Benzoylhydrazones in catalytic hydrophosphorylation

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Reactions of benzoylhydrazones derived from heterocyclic and aromatic aldehydes and aliphatic, heterocyclic, and aliphatic-aromatic ketones with diethyl phosphite in the presence of [tetra(*tert*-butyl)phthalocyanine]aluminum chloride afford α-benzoylhydrazino phosphonates in high yields.

Key words: catalysis, hydrazones, benzohydrazide, α-hydrazino phosphonates, the Pudovik reaction, [tetra(*tert*-butyl)phthalocyanine]aluminum chloride.

α-Hydrazino phosphonic acids are structural analogs of α-amino phosphonic acids. The biological activity of α-hydrazino phosphonic acids[1] and the existence of natural phosphonates[2—4] stimulate scientists to search for new methods of synthesis of this class of compounds.

α-Hydrazino phosphonates are mainly obtained by hydrophosphorylation of compounds containing the C=N bond (the Pudovik reaction[5]). To the best of our knowledge, there are few examples of addition of dialkyl phosphites to hydrazones.[6—9] Thus formaldehyde benzyloxycarbonylhydrazone[6] and *o*-nitrobenzaldehyde phenylhydrazone[7] were hydrophosphorylated under conditions of basic catalysis. Acid-catalyzed hydrophosphorylation of hydrazones of unsaturated aldehydes was also described.[8] Recently, the synthesis of α-hydrazino phosphonates from acetone and cyclopentanone benzoylhydrazones in the presence of $BF_3 \cdot Et_2O$ has been documented; however, the yields of the target products are low (13—44%).[9]

Alternative routes (such as the $LiClO_4$-catalyzed Kabachnik—Fields reaction,[10,11] nucleophilic substitution of modified α-hydroxy phosphonates with hydrazine,[12] and reduction of α-hydrazono phosphonates[13]) afford α-hydrazino phosphonates only from aldehydes.

Thus, according to the literature data, the search for a general method of synthesis of phosphonates from hydrazones of aliphatic and especially aromatic ketones still remains of current interest.

Recently, we have developed a catalytic method of synthesis of α-amino phosphonates in the presence of [tetra(*tert*-butyl)phthalocyanine]aluminum chloride (^{t}PcAlCl), affording the target compounds not only from amines but also from amino acids and not only from aldehydes but also from various ketones.[14—16] In the present work, we used ^{t}PcAlCl for the synthesis of α-hydrazino phosphonates from benzoylhydrazones.

Benzoylhydrazones were obtained in 85—97% yields according to a standard procedure by reactions of benzohydrazide or substituted benzohydrazides with carbonyl compounds in ethanol or without solvent.

Three-component reactions of any carbonyl compounds with benzohydrazide and diethyl phosphite in CH_2Cl_2, toluene, or xylene in the presence of ^{t}PcAlCl resulted in very rapid precipitation of the corresponding hydrazones, which did not undergo hydrophosphorylation under heterogeneous conditions. That is why the preformed benzoylhydrazones were used in subsequent experiments and their ^{t}PcAlCl-catalyzed hydrophosphorylation (a version of the Pudovik reaction) was carried out in the excess of diethyl phosphite as a solvent (Scheme 1).

This catalytic two-component process was used to obtain α-benzoylhydrazino phosphonates from benzoylhydrazones of the following aliphatic, carbocyclic, and heterocyclic ketones: acetone (**1a**), cyclohexanone (**1e**), cyclopentanone (**1i**), *N*-Boc-piperidone (**1m**), and cyclopropyl methyl ketone (**1n**) (see Scheme 1). The yields of the corresponding α-benzoylhydrazino phosphonates **2e**, **2i**, **2m**, and **2n** were 50—85%.

The presence of an electron-donating or -withdrawing substituent in the *para*-position of the phenyl ring of acetone and cyclohexanone benzoylhydrazones virtually does not affect the reactivities of hydrazones **1b—d** and **1f—h**. Thus, the corresponding α-benzoylhydrazino phosphonates **2b—d** and **2f—h** were obtained in 75—85% yields (reaction times 4—6 h).

However, variation of substituents in the phenyl ring of cyclopentanone benzoylhydrazone, which is less reactive than acetone and cyclohexanone benzoylhydrazones, revealed that the corresponding hydrazones (**1f—e**) significantly differ in their reactivity. Thus, electron-donating substituents inhibit, while electron-withdrawing ones promote, the hydrophosphorylation reaction.

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Scheme 1

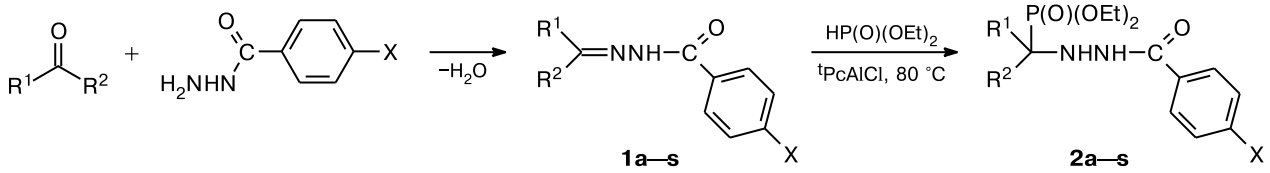
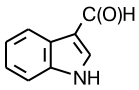
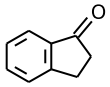
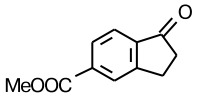


Table 1. Synthesis of benzoylhydrazones **1a**—**s** and the corresponding 2-benzoylhydrazino phosphonates **2a**—**s**

$R^1C(O)R^2$	X	**1**	Yield of **1** (%)	Ratio of **1** : $HP(O)(OEt)_2$	*t*/h*	Product **2**	Yield of **2** (%)
MeC(O)Me	H	**a**	90	1 : 3	2	**a**	75
MeC(O)Me	NO_2	**b**	90	1 : 5	4	**b**	75
MeC(O)Me	Br	**c**	95	1 : 5	6	**c**	80
MeC(O)Me	OMe	**d**	85	1 : 5	6	**d**	85
$(CH_2)_5CO$	H	**e**	90	1 : 3	0.5	**e**	80
$(CH_2)_5CO$	NO_2	**f**	95	1 : 5	4	**f**	80
$(CH_2)_5CO$	Br	**g**	90	1 : 5	6	**g**	85
$(CH_2)_5CO$	OMe	**h**	90	1 : 5	4	**h**	85
$(CH_2)_4CO$	H	**i**	95	1 : 3	24	**i**	50
$(CH_2)_4CO$	NO_2	**j**	97	1 : 5	8	**j**	90
$(CH_2)_4CO$	Br	**k**	95	1 : 5	24	**k**	70
$(CH_2)_4CO$	OMe	**l**	95	1 : 5	32	**l**	65
$(CH_2)_2NBoc(CH_2)_2CO$	H	**m**	95	1 : 5	8	**m**	65
$(CH_2)_3C(O)Me$	H	**n**	85	1 : 3	32	**n**	50
PhC(O)H	H	**o**	92	1 : 3	24	**o**	75
	H	**p**	90	1 : 5	20	**p**	65
PhC(O)Me	H	**q**	85	1 : 5	40	**q**	75
	H	**r**	95	1 : 5	40	**r**	50
	H	**s**	95	1 : 7	50	**s**	55

* The reaction time.

To extend the scope of this method, we carried out reactions of diethyl phosphite with benzoylhydrazones of aromatic and heterocyclic aldehydes (**1o** and **1p**) and benzoylhydrazones of aliphatic-aromatic ketones (acetophenone (**1q**), indan-1-one (**1r**), and methyl 1-oxoindane-5-carboxylate (**1s**)). The yields of the corresponding α-benzoylhydrazino phosphonates **2o**—**s** were 55—75%.

By an example of acetone benzoylhydrazone (**1a**), it was shown that noncatalytic hydrophosphorylation for 2 h also leads to α-benzoylhydrazino phosphonate **2a** in 55% yield. Under the same conditions in the presence of ^{t}PcAlCl, the yield of this product increased to 75%. Noncatalytic hydrophosphorylation of cyclopentanone (**1i**) and indanone hydrazones (**1r**) affords hydrazino phosphonates **2i** and **2r** in 20% yields over 24 and 40 h, respectively. When the reaction time was doubled (48 and 80 h, respectively), the yields of these products increased only to 40 and 30%. This process was accompanied by considerable degradation of the starting diethyl phosphite and the reaction products, which is evident from numerous signals in the ^{31}P NMR spectrum. At the same time, ^{t}PcAlCl-catalyzed hydrophosphorylation of these hydrazones gives α-hydrazino phosphonates **2i** and **2r** in 50% yields over 24 and 40 h, respectively.

The synthesis of phosphonates **2m** and **2s** is of principal importance since, on the one hand, the compounds obtained are bioisosters of the ligands to GABA[17] and glutamate receptors[18] and, on the other hand, it has been shown for the first time that α-hydrazino phosphonates can be synthesized from heterocyclic and aromatic ketones.

The structures of α-hydrazino phosphonates **2p—s** were determined from their ^{1}H, ^{13}C, and ^{31}P NMR (see Ref. 15), IR, and mass spectra; their compositions were confirmed by elemental analysis data. The signals in the ^{31}P NMR spectra of α-hydrazino phosphonates **2a—n** obtained from aliphatic ketones appear at δ 26—30; analogous signals for aromatic derivatives **2o—s** appear at δ 21—25.

Experimental

NMR spectra were recorded on a Bruker Avance 400 instrument (400.13 (^{1}H), 100.61 (^{13}C), and 161.98 MHz (^{31}P)) in $CDCl_3$, CD_3CN, CD_3OD, and DMSO-d_6 with $SiMe_4$ as the internal standard (^{1}H and ^{13}C) and with 85% H_3PO_4 as the external standard (^{31}P). IR spectra were recorded on a UR-20 instrument in CCl_4. Elemental analysis was carried out on a Vario-II CHN-analyzer. Mass spectra were measured on a Finnigan Mat Incos 50 quadrupole mass spectrometer (EI, 70 eV, direct inlet probe).

Diethyl phosphite (Aldrich) was used as purchased. [Tetra-(*tert*-butyl)phthalocyanine]aluminum chloride was prepared according to a known procedure.[19] The course of the reaction was monitored, and the purity of the products was checked, by TLC on ALUGRAM SIL G/UV$_{254}$ plates. The products were separated by column chromatography on Merck 60 silica gel (70—230 mesh ASTM).

Synthesis of benzoylhydrazones 1a—l,n,o,q (general procedure). A mixture of a carbonyl compound (9 mmol) and benzohydrazide (3 mmol) was refluxed for 1—3 h. The mixture was cooled to room temperature and the crystals that formed were filtered off, washed with ether, and dried *in vacuo*.

***N*-(1-Methylethylidene)benzohydrazide (1a)**, m.p. 142—143 °C (*cf.* Ref. 20: m.p. 142—143 °C).

***N*-(1-Methylethylidene)-4-nitrobenzohydrazide (1b).** Yield 90%, m.p. 158—159 °C (*cf.* Ref. 20: m.p. 158—159 °C).

***N*-(1-Methylethylidene)-4-bromobenzohydrazide (1c)**, m.p. 195—197 °C (*cf.* Ref. 21: m.p. 97—198 °C).

***N*-(1-Methylethylidene)-4-methoxybenzohydrazide (1d)**, m.p. 127—129 °C (*cf.* Ref. 20: m.p. 128—129 °C).

***N*-Cyclohexylidenebenzohydrazide (1e)**, m.p. 163—165 °C (*cf.* Ref. 22: m.p. 164—165 °C).

***N*-Cyclohexylidene-4-nitrobenzohydrazide (1f).** Yield 95%, m.p. 149—150 °C (*cf.* Ref. 23: m.p. 150 °C).

***N*-Cyclopentylidenebenzohydrazide (1i).** Yield 95%, m.p. 150—152 °C (*cf.* Ref. 22: m.p. 149—151 °C).

***N*-Cyclopentylidene-4-nitrobenzohydrazide (1j)**, m.p. 150—152 °C (*cf.* Ref. 9: m.p. 150—152 °C).

***N*-(1-Cyclopropylethylidene)benzohydrazide (1n)**, m.p. 122—123 °C (*cf.* Ref. 24: m.p. 121—124 °C).

***N*-Benzylidenebenzohydrazide (1o)**, m.p. 209—210 °C (*cf.* Ref. 25: m.p. 209—210 °C).

***N*-(1-Phenylethylidene)benzohydrazide (1q)**, m.p. 155—157 °C (*cf.* Ref. 26: m.p. 155—157 °C).

***N*-Cyclohexylidene-4-bromobenzohydrazide (1g)**, m.p. 180—182 °C. ^{1}H NMR (CD_3CN), δ: 1.65—1.66 (m, 4 H, ring); 1.70—1.76 (m, 2 H, ring); 2.32—2.40 (m, 4 H, ring); 7.64 (d, 2 H, arom., $^3J_{H,H}$ = 8.4 Hz); 7.72 (d, 2 H, arom., $^3J_{H,H}$ = 8.4 Hz); 9.28 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 25.52, 25.96, 26.91, 27.31, 35.53 (C_{ring}); 126.26, 128.91, 131.80, 132.69 (C_{arom}); 163.42 (s, C=O); 164.05 (s, C=N). IR (CCl_4), ν/cm^{-1}: 1650 (C=N); 1670 (C=O); 3230 (N—H). Found (%): C, 53.10; H, 5.25; N, 9.44. $C_{13}H_{15}BrN_2O$. Calculated (%): C, 52.90; H, 5.12; N, 9.49.

***N*-Cyclohexylidene-4-methoxybenzohydrazide (1h)**, m.p. 149—150 °C. ^{1}H NMR (CD_3CN), δ: 1.62—1.75 (m, 6 H, ring); 2.33—2.36 (m, 2 H, ring); 2.38—2.41 (m, 2 H, ring); 3.84 (s, 3 H, Me); 6.98 (d, 2 H, arom., $^3J_{H,H}$ = 8.7 Hz); 7.80 (d, 2 H, arom., $^3J_{H,H}$ = 9.0 Hz); 9.19 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 25.54, 25.92, 26.88, 27.06, 35.52 (C_{ring}); 55.57 (s, OMe); 113.70, 125.97, 129.09, 162.22 (C_{arom}); 162.52 (s, C=O); 163.83 (s, C=N). IR (CCl_4), ν/cm^{-1}: 1650 (C=N); 1660 (C=O); 3250 (N—H). Found (%): C, 68.26; H, 7.41; N, 11.15. $C_{14}H_{18}N_2O_2$. Calculated (%): C, 68.27; H, 7.37; N, 11.37.

***N*-Cyclopentylidene-4-bromobenzohydrazide (1k)**, m.p. 205—206 °C. ^{1}H NMR (CD_3CN), δ: 1.74—1.81 (m, 2 H, ring); 1.83—1.90 (m, 2 H, ring); 2.36—2.39 (m, 2 H, ring); 2.40—2.47 (br.m, 2 H, ring); 7.64 (d, 2 H, arom., $^3J_{H,H}$ = 8.4 Hz); 7.72 (d, 2 H, arom., $^3J_{H,H}$ = 8.4 Hz); 8.94 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 24.66, 24.85, 27.57, 33.60 (C_{ring}); 126.45, 128.87, 131.91, 132.47 (C_{arom}); 162.97 (s, C=O); 168.49 (s, C=N). IR (CCl_4), ν/cm^{-1}: 1635 (C=N); 1650 (C=O); 3210 (N—H). Found (%): C, 51.28; H, 4.62; N, 9.89. $C_{12}H_{13}BrN_2O$. Calculated (%): C, 51.26; H, 4.66; N, 9.96.

***N*-Cyclopentylidene-4-methoxybenzohydrazide (1l).** Yield 95%, m.p. 177—180 °C. ^{1}H NMR (CD_3CN), δ: 1.73—1.80 (m, 2 H, ring); 1.83—1.90 (m, 2 H, ring); 2.36—2.40 (m, 2 H, ring); 2.41—2.45 (m, 2 H, ring); 3.84 (s, 3 H, Me); 6.98 (d, 2 H, arom., $^3J_{H,H}$ = 9.0 Hz); 7.79 (d, 2 H, arom., $^3J_{H,H}$ = 8.7 Hz); 8.83 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 24.65, 24.82, 27.36, 33.53 (C_{ring}); 55.40 (s, OMe); 113.79, 125.69, 129.07, 162.35 (C_{arom}); 163.48 (s, C=O); 167.17 (s, C=N). IR (CCl_4), ν/cm^{-1}: 1650 (C=N); 1670 (C=O); 3270 (N—H). Found (%): C, 67.30; H, 7.02; N, 11.99. $C_{13}H_{16}N_2O_2$. Calculated (%): C, 67.22; H, 6.94; N, 12.06.

***tert*-Butyl 4-(benzoylhydrazono)piperidine-1-carboxylate (1m).** A melt of *N*-Boc-piperidone (2 mmol) and benzohydrazide (2 mmol) was heated at 80 °C for 40 min. The mixture was cooled to room temperature and the crystals that formed were washed with diethyl ether and dried *in vacuo*. The yield was 95%, m.p. 155—156 °C. ^{1}H NMR ($CDCl_3$), δ: 1.44 (s, 9 H, Bu^t); 2.46—2.49 (m, 4 H, ring); 3.51—3.54 (m, 4 H, ring); 7.35 (m, 1 H, arom.); 7.43—7.47 (m, 2 H, arom.); 7.74 (d, 2 H, arom., $^3J_{H,H}$ = 7.1 Hz); 9.34 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 27.53 (s, C_{ring}); 28.36 (s, Me, Bu^t); 33.97 (s, C_{ring}); 41.09 (s, C_{ring}); 43.78 (s, C_{ring}); 80.18 (s, C, Bu^t); 127.36, 128.35, 131.82, 133.39 (C_{arom}); 154.55 (s, C=O, C(O)OBu^t); 158.93 (s, C=O, C(O)Ph); 164.54 (s, C=N). IR (CCl_4), ν/cm^{-1}: 1650 (C=N); 1670 (C=O); 1690 (C(O)(OBu^t)); 3200 (N—H). Found (%): C, 64.67; H, 7.33; N, 13.12. $C_{17}H_{23}N_2O_3$. Calculated (%): C, 64.33; H, 7.30; N, 13.24.

***N*-(1*H*-Indol-3-ylmethylidene)benzohydrazide (1p).** Indole-3-carbaldehyde (3 mmol) and benzohydrazide (3 mmol) were refluxed in anhydrous ethanol (2 mL) for 2 h. The mixture was cooled to room temperature and the crystals that formed were filtered off, washed with diethyl ether, and dried *in vacuo*. The yield was 90%, m.p. 231—232 °C (*cf.* Ref. 27: m.p. 231—232 °C).

***N*-(2,3-Dihydro-1*H*-inden-1-ylidene)benzohydrazide (1r).** Indan-1-one (2 mmol) and benzohydrazide (2 mmol) were heated at 100 °C for 1 h. The mixture was cooled to room temperature and the crystals that formed were washed with diethyl ether

and dried *in vacuo*. The yield was 95%, m.p. 159—161 °C (*cf.* Ref. 28: m.p. 155 °C).

Methyl 1-(2-benzoylhydrazono)-2,3-dihydro-1*H*-indene-5-carboxylate (1s). Methyl 1-oxoindane-5-carboxylate (2 mmol) and benzohydrazide (2 mmol) were heated at 120 °C for 2 h. The mixture was cooled to room temperature and the crystals that formed were washed with diethyl ether and dried *in vacuo*. The yield was 95%, m.p. 265—266 °C. ^{1}H NMR (DMSO-d_6), δ: 2.98—3.07 (br.m, 2 H, C(2)H_2, ring); 3.09—3.20 (br.m, 2 H, C(3)H_2, ring); 3.87 (s, 3 H, Me); 7.50—7.54 (m, 2 H, arom.); 7.57—7.61 (m, 1 H, arom.); 7.73—7.82 (m, 2 H, arom.); 7.87 (d, 2 H, arom., $^3J_{H,H}$ = 7.4 Hz); 7.91 (d, 1 H, arom., $^3J_{H,H}$ = = 7.7 Hz); 7.97 (s, 1 H, arom.); 10.72 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 28.12 (s, C(3)H_2, ring); 28.49 (s, C(2)H_2, ring); 52.73 (s, OMe); 121.52, 126.50, 127.94, 128.07, 128.19, 131.22, 131.42; 133.93, 142.41, 148.94 (C_{arom}); 162.14 (s, C=O, C(O)Ph); 164.38 (s, C=O, COOMe); 166.50 (s, C=N). IR (CCl_4), ν/cm^{-1}: 1630 (C=N); 1670 (C=O, C(O)Ph), 1720 (C=O, COOMe); 3220 (N—H). Found (%): C, 70.10; H, 5.24; N, 9.15. $C_{18}H_{16}N_2O_3$. Calculated (%): C, 70.12; H, 5.23; N, 9.09.

Synthesis of α-hydrazino phosphonates 2a—s (general procedure). Diethyl phosphite (3—7 mmol) and ^{t}PcAlCl (0.05 mmol) were added to an appropriate hydrazone (1 mmol). The reaction mixture was stirred under argon at 80 °C until the reaction was completed (monitoring by TLC). Then the reaction mixture was dissolved in a minimum amount of CH_2Cl_2—MeOH (70 : 1) and chromatographed on silica gel (column height 15 cm, column diameter 1.5—2.0 cm). The ratios of the reagents, the reaction times, and the yields of the compounds obtained are given in Table 1.

Diethyl [1-(2-benzoylhydrazino)-1-methylethyl]phosphonate (2a), m.p. 79—80 °C. ^{1}H NMR ($CDCl_3$), δ: 1.30 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.0 Hz); 1.33 (d, 6 H, 2 Me, $^3J_{H,P}$ = 15.7 Hz); 4.12—4.19 (m, 4 H, 2 OCH_2); 4.97 (br.s, 1 H, NH); 7.35—7.38 (m, 2 H, arom., $^3J_{H,H}$ = 7.1 Hz); 7.44 (t, 1 H, arom., $^3J_{H,H}$ = = 7.3 Hz); 7.77 (d, 2 H, arom., $^3J_{H,H}$ = 7.1 Hz); 8.73 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.73. ^{13}C NMR ($CDCl_3$), δ: 16.50 (d, Me, POEt, $^3J_{C,P}$ = 5.1 Hz); 21.13 (s, Me); 56.90 (d, C, $^1J_{C,P}$ = 161.0 Hz); 62.85 (d, OCH_2, $^2J_{C,P}$ = 7.3 Hz); 126.83, 128.56, 131.58, 132.58 (C_{arom}); 165.63 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1040, 1070 (P—O—C); 1260 (P=O); 1630 (C=O); 3280 (N—H). Found (%): C, 53.38; H, 7.25; N, 8.99. $C_{14}H_{23}N_2O_4P$. Calculated (%): C, 53.50; H, 7.38; N, 8.91.

Diethyl {1-methyl-1-[2-(4-nitrobenzoyl)hydrazino]ethyl}phosphonate (2b), m.p. 122—123 °C. ^{1}H NMR ($CDCl_3$), δ: 1.28 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.0 Hz); 1.31 (d, 6 H, 2 Me, $^3J_{H,P}$ = 15.1 Hz); 4.10—4.17 (m, 4 H, 2 OCH_2); 5.00 (br.s, 1 H, NH); 7.93, 8.19 (both d, 2 H each, arom., $^3J_{H,H}$ = 8.6 Hz); 9.17 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.39. ^{13}C NMR ($CDCl_3$), δ: 16.46 (d, Me, POEt, $^3J_{C,P}$ = 5.9 Hz); 21.19 (s, Me); 56.82 (d, C, $^1J_{C,P}$ = 159.5 Hz); 62.99 (d, OCH_2, $^2J_{C,P}$ = 7.3 Hz); 123.72, 128.10, 138.21, 149.56 (C_{arom}); 163.26 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1035, 1065 (P—O—C); 1260 (P=O); 1360, 1540 (N=O); 1630 (C=O); 3280 (N—H). Found (%): C, 46.80; H, 6.16; N, 11.74 $C_{14}H_{22}N_3O_6P$. Calculated (%): C, 46.80; H, 6.17; N, 11.69.

Diethyl {1-[2-(4-bromobenzoyl)hydrazino]-1-methylethyl}phosphonate (2c), m.p. 110—112 °C. ^{1}H NMR ($CDCl_3$), δ: 1.31 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 1.33 (d, 6 H, 2 Me, $^3J_{H,P}$ = 15.4 Hz); 4.12—4.20 (m, 4 H, 2 OCH_2); 4.98 (br.s, 1 H, NH); 7.51 (d, 2 H, arom., $^3J_{H,H}$ = 8.6 Hz); 7.65 (d, 2 H, arom., $^3J_{H,H}$ = 8.5 Hz); 8.83 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.63. ^{13}C NMR ($CDCl_3$), δ: 16.51 (d, Me, POEt, $^3J_{C,P}$ = 5.1 Hz); 21.18 (s, Me); 56.87 (d, C, $^1J_{C,P}$ = 161.0 Hz); 62.93 (d, OCH_2, $^2J_{C,P}$ = 7.4 Hz); 126.26, 128.48, 131.44, 131.81 (C_{arom}); 164.51 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1035, 1065 (P—O—C); 1260 (P=O); 1360, 1540 (N=O); 1630 (C=O); 3280 (N—H). Found (%): C, 42.99; H, 5.54; N, 7.21. $C_{14}H_{22}BrN_2O_4P$. Calculated (%): C, 42.76; H, 5.64; N, 7.12.

Diethyl {1-[2-(4-methoxybenzoyl)hydrazino]-1-methylethyl}phosphonate (2d), m.p. 63—64 °C. ^{1}H NMR ($CDCl_3$), δ: 1.29 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.0 Hz); 1.31 (d, 6 H, 2 Me, $^3J_{H,P}$ = 15.6 Hz); 3.76 (s, 3 H, OMe); 4.09—4.18 (m, 4 H, 2 OCH_2); 4.96 (br.d, 1 H, NH, $^3J_{H,P}$ = 24.3 Hz); 6.84, 7.70 (both d, 2 H each, arom., $^3J_{H,H}$ = 8.7 Hz); 8.46 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.94. ^{13}C NMR ($CDCl_3$), δ: 16.58 (d, Me, POEt, $^3J_{C,P}$ = 4.8 Hz); 21.24 (s, Me); 55.43 (s, OMe); 57.04 (d, C, $^1J_{C,P}$ = 161.5 Hz); 62.92 (d, OCH_2, $^2J_{C,P}$ = 8.0 Hz); 113.92, 125.04, 128.68, 162.39 (C_{arom}); 165.32 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1040, 1065 (P—O—C); 1260 (P=O); 1650 (C=O); 3280 (N—H). Found (%): C, 52.25; H, 7.37; N, 8.00. $C_{15}H_{25}N_2O_5P$. Calculated (%): C, 52.32; H, 7.32; N, 8.14.

Diethyl [1-(2-benzoylhydrazino)cyclohexyl]phosphonate (2e), m.p. 65—67 °C. ^{1}H NMR ($CDCl_3$), δ: 1.16—1.21 (m, 1 H, ring); 1.34 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 1.48—1.59 (m, 2 H, ring); 1.60—1.72 (m, 5 H, ring); 1.88—1.95 (m, 2 H, ring); 4.15—4.23 (m, 4 H, 2 OCH_2); 5.46 (br.s, 1 H, NH); 7.38—7.42 (m, 2 H, arom.); 7.44—7.48 (m, 1 H, arom.); 7.79 (d, 2 H, arom., $^3J_{H,H}$ = 8.1 Hz); 8.98 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.16. ^{13}C NMR ($CDCl_3$), δ: 16.53 (d, Me, POEt, $^3J_{C,P}$ = 5.8 Hz); 19.87 (d, $^3J_{C,P}$ = 11.0 Hz); 25.12, 27.50 (C_{ring}); 58.91 (d, C, $^1J_{C,P}$ = 163.2 Hz); 62.94 (d, OCH_2, $^2J_{C,P}$ = 7.3 Hz); 126.69, 128.58, 131.47, 132.63 (C_{arom}); 163.94 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1035, 1070 (P—O—C); 1230 (P=O); 1660 (C=O); 3280 (N—H). Found (%): C, 57.53; H, 7.83; N, 7.81. $C_{17}H_{27}N_2O_4P$. Calculated (%): C, 57.62; H, 7.68; N, 7.90.

Diethyl {1-[2-(4-nitrobenzoyl)hydrazino]cyclohexyl}phosphonate (2f), m.p. 112—113 °C. ^{1}H NMR ($CDCl_3$), δ: 1.11—1.24 (m, 1 H, CH_2, ring); 1.29 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.2 Hz); 1.43—1.71 (m, 7 H, ring); 1.81—1.90 (m, 2 H, ring); 4.11—4.18 (m, 4 H, 2 OCH_2); 5.32 (br.s, 1 H, NH); 7.90 (d, 2 H, arom., $^3J_{H,H}$ = 8.7 Hz); 8.18 (d, 2 H, arom., $^3J_{H,H}$ = 9.0 Hz); 9.30 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 27.93. ^{13}C NMR ($CDCl_3$), δ: 16.44 (d, Me, POEt, $^3J_{C,P}$ = 4.0 Hz); 19.79 (d, $^3J_{C,P}$ = = 10.4 Hz); 25.01, 27.55 (C_{ring}); 58.86 (d, C, $^1J_{C,P}$ = 162.3 Hz); 63.04 (d, OCH_2, $^2J_{C,P}$ = 7.2 Hz); 123.73, 127.87, 138.21, 149.54 (C_{arom}); 161.59 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1040, 1060 (P—O—C); 1240 (P=O); 1350, 1525 (N=O); 1650 (C=O); 3290 (N—H). Found (%): C, 51.19; H, 6.67; N, 10.35. $C_{17}H_{26}N_3O_6P$. Calculated (%): C, 51.12; H, 6.56; N, 10.52.

Diethyl {1-[2-(4-bromobenzoyl)hydrazino]cyclohexyl}phosphonate (2g), m.p. 84—85 °C. ^{1}H NMR ($CDCl_3$), δ: 1.08—1.21 (m, 1 H, CH_2, ring); 1.29 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 1.43—1.66 (m, 7 H, ring); 1.80—1.89 (m, 2 H, ring); 4.09—4.18 (m, 4 H, 2 OCH_2); 5.36 (br.s, 1 H, NH); 7.48 (d, 2 H, arom., $^3J_{H,H}$ = 8.7 Hz); 7.60 (d, 2 H, arom., $^3J_{H,H}$ = 8.7 Hz); 8.98 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.15. ^{13}C NMR ($CDCl_3$), δ: 16.56 (d, Me, POEt, $^3J_{C,P}$ = 4.9 Hz); 19.93 (d, $^3J_{C,P}$ = 10.5 Hz); 25.16, 27.61 (C_{ring}); 58.97 (d, C, $^1J_{C,P}$ = 162.2 Hz); 63.03 (d, OCH_2, $^2J_{C,P}$ = 7.2 Hz); 126.15, 128.36, 131.58, 131.85 (C_{arom}); 163.00 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1035, 1080 (P—O—C);

1230 (P=O); 1650 (C=O); 3290 (N—H). Found (%): C, 47.04; H, 6.22; N, 6.72. $C_{17}H_{26}BrN_2O_4P$. Calculated (%): C, 47.13; H, 6.05; N, 6.74.

Diethyl {1-[2-(4-methoxybenzoyl)hydrazino]cyclohexyl}-phosphonate (2h). ^{1}H NMR ($CDCl_3$), δ: 1.06—1.21 (m, 1 H, CH_2, ring); 1.28 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.0 Hz); 1.40—1.52 (m, 2 H, ring); 1.53—1.66 (m, 5 H, ring); 1.77—1.90 (m, 2 H, ring); 3.75 (s, 3 H, OMe); 4.09—4.18 (m, 4 H, 2 OCH_2); 5.36 (br.s, 1 H, NH); 6.84 (d, 2 H, arom., $^3J_{H,H}$ = 8.8 Hz); 7.69 (d, 2 H, arom., $^3J_{H,H}$ = 9.0 Hz); 8.76 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.31. ^{13}C NMR ($CDCl_3$), δ: 16.52 (d, Me, POEt, $^3J_{C,P}$ = 4.9 Hz); 19.93 (d, $^3J_{C,P}$ = 10.5 Hz); 25.16, 27.55 (C_{ring}); 55.35 (s, OMe); 58.97 (d, C, $^1J_{C,P}$ = 163.0 Hz); 62.88 (d, OCH_2, $^2J_{C,P}$ = 7.2 Hz); 113.81, 125.08, 128.46, 162.20 (C_{arom}); 163.77 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1045, 1075 (P—O—C); 1260 (P=O); 1660 (C=O); 3280 (N—H). Found (%): C, 56.10; H, 7.81; N, 7.35. $C_{18}H_{29}N_2O_5P$. Calculated (%): C, 56.24; H, 7.60; N, 7.29.

Diethyl [1-(2-benzoylhydrazino)cyclopentyl]phosphonate (2i), m.p. 55—58 °C. ^{1}H NMR (CD_3OD), δ: 1.34 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 1.65—1.75 (m, 2 H, ring); 1.85—1.96 (m, 4 H, ring); 1.98—2.11 (m, 2 H, ring); 4.17—4.24 (m, 4 H, 2 OCH_2); 7.46—7.50 (m, 2 H, arom.) 7.52—7.61 (m, 3 H, arom.); 7.82 (d, 2 H, arom., $^3J_{H,H}$ = 7.3 Hz). ^{31}P NMR (CD_3OD), δ: 29.59. ^{13}C NMR (CD_3OD), δ: 15.53 (d, Me, POEt, $^3J_{C,P}$ = 5.9 Hz); 24.82 (d, $^3J_{C,P}$ = 10.2 Hz); 32.40 (d, $^2J_{C,P}$ = 4.4 Hz) (C_{ring}); 62.86 (d, OCH_2, $^2J_{C,P}$ = 7.3 Hz); 66.66 (d, CH, $^1J_{C,P}$ = 157.3 Hz); 126.96, 128.32, 131.62, 132.72 (C_{arom}); 167.71 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1035, 1050 (P—O—C); 1230 (P=O); 1660 (C=O); 3280 (N—H). Found (%): C, 56.51; H, 7.72; N, 8.39. $C_{16}H_{25}N_2O_4P$. Calculated (%): C, 56.46; H, 7.40; N, 8.23.

Diethyl {1-[2-(4-nitrobenzoyl)hydrazino]cyclopentyl}phosphonate (2j), m.p. 86—87 °C. ^{1}H NMR ($CDCl_3$), δ: 1.31 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 6.8 Hz); 1.66—1.95 (m, 8 H, ring); 4.14—4.19 (m, 4 H, 2 OCH_2); 4.99 (br.s, 1 H, NH); 7.95 (d, 2 H, arom., $^3J_{H,H}$ = 7.8 Hz); 8.22 (d, 2 H, arom., $^3J_{H,H}$ = 7.1 Hz); 9.30 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.65. ^{13}C NMR ($CDCl_3$), δ: 16.50 (d, Me, POEt, $^3J_{C,P}$ = 5.1 Hz); 24.54 (d, $^3J_{C,P}$ = 10.2 Hz); 32.35 (d, $^2J_{C,P}$ = 2.9 Hz) (C_{ring}); 63.03 (d, OCH_2, $^2J_{C,P}$ = 7.3 Hz); 66.85 (d, C, $^1J_{C,P}$ = 166.1 Hz); 123.76, 128.08, 138.17, 149.61 (C_{arom}); 162.90 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1040, 1065 (P—O—C); 1230 (P=O); 1350, 1530 (N=O); 1650 (C=O); 3280 (N—H). Found (%): C, 49.95; H, 6.45; N, 10.71. $C_{16}H_{24}N_3O_6P$. Calculated (%): C, 49.87; H, 6.28; N, 10.90.

Diethyl {1-[2-(4-bromobenzoyl)hydrazino]cyclopentyl}phosphonate (2k), m.p. 98—99 °C. ^{1}H NMR ($CDCl_3$), δ: 1.28 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 1.55—1.66 (m, 2 H, ring); 1.67—1.96 (m, 6 H, ring); 4.10—4.17 (m, 4 H, 2 OCH_2); 4.93 (br.s, 1 H, NH); 7.47 (d, 2 H, arom., $^3J_{H,H}$ = 8.4 Hz); 7.60 (d, 2 H, arom., $^3J_{H,H}$ = 8.5 Hz); 8.89 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 28.84. ^{13}C NMR ($CDCl_3$), δ: 16.49 (d, Me, POEt, $^3J_{C,P}$ = 4.8 Hz); 24.54 (d, $^3J_{C,P}$ = 10.5 Hz); 32.31 (d, $^2J_{C,P}$ = 4.1 Hz) (C_{ring}); 62.84 (d, OCH_2, $^2J_{C,P}$ = 7.2 Hz); 66.91 (d, C, $^1J_{C,P}$ = 166.3 Hz); 126.18, 128.40, 131.49, 131.76 (C_{arom}); 164.09 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1040, 1075 (P—O—C); 1240 (P=O); 1650 (C=O); 3280 (N—H). Found (%): C, 45.89; H, 5.91; N, 6.62. $C_{16}H_{24}BrN_2O_4P$. Calculated (%): C, 45.84; H, 5.77; N, 6.48.

Diethyl {1-[2-(4-methoxybenzoyl)hydrazino]cyclopentyl}-phosphonate (2l). ^{1}H NMR ($CDCl_3$), δ: 1.28 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 1.58—1.65 (m, 2 H, ring); 1.69—1.95 (m, 6 H, ring); 3.75 (s, 3 H, OMe); 4.10—4.17 (m, 4 H, 2 OCH_2); 4.91 (br.s, 1 H, NH); 6.83 (d, 2 H, arom., $^3J_{H,H}$ = 8.7 Hz); 7.69 (d, 2 H, arom., $^3J_{H,H}$ = 8.4 Hz); 8.66 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 29.07. ^{13}C NMR ($CDCl_3$), δ: 16.49 (d, Me, POEt, $^3J_{C,P}$ = 4.8 Hz); 24.58 (d, $^3J_{C,P}$ = 10.5 Hz); 32.27 (d, $^2J_{C,P}$ = 3.2 Hz) (C_{ring}); 55.31 (s, OMe); 62.75 (d, OCH_2, $^2J_{C,P}$ = 7.3 Hz); 66.99 (d, C, $^1J_{C,P}$ = 166.2 Hz); 113.79, 124.95, 128.55, 162.25 (C_{arom}); 164.92 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1040, 1070 (P—O—C); 1260 (P=O); 1650 (C=O); 3280 (N—H). Found (%): C, 55.14; H, 7.38; N, 7.63. $C_{17}H_{27}N_2O_5P$. Calculated (%): C, 55.13; H, 7.35; N, 7.56.

***tert*-Butyl 4-(2-benzoylhydrazino)-4-diethoxyphosphorylpiperidine-1-carboxylate (2m)**, m.p. 103—104 °C. ^{1}H NMR ($CDCl_3$), δ: 1.34 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 1.42 (s, 9 H, Bu^t); 1.77—1.88 (br.m, 4 H, ring); 3.17—3.39 (br.m, 2 H, ring); 3.67—3.97 (br.m, 2 H, ring); 4.14—4.25 (m, 4 H, 2 OCH_2); 5.01 (br.s, 1 H, NH); 7.39—7.43 (m, 2 H, arom.); 7.46—7.50 (m, 1 H, arom.); 7.78 (d, 2 H, arom., $^3J_{H,H}$ = 7.3 Hz); 8.90 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 26.35. ^{13}C NMR ($CDCl_3$), δ: 16.55 (d, Me, POEt, $^3J_{C,P}$ = 5.8 Hz); 27.37 (s, C_{ring}); 28.38 (s, Me, Bu^t); 37.50 (br.s, C_{ring}); 38.55 (br.s, C_{ring}); 57.27 (d, C, $^1J_{C,P}$ = 161.8 Hz); 63.02—63.28 (m, OCH_2); 79.60 (s, C, Bu^t); 126.82, 128.68, 131.77, 132.47 (C_{arom}); 154.66 (s, C=O, C(O)OBu^t); 165.11 (s, C=O, C(O)Ph). IR (CCl_4), ν/cm^{-1}: 1030, 1060 (P—O—C); 1260 (P=O); 1650 (C=O, C(O)Ph); 1670 (C=O, C(O)(OBu^t); 3280 (N—H). Found (%): C, 55.30; H, 7.65; N, 9.10. $C_{21}H_{34}N_3O_6P$. Calculated (%): C, 55.37; H, 7.52; N, 9.23. MS (EI, 70 eV), *m/z*: 455 $[M]^+$, 399 $[M + H - Bu^t]^+$, 318 $[M - P(O)(OEt)_2]^+$, 262 $[M + H - P(O)(OEt)_2 - Bu^t]^+$, 105 $[C(O)Ph]^+$, 77 $[Ph]^+$, 57 $[Bu^t]^+$.

Diethyl [1-(2-benzoylhydrazino)-1-cyclopropylethyl]phosphonate (2n). ^{1}H NMR (CD_3OD), δ: 0.43—0.63 (m, 4 H, CH_2, ring); 1.05 (d, 3 H, Me, $^3J_{H,P}$ = 16.4 Hz); 1.27—1.34 (m, 1 H, CH, ring); 1.37 (t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 4.20—4.28 (m, 4 H, 2 OCH_2); 7.46—7.50 (m, 2 H, arom.); 7.54—7.60 (m, 1 H, arom.); 7.81 (d, 2 H, arom., $^3J_{H,H}$ = 7.4 Hz). ^{31}P NMR (CD_3OD), δ: 27.86. ^{13}C NMR (CD_3OD), δ: –0.40 (d, $^3J_{C,P}$ = = 9.5 Hz); 0.61, 12.47 (C_{ring}); 13.41 (s, Me); 15.55, 15.59 (both d, Me, POEt, $^3J_{C,P}$ = 4.3 Hz); 59.47 (d, CH, $^1J_{C,P}$ = 158.1 Hz); 62.01, 63.09 (both d, OCH_2, $^2J_{C,P}$ = 8.0 Hz); 126.96, 128.30, 131.56, 132.70 (C_{arom}); 167.86 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1025, 1050 (P—O—C); 1230 (P=O); 1650 (C=O); 3265 (N—H). Found (%): C, 56.21; H, 7.20; N, 8.36. $C_{16}H_{25}N_2O_4P$. Calculated (%): C, 56.46; H, 7.40; N, 8.23.

Diethyl [(2-benzoylhydrazino)(phenyl)methyl]phosphonate (2o), m.p. 105—106 °C. ^{1}H NMR ($CDCl_3$), δ: 1.23, 1.25 (both t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.0 Hz); 3.98—4.11 (m, 4 H, 2 OCH_2); 4.62 (d, 1 H, $^2J_{H,P}$ = 13.4 Hz); 5.53 (br.s, 1 H, NH); 7.30—7.37 (m, 5 H, arom.); 7.44—7.51 (m, 3 H, arom.); 7.65 (d, 2 H, arom., $^3J_{H,H}$ = 8.4 Hz); 8.37 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 21.18. ^{13}C NMR ($CDCl_3$), δ: 16.37 (d, Me, POEt, $^3J_{C,P}$ = 5.8 Hz); 62.74 (d, CH, $^1J_{C,P}$ = 154.4 Hz); 62.80, 63.41 (both d, OCH_2, $^2J_{C,P}$ = 7.3 Hz, $^2J_{C,P}$ = 7.4 Hz); 126.96, 128.42, 128.45, 128.56, 128.95 (d, $^3J_{C,P}$ = 6.6 Hz); 131.81, 132.53, 133.75 (d, $^2J_{C,P}$ = 6.5 Hz) (C_{arom}); 165.79 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1025, 1055 (P—O—C); 1250 (P=O); 1655 (C=O), 3275 (N—H). Found (%): C, 59.58; H, 6.48; N, 7.64. $C_{18}H_{23}N_2O_4P$. Calculated (%): C, 59.66; H, 6.40; N, 7.73. MS (EI, 70 eV), *m/z*: 362 $[M]^+$, 227 $[M - NHNHC(O)Ph]^+$, 225 $[M - P(O)(OEt)_2]^+$, 119 $[M - P(O)(OEt)_2 - C(O)Ph - H]^+$, 138 $[P(OH)(OEt)_2]^+$ 105 $[C(O)Ph]^+$, 77 $[Ph]^+$.

Diethyl [(2-benzoylhydrazino)(1*H*-indol-3-yl)methyl]phosphonate (2p). ^{1}H NMR, δ: 1.14, 1.24 (both t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.0 Hz); 3.87—3.97 (m, 1 H, 2 OCH_2); 3.99—4.13 (m, 3 H, 2 OCH_2); 4.98 (d, 1 H, $^2J_{H,P}$ = 11.9 Hz); 5.50 (br.s, 1 H, NH); 7.06—7.15 (m, 2 H, arom.); 7.27—7.35 (m, 4 H, arom.); 7.43 (t, 1 H, arom., $^3J_{H,H}$ = 7.5 Hz); 7.64 (d, 2 H, arom., $^3J_{H,H}$ = = 7.1 Hz); 7.80 (d, 1 H, arom., $^3J_{H,H}$ = 7.8 Hz); 9.54 (s, 1 H, NHC(O)Ph). ^{31}P NMR, δ: 22.84. ^{13}C NMR, δ: 16.37, 16.43 (both d, Me, POEt, $^3J_{C,P}$ = 5.1 Hz); 55.30 (d, CH, $^1J_{C,P}$ = = 163.2 Hz); 62.75, 63.42 (both d, OCH_2, $^2J_{C,P}$ = 7.4 Hz, $^2J_{C,P}$ = 7.3 Hz); 106.81, 111.62, 119.49, 119.73, 122.10, 125.25 (d, $^3J_{C,P}$ = 5.9 Hz); 126.79 (d, $^3J_{C,P}$ = 6.6 Hz); 126.97, 128.55, 131.76, 132.62, 136.22 (C_{arom}); 166.87 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1035, 1060 (P—O—C); 1240 (P=O); 1640 (C=O), 3230 (N—H). Found (%): C, 60.01; H, 5.89; N, 10.37. $C_{18}H_{23}N_2O_4P$. Calculated (%): C, 59.84; H, 6.03; N, 10.47. MS (EI, 70 eV), *m/z*: 401 $[M]^+$, 266 $[M - NHNHC(O)Ph]^+$, 264 $[M - P(O)(OEt)_2]^+$, 138 $[P(OH)(OEt)_2]^+$, 130 $[M + H - NHNHC(O)Ph - P(O)(OEt)_2]^+$, 116 $[M - NHNHC(O)Ph - P(O)(OEt)_2 - CH]^+$, 105 $[C(O)Ph]^+$, 77 $[Ph]^+$.

Diethyl [1-(2-benzoylhydrazino)-1-phenylethyl]phosphonate (2q). ^{1}H NMR, δ: 1.26, 1.28 (both t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = = 7.1 Hz); 1.82 (d, 3 H, Me, $^3J_{H,P}$ = 15.7 Hz); 3.95—4.04 (m, 2 H, 2 OCH_2); 4.06—4.17 (m, 2 H, 2 OCH_2); 5.53 (br.d, 1 H, NH, $^3J_{H,P}$ = 15.7 Hz); 7.31—7.34 (m, 1 H, arom.); 7.38—7.42 (t, 4 H, arom., $^3J_{H,H}$ = 7.8 Hz); 7.46—7.50 (m, 1 H, arom.); 7.69—7.71 (m, 4 H, arom.); 8.28 (s, 1 H, NHC(O)Ph). ^{31}P NMR, δ: 24.60. ^{13}C NMR, δ: 16.37, 16.42 (both d, Me, POEt, $^3J_{C,P}$ = 5.1 Hz, $^3J_{C,P}$ = 5.2 Hz); 63.23, 63.63 (both d, $^2J_{C,P}$ = 8.0 Hz, $^2J_{C,P}$ = 7.3 Hz, OCH_2); 63.44 (d, CH, $^1J_{C,P}$ = 155.8 Hz); 126.78, 127.38 (d, $^3J_{C,P}$ = = 4.4 Hz); 127.94, 128.38, 128.65, 131.71, 132.51, 138.11 (d, $^2J_{C,P}$ = 3.7 Hz) (C_{arom}); 165.70 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1035, 1060 (P—O—C); 1240 (P=O); 1660 (C=O); 3280 (N—H). Found (%): C, 60.86; H, 6.71; N, 7.33. $C_{19}H_{25}N_2O_4P$. Calculated (%): C, 60.63; H, 6.69; N, 7.44.

Diethyl [1-(2-benzoylhydrazino)-2,3-dihydro-1*H*-inden-1-yl]phosphonate (2r), m.p. 85—86 °C. ^{1}H NMR ($CDCl_3$), δ: 1.14, 1.21 (both t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.0 Hz); 2.15—2.28 (m, 1 H, C(2)H_2, ring); 2.50—2.61 (m, 1 H, C(2)H_2, ring); 2.86—3.03 (m, 2 H, C(3)H_2, ring); 3.89—4.11 (m, 4 H, 2 OCH_2); 5.56 (br.s, 1 H, NH); 7.09—7.21 (m, 3 H, arom.); 7.27—7.33 (m, 2 H, arom.); 7.35—7.42 (m, 1 H, arom.); 7.45—7.50 (m, 1 H, arom.); 7.57—7.60 (m, 2 H, arom.); 8.83 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 24.56. ^{13}C NMR ($CDCl_3$), δ: 16.16, 16.21 (both d, Me, POEt, $^3J_{C,P}$ = 4.4 Hz, $^3J_{C,P}$ = 5.1 Hz); 30.12 (d, C(3)H_2, ring, $^3J_{C,P}$ = 3.7 Hz); 32.32 (d, C(2)H_2, ring, $^2J_{C,P}$ = 2.9 Hz); 63.16, 63.84 (both d, OCH_2, $^2J_{C,P}$ = 8.0 Hz, $^2J_{C,P}$ = 7.3 Hz); 71.54 (d, C, $^1J_{C,P}$ = 166.1 Hz); 124.93, 125.70, 126.32, 126.77, 128.48, 129.11, 131.72, 132.16, 138.05, 145.11 (d, $^2J_{C,P}$ = 8.8 Hz) (C_{arom}); 166.66 (s, C=O). IR (CCl_4), ν/cm^{-1}: 1040, 1060 (P—O—C); 1235 (P=O); 1660 (C=O); 3280 (N—H). Found (%): C, 61.70; H, 6.35; N, 7.32. $C_{20}H_{25}N_2O_4P$. Calculated (%): C, 61.85; H, 6.49; N, 7.21.

Methyl 1-(2-benzoylhydrazino)-1-diethoxyphosphoryl-2,3-dihydro-1*H*-indene-5-carboxylate (2s), m.p. 235—237 °C. ^{1}H NMR ($CDCl_3$), δ: 1.18, 1.20 (both t, 6 H, 2 Me, POEt, $^3J_{H,H}$ = 7.1 Hz); 2.18—2.29 (m, 1 H, C(2)H_2, ring); 2.58—2.68 (m, 1 H, C(2)H_2, ring); 2.90—3.06 (m, 2 H, C(3)H_2, ring); 3.80 (s, 3 H, OMe); 3.97—4.13 (m, 4 H, 2 OCH_2); 5.58 (br.s, 1 H, NH); 7.28—7.31 (m, 2 H, arom.); 7.38 (t, 1 H, arom., $^3J_{H,H}$ = = 7.2 Hz); 7.54 (d, 1 H, arom., $^3J_{H,H}$ = 7.7 Hz); 7.61 (d, 1 H, arom., $^3J_{H,H}$ = 7.5 Hz); 7.79 (d, 1 H, arom., $^3J_{H,H}$ = 8.1 Hz); 8.81 (s, 1 H, arom.); 8.59 (s, 1 H, NHC(O)Ph). ^{31}P NMR ($CDCl_3$), δ: 23.70. ^{13}C NMR ($CDCl_3$), δ: 16.38 (d, Me, POEt, $^3J_{C,P}$ = 4.1 Hz); 29.98 (d, C(3)H_2, ring, $^3J_{C,P}$ = 2.4 Hz); 32.82 (s, C(2)H_2, ring); 52.02 (s, OMe); 63.10, 63.73 (both d, OCH_2, $^2J_{C,P}$ = 7.2 Hz, $^2J_{C,P}$ = 7.3 Hz); 71.54 (d, C, $^1J_{C,P}$ = 167.0 Hz); 125.62, 126.11, 126.75, 127.94, 128.56, 130.08, 131.67, 132.28, 143.90, 145.37 (d, C_{arom}, $^2J_{C,P}$ = 7.0 Hz); 165.56 (s, C=O, C(O)Ph); 166.87 (s, C=O, COOMe). IR (CCl_4), ν/cm^{-1}: 1040, 1060 (P—O—C); 1230 (P=O); 1660 (C=O, C(O)Ph); 1730 (C=O, COOMe); 3230 (N—H). Found (%): C, 59.11; H, 6.09; N, 6.19. $C_{22}H_{27}N_2O_6P$. Calculated (%): C, 59.16; H, 6.10; N, 6.27.

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