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Reaction of 1,2-Diaza-1,3-butadienes with Aminophosphorus Nucleophiles: A Practical Access to New Phosphorylated Pyrazolones

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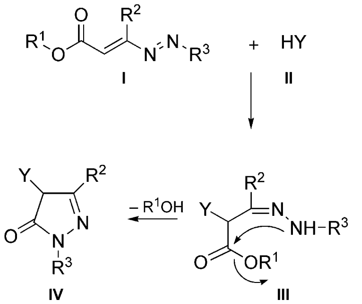
The reaction of 1,2-diaza-1,3-butadienes with dibenzyl diisopropylphosphoramidite, methyl tetraisopropylphosphorodiamidite or tris(dimethylamino)phosphane under solvent-free conditions gave stable α-phosphoranylidene-hydrazones that, in turn, were transformed into the corresponding 5-oxo-4-phosphoranylidene-4,5-dihydro-1*H*-pyrazoles. X-ray diffraction analysis of one of these derivatives is reported. α-Phosphoranylidene-hydrazones, derived from the reaction between 1,2-diaza-1,3-butadienes with dibenzyl diisopropylphosphoramidite, were converted by hydrolytic cleavage into (*E*)-hydrazono-phosphonates, which are useful for the preparation of the corresponding (3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)phosphonamidates.

Introduction

Organophosphorus compounds are noteworthy for their biological activity,[1] especially when they are associated with various heterocycles.[2] One of the most important of these bioactive heterocycles is the pyrazole moiety.[3] In spite of their importance, methods for the direct synthesis of substituted pyrazoles containing phosphorus groups are quite limited.[4] In particular, amino-phoshoranylidene- and phosphonamido-pyrazolones have not been widely reported in the literature.[5]

On the other hand, 1,2-diaza-1,3-butadienes have been intensively studied by several researchers because of their usefulness in organic synthesis.[6,7] Our group has employed these substrates mainly as building blocks for the synthesis of five- or six-membered heterocycles.[6,8] In particular, 1,2-diaza-1,3-butadienes **I** readily react with a large variety of nucleophiles **II** by 1,4-conjugate addition (Michael-type) of the latter to the terminal carbon atom of the heterodiene system to give 1,4-adduct hydrazone intermediates **III**. These compounds can furnish polyfunctionalized pyrazolones **IV**[6,9] by intermolecular nucleophilic attack of the C=N–*N*H nitrogen on the ester group in the γ-position and subsequent loss of an alcohol molecule (Scheme 1).



Scheme 1.

Also, in the past few years, we have examined the phospha-Michael (P-Michael) addition of some phosphorus nucleophiles to 1,2-diaza-1,3-butadienes, which is one of the most versatile tools for the formation of the P–C bond.[10] In detail, the reaction of 1,2-diaza-1,3-butadienes with triphenyl-[11a] or trialkylphosphanes[11b] gives pyrazoles or pyrazol-5-ones, whereas with trialkyl phosphites and dialkyl phenylphosphonites they furnish new 1,2,3-diazaphospholes or (*E*)-hydrazono-phosphonates.[12]

Based on these considerations and with the aim of synthesizing new phosphorylated pyrazolones containing one, two or three amino functions directly linked to the phosphorus atom, we describe herein the reaction between 1,2-diaza-1,3-butadienes and dibenzyl diisopropylphosphoramidite, methyl tetraisopropylphosphorodiamidite or tris-

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(dimethylamino)phosphane to form stable α-phosphoranylidene-hydrazones. These ylide derivatives can be converted into the desired 5-oxo-4-phosphoranylidene-4,5-dihydro-1*H*-pyrazoles or (*E*)-hydrazono-phosphonates. These latter compounds have been demonstrated in recent years to be important tools in the synthesis of various heterocyclic compounds.[12] In this work, they are employed in the preparation of interesting (3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)-phosphonamidates.

Results and Discussion

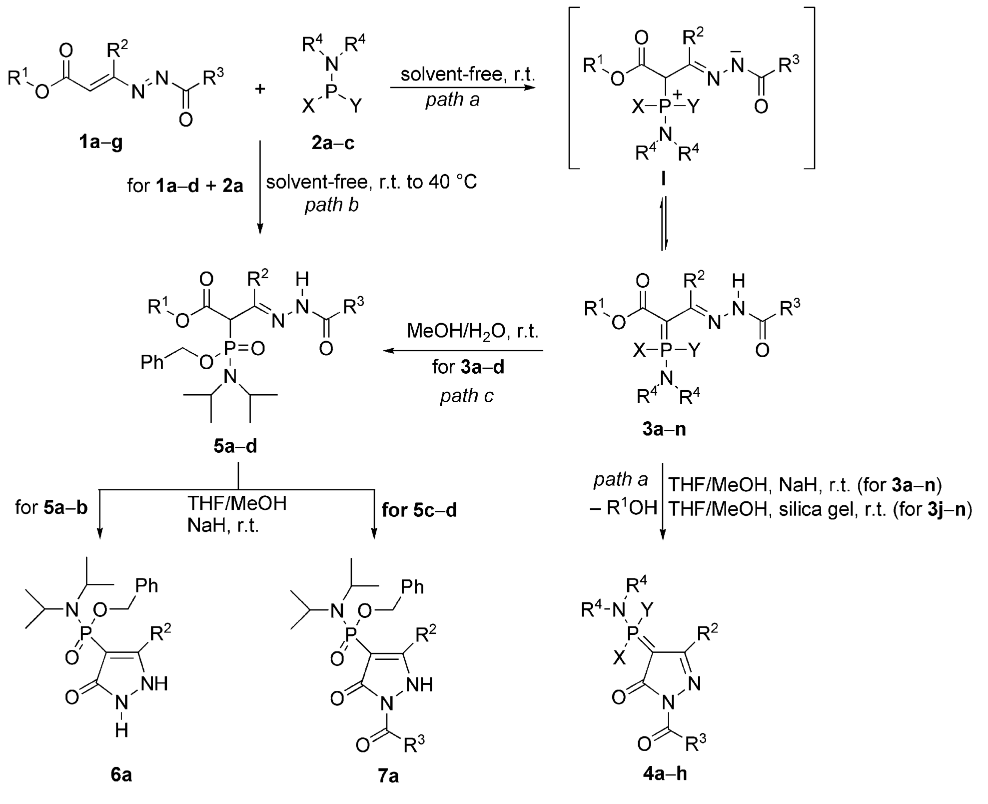
1,2-Diaza-1,3-butadienes **1a**–**g** readily reacted with dibenzyl diisopropylphosphoramidite (**2a**), methyl tetraisopropylphosphorodiamidite (**2b**) or tris(dimethylamino)-phosphane (**2c**) under solvent-free conditions in 0.2–3.0 h to give α-phosphoranylidene-hydrazones **3a**–**n**, which precipitated from the reaction medium in good yields (Scheme 2, path a, Table 1).

The ylide derivatives **3a**–**n** are formed by nucleophilic 1,4-addition of the phosphorus atom to the terminal carbon atom of the heterodiene system to form a zwitterionic intermediate **I**, which exists in equilibrium with its ylide form **3** through a 1,4-proton shift (Scheme 2).

Ylide intermediates **3a**–**n** can be easily converted into the corresponding 5-oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles **4a**–**h** by treatment with a catalytic (for **3a**–**i**) or a stoichiometric (for **3k**–**n**) amount of sodium hydride in a mixture of tetrahydrofuran/methanol (1:1) at room temperature (Scheme 2, path a, Table 1). Ring closure to the pyrazolone ring is ascribable to an intramolecular nucleophilic attack of the base-activated hydrazone nitrogen atom on the ester group with loss of an alcohol molecule (see Scheme 1).

The ^{13}C NMR chemical shifts of the P–C signals of the hydrazones **3** (δ = 45.9–56.7 ppm) and 5-oxopyrazoles **4** (δ = 71.5–84.5 ppm) and the values of their coupling constants (J = 119.1–198.8 Hz for **3** and J = 192.7–205.0 Hz for **4**) clearly supported the ylide nature of these compounds.[12,13] However, the molecular structure of 5-oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles was unequivocally established by X-ray diffraction analysis of **4c** (Figure 1).[14]

The conversion of the ylide derivatives **3j**–**n**, derived from **1a**–**d**,**g**, with **2c** into the corresponding 5-oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles **4f**–**h** also occurs in the presence of some acidic resins,[15a] such as montmorillonite,[15b] zeolite,[15c] amberlyst 15 H[15d] or silica gel,[15e] in a mixture of tetrahydrofuran/methanol (95:5). For the conversion of ethyl 3-[(anilinocarbonyl)hydrazono]-2-[tris(dimethylamino)phosphoranylidene]butanoate (**3m**) into 3-methyl-5-oxo-*N*-phenyl-4-[tris(dimethylamino)phosphoranylidene]-4,5-dihydro-1*H*-pyrazole-1-carboxamide (**4g**) different amounts of some of these resins were tested and also different temperatures. The results of this study are reported in Table 2. Silica gel was found to be the best in terms of higher yields and shorter reaction times, even at room temperature. Thus, the use of these optimal conditions was extended to the conversion of α-phosphoranylid-



Scheme 2.

Table 1. Yields and reaction times for the preparation of α-phosphoranylidene-hydrazones **3a**–**n** and 5-oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles **4a**–**h**.

1	R^1	R^2	R^3	2	X	Y	R^4	3	Yield [%][a]	Time [h][b]	4[c]	Yield [%][d]	Time [h][e]
1a	Me	Me	NH_2	**2a**	OBn	OBn	*i*Pr	**3a**	64	3.0	**4a**	67	2.5
1b	Et	Me	NH_2	**2a**	OBn	OBn	*i*Pr	**3b**	67	3.0	**4a**	64	3.0
1c	Me	Me	NHPh	**2a**	OBn	OBn	*i*Pr	**3c**	68	4.0	**4b**	69	2.0
1d	Et	Me	NHPh	**2a**	OBn	OBn	*i*Pr	**3d**	63	4.5	**4b**	75	2.0
1a	Me	Me	NH_2	**2b**	OMe	$N(R^4)_2$	*i*Pr	**3e**	92	0.5	**4c**	75	48.0
1b	Et	Me	NH_2	**2b**	OMe	$N(R^4)_2$	*i*Pr	**3f**	100	0.5	**4c**	68	48.0
1c	Me	Me	NHPh	**2b**	OMe	$N(R^4)_2$	*i*Pr	**3g**	66	0.2	**4d**	90	48.0
1e	Me	Et	NH_2	**2b**	OMe	$N(R^4)_2$	*i*Pr	**3h**	65	1.0	[f]		
1f	Et	Me	O*t*Bu	**2b**	OMe	$N(R^4)_2$	*i*Pr	**3i**	88	1.0	**4e**	70	72.0
1a	Me	Me	NH_2	**2c**	$N(R^4)_2$	$N(R^4)_2$	Me	**3j**	81	3.0	**4f**	66	6.0
1b	Et	Me	NH_2	**2c**	$N(R^4)_2$	$N(R^4)_2$	Me	**3k**	84	3.0	**4f**	68	6.0
1c	Me	Me	NHPh	**2c**	$N(R^4)_2$	$N(R^4)_2$	Me	**3l**	72	0.4	**4g**	89	1.0
1d	Et	Me	NHPh	**2c**	$N(R^4)_2$	$N(R^4)_2$	Me	**3m**	77	0.3	**4g**	91	1.0
1g	Me	Et	NHPh	**2c**	$N(R^4)_2$	$N(R^4)_2$	Me	**3n**	72	1.5	**4h**	76	0.5

[a] Yields of the pure isolated products, based on **1a**–**g**. [b] Time for the disappearance of **1a**–**g**. [c] Prepared starting from **3a**–**n** with sodium hydride. [d] Yields of the pure isolated products, based on **3a**–**n**. [e] Time for the disappearance of compounds **3a**–**n**. [f] The reaction gave a complicated mixture.

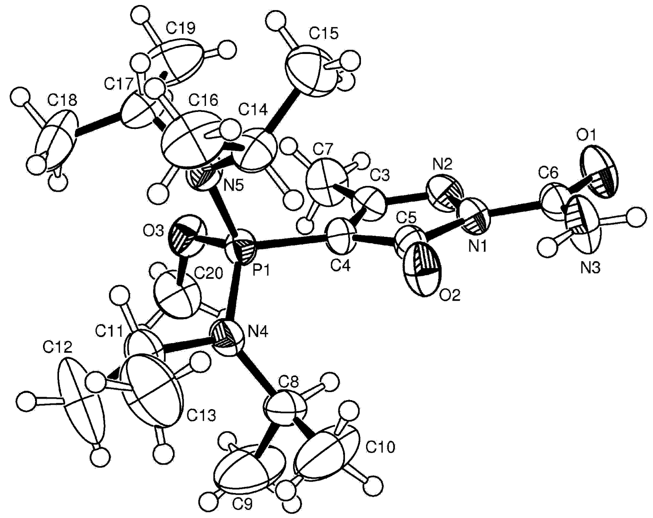


Figure 1. X-ray structure of compound **4c** with 50% probability thermal ellipsoids.

ene-hydrazones **3j**–**n** into **4f**–**h**. Yields and reaction times are reported in Table 3. Under the mild acidic conditions used in the reactions, the ester electrophilic centre is probably activated during the ring-closure step.

Acidic treatment of α-phosphoranylidene-hydrazones **3a**–**i**, derived from **1a**–**h** and **2a**,**b**, with resins gave complicated reaction mixtures, probably because of the presence of one or two oxygen atoms linked to the phosphorus atom that makes possible other concomitant reactions.

When the temperature for the reaction between 1,2-diaza-1,3-butadienes **1a**–**d** and dibenzyl diisopropylphosphoramidite (**2a**) under solvent-free conditions was raised to 40 °C and the mixture allowed to stand at this temperature for the appropriate time (7.0–12.0 h), (*E*)-hydrazono-phosphonates **5a**–**d** were formed in good yields (Scheme 2, path b, Table 4). Compounds **5a**–**d** can also be obtained by hydrolytic cleavage of α-phosphoranylidene-hydrazones **3a**–**d**, by magnetically stirring in methanol/water (95:5) at room temperature (Scheme 2, path c, Table 4).

Table 2. Yields and reaction times for the conversion of ethyl 3-[(anilinocarbonyl)hydrazono]-2-[tris(dimethylamino)phosphoranylidene]butanoate (**3m**) into 3-methyl-5-oxo-*N*-phenyl-4-[tris(dimethylamino)phosphoranylidene]-4,5-dihydro-1*H*-pyrazole-1-carboxamide (**4g**) by using different resins and temperatures.

Resin	Amount[a]	*T* [°C]	Time [h]	Yield [%]
Montmorillonite	1.0 equiv.	60	1.0	85
Montmorillonite	2.0 equiv.	25	0.5	50
Zeolite	1.0 equiv.	60	1.0	85
Zeolite	2.0 equiv.	25	3.3	65
Amberlyst 15H	1.0 equiv.	60	1.0	46
Amberlyst 15H	2.0 equiv.	25	0.2	58
Silica gel	5.0 g	25	0.1	87

[a] Amount relative to 1 mmol of the starting **3m**.

Table 3. Yields and reaction times for the preparation of 5-oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles **4f**–**h** with silica gel starting from **3j**–**n**.

3	4	Yield [%][a]	Time [h][b]
3j	**4f**	85	0.2
3k	**4f**	81	0.1
3l	**4g**	81	0.2
3m	**4g**	87	0.1
3n	**4h**	86	0.1

[a] Yields of the pure isolated products, based on **3j**–**n**. [b] Time for the disappearance of compounds **3j**–**n**.

In the reactions between 1,2-diaza-1,3-butadienes **1a**–**g** and **2b**,**c**, (*E*)-hydrazono-phosphonates **5** did not form, perhaps because of electronic and/or steric effects caused by the additional nitrogen atoms bound to the phosphorus atom making it a poorer electrophile.

The hydrazone derivatives **5a**–**d** have proven once again their synthetic utility as they were converted in good yields into (3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)phosphonamidates **6a** and **7a** by treatment with a catalytic amount of sodium hydride in tetrahydrofuran/methanol (1:1) (Scheme 2,

Table 4. Yields and reaction times for the preparation of (*E*)-hydrazono-phosphonates **5a**–**d**.

1	R^1	R^2	R^3	2	3	5	Yield [%][a]	Time [h][b]	Yield [%][c]	Time [h][d]
1a	Me	Me	NH_2	**2a**	**3a**	**5a**	78	7.0	68	7
1b	Et	Me	NH_2	**2a**	**3b**	**5b**	87	12.0	62	12
1c	Me	Me	NHPh	**2a**	**3c**	**5c**	67	12.0	66	15
1d	Et	Me	NHPh	**2a**	**3d**	**5d**	70	8.0	76	27

[a] Yields of the pure isolated products, based on **1a**–**d** (path b, Scheme 2). [b] Time for the formation of compounds **5a**–**d**, refers to path b of Scheme 2. [c] Yields of the pure isolated products, based on **3a**–**d** (path c, Scheme 2). [d] Time for the disappearance of compounds **3a**–**d** refers to path c of Scheme 2.

Table 5) according to the same base-promoted mechanism as described for the synthesis of **4a**–**h**. The formation of 2-unsubstituted 3-oxopyrazole **6a** took place by base-promoted hydrolytic cleavage of the aminocarbonyl group linked to the nitrogen atom at the 2-position of the pyrazole ring.

Table 5. Yields and reaction times for the preparation of (3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)phosphonamidates **6a** and **7a**.

5	6	Yield [%] [a]	Time [h] [b]	7	Yield [%] [c]	Time[h] [d]
5a	**6a**	64	3.0			
5b	**6a**	67	3.0			
5c				**7a**	75	0.1
5d				**7a**	77	0.2

[a] Yields of the pure isolated products, based on **5a**,**b**. [b] Time for the disappearance of compounds **5a**,**b**. [c] Yields of the pure isolated products, based on **5c**,**d**. [d] Time for the disappearance of compounds **5c**,**d**.

Conclusions

We have implemented a practical procedure for the synthesis of 5-oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles and (3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)phosphonamidates via α-phosphoranylidene-hydrazones and (*E*)-hydrazono-phosphonates, respectively. Pyrazoles directly substituted with phosphorus-containing groups are of interest as a result of their biological activity.[1–3] Furthermore, to the best of our knowledge, few examples of the synthesis of amino-phosphorylated pyrazolones have been reported in the literature,[5] and thus our investigation represents an important contribution to this field. The use of heterogeneous catalysis in the conversion of (*E*)-hydrazono-phosphonates into 5-oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles makes this method advantageous by virtue of the easy regeneration of the resins and the simple workup of the reaction mixtures (only filtration).[15]

Experimental Section

General: Dibenzyl diisopropylphosphoramidite, methyl tetraisopropylphosphorodiamidite, tris(dimethylamino)phosphane, sodium hydride, Amberlyst 15 H, montmorillonite KSF, HY zeolite (DAHY) and silica gel 35–70 µm 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 from sodium hydroxide. Melting points were determined in open capillary tubes with a Gallenkamp apparatus. Mass spectra (EI) were recorded at an ionizing voltage of 70 eV with a Shimadzu QP5000 spectrometer. ^1H and ^{13}C NMR spectra were recorded at 400 and 100.32 MHz, respectively, with a Varian Mercury 400VX spectrometer. All NMR spectra were recorded in $CDCl_3$ or [D$_6$]DMSO, as specified below. ^1H chemical shifts (δ_H) are reported in parts per million (ppm) relative to TMS as the internal standard. All coupling constant (*J*) values are given in Hz. ^{13}C chemical shifts (δ_C) are reported in parts per million (ppm) relative to $CDCl_3$ or [D$_6$]DMSO as the internal standard in broadband decoupled mode; the multiplicities were obtained by 135° and 90° DEPT experiments to aid assignment. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet; br., broad. All the NH and NH_2 groups exchanged with D_2O. Precoated silica gel plates (0.25 mm) were employed in analytical thin-layer chromatography and silica gel 35–70 µm for column chromatography. All new compounds showed satisfactory elemental analysis (C ±0.35, H ±0.30, N ±0.30). The nomenclature was generated by using ACD/IUPAC Name.[16]

General Procedure for the Synthesis of α-Phosphoranylidene-hydrazones 3a–n: 1,2-Diaza-1,3-butadienes **1a**–**g** (1 mmol) as a mixture of (*E*)/(*Z*) isomers[17] and dibenzyl diisopropylphosphoramidite (**2a**), methyl tetraisopropylphosphorodiamidite (**2b**) or tris(dimethylamino)phosphane (**2c**; 4 mmol) were magnetically stirred at room temperature for 0.2–4.5 h until the red colour of the starting material **1** had disappeared. The α-phosphoranylidene-hydrazones **3a**–**n** precipitated from the reaction medium and were collected by filtration.

Methyl 3-[(Aminocarbonyl)hydrazono]-2-[bis(benzyloxy)(diisopropylamino)phosphoranylidene]butanoate (3a): White powder; yield: 330.6 mg (64%); m.p. 118–120 °C. ^1H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.14 [d, J = 6.8 Hz, 12 H, 2 CH(CH_3)$_2$], 2.04 (s, 3 H, CH_3), 3.42 (s, 3 H, CO_2CH_3), 3.78–3.86 [m, 2 H, 2 CH(CH_3)$_2$], 4.92–5.03 (m, 4 H, 2 OCH_2Ph), 6.01 (br. s, 2 H, NH_2), 7.30–7.36 (m, 10 H, CH$_{arom}$), 8.72 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.2 (d, $^3J_{CP}$ = 8.4 Hz, CH_3), 21.6 (d, $^3J_{CP}$ = 23.5 Hz, CH_3), 23.2 (d, $^3J_{CP}$ = 19.7 Hz, CH_3), 47.8 (d, $^2J_{CP}$ = 53.9 Hz, CH), 52.0 (s, CH_3), 55.5 (d, $^1J_{CP}$ = 119.2 Hz, 1 C), 64.4 (d, $^2J_{CP}$ = 28.1 Hz, CH_2), 127.0 (s, CH), 127.1 (s, CH), 127.8 (s, CH), 128.3 (s, CH), 129.1 (s, CH), 129.4 (s, CH), 136.2 (d, $^3J_{CP}$ = 8.3 Hz, 1 C), 136.8 (d, $^3J_{CP}$ = 8.8 Hz, 1 C), 140.6 (d, $^2J_{CP}$ = 14.0 Hz, 1 C), 156.8 (s, 1 C), 167.1 (d, $^2J_{CP}$ = 5.3 Hz, 1 C) ppm. MS: *m*/*z* (%) = 516 (14) [M]$^+$, 441 (34), 426 (100). $C_{26}H_{37}N_4O_5P$ (516.56): calcd. C 60.45, H 7.22, N 10.85; found C 60.39, H 7.17, N 10.91.

Ethyl 3-[(Aminocarbonyl)hydrazono]-2-[bis(benzyloxy)(diisopropylamino)phosphoranylidene]butanoate (3b): White powder; yield: 355.5 mg (67%); m.p. 138–140 °C. ^1H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.09 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.14 [d, J = 6.8 Hz, 12 H, 2 CH(CH_3)$_2$], 2.09 (s, 3 H, CH_3), 3.81–3.90 [m, 2 H, 2 CH(CH_3)$_2$], 3.95 (q, J = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 4.93–5.08 (m, 4 H, 2 OCH_2Ph), 6.08 (br. s, 2 H, NH_2), 7.29–7.34 (m, 10 H, CH$_{arom}$), 8.72 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 13.8 (s, CH$_3$), 15.3 (d, $^3J_{CP}$ = 8.3 Hz, CH$_3$), 21.3 (d, $^3J_{CP}$ = 22.8 Hz, CH$_3$), 23.4 (d, $^3J_{CP}$ = 20.0 Hz, CH$_3$), 45.6 (d, $^2J_{CP}$ = 53.9 Hz, CH), 55.7 (d, $^1J_{CP}$ = 119.9 Hz, 1 C), 64.5 (d, $^2J_{CP}$ = 28.0 Hz, CH$_2$), 68.1 (s, CH$_2$), 127.0 (s, CH), 127.2 (s, CH), 127.9 (s, CH), 128.1 (s, CH), 129.0 (s, CH), 129.4 (s, CH), 136.1 (d, $^3J_{CP}$ = 8.3 Hz, 1 C), 136.7 (d, $^3J_{CP}$ = 8.2 Hz, 1 C), 140.8 (d, $^2J_{CP}$ = 15.0 Hz, 1 C), 156.9 (s, 1 C), 167.3 (d, $^2J_{CP}$ = 5.5 Hz, 1 C) ppm. MS: *m*/*z* (%) = 530 (11) [M]$^+$, 455 (39), 440 (100). $C_{27}H_{39}N_4O_5P$ (530.59): calcd. C 61.12, H 7.41, N 10.56; found C 61.19, H 7.38, N 10.69.

Methyl 3-[(Anilinocarbonyl)hydrazono]-2-[bis(benzyloxy)(diisopropylamino)phosphoranylidene]butanoate (3c): White powder; yield: 403.1 mg (68%); m.p. 123–125 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.14 [d, *J* = 6.8 Hz, 12 H, 2 CH(C*H*$_3$)$_2$], 2.14 (s, 3 H, CH$_3$), 3.45 (s, 3 H, CO$_2$CH$_3$), 3.81–3.90 [m, 2 H, 2 C*H*(CH$_3$)$_2$], 4.98–5.10 (m, 4 H, 2 OC*H*$_2$Ph), 6.91–7.37 (m, 15 H, CH$_{arom}$), 8.25 (s, 1 H, NH), 9.25 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.4 (s, CH$_3$), 21.3 (d, $^3J_{CP}$ = 22.9 Hz, CH$_3$), 23.4 (d, $^3J_{CP}$ = 20.1 Hz, CH$_3$), 46.3 (d, $^2J_{CP}$ = 53.8 Hz, CH), 52.1 (s, CH$_3$), 55.7 (d, $^1J_{CP}$ = 119.1 Hz, 1 C), 64.2 (d, $^2J_{CP}$ = 20.0 Hz, CH$_2$), 118.3 (s, CH), 119.0 (s, CH), 121.9 (s, CH), 127.2 (s, CH), 127.4 (s, CH), 127.9 (s, CH), 128.0 (s, CH), 128.3 (s, CH), 128.5 (s, CH), 135.6 (d, $^3J_{CP}$ = 8.2 Hz, 1 C), 136.2 (d, $^3J_{CP}$ = 8.3 Hz, 1 C), 138.9 (s, 1 C), 139.6 (d, $^2J_{CP}$ = 15.0 Hz, 1 C), 153.3 (s, 1 C), 168.4 (d, $^2J_{CP}$ = 5.8 Hz, 1 C) ppm. MS: *m*/*z* (%) = 592 (1) [M]$^+$, 502 (16), 488 (29), 441 (19), 426 (100). $C_{32}H_{41}N_4O_5P$ (592.66): calcd. C 64.85, H 6.97, N 9.45; found C 64.91, H 6.79, N 9.55.

Ethyl 3-[(Anilinocarbonyl)hydrazono]-2-[bis(benzyloxy)(diisopropylamino)phosphoranylidene]butanoate (3d): White powder; yield: 382.3 mg (63%); m.p. 130–132 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.10 (t, *J* = 7.2 Hz, 3 H, CO$_2$CH$_2$C*H*$_3$), 1.19 [d, *J* = 6.8 Hz, 12 H, 2 CH(C*H*$_3$)$_2$], 2.15 (s, 3 H, CH$_3$), 3.83–3.89 [m, 2 H, 2 C*H*(CH$_3$)$_2$], 3.95 (q, *J* = 7.2 Hz, 2 H, CO$_2$C*H*$_2$CH$_3$), 5.00 and 5.08 (2 dd, *J* = 11.6, $^3J_{HP}$ = 7.2 Hz, 4 H, 2 OC*H*$_2$Ph), 6.93 (t, *J* = 7.2 Hz, 1 H$_{arom}$), 7.18–7.38 (m, 14 H, CH$_{arom}$), 8.22 (s, 1 H, NH), 9.22 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 13.7 (s, CH$_3$), 14.8 (s, CH$_3$), 21.5 (d, $^3J_{CP}$ = 23.1 Hz, CH$_3$), 23.6 (d, $^3J_{CP}$ = 19.8 Hz, CH$_3$), 45.6 (d, $^2J_{CP}$ = 53.8 Hz, CH), 56.7 (d, $^1J_{CP}$ = 119.9 Hz, 1 C), 64.6 (d, $^2J_{CP}$ = 17.4 Hz, CH$_2$), 68.2 (s, CH$_2$), 118.3 (s, CH), 119.0 (s, CH), 121.9 (s, CH), 126.7 (s, CH), 127.2 (s, CH), 127.8 (s, CH), 128.0 (s, CH), 128.3 (s, CH), 128.5 (s, CH), 135.6 (d, $^3J_{CP}$ = 8.3 Hz, 1 C), 136.2 (d, $^3J_{CP}$ = 8.4 Hz, 1 C), 138.9 (s, 1 C), 139.2 (d, $^2J_{CP}$ = 15.9 Hz, 1 C), 153.3 (s, 1 C), 168.3 (d, $^2J_{CP}$ = 5.8 Hz, 1 C) ppm. MS: *m*/*z* (%) = 606 (11) [M]$^+$, 560 (8), 515 (35), 426 (100). $C_{33}H_{43}N_4O_5P$ (606.69): calcd. C 65.33, H 7.14, N 9.23; found C 65.29, H 7.28, N 9.17.

Methyl 3-[(Aminocarbonyl)hydrazono]-2-[bis(diisopropylamino)(methoxy)phosphoranylidene]butanoate (3e): White powder; yield: 399.1 mg (92%); m.p. 160–162 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.14 and 1.17 [2 d, *J* = 6.8 Hz, 24 H, 4 CH(C*H*$_3$)$_2$], 1.96 (s, 3 H, CH$_3$), 3.35 (s, 3 H, CO$_2$CH$_3$), 3.70–3.81 [m, 4 H, 4 C*H*(CH$_3$)$_2$], 3.74 (d, $^3J_{HP}$ = 11.6 Hz, 3 H, OCH$_3$), 5.75 and 6.22 (2 br. s, 2 H, NH$_2$), 8.71 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.0 (s, CH$_3$), 22.8 (d, $^3J_{CP}$ = 6.0 Hz, CH$_3$), 46.8 (d, $^2J_{CP}$ = 6.8 Hz, CH$_3$), 48.5 (d, $^2J_{CP}$ = 21.2 Hz, CH), 54.4 (s, CH$_3$), 56.0 (d, $^1J_{CP}$ = 198.8 Hz, 1 C), 147.3 (s, 1 C), 156.2 (s, 1 C), 167.7 (d, $^2J_{CP}$ = 18.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 433 (85) [M]$^+$, 390 (100). $C_{19}H_{40}N_5O_4P$ (433.52): calcd. C 52.64, H 9.30, N 16.15; found C 52.78, H 9.27, N 15.99.

Ethyl 3-[(Aminocarbonyl)hydrazono]-2-[bis(diisopropylamino)(methoxy)phosphoranylidene]butanoate (3f): Pale-pink powder; yield: 446.7 mg (100%); m.p. 168–170 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.07–1.22 [m, 27 H, CO$_2$CH$_2$C*H*$_3$ and 4 CH(C*H*$_3$)$_2$], 1.95 (s, 3 H, CH$_3$), 3.70–3.79 [m, 4 H, 4 C*H*(CH$_3$)$_2$], 3.72 (d, $^3J_{HP}$ = 12.0 Hz, 3 H, OCH$_3$), 3.86 (q, *J* = 7.2 Hz, 2 H, CO$_2$C*H*$_2$CH$_3$), 5.76 and 6.21 (2 br. s, 2 H, NH$_2$), 8.70 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 14.9 (s, CH$_3$), 21.3 (s, CH$_3$), 23.2 (d, $^3J_{CP}$ = 5.6 Hz, CH$_3$), 46.9 (d, $^2J_{CP}$ = 6.8 Hz, CH$_3$), 47.9 (d, $^2J_{CP}$ = 29.6 Hz, CH), 55.9 (d, $^1J_{CP}$ = 198.8 Hz, 1 C), 57.3 (s, CH$_2$), 148.2 (s, 1 C), 157.0 (s, 1 C), 168.3 (d, $^2J_{CP}$ = 17.5 Hz, 1 C) ppm. MS: *m*/*z* (%) = 447 (77) [M]$^+$, 404 (100). $C_{20}H_{42}N_5O_4P$ (447.55): calcd. C 53.67, H 9.46, N 15.65; found C 53.71, H 9.33, N 15.73.

Methyl 3-[(Anilinocarbonyl)hydrazono]-2-[bis(diisopropylamino)(methoxy)phosphoranylidene]butanoate (3g): Pale-yellow powder; yield: 336.3 mg (66%); m.p. 138–140 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.14 and 1.17 [2 d, *J* = 6.8 Hz, 24 H, 4 CH(C*H*$_3$)$_2$], 2.03 (s, 3 H, CH$_3$), 3.38 (s, 3 H, CO$_2$CH$_3$), 3.70–3.79 [m, 4 H, 4 C*H*(CH$_3$)$_2$], 3.73 (d, $^3J_{HP}$ = 11.6 Hz, 3 H, OCH$_3$), 6.95 (t, *J* = 8.0 Hz, 1 H, CH$_{arom}$), 7.24 (t, *J* = 8.0 Hz, 2 H, CH$_{arom}$), 7.41 (d, *J* = 8.0 Hz, 2 H, CH$_{arom}$), 8.24 (s, 1 H, NH), 9.24 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 14.7 (s, CH$_3$), 23.1 (d, $^3J_{CP}$ = 5.1 Hz, CH$_3$), 46.9 (d, $^2J_{CP}$ = 6.1 Hz, CH$_3$), 48.7 (d, $^2J_{CP}$ = 21.9 Hz, CH), 54.5 (s, CH$_3$), 56.2 (d, $^1J_{CP}$ = 198.8 Hz, 1 C), 118.4 (s, CH), 122.0 (s, CH), 128.7 (s, CH), 138.9 (s, 1 C), 150.0 (s, 1 C), 153.1 (s, 1 C), 168.4 (d, $^2J_{CP}$ = 17.5 Hz, 1 C) ppm. MS: *m*/*z* (%) = 509 (100) [M]$^+$. $C_{25}H_{44}N_5O_4P$ (509.22): calcd. C 58.92, H 8.70, N 13.74; found C 58.79, H 8.78, N 13.88.

Methyl 3-[(Aminocarbonyl)hydrazono]-2-[bis(diisopropylamino)(methoxy)phosphoranylidene]pentanoate (3h): White powder; yield: 292.0 mg (65%); m.p. 124–126 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.04–1.16 [m, 27 H, CH$_2$C*H*$_3$ and 4 CH(C*H*$_3$)$_2$], 2.31 (q, *J* = 7.6 Hz, 2 H, C*H*$_2$CH$_3$), 3.35 (s, 3 H, CO$_2$CH$_3$), 3.70–3.80 [m, 4 H, 4 C*H*(CH$_3$)$_2$], 3.74 (d, $^3J_{HP}$ = 11.6 Hz, 3 H, OCH$_3$), 5.74 and 6.17 (2 br. s, 2 H, NH$_2$), 8.71 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 9.8 (s, CH$_3$), 23.0 (d, $^3J_{CP}$ = 6.0 Hz, CH$_3$), 25.9 (s, CH$_2$), 46.5 (d, $^2J_{CP}$ = 6.8 Hz, CH$_3$), 49.0 (d, $^2J_{CP}$ = 30.0 Hz, CH), 54.2 (s, CH$_3$), 55.8 (d, $^1J_{CP}$ = 198.8 Hz, 1 C), 151.7 (s, 1 C), 156.8 (s, 1 C), 168.4 (d, $^2J_{CP}$ = 18.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 447 (79) [M]$^+$, 404 (100). $C_{20}H_{42}N_5O_4P$ (447.55): calcd. C 53.67, H 9.46, N 15.65; found C 53.66, H 9.21, N 15.58.

Ethyl 2-[Bis(diisopropylamino)(methoxy)phosphoranylidene]-3-[(*tert*-butoxycarbonyl)hydrazono]butanoate (3i): White powder; yield: 444.8 mg (88%); m.p. 124–126 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.07–1.15 [m, 27 H, CO$_2$CH$_2$C*H*$_3$ and 4 CH(C*H*$_3$)$_2$], 1.39 [s, 9 H, C(CH$_3$)$_3$], 1.93 (s, 3 H, CH$_3$), 3.69–3.81 [m, 4 H, 4 C*H*(CH$_3$)$_2$], 3.71 (d, $^3J_{HP}$ = 12.0 Hz, 3 H, OCH$_3$), 3.85 (q, *J* = 7.2 Hz, 2 H, CO$_2$C*H*$_2$CH$_3$), 8.90 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 14.7 (s, CH$_3$), 20.7 (s, CH$_3$), 23.2 (d, $^3J_{CP}$ = 5.8 Hz, CH$_3$), 29.1 (s, CH$_3$), 44.4 (d, $^2J_{CP}$ = 21.9 Hz, CH), 46.5 (d, $^2J_{CP}$ = 6.8 Hz, CH$_3$), 56.6 (d, $^1J_{CP}$ = 196.8 Hz, 1 C), 59.2 (s, CH$_2$), 80.1 (s, 1 C), 150.1 (s, 1 C), 153.7 (s, 1 C), 168.3 (d, $^2J_{CP}$ = 18.0 Hz, 1 C) ppm. MS: *m*/*z* (%) = 504 (58) [M]$^+$, 431 (100). $C_{24}H_{49}N_4O_5P$ (504.64): calcd. C 57.12, H 9.79, N 11.10; found C 57.21, H 9.83, N 11.13.

Methyl 3-[(Aminocarbonyl)hydrazono]-2-[tris(dimethylamino)phosphoranylidene]butanoate (3j): Pale-pink powder; yield: 271.1 mg (81%); m.p. 162–164 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.92 (d, $^4J_{HP}$ = 2.0 Hz, 3 H, CH$_3$), 2.55 [d, $^3J_{HP}$ = 9.6 Hz, 18 H, 3 N(CH$_3$)$_2$], 3.36 (s, 3 H, CO$_2$CH$_3$), 6.20 (br. s, 2 H, NH$_2$), 7.79 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 16.0 (s, CH$_3$), 37.4 (d, $^2J_{CP}$ = 4.6 Hz, CH$_3$), 38.0 (d, $^2J_{CP}$ = 4.5 Hz, CH$_3$), 46.1 (d, $^1J_{CP}$ = 188.1 Hz, 1 C), 50.0 (s, CH$_3$), 146.5 (s, $^2J_{CP}$

= 9.1 Hz, 1 C), 156.8 (s, 1 C), 166.8 (d, $^2J_{CP}$ = 16.0 Hz, 1 C) ppm. MS: *m*/*z* (%) = 334 (39) [M]$^+$, 317 (8), 303 (36), 260 (100). $C_{12}H_{27}N_6O_3P$ (334.35): calcd. C 43.11, H 8.14, N 25.14; found C 43.23, H 8.24, N 25.18.

Ethyl 3-[(Aminocarbonyl)hydrazono]-2-[tris(dimethylamino)phosphoranylidene]butanoate (3k): Pale-pink powder; yield: 392.7 mg (84%); m.p. 174–176 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.05 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.93 (d, $^4J_{HP}$ = 1.6 Hz, 3 H, CH_3), 2.55 [d, $^3J_{HP}$ = 9.6 Hz, 18 H, 3 $N(CH_3)_2$], 3.84 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 6.18 (br. s, 2 H, NH_2), 7.77 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.8 (s, CH_3), 20.7 (s, CH_3), 37.4 (d, $^2J_{CP}$ = 5.8 Hz, CH_3), 38.0 (d, $^2J_{CP}$ = 5.3 Hz, CH_3), 46.2 (d, $^1J_{CP}$ = 187.4 Hz, 1 C), 57.4 (s, CH_2), 146.6 (s, $^2J_{CP}$ = 9.9 Hz, 1 C), 156.8 (s, 1 C), 166.4 (d, $^2J_{CP}$ = 15.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 348 (1) [M]$^+$, 302 (4), 259 (100). $C_{13}H_{29}N_6O_3P$ (348.38): calcd. C 44.82, H 8.39, N 24.12; found C 44.91, H 8.43, N 24.31.

Methyl 3-[(Anilinocarbonyl)hydrazono]-2-[tris(dimethylamino)phosphoranylidene]butanoate (3l): Pale-pink powder; yield: 296.2 mg (72%); m.p. 102–104 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 2.02 (s, 3 H, CH_3), 2.56 [d, $^3J_{HP}$ = 9.6 Hz, 18 H, 3 $N(CH_3)_2$], 3.41 (s, 3 H, CO_2CH_3), 6.95–7.59 (m, 5 H, CH_{arom}), 8.39 (s, 1 H, NH), 9.14 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.3 (s, CH_3), 36.9 (d, $^2J_{CP}$ = 4.6 Hz, CH_3), 37.4 (d, $^2J_{CP}$ = 4.5 Hz, CH_3), 45.9 (d, $^1J_{CP}$ = 188.9 Hz, 1 C), 49.3 (s, CH_3), 118.9 (s, CH), 122.0 (s, CH), 128.5 (s, CH), 139.3 (s, 1 C), 147.6 (s, $^2J_{CP}$ = 9.9 Hz, 1 C), 152.4 (s, 1 C), 166.1 (d, $^2J_{CP}$ = 15.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 410 (2) [M]$^+$, 378 (10), 259 (100). $C_{18}H_{31}N_6O_3P$ (410.45): calcd. C 52.67, H 7.61, N 20.48; found C 52.73, H 7.75, N 20.31.

Ethyl 3-[(Anilinocarbonyl)hydrazono]-2-[tris(dimethylamino)phosphoranylidene]butanoate (3m): Pale-pink powder; yield: 327.2 mg (77%); m.p. 102–104 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.17 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 2.13 (s, 3 H, CH_3), 2.67 [d, $^3J_{HP}$ = 9.6 Hz, 18 H, 3 $N(CH_3)_2$], 4.01 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 6.96–7.54 (m, 5 H, CH_{arom}), 8.19 (s, 1 H, NH), 8.77 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.5 (s, CH_3), 20.9 (s, CH_3), 37.0 (d, $^2J_{CP}$ = 4.6 Hz, CH_3), 38.0 (d, $^2J_{CP}$ = 4.5 Hz, CH_3), 46.0 (d, $^1J_{CP}$ = 188.8 Hz, 1 C), 57.6 (s, CH_2), 118.8 (s, CH), 121.9 (s, CH), 128.7 (s, CH), 139.5 (s, 1 C), 147.3 (d, $^2J_{CP}$ = 9.9 Hz, 1 C), 152.8 (s, 1 C), 166.4 (d, $^2J_{CP}$ = 15.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 424 (1) [M]$^+$, 410 (81), 379 (30), 365 (11), 318 (100). $C_{19}H_{33}N_6O_3P$ (424.47): calcd. C 53.76, H 7.84, N 19.80; found C 53.81, H 7.91, N 19.72.

Methyl 3-[(Anilinocarbonyl)hydrazono]-2-[tris(dimethylamino)phosphoranylidene]pentanoate (3n): Pale-pink powder; yield: 304.9 mg (72%); m.p. 110–112 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.01 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 2.29 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 2.56 [d, $^3J_{HP}$ = 9.6 Hz, 18 H, 3 $N(CH_3)_2$], 3.38 (s, 3 H, CO_2CH_3), 6.94–7.56 (m, 5 H, CH_{arom}), 8.21 (s, 1 H, NH), 8.66 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 11.8 (s, CH_3), 22.8 (s, CH_2), 37.4 (d, $^2J_{CP}$ = 4.5 Hz, CH_3), 37.6 (d, $^2J_{CP}$ = 4.6 Hz, CH_3), 46.0 (d, $^1J_{CP}$ = 189.6 Hz, 1 C), 50.0 (s, CH_3), 119.7 (s, CH), 122.9 (s, CH), 129.3 (s, CH), 139.8 (s, 1 C), 152.3 (s, $^2J_{CP}$ = 9.1 Hz, 1 C), 153.2 (s, 1 C), 167.0 (d, $^2J_{CP}$ = 15.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 424 (50) [M]$^+$, 393 (11), 332 (58), 274 (100). $C_{19}H_{33}N_6O_3P$ (424.47): calcd. C 53.76, H 7.84, N 19.80; found C 53.66, H 7.94, N 19.69.

General Procedure for the Synthesis of 5-Oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles 4a–h with Sodium Hydride: α-Phosphoranylidene-hydrazones **3a**–**n** (1 mmol) were dissolved in a mixture of tetrahydrofuran (5 mL)/methanol (5 mL) at room temperature and a catalytic amount in the case of **3a**–**i** and a stoichiometric amount (1.0 mmol) in the case of **3k**–**n** of sodium hydride was added. The reaction mixture was magnetically stirred for 0.5–72.0 h until the disappearance of the starting compound **3**. 5-Oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles **4a**–**h** were obtained by column chromatography on silica gel (elution mixtures: ethyl acetate/methanol) and by subsequent crystallization from diethyl ether/light petroleum ether (40–60 °C).

General Procedure for the Synthesis of 5-Oxo-4-phoshoranylidene-4,5-dihydro-1*H*-pyrazoles 4f–h with Silica Gel: Phosphoranylidene-hydrazones **3j**–**n** (1 mmol) were dissolved in a mixture of tetrahydrofuran (9.5 mL)/methanol (0.5 mL) at room temperature, and silica gel (5 g) was added. The reaction mixture was magnetically stirred for 0.1–0.2 h until the disappearance of the starting compound **3**. The resin was removed by filtration, and the reaction solvents were evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel column (elution mixtures: ethyl acetate/methanol) to give 5-oxo-4-phosphoranylidene-4,5-dihydro-1*H*-pyrazoles **4f**–**h**, which were crystallized from diethyl ether/light petroleum ether (40–60 °C).

4-[Bis(benzyloxy)(diisopropylamino)phosphoranylidene]-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazole-1-carboxamide (4a): Pale-pink powder; yield: 324.9 mg (67%) from **3a**, 309.6 mg (64%) from **3b**; m.p. 190–192 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.19 [d, *J* = 6.8 Hz, 12 H, 2 $CH(CH_3)_2$], 2.06 (s, 3 H, CH_3), 3.32–3.64 [m, 2 H, 2 $CH(CH_3)_2$], 4.85–5.09 (m, 4 H, 2 OCH_2Ph), 6.29 and 9.25 (2 br. s, 2 H, NH_2), 7.33–7.38 (m, 10 H, CH_{arom}) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 16.0 (s, CH_3), 23.3 (d, $^3J_{CP}$ = 19.0 Hz, CH_3), 45.2 (d, $^2J_{CP}$ = 43.4 Hz, CH), 64.4 (d, $^2J_{CP}$ = 28.1 Hz, CH_2), 84.4 (d, $^1J_{CP}$ = 201.0 Hz, 1 C), 127.6 (s, CH), 127.8 (s, CH), 128.0 (s, CH), 128.3 (s, CH), 128.8 (s, CH), 128.9 (s, CH), 139.1 (d, $^3J_{CP}$ = 12.2 Hz, 1 C), 139.7 (d, $^3J_{CP}$ = 12.0 Hz, 1 C), 151.7 (s, 1 C), 153.9 (d, $^2J_{CP}$ = 5.1 Hz, 1 C), 167.4 (d, $^2J_{CP}$ = 19.6 Hz, 1 C) ppm. MS: *m*/*z* (%) = 484 (2) [M]$^+$, 470 (6), 152 (21), 125 (48), 111 (100). $C_{25}H_{33}N_4O_4P$ (484.52): calcd. C 61.97, H 6.86, N 11.56; found C 61.91, H 6.71, N 11.63.

4-[Bis(benzyloxy)(diisopropylamino)phosphoranylidene]-3-methyl-5-oxo-*N*-phenyl-4,5-dihydro-1*H*-pyrazole-1-carboxamide (4b): White powder; yield: 387.2 mg (69%) from **3c**, 419.8 mg (75%) from **3d**; m.p. 201–203 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.19 [d, *J* = 6.8 Hz, 12 H, 2 $CH(CH_3)_2$], 2.12 (s, 3 H, CH_3), 3.48–3.56 [m, 2 H, 2 $CH(CH_3)_2$], 4.86–4.96 (m, *J* = 11.6 Hz, 4 H, 2 OCH_2Ph), 6.99–7.55 (m, 15 H, CH_{arom}), 12.62 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 16.1 (s, CH_3), 23.4 (d, $^3J_{CP}$ = 15.2 Hz, CH_3), 45.2 (d, $^2J_{CP}$ = 43.0 Hz, CH), 64.4 (d, $^2J_{CP}$ = 28.1 Hz, CH_2), 84.5 (d, $^1J_{CP}$ = 205.0 Hz, 1 C), 118.4 (s, CH), 119.7 (s, CH), 123.1 (s, CH), 127.6 (s, CH), 127.7 (s, CH), 128.8 (s, CH), 120.0 (s, CH), 129.3 (s, CH), 129.6 (s, CH), 138.9 (s, 1 C), 139.3 (d, $^3J_{CP}$ = 12.2 Hz, 1 C), 139.6 (d, $^3J_{CP}$ = 12.2 Hz, 1 C), 150.7 (s, 1 C), 153.5 (d, $^2J_{CP}$ = 4.8 Hz, 1 C), 167.5 (d, $^2J_{CP}$ = 19.8 Hz, 1 C) ppm. MS: *m*/*z* (%) = 560 (1) [M]$^+$, 546 (5), 167 (22), 152 (24), 125 (57), 111 (100). $C_{31}H_{37}N_4O_4P$ (560.62): calcd. C 66.41, H 6.65, N 9.99; found C 66.33, H 6.78, N 9.79.

4-[Bis(diisopropylamino)(methoxy)phosphoranylidene]-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazole-1-carboxamide (4c): White powder; yield: 302.1 mg (75%) from **3e**, 273.8 mg (68%) from **3f**; m.p. 148–150 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.20 [d, *J* = 6.8 Hz, 12 H, 2 $CH(CH_3)_2$], 1.27 [d, *J* = 6.8 Hz, 12 H, 2 $CH(CH_3)_2$], 2.02 (s, 3 H, CH_3), 3.83–3.94 [m, 4 H, 4 $CH(CH_3)_2$], 3.89 (d, $^3J_{HP}$ = 12.0 Hz, 3 H, OCH_3), 6.84 and 8.70 (2 s, 2 H, NH_2) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 16.1 (s, CH_3), 23.1 (q, CH_3), 47.9 (d, $^2J_{CP}$ = 6.8 Hz, CH_3), 55.5 (d, $^2J_{CP}$ = 5.3 Hz, CH), 75.0 (d, $^{1}J_{CP}$ = 197.9 Hz, 1 C), 148.8 (d, $^{2}J_{CP}$ = 13.7 Hz, 1 C), 151.6 (s, 1 C), 167.8 (d, $^{2}J_{CP}$ = 25.0 Hz, 1 C) ppm. MS: *m*/*z* (%) = 401 (1) [M]$^{+}$, 358 (8), 315 (8), 258 (100). $C_{18}H_{36}N_5O_3P$ (401.48): calcd. C 53.85, H 9.04, N 17.44; found C 53.94, H 9.12, N 17.54.

4-[Bis(diisopropylamino)(methoxy)phosphoranylidene]-3-methyl-5-oxo-*N*-phenyl-4,5-dihydro-1*H*-pyrazole-1-carboxamide (4d): White powder; yield: 431.1 mg (90%); m.p. 150–152 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.20 [d, *J* = 6.8 Hz, 12 H, 2 CH(C*H*$_3$)$_2$], 1.31 [d, *J* = 6.8 Hz, 12 H, 2 CH(C*H*$_3$)$_2$], 2.11 (s, 3 H, CH$_3$), 3.87–3.96 [m, 4 H, 4 C*H*(CH$_3$)$_2$], 3.90 (d, $^{3}J_{HP}$ = 12.0 Hz, 3 H, OCH$_3$), 6.99–7.53 (m, *J* = 5 H, CH$_{arom}$), 11.95 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 16.2 (s, CH$_3$), 23.1 (d, $^{3}J_{CP}$ = 3.8 Hz, CH$_3$), 47.3 (d, $^{2}J_{CP}$ = 6.0 Hz, CH$_3$), 55.0 (d, $^{2}J_{CP}$ = 6.1 Hz, CH), 76.2 (d, $^{1}J_{CP}$ = 196.6 Hz, 1 C), 119.2 (s, CH), 122.9 (s, CH), 129.0 (s, CH), 138.3 (s, 1 C), 148.7 (d, $^{2}J_{CP}$ = 13.7 Hz, 1 C), 150.4 (s, 1 C), 167.8 (d, $^{2}J_{CP}$ = 25.0 Hz, 1 C) ppm. MS: *m*/*z* (%) = 477 (1) [M]$^{+}$, 358 (8), 258 (100). $C_{24}H_{40}N_5O_3P$ (477.58): calcd. C 60.36, H 8.44, N 14.66; found C 60.31, H 8.55, N 14.72.

***tert*-Butyl 4-[Bis(diisopropylamino)(methoxy)phosphoranylidene]-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazole-1-carboxylate (4e):** White powder; yield: 322.1 mg (70%); m.p. 151–153 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.30 [d, *J* = 6.8 Hz, 12 H, 2 CH(C*H*$_3$)$_2$], 1.34 [d, *J* = 6.8 Hz, 12 H, 2 CH(C*H*$_3$)$_2$], 1.61 [s, 9 H, C(CH$_3$)$_3$], 2.18 (d, $^{4}J_{HP}$ = 0.8 Hz, 3 H, CH$_3$), 3.88 (d, $^{3}J_{HP}$ = 12.0 Hz, 3 H, OCH$_3$), 3.90–3.98 [m, 4 H, 4 C*H*(CH$_3$)$_2$] ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 16.3 (s, CH$_3$), 20.9 (s, CH$_3$), 23.3 (s, CH$_3$), 46.8 (d, $^{2}J_{CP}$ = 6.8 Hz, CH$_3$), 54.0 (d, $^{2}J_{CP}$ = 6.8 Hz, CH), 76.1 (d, $^{1}J_{CP}$ = 196.6 Hz, 1 C), 80.1 (s, 1 C), 146.6 (d, $^{2}J_{CP}$ = 13.0 Hz, 1 C), 153.6 (s, 1 C), 169.5 (d, $^{2}J_{CP}$ = 21.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 458 (11) [M]$^{+}$, 359 (6), 315 (24), 258 (100). $C_{22}H_{43}N_4O_4P$ (458.57): calcd. C 57.62, H 9.45, N 12.22; found C 57.58, H 9.61, N 12.03.

3-Methyl-5-oxo-4-[tris(dimethylamino)phosphoranylidene]-4,5-dihydro-1*H*-pyrazole-1-carboxamide (4f): White powder; yield: 200.1 mg (66%) from **3j** and 204.9 mg (68%) from **3k** using NaH, 257.1 mg (85%) from **3j** and 244.5 mg (81%) from **3k** using silica gel; m.p. 174–176 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.98 (s, 3 H, CH$_3$), 2.65 [d, $^{3}J_{HP}$ = 10.0 Hz, 18 H, 3 N(CH$_3$)$_2$], 6.88 and 8.78 (2 br. s, 2 H, NH$_2$) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.3 (s, CH$_3$), 36.9 (d, $^{2}J_{CP}$ = 4.6 Hz, CH$_3$), 71.5 (d, $^{1}J_{CP}$ = 193.5 Hz, 1 C), 149.5 (s, $^{2}J_{CP}$ = 12.1 Hz, 1 C), 151.7 (s, 1 C), 168.2 (d, $^{2}J_{CP}$ = 22.8 Hz, 1 C) ppm. MS: *m*/*z* (%) = 302 (1) [M]$^{+}$, 259 (100). $C_{11}H_{23}N_6O_2P$ (302.31): calcd. C 43.70, H 7.67, N 27.80; found C 43.81, H 7.72, N 27.66.

3-Methyl-5-oxo-*N*-phenyl-4-[tris(dimethylamino)phosphoranylidene]-4,5-dihydro-1*H*-pyrazole-1-carboxamide (4g): White powder; yield: 338.1 mg (89%) from **3l** and 343.8 mg (91%) from **3m** using NaH, 307.1 mg (81%) from **3l** and 330.1 mg (87%) from **3m** using silica gel; m.p. 174–176 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 2.02 (s, 3 H, CH$_3$), 2.67 [d, $^{3}J_{HP}$ = 10.0 Hz, 18 H, 3 N(CH$_3$)$_2$], 7.04 (t, *J* = 7.6 Hz, 1 H, CH$_{arom}$), 7.30 (t, *J* = 7.6 Hz, 2 H, CH$_{arom}$), 7.49 (d, *J* = 7.6 Hz, 2 H, CH$_{arom}$), 11.98 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 16.0 (s, CH$_3$), 37.6 (d, $^{2}J_{CP}$ = 4.5 Hz, CH$_3$), 73.1 (d, $^{1}J_{CP}$ = 192.7 Hz, 1 C), 119.8 (s, CH), 123.5 (s, CH), 129.7 (s, CH), 139.2 (s, 1 C), 149.4 (s, 1 C), 151.2 (d, $^{2}J_{CP}$ = 12.1 Hz, 1 C), 169.0 (d, $^{2}J_{CP}$ = 22.7 Hz, 1 C) ppm. MS: *m*/*z* (%) = 378 (2) [M]$^{+}$, 259 (100). $C_{17}H_{27}N_6O_2P$ (378.40): calcd. C 53.96, H 7.19, N 22.21; found C 53.88, H 7.21, N 22.12.

3-Ethyl-5-oxo-*N*-phenyl-4-[tris(dimethylamino)phosphoranylidene]-4,5-dihydro-1*H*-pyrazole-1-carboxamide (4h): White powder; yield: 299.1 mg (76%) using NaH, 378.1 mg (86%) using silica gel; m.p. 144–146 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.20 (t, *J* = 7.6 Hz, 3 H, CH$_2$C*H*$_3$), 2.37 (q, *J* = 7.6 Hz, 2 H, C*H*$_2$CH$_3$), 2.68 [d, $^{3}J_{HP}$ = 9.6 Hz, 18 H, 3 N(CH$_3$)$_2$], 7.04 (t, *J* = 7.6 Hz, 1 H, CH$_{arom}$), 7.32 (t, *J* = 7.6 Hz, 2 H, CH$_{arom}$), 7.51 (d, *J* = 7.6 Hz, 2 H, CH$_{arom}$), 12.07 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 12.2 (s, CH$_3$), 22.4 (s, CH$_2$), 37.6 (d, $^{2}J_{CP}$ = 5.3 Hz, CH$_3$), 72.5 (d, $^{1}J_{CP}$ = 193.5 Hz, 1 C), 119.9 (s, CH), 123.5 (s, CH), 129.7 (s, CH), 139.2 (s, 1 C), 149.5 (s, 1 C), 155.6 (d, $^{2}J_{CP}$ = 12.1 Hz, 1 C), 168.9 (d, $^{2}J_{CP}$ = 22.7 Hz, 1 C) ppm. MS: *m*/*z* (%) = 392 (5) [M]$^{+}$, 349 (1), 273 (100). $C_{18}H_{29}N_6O_2P$ (392.43): calcd. C 55.09, H 7.45, N 21.42; found C 55.18, H 7.67, N 21.53.

General Procedure for the Synthesis of (*E*)-Hydrazono-phosphonates 5a–d Starting from 1,2-Diaza-1,3-butadienes (Scheme 1, Path b): 1,2-Diaza-1,3-butadienes **1a**–**d** (1 mmol) as a mixture of (*E*)/(*Z*) isomers[17] and dibenzyl diisopropylphosphoramidite (**2a**) (4 mmol) were magnetically stirred at room temperature for 3.0–4.5 h until the red colour of the starting compound **1** disappeared and α-phosphoranylidene-hydrazones **3a**–**d** precipitated from the reaction medium. Then the temperature of the reaction mixture was raised to 40 °C, and the mixture was allowed to stand under these conditions for 7.0–12.0 h. (*E*)-Hydrazono-phosphonates **5a**–**d** were obtained by column chromatography on silica gel (elution mixtures: ethyl acetate/methanol). Further purification of these compounds was achieved by crystallization from ethyl acetate/light petroleum ether (40–60 °C).

General Procedure for the Synthesis of (*E*)-Hydrazono-phosphonates 5a–d Starting from α-Phosphoranylidene-hydrazones 3a–d (Scheme 1, Path c): A solution of α-phosphoranylidene-hydrazones **3a**–**d** (1 mmol) in methanol (9.5 mL)/water (0.5 mL) was magnetically stirred for 7.0–27.0 h until TLC revealed the disappearance of the starting compound **3**. The mixture was then dried with anhydrous sodium sulfate and, after evaporation of the solvent, purified by chromatography on a silica gel column (elution mixtures: ethyl acetate/methanol) to give hydrazono-phosphonates **5a**–**d** in good purity. Further purification of these compounds was achieved by crystallization from ethyl acetate/light petroleum ether (40–60 °C).

Methyl 3-[(Aminocarbonyl)hydrazono]-2-[(benzyloxy)(diisopropylamino)phosphoryl]butanoate (5a): Pale-pink powder; yield: 332.8 mg (78%) by path b, 290.1 mg (68%) by path c; m.p. 140–142 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.06 [d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.17 [d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 2.04 (d, $^{4}J_{HP}$ = 2.8 Hz, 3 H, CH$_3$), 3.32–3.39 [m, 2 H, 2 C*H*(CH$_3$)$_2$], 3.55 (s, 3 H, CO$_2$CH$_3$), 4.08 (d, $^{1}J_{HP}$ = 20.4 Hz, 1 H, CH), 4.94 (2 dd, *J* = 7.2, $^{3}J_{HP}$ = 12.4 Hz, 2 H, OC*H*$_2$Ph), 6.29 (br. s, 2 H, NH$_2$), 7.30–7.39 (m, 5 H, CH$_{arom}$), 9.25 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 15.9 (d, $^{3}J_{CP}$ = 8.3 Hz, CH$_3$), 22.3 (d, $^{3}J_{CP}$ = 23.6 Hz, CH$_3$), 23.9 (d, $^{3}J_{CP}$ = 19.7 Hz, CH$_3$), 46.3 (s, CH), 52.7 (s, CH$_3$), 56.3 (d, $^{1}J_{CP}$ = 119.1 Hz, CH), 65.3 (d, $^{2}J_{CP}$ = 6.1 Hz, CH$_2$), 127.9 (s, CH), 128.5 (s, CH), 129.0 (s, CH), 137.6 (d, $^{3}J_{CP}$ = 6.8 Hz, 1 C), 141.3 (d, $^{2}J_{CP}$ = 6.1 Hz, 1 C), 157.6 (s, 1 C), 167.8 (d, $^{2}J_{CP}$ = 5.3 Hz, 1 C) ppm. MS: *m*/*z* (%) = 426 (48) [M]$^{+}$, 411 (8), 395 (1), 383 (4), 368 (18), 351 (34), 336 (15), 326 (27), 309 (6), 294 (7), 283 (13), 272 (100). $C_{19}H_{31}N_4O_5P$ (426.44): calcd. C 53.51, H 7.33, N 13.14; found C 53.66, H 7.23, N 13.01.

Ethyl 3-[(Aminocarbonyl)hydrazono]-2-[(benzyloxy)(diisopropylamino)phosphoryl]butanoate (5b): Pale-pink powder; yield: 383.9 mg (87%) by path b, 274.0 mg (62%) by path c; m.p. 150–152 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.04 (t, *J* = 7.2 Hz, 3 H, CO$_2$CH$_2$C*H*$_3$), 1.08 [d, *J* = 7.2 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.19 [d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$], 2.07 (s, 3 H, CH$_3$), 3.32–3.41 [m, 2 H, 2 C*H*(CH$_3$)$_2$], 4.00–4.08 (m, 3 H, CO$_2$C*H*$_2$CH$_3$ and CH), 4.87–4.90 and 5.02–5.05 (2 m, 2 H, OCH_2Ph), 6.29 (br. s, 2 H, NH_2), 7.30–7.39 (m, 5 H, CH_{arom}), 9.23 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $[D_6]DMSO$, 25 °C): δ = 13.7 (s, CH_3), 15.3 (d, $^3J_{CP}$ = 8.1 Hz, CH_3), 21.6 (d, $^3J_{CP}$ = 21.2 Hz, CH_3), 23.2 (d, $^3J_{CP}$ = 18.2 Hz, CH_3), 45.6 (s, CH), 55.7 (d, $^1J_{CP}$ = 119.1 Hz, CH), 60.9 (s, CH_2), 64.5 (d, $^2J_{CP}$ = 6.1 Hz, CH_2), 127.2 (s, CH), 127.8 (s, CH), 128.2 (s, CH), 136.8 (d, $^3J_{CP}$ = 6.8 Hz, 1 C), 140.8 (d, $^2J_{CP}$ = 6.1 Hz, 1 C), 156.9 (s, 1 C), 166.6 (d, $^2J_{CP}$ = 5.3 Hz, 1 C) ppm. MS: *m*/*z* (%) = 440 (17) $[M]^+$, 425 (8), 382 (18), 370 (43), 340 (39), 297 (15), 272 (100). $C_{20}H_{33}N_4O_5P$ (440.47): calcd. C 54.54, H 7.55, N 12.72; found C 54.61, H 7.58, N 12.88.

Methyl 3-[(Anilinocarbonyl)hydrazono]-2-[(benzyloxy)(diisopropylamino)phosphoryl]butanoate (5c): White powder; yield: 337.2 mg (67%) by path b, 331.4 mg (66%) by path c; m.p. 198–200 °C. ^1H NMR (400 MHz, $[D_6]DMSO$, 25 °C): δ = 1.09 [d, *J* = 6.4 Hz, 6 H, $CH(CH_3)_2$], 1.20 [d, *J* = 6.0 Hz, 6 H, $CH(CH_3)_2$], 2.13 (s, 3 H, CH_3), 3.30–3.40 [m, 2 H, 2 $CH(CH_3)_2$], 3.59 (s, 3 H, CO_2CH_3), 4.43 (d, $^1J_{HP}$ = 20.4 Hz, 1 H, CH), 4.89–4.93 and 5.04–5.07 (2 m, 2 H, OCH_2Ph), 6.98 (t, *J* = 6.8 Hz, 1 H, CH_{arom}), 7.25–7.39 (m, 8 H, CH_{arom}), 7.57 (d, *J* = 7.6 Hz, 1 H, CH_{arom}), 8.89 (s, 1 H, NH), 9.82 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $[D_6]DMSO$, 25 °C): δ = 15.5 (d, $^3J_{CP}$ = 8.3 Hz, CH_3), 21.8 (d, $^3J_{CP}$ = 21.6 Hz, CH_3), 23.1 (d, $^3J_{CP}$ = 19.2 Hz, CH_3), 45.6 (s, CH), 52.1 (s, CH_3), 55.1 (d, $^1J_{CP}$ = 119.9 Hz, CH), 64.7 (d, $^2J_{CP}$ = 6.1 Hz, CH_2), 118.9 (s, CH), 122.2 (s, CH), 127.2 (s, CH), 127.8 (s, CH), 127.9 (s, CH), 128.2 (s, CH), 136.8 (d, $^3J_{CP}$ = 6.8 Hz, 1 C), 139.1 (s, 1 C), 141.9 (d, $^2J_{CP}$ = 6.1 Hz, 1 C), 153.2 (s, 1 C), 167.2 (d, $^2J_{CP}$ = 5.3 Hz, 1 C) ppm. MS: *m*/*z* (%) = 502 (35) $[M]^+$, 410 (81), 247 (100). $C_{25}H_{35}N_4O_5P$ (502.54): calcd. C 59.75, H 7.02, N 11.15; found C 59.90, H 7.11, N 11.29.

Ethyl 3-[(Anilinocarbonyl)hydrazono]-2-[(benzyloxy)(diisopropylamino)phosphoryl]butanoate (5d): White powder; yield: 360.9 mg (70%) by path b, 393.1 mg (76%) by path c; m.p. 208–210 °C. ^1H NMR (400 MHz, $[D_6]DMSO$, 25 °C): δ = 1.06 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.10 [d, *J* = 6.0 Hz, 6 H, $CH(CH_3)_2$], 1.20 [d, *J* = 6.0 Hz, 6 H, $CH(CH_3)_2$], 2.13 (s, 3 H, CH_3), 3.35–3.43 [m, 2 H, 2 $CH(CH_3)_2$], 4.01–4.06 (m, 2 H, $CO_2CH_2CH_3$), 4.40 (d, *J* = 6.8 Hz, 1 H, CH), 4.87–4.90 and 5.02–5.06 (2 m, 2 H, OCH_2Ph), 6.99 (t, *J* = 6.8 Hz, 1 H_{arom}), 7.27–7.39 (m, 8 H, CH_{arom}), 7.57 (d, *J* = 6.8 Hz, 1 H_{arom}), 8.89 (s, 1 H, NH), 9.80 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $[D_6]DMSO$, 25 °C): δ = 13.7 (s, CH_3), 15.2 (d, $^3J_{CP}$ = 8.8 Hz, CH_3), 21.7 (d, $^3J_{CP}$ = 21.8 Hz, CH_3), 23.1 (d, $^3J_{CP}$ = 19.0 Hz, CH_3), 45.6 (s, CH), 55.2 (d, $^1J_{CP}$ = 119.1 Hz, CH), 61.0 (s, CH_2), 64.6 (d, $^2J_{CP}$ = 6.1 Hz, CH_2), 118.9 (s, CH), 122.3 (s, CH), 127.3 (s, CH), 127.8 (s, CH), 127.9 (s, CH), 128.3 (s, CH), 137.0 (d, $^3J_{CP}$ = 6.8 Hz, 1 C), 139.1 (s, 1 C), 142.1 (d, $^2J_{CP}$ = 6.1 Hz, 1 C), 153.3 (s, 1 C), 166.7 (d, $^2J_{CP}$ = 5.3 Hz, 1 C) ppm. MS: *m*/*z* (%) = 516 (39) $[M]^+$, 424 (71), 261 (100). $C_{26}H_{37}N_4O_5P$ (516.56): calcd. C 60.45, H 7.22, N 10.85; found C 60.33, H 7.29, N 10.69.

General Procedure for the Synthesis of (3-Oxo-2,3-dihydro-1*H*-pyrazol-4-yl)phosphonamidates 6a and 7a: (*E*)-Hydrazono-phosphonates **5a**–**d** (1 mmol) were dissolved in a mixture of tetrahydrofuran (5 mL)/methanol (5 mL), and a catalytic amount of sodium hydride (0.1 mmol) was added. The reaction mixture was magnetically stirred for 0.1–1.0 h until the disappearance of the starting compound **5**. Benzyl *N*,*N*-diisopropyl-*P*-(5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)phosphonamidate (**6a**) was obtained from **5a**,**b**, and benzyl *P*-[2-(anilinocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-*N*,*N*-diisopropylphosphonamidate (**7a**) was obtained from **5c**,**d**. Products **6a** and **7a** were purified by column chromatography on silica gel (elution mixtures: ethyl acetate/methanol) and by subsequent crystallization from diethyl ether/light petroleum ether (40–60 °C).

Benzyl *N*,*N*-Diisopropyl-*P*-(5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)phosphonamidate (6a): Pale-pink powder; yield: 225.1 mg (64%) from **5a**, 234.9 mg (67%) from **5b**; m.p. 177–179 °C. ^1H NMR (400 MHz, $[D_6]DMSO$, 25 °C): δ = 1.09 [d, *J* = 6.0 Hz, 6 H, $CH(CH_3)_2$], 1.15 [d, *J* = 6.4 Hz, 6 H, $CH(CH_3)_2$], 2.10 (s, 3 H, CH_3), 3.37–3.50 [m, 2 H, 2 $CH(CH_3)_2$], 4.81–4.85 (m, 2 H, OCH_2Ph), 6.91 (br. s, 1 H, NH), 7.25–7.43 (m, 5 H, CH_{arom}), 9.09 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $[D_6]DMSO$, 25 °C): δ = 15.2 (s, CH_3), 22.6 (d, $^3J_{CP}$ = 19.8 Hz, CH_3), 44.4 (d, $^2J_{CP}$ = 5.3 Hz, CH), 63.6 (d, $^2J_{CP}$ = 5.0 Hz, CH_2), 65.8 (d, $^1J_{CP}$ = 95.1 Hz, 1 C), 126.98 (s, CH), 128.1 (s, CH), 128.9 (s, CH), 138.9 (d, $^3J_{CP}$ = 5.9 Hz, 1 C), 152.8 (d, $^2J_{CP}$ = 12.3 Hz, 1 C), 166.1 (d, $^2J_{CP}$ = 9.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 351 (14) $[M]^+$, 283 (11), 265 (11), 258 (100). $C_{17}H_{26}N_3O_3P$ (351.38): calcd. C 58.11, H 7.46, N 11.96; found C 58.23, H 7.39, N 12.03.

Benzyl *P*-[2-(Anilinocarbonyl)-5-methyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl]-*N*,*N*-diisopropylphosphonamidate (7a): White powder; yield: 353.3 mg (75%) from **5c**, 362.0 mg (77%) from **5d**; m.p. 202–204 °C. ^1H NMR (400 MHz, $[D_6]DMSO$, 25 °C): δ = 1.11 [d, *J* = 6.4 Hz, 6 H, $CH(CH_3)_2$], 1.19 [d, *J* = 6.8 Hz, 6 H, $CH(CH_3)_2$], 2.14 (s, 3 H, CH_3), 3.42–3.53 [m, 2 H, 2 $CH(CH_3)_2$], 4.86–4.97 (m, 2 H, OCH_2Ph), 7.01 (t, *J* = 6.8 Hz, 1 H, CH_{arom}), 7.26–7.55 (m, 9 H, CH_{arom}), 12.63 (2 s, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, $[D_6]DMSO$, 25 °C): δ = 15.3 (s, CH_3), 22.7 (d, $^3J_{CP}$ = 15.9 Hz, CH_3), 44.4 (d, $^2J_{CP}$ = 5.3 Hz, CH), 63.6 (d, $^2J_{CP}$ = 4.6 Hz, CH_2), 65.2 (d, $^1J_{CP}$ = 93.3 Hz, 1 C), 117.7 (s, CH), 119.0 (s, CH), 122.4 (s, CH), 126.8 (s, CH), 128.0 (s, CH), 128.9 (s, CH), 138.9 (d, $^3J_{CP}$ = 5.9 Hz, 1 C), 139.3 (s, 1 C), 149.8 (s, 1 C), 152.7 (d, $^2J_{CP}$ = 12.3 Hz, 1 C), 166.8 (d, $^2J_{CP}$ = 9.2 Hz, 1 C) ppm. MS: *m*/*z* (%) = 470 (1) $[M]^+$, 426 (27), 351 (100). $C_{24}H_{31}N_4O_4P$ (470.50): calcd. C 61.27, H 6.64, N 11.91; found C 61.34, H 6.81, N 11.88.

X-ray Crystallography of Compound 4c: Single crystals of **4c** were obtained by dissolving a few milligrams of powder in dioxane and allowing the solution to concentrate at room temperature. A Siemens P4 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and the ω-scan technique were used for data collection. The structure was solved by direct methods implemented in the SHELXS-97 program.[18] Refinement was carried out by full-matrix anisotropic least-squares methods on F^2 for all reflections for non-hydrogen atoms by using the SHELXL-97 program.[19]

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