d, $^1J_{CP}$=152.5 Hz, C), 128.5 (d, $^2J_{CP}$=15.2 Hz, CH), 131.1 (d, $^3J_{CP}$=10.6 Hz, CH), 132.6 (s, CH), 148.3 (d, $^2J_{CP}$=7.6 Hz, C), 157.2 (s, C), 167.9 (d, $^2J_{CP}$=18.2 Hz, C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 67.07; MS *m*/*z* 355 (37) [M$^+$], 324 (20), 310 (25), 280 (62), 266 (100). Anal. Calcd for $C_{15}H_{22}N_3O_5P$: C, 50.70; H, 6.24; N, 11.83. Found: C, 50.57; H, 6.17; N, 11.70.

*4.4.3. Methyl 3-[2-(aminocarbonyl)hydrazono]-2-(1,1-diethoxy-1-phenyl-λ^5-phosphanylidene)butanoate (**3c**)*

White powder; mp 82–86 °C; IR (Nujol) ν_{max} 3462, 3189, 1699, 1650 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.20 (t, 6H, J=7.0 Hz, $2OCH_2CH_3$), 1.99 (s, 3H, CH_3), 3.35 (s, 3H, CO_2CH_3), 4.02–4.08 (m, 4H, $2OCH_2CH_3$), 5.67 (br s, 2H, NH_2), 7.49–7.72 (m, 5H, CH_{arom}), 8.55 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 16.5 (d, $^3J_{CP}$=6.0 Hz, CH_3), 19.3 (d, $^3J_{CP}$=6.8 Hz, CH_3), 49.7 (s, CH_3), 56.6 (d, $^1J_{CP}$=167.0 Hz, C), 64.2 (d, $^2J_{CP}$=6.1 Hz, CH_2), 129.3 (d, $^2J_{CP}$=14.4 Hz, CH), 129.4 (d, $^1J_{CP}$=154.0 Hz, C), 131.6 (d, $^3J_{CP}$=10.6 Hz, CH), 132.5 (s, CH), 149.0 (d, $^2J_{CP}$=7.6 Hz, C), 157.9 (s, C), 169.0 (d, $^2J_{CP}$=18.2 Hz, C); MS *m*/*z* 369 (6) [M$^+$], 326 (47), 323 (59), 295 (11), 280 (100). Anal. Calcd for $C_{16}H_{24}N_3O_5P$: C, 52.03; H, 6.55; N, 11.38. Found: C, 52.07; H, 6.47; N, 11.42.

*4.4.4. Ethyl 3-[2-(aminocarbonyl)hydrazono]-2-(1,1-diethoxy-1-phenyl-λ^5-phosphanylidene)butanoate (**3d**)*

White powder; mp 89–93 °C; IR (Nujol) ν_{max} 3462, 3198, 1699, 1641 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 0.93 (t, 3H, J=7.2 Hz, $CO_2CH_2CH_3$), 1.20 (t, 6H, J=7.0 Hz, $2OCH_2CH_3$), 2.00 (s, 3H, CH_3), 3.80 (q, 2H, J=7.2 Hz, $CO_2CH_2CH_3$), 4.02–4.08 (m, 4H, 2 OCH_2CH_3), 5.69 (br s, 2H, NH_2), 7.49–7.73 (m, 5H, CH_{arom}), 8.56 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.5 (s, CH_3), 15.8 (d, $^3J_{CP}$=6.8 Hz, CH_3), 18.7 (d, $^3J_{CP}$=6.8 Hz, CH_3), 56.0 (d, $^1J_{CP}$=167.0 Hz, C), 57.6 (s, CH_2), 63.4 (d, $^2J_{CP}$=6.8 Hz, CH_2), 63.5 (d, $^2J_{CP}$=6.8 Hz, CH_2), 128.6 (d, $^2J_{CP}$=13.6 Hz, CH), 128.9 (d, $^1J_{CP}$=150.9 Hz, C), 131.0 (d, $^3J_{CP}$=10.7 Hz, CH), 132.4 (s, CH), 148.4 (d, $^2J_{CP}$=7.6 Hz, C), 157.2 (s, C), 167.9 (d, $^2J_{CP}$=17.5 Hz, C); MS m/z 383 (1) [M^+], 337 (35), 294 (62), 240 (67), 220 (100). Anal. Calcd for $C_{17}H_{26}N_3O_5P$: C, 53.26; H, 6.84; N, 10.96. Found: C, 53.37; H, 6.78; N, 10.62.

*4.4.5. Methyl 2-(aminocarbonyl)-3-methoxy-5-methyl-3-phenyl-2H-1,2,3λ^5-diazaphosphole-4-carboxylate (**4a**)*

Colorless crystals; mp 125–127 °C; IR (Nujol) ν_{max} 3415, 3212, 1704, 1657 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.24 (s, 3H, CH_3), 3.36 (s, 3H, CO_2CH_3), 3.61 (d, 3H, $^3J_{HP}$=14.4 Hz, OCH_3), 6.90 and 7.18 (2br s, 2H, NH_2), 7.54–7.76 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 17.1 (s, CH_3), 49.7 (s, CH_3), 52.4 (d, $^2J_{CP}$=13.7 Hz, CH_3), 63.0 (d, $^1J_{CP}$=158.0 Hz, C), 124.3 (d, $^1J_{CP}$=160.1 Hz, C), 128.5 (d, $^2J_{CP}$=16.0 Hz, CH), 132.8 (d, $^3J_{CP}$=12.2 Hz, CH), 133.3 (s, CH), 153.7 (d, $^2J_{CP}$=8.4 Hz, C), 155.2 (d, $^2J_{CP}$=25.0 Hz, C), 164.2 (d, $^2J_{CP}$=19.7 Hz, C); MS m/z 309 (31) [M^+], 278 (7), 266 (100). Anal. Calcd for $C_{13}H_{16}N_3O_5P$: C, 50.49; H, 5.21; N, 13.59. Found: C, 50.29; H, 5.08; N, 13.66.

*4.4.6. Ethyl 2-(aminocarbonyl)-3-methoxy-5-methyl-3-phenyl-2H-1,2,3λ^5-diazaphosphole-4-carboxylate (**4b**)*

Colorless crystals; mp 127–130 °C; IR (Nujol) ν_{max} 3467, 3313, 3275, 1713, 1662 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 0.84 (t, 3H, J=7.2 Hz, $CO_2CH_2CH_3$), 2.23 (s, 3H, CH_3), 3.61 (d, 3H, $^3J_{HP}$=14.4 Hz, OCH_3), 3.75–3.91 (m, 2H, $CO_2CH_2CH_3$), 6.90 and 7.18 (2br s, 2H, NH_2), 7.53–7.75 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.1 (s, CH_3), 16.9 (d, $^3J_{CP}$=5.3 Hz, CH_3), 52.3 (d, $^2J_{CP}$=6.8 Hz, CH_3), 57.6 (s, CH_2), 63.1 (d, $^1J_{CP}$=157.0 Hz, C), 124.6 (d, $^1J_{CP}$=160.1 Hz, C), 128.4 (d, $^2J_{CP}$=15.9 Hz, CH), 132.7 (d, $^3J_{CP}$=12.1 Hz, CH), 133.2 (s, CH), 153.7 (d, $^2J_{CP}$=8.4 Hz, C), 155.1 (d, $^2J_{CP}$=25.1 Hz, C), 163.6 (d, $^2J_{CP}$=18.8 Hz, C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 58.51; MS m/z 323 (33) [M^+], 280 (100). Anal. Calcd for $C_{14}H_{18}N_3O_4P$: C, 52.01; H, 5.61; N, 13.00. Found: C, 51.97; H, 5.57; N, 13.58.

*4.4.7. N4,N4,5-Trimethyl-3-methoxy-3-phenyl-2H-1,2,3λ^5-diazaphosphole-2,4-dicarboxamide (**4c**)*

White solid; mp 125–127 °C; IR (Nujol) ν_{max} 3354, 3221, 1713, 1698 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.12 (s, 3H, CH_3), 2.79 (s, 6H, $N(CH_3)_2$), 3.58 (d, 3H, $^3J_{HP}$=14.0 Hz, OCH_3), 6.85 and 7.17 (2br s, 2H, NH_2), 7.52–7.76 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 17.1 (d, $^3J_{CP}$=6.1 Hz, CH_3), 37.5 (s, CH_3), 52.4 (d, $^2J_{CP}$=6.8 Hz, CH_3), 65.2 (d, $^1J_{CP}$=154.7 Hz, C), 124.7 (d, $^1J_{CP}$=160.0 Hz, C), 128.6 (d, $^2J_{CP}$=15.0 Hz, CH), 133.2 (d, $^3J_{CP}$=11.3 Hz, CH), 133.3 (s, CH), 153.8 (d, $^2J_{CP}$=8.3 Hz, C), 154.0 (d, $^2J_{CP}$=23.5 Hz, C), 167.7 (d, $^2J_{CP}$=19.0 Hz, C); MS m/z 322 (5) [M^+], 252 (5), 220 (26), 205 (100). Anal. Calcd for $C_{14}H_{19}N_4O_3P$: C, 52.17; H, 5.94; N, 17.38. Found: C, 52.31; H, 6.01; N, 17.33.

*4.4.8. Methyl 2-(aminocarbonyl)-5-ethyl-5-methoxy-3-phenyl-2H-1,2,3λ^5-diazaphosphole-4-carboxylate (**4d**)*

White solid; mp 124–125 °C; IR (Nujol) ν_{max} 3430, 3210, 1691, 1654 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.84 (t, 3H, J=7.2 Hz, CH_2CH_3), 2.59–2.77 (m, 2H, CH_2CH_3), 3.36 (s, 3H, CO_2CH_3), 3.61 (d, 3H, $^3J_{HP}$=10.4 Hz, OCH_3), 6.88 and 7.21 (2br s, 2H, NH_2), 7.55–7.76 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 12.2 (s, CH_3), 23.8 (s, CH_2), 49.7 (s, CH_3), 52.3 (d, $^2J_{CP}$=8.1 Hz, CH_3), 61.6 (d, $^1J_{CP}$=154.8 Hz, C), 124.4 (d, $^1J_{CP}$=159.4 Hz, C), 128.5 (d, $^2J_{CP}$=16.0 Hz, CH), 132.7 (d, $^3J_{CP}$=12.1 Hz, CH), 133.2 (s, CH), 153.7 (d, $^2J_{CP}$=8.4 Hz, C), 159.9 (d, $^2J_{CP}$=22.7 Hz, C), 163.7 (d, $^2J_{CP}$=19.7 Hz, C); MS m/z 323 (31) [M^+], 292 (5), 280 (100). Anal. Calcd for $C_{14}H_{18}N_3O_4P$: C, 52.01; H, 5.61; N, 13.00. Found: C, 52.14; H, 5.71; N, 12.89.

*4.4.9. Methyl 2-(aminocarbonyl)-3-ethoxy-5-methyl-3-phenyl-2H-1,2,3λ^5-diazaphosphole-4-carboxylate (**4e**)*

Colorless crystals; mp 112–115 °C; IR (Nujol) ν_{max} 3398, 3299, 3218, 1696, 1657 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.24 (t, 3H, J=7.2 Hz, OCH_2CH_3), 2.22 (s, 3H, CH_3), 3.36 (s, 3H, CO_2CH_3), 3.88–4.04 (m, 2H, OCH_2CH_3), 6.87 and 7.15 (2br s, 2H, NH_2), 7.54–7.75 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.1 (s, CH_3), 17.0 (d, $^3J_{CP}$=6.1 Hz, CH_3), 49.8 (s, CH_3), 63.3 (d, $^2J_{CP}$=7.1 Hz, CH_2), 65.1 (d, $^1J_{CP}$=157.6 Hz, C), 124.9 (d, $^1J_{CP}$=160.1 Hz, C), 129.0 (d, $^2J_{CP}$=16.0 Hz, CH), 132.2 (d, $^3J_{CP}$=12.0 Hz, CH), 133.3 (s, CH), 154.1 (d, $^2J_{CP}$=8.3 Hz, C), 155.6 (d, $^2J_{CP}$=25.0 Hz, C), 164.2 (d, $^2J_{CP}$=19.5 Hz, C); MS m/z 323 (53) [M^+], 292 (6), 280 (100). Anal. Calcd for $C_{14}H_{18}N_3O_4P$: C, 52.01; H, 5.61; N, 13.00. Found: C, 52.09; H, 5.49; N, 13.29.

*4.4.10. Ethyl 2-(aminocarbonyl)-3-ethoxy-5-methyl-3-phenyl-2H-1,2,3λ^5-diazaphosphole-4-carboxylate (**4f**)*

Colorless crystals; mp 119–121 °C; IR (Nujol) ν_{max} 3372, 3291, 3205, 1704, 1687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 0.86 (t, 3H, J=6.8 Hz, $CO_2CH_2CH_3$), 1.25 (t, 3H, J=7.2 Hz, OCH_2CH_3), 2.21 (s, 3H, CH_3), 3.82 (q, 2H, J=6.8 Hz, $CO_2CH_2CH_3$), 3.96–4.01 (m, 2H, OCH_2CH_3), 6.92 and 7.16 (2br s, 2H, NH_2), 7.52–7.74 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.4 (s, CH_3), 16.8 (d, $^3J_{CP}$=6.0 Hz, CH_3), 17.7 (d, $^3J_{CP}$=5.3 Hz, CH_3), 58.3 (s, CH_3), 63.1 (d, $^2J_{CP}$=6.9 Hz, CH_2), 65.2 (d, $^1J_{CP}$=157.0 Hz, C), 125.8 (d, $^1J_{CP}$=160.1 Hz, C), 129.2 (d, $^2J_{CP}$=16.0 Hz, CH), 131.9 (d, $^3J_{CP}$=10.0 Hz, CH), 133.3 (s, CH), 154.5 (d, $^2J_{CP}$=8.3 Hz, C), 155.8 (d, $^2J_{CP}$=25.1 Hz, C), 164.3 (d, $^2J_{CP}$=19.0 Hz, C); MS m/z 337 (58) [M^+], 294 (100). Anal. Calcd for $C_{15}H_{20}N_3O_4P$: C, 53.41; H, 5.98; N, 12.46. Found: C, 53.47; H, 5.79; N, 12.61.

*4.4.11. N4,N4,5-Trimethyl-3-ethoxy-3-phenyl-2H-1,2,3λ^5-diazaphosphole-2,4-dicarboxamide (**4g**)*

White solid; mp 138–141 °C; IR (Nujol) ν_{max} 3361, 3218, 1741, 1680 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.24 (t, 3H, J=6.8 Hz, OCH_2CH_3), 2.11 (s, 3H, CH_3), 2.79 (s, 6H, $N(CH_3)_2$), 3.82–4.06 (m, 2H, OCH_2CH_3), 6.79 and 7.07 (2br s, 2H, NH_2), 7.52–7.76 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.3 (d, $^3J_{CP}$=6.8 Hz, CH_3), 17.1 (d, $^3J_{CP}$=6.0 Hz, CH_3), 38.2 (s, CH_3), 61.9 (d, $^2J_{CP}$=6.1 Hz, CH_2), 66.0 (d, $^1J_{CP}$=155.6 Hz, C), 125.3 (d, $^1J_{CP}$=159.3 Hz, C), 128.5 (d, $^2J_{CP}$=16.0 Hz, CH), 133.1 (d, $^3J_{CP}$=11.3 Hz, CH), 133.3 (s, CH), 153.7 (d, $^2J_{CP}$=9.1 Hz, C), 153.8 (d, $^2J_{CP}$=21.3 Hz, C), 167.8 (d, $^2J_{CP}$=19.7 Hz, C); MS m/z 337 (7) [M^+], 310 (40), 267 (100). Anal. Calcd for $C_{15}H_{21}N_4O_3P$: C, 53.57; H, 6.29; N, 16.66. Found: C, 53.39; H, 6.41; N, 16.38.

*4.4.12. Ethyl 2-(aminocarbonyl)-3-ethoxy-5-methyl-3-phenyl-2H-1,2,3λ^5-diazaphosphole-4-carboxylate (**4h**)*

White solid; mp 126–127 °C; IR (Nujol) ν_{max} 3457, 3195, 1696, 1687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.18 (t, 3H, J=7.2 Hz, CH_2CH_3), 1.26 (t, 3H, J=6.8 Hz, OCH_2CH_3), 2.58–2.76 (m, 2H, CH_2CH_3), 3.37 (s, 3H, CH_3), 3.88–4.03 (m, 2H, OCH_2CH_3), 6.86 and 7.18 (2br s, 2H, NH_2), 7.53–7.74 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 12.3 (s, CH_3), 15.4 (d, $^3J_{CP}$=5.6 Hz, CH_3), 23.8 (s, CH_2), 49.6 (s, CH_3), 62.4 (d, $^1J_{CP}$=156.3 Hz, C), 62.5 (d, $^2J_{CP}$=6.1 Hz, CH_2), 124.9 (d, $^1J_{CP}$=160.1 Hz, CH), 128.5 (d, $^2J_{CP}$=15.9 Hz, CH), 132.6 (d, $^3J_{CP}$=12.2 Hz, CH), 133.1 (s, CH), 153.8 (d, $^2J_{CP}$=8.3 Hz, C), 159.9 (d, $^2J_{CP}$=24.3 Hz, C), 163.8 (d, $^2J_{CP}$=19.7 Hz, C); MS m/z 337 (58) [M^+], 306 (7), 294 (100). Anal. Calcd for $C_{15}H_{20}N_3O_4P$: C, 53.41; H, 5.98; N, 12.46. Found: C, 53.55; H, 5.74; N, 12.58.

4.5. General procedure for the synthesis of *E*-hydrazonophosphonates 5a–h

A solution of 3-phenyl-2*H*-1,2,3λ^5-diazaphospholes **4a–h** (1 mmol) in methanol–water (9.5:0.5 mL) was magnetically stirred for 6.0–10.0 h, until a TLC check revealed the disappearance of the starting compound **4**. The mixture was then dried over anhydrous sodium sulfate and, after evaporation of the solvent, it was chromatographed on a silica gel column (elution mixture: ethyl acetate–methanol) to give hydrazonophosphonates **5a–h** in good purity. Further purification of these compounds can be obtained by crystallization from ethyl acetate–light petroleum (bp 40–60 °C).

4.5.1. Methyl 3-[2-(aminocarbonyl)hydrazono]-2-[methoxy-(phenyl)phosphoryl]butanoate (**5a**)

White solid; mp 148–150 °C; IR (Nujol) ν_{max} 3469, 3310, 1740, 1692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 3H, CH_3), 3.57 (s, 3H, CO_2CH_3), 3.66–3.72 (m, 3H, OCH_3), 4.16 (d, 1H, $^2J_{HP}$=18.8 Hz, CH), 5.77 (br s, 2H, NH_2), 7.40–7.76 (m, 5H, CH_{arom}), 8.95 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (s, CH_3), 52.6 (s, CH_3), 53.6 (d, $^2J_{CP}$=6.8 Hz, CH_3), 53.9 (d, $^1J_{CP}$=136.0 Hz, CH), 129.4 (d, $^2J_{CP}$=14.4 Hz, CH), 130.0 (d, $^1J_{CP}$=107.0 Hz, C), 132.2 (d, $^3J_{CP}$=11.4 Hz, CH), 132.6 (d, $^2J_{CP}$=10.6 Hz, C), 133.6 (s, C), 162.5 (s, C), 165.8 (d, $^2J_{CP}$=5.2 Hz, C); MS *m*/*z* 327 (11) [M$^+$], 296 (100). Anal. Calcd for $C_{13}H_{18}N_3O_5P$: C, 47.71; H, 5.54; N, 12.84. Found: C, 47.68; H, 5.44; N, 12.65.

4.5.2. Ethyl 3-[2-(aminocarbonyl)hydrazono]-2-[methoxy-(phenyl)phosphoryl]butanoate (**5b**)

White solid; mp 146–147 °C; IR (Nujol) ν_{max} 3478, 3300, 1744, 1700, 1687 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.93 (t, 3H, *J*=6.8 Hz, $CO_2CH_2CH_3$), 1.95 (d, 3H, $^4J_{HP}$=1.6 Hz, CH_3), 3.56 (d, 3H, $^3J_{HP}$=11.2 Hz, OCH_3), 3.90–3.93 (m, 2H, $CO_2CH_2CH_3$), 4.41 (d, 1H, $^2J_{HP}$=18.8 Hz, CH), 6.26 (br s, 2H, NH_2), 7.52–7.75 (m, 5H, CH_{arom}), 9.33 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.5 (s, CH_3), 15.8 (s, CH_3), 51.7 (d, $^2J_{CP}$=6.8 Hz, CH_3), 56.9 (d, $^1J_{CP}$=88.0 Hz, CH), 61.1 (s, CH_2), 128.5 (d, $^2J_{CP}$=12.9 Hz, CH), 129.2 (d, $^1J_{CP}$=162.0 Hz, C), 131.9 (d, $^3J_{CP}$=9.9 Hz, CH), 132.8 (s, CH), 139.8 (d, $^2J_{CP}$=6.9 Hz, C), 156.8 (s, C), 166.2 (d, $^2J_{CP}$=5.3 Hz, C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 36.40; MS *m*/*z* 341 (7) [M$^+$], 278 (15), 266 (18), 252 (100). Anal. Calcd for $C_{14}H_{20}N_3O_5P$: C, 49.27; H, 5.91; N, 12.31. Found: C, 49.33; H, 5.88; N, 12.43.

4.5.3. Methyl {2-[2-(aminocarbonyl)hydrazono]-1-[(dimethylamino)carbonyl]propyl}phenylphosphinate (**5c**)

White solid; mp 173–177 °C; IR (Nujol) ν_{max} 3472, 3298, 1725, 1692 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.87 (d, 3H, $^4J_{HP}$=2.0 Hz, CH_3), 2.79 and 2.94 (2s, 6H, $N(CH_3)_2$), 3.56 (d, 3H, $^3J_{HP}$=10.8 Hz, OCH_3), 4.69 (d, 1H, $^2J_{HP}$=18.8 Hz, CH), 6.18 (br s, 2H, NH_2), 7.48–7.71 (m, 5H, CH_{arom}), 9.25 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.9 (s, CH_3), 35.9 (s, CH_3), 38.1 (s, CH_3), 52.1 (d, $^2J_{CP}$=6.0 Hz, CH_3), 54.8 (d, $^1J_{CP}$=78.9 Hz, CH), 128.8 (d, $^2J_{CP}$=12.2 Hz, CH), 130.8 (d, $^1J_{CP}$=132.0 Hz, C), 132.5 (d, $^3J_{CP}$=9.9 Hz, CH), 132.8 (s, CH), 141.6 (d, $^2J_{CP}$=6.8 Hz, C), 157.6 (s, C), 165.9 (d, $^2J_{CP}$=4.5 Hz, C); MS *m*/*z* 340 (1) [M$^+$], 296 (41), 266 (100). Anal. Calcd for $C_{14}H_{21}N_4O_4P$: C, 49.41; H, 6.22; N, 16.46. Found: C, 49.67; H, 6.18; N, 16.59.

4.5.4. Methyl 3-[2-(aminocarbonyl)hydrazono]-2-[methoxy-(phenyl)phosphoryl]pentanoate (**5d**)

White solid; mp 120–123 °C; IR (Nujol) ν_{max} 3465, 3290, 1748, 1700, 1684 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, 3H, *J*=7.6 Hz, CH_2CH_3), 2.32–2.50 (m, 2H, CH_2CH_3), 3.62 (s, 3H, CO_2CH_3), 3.70–3.72 (m, 3H, OCH_3), 4.14 (d, 1H, $^2J_{HP}$=18.6 Hz, CH), 6.21 (br s, 2H, NH_2), 7.44–7.80 (m, 5H, CH_{arom}), 8.82 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0 (s, CH_3), 23.1 (s, CH_2), 52.1 (s, CH_3), 52.9 (d, $^2J_{CP}$=6.8 Hz, CH_3), 55.8 (d, $^1J_{CP}$=91.8 Hz, CH), 128.5 (d, $^2J_{CP}$=13.7 Hz, CH), 131.0 (d, $^3J_{CP}$=11.3 Hz, CH), 131.4 (d, $^1J_{CP}$=111.6 Hz, C), 133.1 (s, CH), 145.1 (d, $^2J_{CP}$=6.8 Hz, C), 158.1 (s, C), 166.8 (d, $^2J_{CP}$=5.7 Hz, C); MS *m*/*z* 341 (11) [M$^+$], 310 (28), 266 (100). Anal. Calcd for $C_{14}H_{20}N_3O_5P$: C, 49.27; H, 5.91; N, 12.31. Found: C, 49.44; H, 5.96; N, 12.03.

4.5.5. Methyl 3-[2-(aminocarbonyl)hydrazono]-2-[ethoxy-(phenyl)phosphoryl]butanoate (**5e**)

White solid; mp 126–128 °C; IR (Nujol) ν_{max} 3469, 3296, 1750, 1705, 1684 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.18 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.92 (d, 3H, $^4J_{HP}$=1.6 Hz, CH_3), 3.65 (s, 3H, CO_2CH_3), 3.89–3.91 (m, 2H, OCH_2CH_3), 4.40 (d, 1H, $^2J_{HP}$=19.2 Hz, CH), 6.23 (br s, 2H, NH_2), 7.51–7.74 (m, 5H, CH_{arom}), 9.30 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.8 (s, CH_3), 16.2 (d, $^2J_{CP}$=6.0 Hz, CH_3), 52.3 (s, CH_3), 57.1 (d, $^1J_{CP}$=88.0 Hz, CH), 61.1 (d, $^2J_{CP}$=6.3 Hz, CH_2), 128.4 (d, $^2J_{CP}$=12.9 Hz, CH), 129.8 (d, $^1J_{CP}$=132.0 Hz, C), 131.7 (d, $^3J_{CP}$=9.9 Hz, CH), 132.6 (s, CH), 139.4 (d, $^2J_{CP}$=6.9 Hz, C), 156.8 (s, C), 166.7 (d, $^2J_{CP}$=5.3 Hz, C); MS *m*/*z* 341 (1) [M$^+$], 325 (31), 296 (44), 266 (100). Anal. Calcd for $C_{14}H_{20}N_3O_5P$: C, 49.27; H, 5.91; N, 12.31. Found: C, 49.38; H, 5.65; N, 12.37.

4.5.6. Ethyl 3-[2-(aminocarbonyl)hydrazono]-2-[ethoxy-(phenyl)phosphoryl]butanoate (**5f**)

White solid; mp 129–130 °C; IR (Nujol) ν_{max} 3471, 3306, 1747, 1692, 1684 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.94 (t, 3H, *J*=7.2 Hz, $CO_2CH_2CH_3$), 1.17 (t, 3H, *J*=6.8 Hz, OCH_2CH_3), 1.94 (s, 3H, CH_3), 3.88–3.97 (m, 4H, $CO_2CH_2CH_3$ and OCH_2CH_3), 4.37 (d, 1H, $^2J_{HP}$=19.2 Hz, CH), 6.26 (br s, 2H, NH_2), 7.51–7.75 (m, 5H, CH_{arom}), 9.31 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.5 (s, CH_3), 15.8 (s, CH_3), 16.2 (d, $^3J_{CP}$=5.3 Hz, CH_3), 57.2 (d, $^1J_{CP}$=88.0 Hz, CH), 61.1 (d, $^2J_{CP}$=13.6 Hz, CH_2), 61.2 (s, CH_2), 128.4 (d, $^2J_{CP}$=12.9 Hz, CH), 130.1 (d, $^1J_{CP}$=131.3 Hz, C), 131.7 (d, $^3J_{CP}$=9.8 Hz, CH), 132.5 (s, CH), 139.9 (d, $^2J_{CP}$=6.8 Hz, C), 156.9 (s, C), 166.2 (d, $^2J_{CP}$=7.6 Hz, C); MS *m*/*z* 355 (7) [M$^+$], 338 (12), 309 (10), 292 (13), 266 (100). Anal. Calcd for $C_{15}H_{22}N_3O_5P$: C, 50.70; H, 6.24; N, 11.83. Found: C, 50.53; H, 6.33; N, 11.71.

4.5.7. Ethyl {2-[2-(aminocarbonyl)hydrazono]-1-[(dimethylamino)carbonyl]propyl}phenylphosphinate (**5g**)

White solid; mp 165–168 °C; IR (Nujol) ν_{max} 3470, 3305, 1718, 1685 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.17 and 1.18 (dt, 3H, *J*=6.8 Hz, $^4J_{HP}$=2.0 Hz, OCH_2CH_3), 1.86 (d, 3H, $^4J_{HP}$=2.0 Hz, CH_3), 2.79 and 2.94 (2s, 6H, $N(CH_3)_2$), 3.82–4.03 (m, 2H, OCH_2CH_3), 4.67 (d, 1H, $^2J_{HP}$=18.8 Hz, CH), 6.17 (br s, 2H, NH_2), 7.46–7.72 (m, 5H, CH_{arom}), 9.22 (2s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.0 (s, CH_3), 15.3 (s, CH_3), 35.3 (s, CH_3), 37.5 (s, CH_3), 55.0 (d, $^2J_{CP}$=94.1 Hz, CH), 60.7 (d, $^2J_{CP}$=6.8 Hz, CH_2), 128.0 (d, $^2J_{CP}$=12.2 Hz, CH), 130.4 (d, $^1J_{CP}$=132.2 Hz, C), 131.6 (d, $^3J_{CP}$=9.9 Hz, CH), 132.1 (s, CH), 141.0 (d, $^2J_{CP}$=7.5 Hz, C), 156.9 (s, C), 165.2 (d, $^2J_{CP}$=3.8 Hz, C); MS *m*/*z* 354 (2) [M$^+$], 337 (13), 310 (51), 266 (100). Anal. Calcd for $C_{15}H_{23}N_4O_4P$: C, 50.84; H, 6.54; N, 15.51. Found: C, 50.77; H, 6.39; N, 15.48.

4.5.8. Methyl 3-[2-(aminocarbonyl)hydrazono]-2-[ethoxy-(phenyl)phosphoryl]pentanoate (**5h**)

White solid; mp 128–132 °C; IR (Nujol) ν_{max} 3480, 3270, 1752, 1695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, 3H, *J*=7.6 Hz, CH_2CH_3), 1.16 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 2.30–2.48 (m, 2H, CH_2CH_3), 3.62 (s, 3H, CO_2CH_3), 3.69–3.74 (m, 2H, OCH_2CH_3), 4.14 (d, 1H, $^2J_{HP}$=18.6 Hz, CH), 6.15 (br s, 2H, NH_2), 7.42–7.79 (m, 5H, CH_{arom}), 8.93 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.1 (s, CH_3), 16.0 (d, $^3J_{CP}$=6.1 Hz, CH_3), 23.3 (s, CH_2), 52.3 (s, CH_3), 61.0 (d, $^2J_{CP}$=6.3 Hz, CH_2), 53.9 (d, $^1J_{CP}$=91.6 Hz, CH), 129.1 (d, $^2J_{CP}$=13.7 Hz, CH), 131.2 (d, $^3J_{CP}$=11.3 Hz, CH), 131.6 (d, $^1J_{CP}$=111.0 Hz, C), 132.9 (s, CH), 144.7 (d, $^2J_{CP}$=7.2 Hz, C), 158.7 (s, C), 166.9 (d, $^2J_{CP}$=6.2 Hz, C); MS *m*/*z* 355 (6) [M$^+$], 338 (15), 280 (100). Anal. Calcd for

$C_{15}H_{22}N_3O_5P$: C, 49.27; H, 5.91; N, 12.31. Found: C, 49.12; H, 5.87; N, 12.37.

4.6. General procedure for the synthesis of β-ketophosphonates 6a–e

To a solution of *E*-hydrazonophosphonates **5a**,**b**,**d**,**f**,**g** (1 mmol) in acetone–water (9:1, 15 mL), 4 equiv of Amberlyst 15H was added and the reaction was refluxed for 3.0–5.0 h, until the disappearance of the starting compound **5** (monitored by TLC). The resin was removed by filtration and the reaction solvent was evaporated under reduced pressure. Then the crude was chromatographed on silica gel column (elution mixture: ethyl acetate–cyclohexane) to give products **6a–d** as oils, while **6e** was crystallized from ethyl acetate–cyclohexane.

*4.6.1. Methyl 2-[methoxy(phenyl)phosphoryl]-3-oxobutanoate (keto tautomer: 3%)/methyl 3-hydroxy-2-[methoxy(phenyl)-phosphoryl]-2-butenoate (enol tautomer: 97%) (**6a**)*

Colorless oil; IR (Nujol) ν_{max} 3279 (br), 1741, 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 0.09H, CH_3 keto tautomer), 2.49 (s, 2.91H, CH_3 enol tautomer), 3.51 (s, 2.91H, CO_2CH_3 enol tautomer), 3.62 (s, 0.09H, CO_2CH_3 keto tautomer), 3.82 (d, 3H, $^2J_{HP}$=12.4 Hz, OCH_3 keto and enol tautomers), 5.56–5.58 (m, 0.03H, CH keto tautomer), 7.44–7.84 (m, 5H, CH_{arom} keto and enol tautomers), 14.69 (s, 0.97H, OH enol tautomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0 (d, $^3J_{CP}$=9.1 Hz, CH_3), 24.1 (d, $^3J_{CP}$=9.1 Hz, CH_3), 51.0 (s, CH_3), 51.9 (d, $^2J_{CP}$=6.8 Hz, CH_3), 89.1 (d, $^1J_{CP}$=129.0 Hz, C), 108.1 (d, $^1J_{CP}$=129.0 Hz, CH), 128.4 (d, $^2J_{CP}$=14.4 Hz, CH), 131.2 (d, $^1J_{CP}$=154.8 Hz, C), 131.7 (d, $^3J_{CP}$=10.6 Hz, CH), 132.5 (d, $^4J_{CP}$=3.0 Hz, CH), 165.5 (d, $^2J_{CP}$=11.3 Hz, C), 190.3 (s, C), 197.0 (s, C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 33.45, 46.60; MS *m*/*z* 270 (60) [M^+], 255 (60), 238 (20), 223 (14), 197 (18), 173 (25), 155 (100). Anal. Calcd for $C_{12}H_{15}O_5P$: C, 53.34; H, 5.59. Found: C, 53.39; H, 5.54.

*4.6.2. Ethyl 3-hydroxy-2-[methoxy(phenyl)phosphoryl]-2-butenoate (enol tautomer: 100%) (**6b**)*

Colorless oil; IR (Nujol) ν_{max} 3300 (br), 1740, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, 3H, *J*=7.2 Hz, $CO_2CH_2CH_3$), 2.50 (3H, s, CH_3), 3.82 (d, 3H, $^3J_{HP}$=11.6 Hz, OCH_3), 3.94–4.00 (m, 2H, $CO_2CH_2CH_3$), 7.42–7.83 (m, 5H, CH_{arom}), 14.67 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (s, CH_3), 23.9 (d, $^3J_{CP}$=9.1 Hz, CH_3), 51.8 (d, $^2J_{CP}$=6.8 Hz, CH_3), 60.0 (s, CH_2), 89.0 (d, $^1J_{CP}$=129.0 Hz, C), 128.3 (d, $^2J_{CP}$=13.6 Hz, CH), 131.5 (d, $^1J_{CP}$=155.5 Hz, C), 131.6 (d, $^3J_{CP}$=10.6 Hz, CH), 132.5 (s, CH), 166.0 (d, $^2J_{CP}$=10.6 Hz, C), 190.3 (s, C); MS *m*/*z* 284 (61) [M^+], 269 (58), 239 (20), 311 (38), 155 (100). Anal. Calcd for $C_{13}H_{17}O_5P$: C, 54.93; H, 6.03. Found: C, 54.81; H, 5.99.

*4.6.3. Methyl 3-hydroxy-2-[methoxy(phenyl)phosphoryl]-2-pentenoate (enol tautomer: 100%) (**6c**)*

Pale yellow oil; IR (Nujol) ν_{max} 3305 (br), 1738, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 2.85 (q, 2H, *J*=7.2 Hz, $CO_2CH_2CH_3$), 3.48 (s, 3H, CO_2CH_3), 3.80 (d, 3H, $^3J_{HP}$=12.4 Hz, OCH_3), 7.40–7.81 (m, 5H, CH_{arom}), 14.81 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6 (s, CH_3), 51.1 (s, CH_3), 63.2 (d, $^3J_{CP}$=6.8 Hz, CH_2), 51.9 (d, $^2J_{CP}$=6.8 Hz, CH_3), 88.9 (d, $^1J_{CP}$=127.5 Hz, C), 128.2 (d, $^2J_{CP}$=13.6 Hz, CH), 131.4 (d, $^1J_{CP}$=155.0 Hz, C), 131.7 (d, $^3J_{CP}$=10.6 Hz, CH), 132.6 (s, CH), 166.4 (d, $^2J_{CP}$=11.3 Hz, C), 190.1 (s, C); MS *m*/*z* 284 (37) [M^+], 255 (100). Anal. Calcd for $C_{13}H_{17}O_5P$: C, 54.93; H, 6.03. Found: C, 54.81; H, 5.99.

*4.6.4. Ethyl 2-[ethoxy(phenyl)phosphoryl]-3-oxobutanoate (keto tautomer: 5%)/ethyl 2-[ethoxy(phenyl)phosphoryl]-3-hydroxy-2-butenoate (enol tautomer: 95%) (**6d**)*

Pale yellow oil; IR (Nujol) ν_{max} 3305 (br), 1742, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, 2.85H, *J*=7.2 Hz, $CO_2CH_2CH_3$ enol tautomer), 1.09 (t, 0.15H, *J*=7.2 Hz, $CO_2CH_2CH_3$ keto tautomer), 1.39 (t, 3H, *J*=7.2 Hz, OCH_2CH_3 keto and enol tautomers), 2.38 (s, 0.15H, CH_3 keto tautomer), 2.49 (s, 2.85H, CH_3 enol tautomer), 3.89–4.22 (m, 4H, $CO_2CH_2CH_3$ and OCH_2CH_3 keto and enol tautomers), 5.56–5.58 (m, 0.05H, CH keto tautomer), 7.40–7.84 (m, 5H, CH_{arom} keto and enol tautomers), 14.46 (s, 0.95H, OH enol tautomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (s, CH_3), 14.1 (s, CH_3), 16.5 (d, $^3J_{CP}$=6.8 Hz, CH_3), 23.9 (d, $^3J_{CP}$=9.1 Hz, CH_3), 60.0 (s, CH_2), 61.6 (d, $^2J_{CP}$=9.1 Hz, CH_2), 89.8 (d, $^1J_{CP}$=127.5 Hz, C), 108.1 (d, $^1J_{CP}$=119.0 Hz, CH), 128.2 (d, $^2J_{CP}$=13.6 Hz, CH), 131.4 (d, $^1J_{CP}$=155.0 Hz, C), 131.7 (d, $^3J_{CP}$=10.6 Hz, CH), 132.6 (s, CH), 166.1 (d, $^2J_{CP}$=11.3 Hz, C), 190.0 (s, C), 197.0 (s, C); MS *m*/*z* 298 (64) [M^+], 283 (45), 252 (24), 225 (37), 211 (30), 183 (32), 169 (100). Anal. Calcd for $C_{14}H_{19}O_5P$: C, 53.34; H, 5.59. Found: C, 53.39; H, 5.54.

*4.6.5. Ethyl {1-[(dimethylamino)carbonyl]-2-hydroxy-1-propenyl}-phenylphosphinate (enol tautomer: 100%) (**6e**)*

White solid; mp 88–91 °C; IR (Nujol) ν_{max} 3300 (br), 1742, 1712 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.19 (t, 3H, *J*=7.6 Hz, OCH_2CH_3), 2.24 (s, 3H, CH_3), 2.70 and 2.89 (2s, 6H, $N(CH_3)_2$), 3.89–4.21 (m, 2H, OCH_2CH_3), 7.44–7.76 (m, 5H, CH_{arom}), 12.22 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.3 (s, CH_3), 15.4 (s, CH_3), 24.7 (d, $^3J_{CP}$=9.1 Hz, CH_3), 16.8 (d, $^3J_{CP}$=6.8 Hz, CH_3), 61.6 (d, $^2J_{CP}$=9.1 Hz, CH_2), 89.1 (d, $^1J_{CP}$=129.1 Hz, C), 128.2 (d, $^2J_{CP}$=13.6 Hz, CH), 131.1 (d, $^1J_{CP}$=155.1 Hz, C), 131.6 (d, $^3J_{CP}$=10.6 Hz, CH), 132.5 (s, CH), 166.7 (d, $^2J_{CP}$=11.1 Hz, C), 190.0 (s, C); MS *m*/*z* 297 (20) [M^+], 279 (58), 253 (100). Anal. Calcd for $C_{14}H_{20}NO_4P$: C, 56.56; H, 6.78. Found: C, 56.47; H, 6.79.

4.7. General procedure for the synthesis of 4-[alkoxy(phenyl)-phosphoryl]-1,2-diaza-1,3-butadienes 9a–e

To a magnetically stirred solution of *E*-hydrazonophosphonates **5a**,**b**,**d**,**f**,**g** (1 mmol) in dichloromethane (150 mL), 2,4,4,6-tetrabromo-3-*n*-pentadecyl-2,5-cyclohexadienone (TBPCO)[25] (1.1 mmol) was added portion-wise at room temperature obtaining the corresponding α-bromohydrazones **8** (check by TLC), in 2.0 h. The mixture was then treated with an aqueous solution of sodium acetate (20 mL×2) and the organic layer was dried on sodium sulfate. Dichloromethane was evaporated under reduced pressure and the final 4-[alkoxy(phenyl)phosphoryl]-1,2-diaza-1,3-butadienes **9a–e** were purified by chromatography on silica gel column (elution mixture: ethyl acetate–cyclohexane) and were obtained as red oils.

*4.7.1. Methyl 3-[2-(aminocarbonyl)-1-diazenyl]-2-[methoxy-(phenyl)phosphoryl]-2-butenoate (**9a**)*

Red oil; IR (Nujol) ν_{max} 3291, 3170, 1734, 1615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (d, 3H, $^4J_{HP}$=2.4 Hz, CH_3), 3.69 (d, 3H, $^3J_{HP}$=11.6 Hz, OCH_3), 3.89 (s, 3H, CO_2CH_3), 5.17 and 7.10 (2br s, 2H, NH_2), 7.45–7.84 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (d, $^3J_{CP}$=9.8 Hz, CH_3), 51.4 (s, CH_3), 52.7 (d, $^2J_{CP}$=28.8 Hz, CH_3), 128.8 (d, $^2J_{CP}$=13.6 Hz, CH), 130.7 (d, $^1J_{CP}$=146.4 Hz, C), 131.5 (d, $^3J_{CP}$=12.0 Hz, CH), 133.2 (s, CH), 136.4 (d, $^1J_{CP}$=123.0 Hz, C), 159.4 (s, C), 163.3 (d, $^2J_{CP}$=21.0 Hz, C), 165.4 (d, $^2J_{CP}$=7.6 Hz, C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 26.78; MS *m*/*z* 326 (3) [M^++1], 308 (11), 267 (15), 253 (63), 221 (45), 207 (81), 195 (100). Anal. Calcd for $C_{13}H_{16}N_3O_5P$: C, 48.01; H, 4.96; N, 12.92. Found: C, 47.99; H, 4.94; N, 12.97.

*4.7.2. Ethyl 3-[2-(aminocarbonyl)-1-diazenyl]-2-[methoxy-(phenyl)phosphoryl]-2-butenoate (**9b**)*

Red oil; mixture of isomers; IR (Nujol) ν_{max} 3284, 3168, 1731, 1616 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 and 1.35 (2t, 3H, *J*=7.2 Hz, $CO_2CH_2CH_3$), 2.03 and 2.14 (2d, 3H, $^4J_{HP}$=1.2 Hz, CH_3), 3.69 and 3.82 (2d, 3H, $^3J_{HP}$=11.6 Hz, OCH_3), 4.22–4.39 (m, 2H,

$CO_2CH_2CH_3$), 5.56, 5.97, 6.02, and 7.01 (4br s, 2H, NH_2), 7.45–7.95 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0 (s, CH_3), 13.5 (d, $^3J_{CP}$=9.8 Hz, CH_3), 14.3 (d, $^3J_{CP}$=9.8 Hz, CH_3), 52.2 (d, $^2J_{CP}$=28.8 Hz, CH_3), 62.4 (s, CH_2), 62.6 (s, CH_2), 128.9 (d, $^2J_{CP}$=14.0 Hz, CH), 129.0 (d, $^2J_{CP}$=13.7 Hz, CH), 129.6 (d, $^1J_{CP}$=135.0 Hz, C), 131.7 (d, $^3J_{CP}$=11.4 Hz, CH), 132.1 (d, $^3J_{CP}$=10.6 Hz, CH), 133.0 (s, CH), 137.1 (d, $^1J_{CP}$=123.7 Hz, C), 140.4 (d, $^1J_{CP}$=122.9 Hz, C), 159.0 (s, C), 162.1 (d, $^2J_{CP}$=21.2 Hz, C), 162.4 (d, $^2J_{CP}$=24.3 Hz, C), 165.2 (d, $^2J_{CP}$=8.3 Hz, C), 165.7 (d, $^2J_{CP}$=9.1 Hz, C); MS *m/z* 340 (2) [M^++1], 322 (13), 267 (12), 253 (60), 221 (33), 207 (83), 195 (100). Anal. Calcd for $C_{14}H_{18}N_3O_5P$: C, 49.56; H, 5.35; N, 12.38. Found: C, 49.63; H, 5.46; N, 12.01.

*4.7.3. Methyl 3-[2-(aminocarbonyl)-1-diazenyl]-2-[methoxy-(phenyl)phosphoryl]-2-pentenoate (**9c**)*

Red oil; IR (Nujol) ν_{max} 3290, 3150, 1725, 1623 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.06 (t, 3H, *J*=7.2 Hz, CH_2CH_3), 2.43–2.55 (m, 2H, CH_2CH_3), 3.70 (d, 3H, $^3J_{HP}$=11.6 Hz, OCH_3), 3.87 (s, 3H, CO_2CH_3), 5.17 and 7.10 (2br s, 2H, NH_2), 7.45–7.85 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 12.3 (s, CH_3), 13.1 (d, $^3J_{CP}$=7.3 Hz, CH_2), 52.0 (s, CH_3), 53.1 (d, $^2J_{CP}$=28.6 Hz, CH_3), 128.7 (d, $^2J_{CP}$=14.4 Hz, CH), 130.8 (d, $^1J_{CP}$=135.1 Hz, C), 131.4 (d, $^3J_{CP}$=11.4 Hz, CH), 133.0 (s, CH), 136.3 (d, $^1J_{CP}$=123.0 Hz, C), 159.3 (s, C), 162.5 (d, $^2J_{CP}$=32.0 Hz, C), 165.2 (d, $^2J_{CP}$=8.3 Hz, C); MS *m/z* 340 (1) [M^++1], 267 (10), 253 (45), 239 (33), 222 (23), 207 (100). Anal. Calcd for $C_{14}H_{18}N_3O_5P$: C, 49.56; H, 5.35; N, 12.38. Found: C, 49.63; H, 5.68; N, 12.55.

*4.7.4. Methyl 3-[2-(aminocarbonyl)-1-diazenyl]-2-[ethoxy-(phenyl)phosphoryl]-2-butenoate (**9d**)*

Red oil; IR (Nujol) ν_{max} 3288, 3162, 1730, 1628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, 3H, *J*=7.2 Hz, $CO_2CH_2CH_3$), 2.03 (d, 3H, $^4J_{HP}$=2.4 Hz, CH_3), 3.89 (s, 3H, CO_2CH_3), 3.96–4.00 and 4.09–4.15 (2m, 2H, $CO_2CH_2CH_3$), 5.41 and 7.03 (2br s, 2H, NH_2), 7.26–7.48 (m, 2H, CH_{arom}), 7.52–7.54 (m, 1H, CH_{arom}), 7.81–7.87 (m, 2H, CH_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (d, $^3J_{CP}$=9.8 Hz, CH_3), 16.3 (d, $^3J_{CP}$=6.8 Hz, CH_3), 52.2 (s, CH_3), 61.8 (d, $^2J_{CP}$=6.0 Hz, CH_2), 128.7 (d, $^2J_{CP}$=13.6 Hz, CH), 131.4 (d, $^3J_{CP}$=10.7 Hz, CH), 131.5 (d, $^1J_{CP}$=144.1 Hz, C), 132.7 (s, CH), 137.0 (d, $^1J_{CP}$=123.0 Hz, C), 159.3 (s, C), 162.2 (d, $^2J_{CP}$=31.8 Hz, C), 165.8 (d, $^2J_{CP}$=8.3 Hz, C); MS *m/z* 340 (2) [M^++1], 322 (15), 281 (17), 266 (58), 207 (100). Anal. Calcd for $C_{14}H_{18}N_3O_5P$: C, 49.56; H, 5.35; N, 12.38. Found: C, 49.68; H, 5.26; N, 12.60.

*4.7.5. Ethyl 3-[2-(aminocarbonyl)-1-diazenyl]-2-[ethoxy(phenyl)-phosphoryl]-2-butenoate (**9e**)*

Red oil; mixture of isomers; IR (Nujol) ν_{max} 3284, 3160, 1730, 1625 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.14 and 1.18 (2t, 3H, *J*=6.8 Hz, OCH_2CH_3), 1.26 and 1.27 (2t, 3H, *J*=7.2 Hz, $CO_2CH_2CH_3$), 1.83 and 1.98 (2d, 3H, $^4J_{HP}$=0.8 Hz, CH_3), 3.85–4.11 (m, 2H, OCH_2CH_3), 4.15 and 4.29 (2q, 2H, *J*=7.2 Hz, $CO_2CH_2CH_3$), 5.19, 5.65, 5.96, and 7.10 (4br s, 2H, NH_2), 7.46–7.85 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ 11.8 (s, CH_3), 13.5 (d, $^3J_{CP}$=9.1 Hz, CH_3), 14.5 (d, $^3J_{CP}$=9.1 Hz, CH_3), 16.7 (d, $^3J_{CP}$=6.9 Hz, CH_3), 61.8 (d, $^2J_{CP}$=6.0 Hz, CH_2), 62.1 (s, CH_2), 62.5 (d, $^2J_{CP}$=6.0 Hz, CH_2), 129.0 (d, $^2J_{CP}$=13.7 Hz, CH), 129.7 (d, $^2J_{CP}$=13.6 Hz, CH), 130.3 (d, $^1J_{CP}$=144.0 Hz, C), 132.1 (d, $^3J_{CP}$=10.6 Hz, CH), 132.3 (d, $^3J_{CP}$=11.3 Hz, CH), 133.9 (s, CH), 136.0 (d, $^1J_{CP}$=123.0 Hz, C), 138.2 (d, $^1J_{CP}$=123.0 Hz, C), 159.7 (s, C), 164.3 (d, $^2J_{CP}$=20.0 Hz, C), 165.5 (d, $^2J_{CP}$=8.3 Hz, C), 165.8 (d, $^2J_{CP}$=8.4 Hz, C); MS *m/z* 354 (3) [M^++1], 336 (12), 281 (21), 266 (61), 221 (100). Anal. Calcd for $C_{15}H_{20}N_3O_5P$: C, 50.99; H, 5.71; N, 11.89. Found: C, 51.03; H, 5.88; N, 11.73.

4.8. General procedure for the synthesis of 2-[alkoxy(phenyl)-phosphoryl]-2-methoxyhydrazones 10a,b

To a magnetically stirred solution of 4-[alkoxy(phenyl)-phosphoryl]-1,2-diaza-1,3-butadienes **9b**,**e** (1 mmol) in methanol (10 mL) at room temperature, a catalytic amount of sodium methoxide (0.1 mmol) was added. The reaction was allowed to stand in these conditions for 0.5–1.0 h, until the disappearance of the red color of the starting compound **6**. After evaporation of the solvent under reduced pressure, the products **10a**,**b** were obtained by chromatography on a silica gel column (elution mixture: ethyl acetate–cyclohexane) and were crystallized from ethyl acetate–light petroleum (bp 40–60 °C).

*4.8.1. Ethyl 3-[2-(aminocarbonyl)hydrazono]-2-methoxy-2-[methoxy(phenyl)phosphoryl]butanoate (**10a**)*

White powder; mp 111–113 °C; IR (Nujol) ν_{max} 3358, 3100, 1705, 1620 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88–0.93 (m, 3H, $CO_2CH_2CH_3$), 2.45 and 2.54 (2s, 3H, CH_3), 3.66 and 3.69 (2s, 3H, OCH_3), 3.74 and 3.76 (2d, 3H, $^3J_{HP}$=2.1 Hz, $POCH_3$), 3.81–3.93 (m, 2H, $CO_2CH_2CH_3$), 5.64 and 6.12 (2br s, 2H, NH_2), 7.38–7.43 (m, 3H, CH_{arom}), 7.75–7.79 (m, 2H, CH_{arom}), 9.81 and 10.61 (2s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.2 (s, CH_3), 14.3 (s, CH_3), 25.3 (d, $^3J_{CP}$=10.6 Hz, CH_3), 29.9 (s, CH_3), 54.0 (d, $^2J_{CP}$=13.9 Hz, CH_3), 59.2 (s, CH_2), 59.6 (s, CH_2), 80.6 (d, $^1J_{CP}$=135.8 Hz, C), 128.0 (d, $^2J_{CP}$=13.7 Hz, CH), 130.7 (d, $^3J_{CP}$=6.1 Hz, CH), 130.8 (d, $^3J_{CP}$=6.1 Hz, CH), 131.3 (d, $^4J_{CP}$=2.5 Hz, CH), 134.6 (d, $^1J_{CP}$=147.4 Hz, C), 135.6 (d, $^1J_{CP}$=149.5 Hz, C), 167.5 (d, $^2J_{CP}$=12.2 Hz, C), 169.7 (d, $^2J_{CP}$=12.2 Hz, C), 172.6 (s, C), 174.1 (d, $^2J_{CP}$=6.1 Hz, C); MS *m/z* 371 (1) [M^+], 283 (100). Anal. Calcd for $C_{15}H_{22}N_3O_6P$: C, 48.52; H, 5.97; N, 11.32. Found: C, 48.57; H, 6.01; N, 11.44.

*4.8.2. Methyl 3-[2-(aminocarbonyl)hydrazono]-2-[ethoxy-(phenyl)phosphoryl]-2-methoxybutanoate (**10b**)*

White powder; mp 117–119 °C; IR (Nujol) ν_{max} 3360, 3090, 1698, 1622 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20–1.40 (m, 3H, OCH_2CH_3), 2.46 and 2.58 (2s, 3H, CH_3), 3.42 and 3.44 (2s, 3H, CO_2CH_3), 3.64 and 3.88 (2s, 3H, OCH_3), 4.06–4.16 (m, 2H, OCH_2CH_3), 5.17 and 5.58 (2br s, 2H, NH_2), 7.38–7.44 (m, 3H, CH_{arom}), 7.78–7.82 (m, 2H, CH_{arom}), 9.75 and 10.15 (2s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.2 (d, $^3J_{CP}$=6.0 Hz, CH_3), 25.5 (d, $^3J_{CP}$=10.6 Hz, CH_3), 29.8 (s, CH_3), 49.6 (s, CH_3), 64.8 (d, $^2J_{CP}$=7.1 Hz, CH_2), 80.8 (d, $^1J_{CP}$=137.4 Hz, C), 128.1 (d, $^2J_{CP}$=13.6 Hz, CH), 130.8 (d, $^3J_{CP}$=6.1 Hz, CH), 131.1 (s, CH), 134.8 (d, $^1J_{CP}$=147.4 Hz, C), 167.8 (d, $^2J_{CP}$=12.0 Hz, C), 172.8 (s, C), 174.0 (d, $^2J_{CP}$=6.1 Hz, C); MS *m/z* 371 (2) [M^+], 339 (15), 283 (100). Anal. Calcd for $C_{15}H_{22}N_3O_6P$: C, 48.52; H, 5.97; N, 11.32. Found: C, 48.52; H, 5.97; N, 11.12.

4.9. General procedure for the synthesis of 5-phosphinate-substituted thiazol-4-ones 12a–c

A solution of 4-[alkoxy(phenyl)phosphoryl]-1,2-diaza-1,3-butadienes **9a**,**c**,**d** (1 mmol) and thiourea **11** (1 mmol) in methanol (10 mL) was magnetically stirred at room temperature for 1.0–2.0 h, until the disappearance of the reagents (monitored by TLC). The compounds **12a–c** were directly crystallized from the reaction medium and collected as pure products by filtration.

*4.9.1. Methyl (5-{1-[2-(aminocarbonyl)hydrazono]ethyl}-2-imino-4-oxo-1,3-thiazolan-5-yl)phenylphosphinate (**12a**)*

White powder; mp 172–175 °C; IR (Nujol) ν_{max} 3315, 3280, 3110, 1715 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.72 (s, 3H, CH_3), 3.58 (d, 3H, $^3J_{HP}$=10.8 Hz, OCH_3), 6.26 (br s, 2H, NH_2), 7.43–7.79 (m, 5H, CH_{arom}), 9.07 (s, 1H, NH), 9.30 (s, 1H, NH), 9.58 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.2 (s, CH_3), 52.4 (s, CH_3), 75.9 (d, $^1J_{CP}$=93.3 Hz, C), 127.8 (d, $^2J_{CP}$=12.2 Hz, CH), 129.8 (d, $^1J_{CP}$=139.8 Hz, C), 132.5 (s, CH), 133.4 (d, $^3J_{CP}$=9.1 Hz, CH), 141.3 (s, C), 157.0 (d, $^2J_{CP}$=22.0 Hz, C), 179.7 (s, C), 182.0 (s, C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 34.88; MS *m/z* 369 (1) [M^+], 294 (7), 266 (14), 212 (43), 185 (23), 171 (42), 155 (100). Anal. Calcd for $C_{13}H_{16}N_5O_4PS$: C, 42.28; H, 4.37; N, 18.96. Found: C, 42.49; H, 4.22; N, 19.02.

*4.9.2. Methyl (5-{1-[2-(aminocarbonyl)hydrazono]propyl}-2-imino-4-oxo-1,3-thiazolan-5-yl)phenylphosphinate (**12b**)*

White powder; mp 142–145 °C with decomposition; IR (Nujol) ν_{max} 3325, 3280, 3105, 1720 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 0.87 (t, 3H, J=7.2 Hz, CH_2CH_3), 2.44 (t, 2H, J=7.2 Hz, CH_2CH_3), 3.61 (d, 3H, $^3J_{CP}$=10.8 Hz, OCH_3), 6.19 (br s, 2H, NH_2), 7.45–7.81 (m, 5H, CH_{arom}), 9.05 (s, 1H, NH), 9.27 (s, 1H, NH), 9.67 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 9.8 (s, CH_3), 20.4 (s, CH_2), 52.5 (s, CH_3), 76.0 (d, $^1J_{CP}$=93.8 Hz, C), 127.8 (d, $^2J_{CP}$=12.9 Hz, CH), 129.3 (d, $^1J_{CP}$=136.5 Hz, C), 132.5 (s, CH), 133.4 (d, $^3J_{CP}$=9.1 Hz, CH), 144.9 (s, C), 156.9 (d, $^2J_{CP}$=22.0 Hz, C), 179.7 (s, C), 182.0 (s, C); MS m/z 383 (1) [M^+], 368 (20), 340 (8), 266 (59), 172 (100). Anal. Calcd for $C_{14}H_{18}N_5O_4PS$: C, 43.86; H, 4.73; N, 18.27. Found: C, 43.93; H, 4.84; N, 18.16.

*4.9.3. Ethyl (5-{1-[2-(aminocarbonyl)hydrazono]ethyl}-2-imino-4-oxo-1,3-thiazolan-5-yl)phenylphosphinate (**12c**)*

White powder; mp 176–179 °C; IR (Nujol) ν_{max} 3330, 3275, 3108, 1710 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.14–1.27 (m, 3H, OCH_2CH_3), 1.74 (s, 3H, CH_3), 3.92–4.02 (m, 2H, OCH_2CH_3), 6.41 (br s, 2H, NH_2), 7.47–7.81 (m, 5H, CH_{arom}), 9.07 (s, 1H, NH), 9.30 (s, 1H, NH), 9.60 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.1 (s, CH_3), 16.2 (s, CH_3), 61.7 (d, $^2J_{CP}$=6.0 Hz, CH_2), 76.0 (d, $^1J_{CP}$=93.3 Hz, C), 127.8 (d, $^2J_{CP}$=12.9 Hz, CH), 129.9 (d, $^1J_{CP}$=142.2 Hz, C), 132.4 (s, CH), 133.4 (d, $^3J_{CP}$=9.1 Hz, CH), 141.3 (s, C), 156.9 (d, $^2J_{CP}$=22.0 Hz, C), 179.9 (s, C), 182.3 (s, C); MS m/z 383 (1) [M^+], 368 (21), 340 (18), 283 (31), 214 (100). Anal. Calcd for $C_{14}H_{18}N_5O_4PS$: C, 43.86; H, 4.73; N, 18.27. Found: C, 43.78; H, 4.59; N, 18.31.

Acknowledgements

This work was supported by the financial assistance from the Ministero dell'Università, dell'Istruzione e della Ricerca (MIUR)-PRIN and the Università degli Studi di Urbino 'Carlo Bo'.

References and notes

1. (a) Attanasi, O. A.; Caglioti, L. *Org. Prep. Proced. Int.* **1986**, *18*, 299; (b) Attanasi, O. A.; Filippone, P. *Synlett* **1997**, 1128; (c) Attanasi, O. A.; De Crescentini, L.; Filippone, P.; Mantellini, F.; Santeusanio, S. *ARKIVOC* **2002**, *xi*, 274.
2. (a) Banert, K. *Targets in Heterocyclic Systems: Chemistry and Properties*; Attanasi, O. A., Spinelli, D., Eds.; Società Chimica Italiana: Rome, 2000; Vol. 3, p 1; (b) Polanc, S. *Targets in Heterocyclic Systems: Chemistry and Properties*; Attanasi, O. A., Spinelli, D., Eds.; Società Chimica Italiana: Rome, 2000; Vol. 3, p 33; (c) Boeckman, R. K., Jr.; Reed, J. E.; Ge, P. *Org. Lett.* **2001**, *3*, 3651; (d) van Bergen, M.; Gais, H.-J. *J. Am. Chem. Soc.* **2002**, *124*, 4321; (e) Kim, M.; Gais, H.-J. *J. Org. Chem.* **2006**, *71*, 4642.
3. (a) Attanasi, O. A.; De Crescentini, L.; Filippone, P.; Mantellini, F.; Tietze, L. F. *Tetrahedron* **2001**, *57*, 5855; (b) Attanasi, O. A.; De Crescentini, L.; Filippone, P.; Mantellini, F.; Santeusanio, S. *Synlett* **2003**, 1183; (c) Attanasi, O. A.; De Crescentini, L.; Favi, G.; Filippone, P.; Lillini, S.; Mantellini, F.; Santeusanio, S. *Org. Lett.* **2005**, *7*, 2469.
4. (a) Attanasi, O. A.; De Crescentini, L.; Favi, G.; Filippone, P.; Mantellini, F.; Santeusanio, S. *J. Org. Chem.* **2004**, *69*, 2686; (b) Attanasi, O. A.; Favi, G.; Filippone, P.; Lillini, S.; Mantellini, F.; Spinelli, D.; Stenta, M. *Adv. Synth. Catal.* **2007**, *349*, 907; (c) Schmidt, A.; Karapetyan, V.; Attanasi, O. A.; Favi, G.; Görls, H.; Mantellini, F.; Langer, P. *Synlett* **2007**, 2965.
5. Attanasi, O. A.; Berretta, S.; De Crescentini, L.; Favi, G.; Filippone, P.; Giorgi, G.; Lillini, S.; Mantellini, F. *Tetrahedron Lett.* **2007**, *48*, 2449.
6. Attanasi, O. A.; Favi, G.; Filippone, P.; Giorgi, G.; Lillini, S.; Mantellini, F.; Perrulli, F. R. *Synlett* **2006**, 2731.
7. Attanasi, O. A.; De Crescentini, L.; Favi, G.; Filippone, P.; Giorgi, G.; Mantellini, F.; Santeusanio, S. *J. Org. Chem.* **2003**, *68*, 1947.
8. Attanasi, O. A.; De Crescentini, L.; Favi, G.; Filippone, P.; Golobič, A.; Lillini, S.; Mantellini, F. *Synlett* **2006**, 2735.
9. (a) Attanasi, O. A.; De Crescentini, L.; Favi, G.; Filippone, P.; Mantellini, F.; Santeusanio, S. *Synlett* **2004**, 549; (b) Attanasi, O. A.; Davoli, P.; Favi, G.; Filippone, P.; Forni, A.; Moscatelli, G.; Prati, F. *Org. Lett.* **2007**, *9*, 3461.
10. Aparicio, D.; Attanasi, O. A.; Filippone, P.; Ignacio, R.; Lillini, S.; Mantellini, F.; Palacios, F.; de los Santos, J. M. *J. Org. Chem.* **2006**, *71*, 5897.
11. Attanasi, O. A.; Favi, G.; Filippone, P.; Golobič, A.; Perrulli, F. R.; Stanovnik, B.; Svete, J. *Synlett* **2007**, 2971.
12. Enders, D.; Saint-Dizier, A.; Lannou, M.-I.; Lenzen, A. *Eur. J. Org. Chem.* **2006**, 29.
13. (a) Seto, H.; Kuzuyama, T. *Nat. Prod. Rep.* **1999**, *16*, 589; (b) Fields, S. C. *Tetrahedron* **1999**, *55*, 12237.
14. (a) Attanasi, O. A.; Filippone, P.; Mei, A. *Tetrahedron* **1992**, *48*, 1707; (b) Attanasi, O. A.; Filippone, P.; Giovagnoli, D. *Org. Prep. Proced. Int.* **1994**, *26*, 321.
15. Attanasi, O. A.; Baccolini, G.; Boga, C.; De Crescentini, L.; Filippone, P.; Mantellini, F. *J. Org. Chem.* **2005**, *70*, 4033.
16. Schmidpeter, A. *Comprehensive Heterocyclic Chemistry-II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, UK, 1996; Vol. 4, p 771 and references cited therein.
17. Baccolini, G.; Orsolan, G.; Mezzina, E. *Tetrahedron Lett.* **1995**, *36*, 447.
18. (a) Albrigt, T.; Freeman, W.; Schweizer, E. *J. Am. Chem. Soc.* **1975**, *97*, 940; (b) Simons, W. *The Sadtler Guide to Carbon-13 NMR Spectra*; Sadtler Research Laboratories: Philadelphia, PA, 1983.
19. Ballini, R.; Petrini, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2563.
20. (a) Horner, L.; Hoffmann, H.; Wippel, H. G.; Klahre, G. *Chem. Ber.* **1959**, *92*, 2499; (b) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733; (c) Wadsworth, W. S., Jr. *Org. React. (N.Y.)* **1977**, *25*, 73.
21. Maryanoff, B.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.
22. (a) Aboujaoude, E. E.; Colligan, N.; Savignac, P. *J. Organomet. Chem.* **1984**, *264*, 9; (b) Mikolajczyk, M.; Balezewski, P. *Synthesis* **1984**, 691.
23. Baccolini, G.; Todesco, P. E.; Dalpozzo, R.; De Nino, A. *Gazz. Chim. Ital.* **1996**, *126*, 271.
24. (a) Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 671; (b) Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 873.
25. Attanasi, O. A.; Berretta, S.; Favi, G.; Filippone, P.; Mele, G.; Moscatelli, G.; Saladino, R. *Org. Lett.* **2006**, *8*, 4293.
26. Attanasi, O. A.; De Crescentini, L.; Filippone, P.; Foresti, E.; Galeazzi, R.; Ghiviriga, I.; Katritzky, A. R. *Tetrahedron* **1997**, *53*, 5617.
27. Attanasi, O. A.; De Crescentini, L.; Foresti, E.; Galarini, R.; Santeusanio, S.; Serra-Zanetti, F. *Synthesis* **1995**, 1397.