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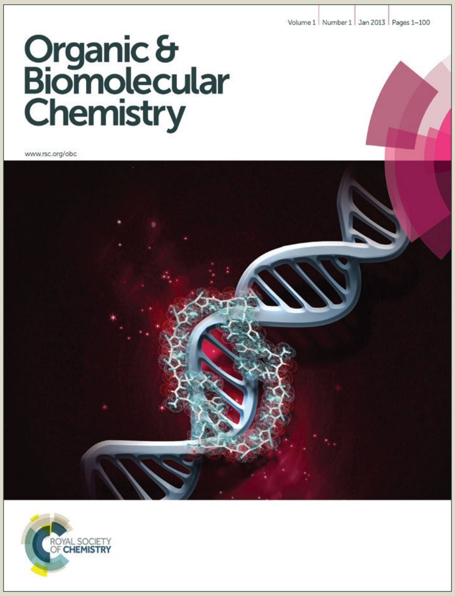

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ARTICLE

Base Mediated 1,3-Dipolar Cycloaddition of α-Substituted Vinyl Phosphonates with Diazo Compounds for Synthesis of 3-Pyrazolylphosphonates and 5-Pyrazolcarboxylates

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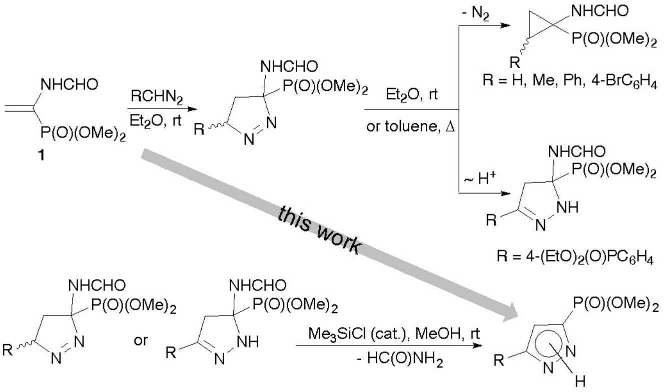
Nataliya S. Goulioukina,*[a,b] Nikolay N. Makukhin,[a] Egor D. Shinkarev,[a] Yuri K. Grishin,[a] Vitaly A. Roznyatovsky,[a] Irina P. Beletskaya*[a,b]

5-Aryl-substituted pyrazol-3-ylphosphonates have been conveniently synthesized by 1,3-dipolar cycloaddition of 1-formamidovinylphosphonate and aryldiazomethanes under K_2CO_3/MeOH conditions at room temperature. These pyrazoles are formed in one pot *via* spontaneous elimination of formamide. Basic conditions prevent competitive formation of cyclopropylphosphonates. 3-Aryl substituted pyrazol-5-carboxylates can be synthesized by the same methodology from 1-arylvinylphosphonates and ethyl diazoacetate, although the stronger base NaH is necessary to ensure the success of the aromatization stage with the elimination of diethoxylphosphoryl moiety.

Introduction

The pyrazole moiety is regarded as a privileged heterocyclic skeleton with multifarious applications. Pyrazoles represent the core structure of numerous naturally occurring molecules (e.g., pyrazol-3(5)-carboxylic acid from the sponge *Tedania anhelans*, (*S*)-β-pyrazolylalanine from *Citrullus vulgaris*, and alkaloid Withasomnine from Indian medicinal plant *Withania Somnifera*),[1] pharmaceuticals (e.g., the marketed drugs Celebrex and Viagra), and crop protection agents.[2] Pyrazoles are also efficient coordinating ligands in catalysis[3] and supramolecular chemistry.[4] Among various functionalized pyrazoles, pyrazolylphosphonates have received considerable attention over the past decade due to their remarkable bioactivity profiles[5] and possible applications as organic precursors.[6] An increasing interest in pyrazolylphosphonates has been reflected by the development of various synthetic methodologies allowing straightforward access to these structural motifs, however, the main focus had been on 4-pyrazolylphosphonates,[7] while 3(5)-pyrazolylphosphonates[8] received much less attention. A remarkable progress had been initiated by pioneering work of Namboothiri et al. who proposed to employ the Bestmann-Ohira reagent as a 1,3-dipolar precursor in base-mediated cycloaddition reactions with conjugated nitroalkenes.[9] This methodology was further extended on a variety of dipolarophiles and nowadays presents the most developed synthetic route to 3(5)-pyrazolylphosphonates.[8,10,11] By contrast, the alternative approach utilizing α,β-unsaturated phosphonates as cycloaddition partners has been scarcely reported, is frequently complicated by competitive formation of cyclopropylphosphonates, and thus remains a challenging task.

Recently we have reported an efficient approach to the synthesis of 2-substituted 1-aminocyclopropylphosphonates based on the regioselective 1,3-dipolar cycloaddition reaction of diazo compounds with dimethyl 1-formamidovinylphosphonate (**1**) (Scheme 1).[12,13] The reaction pathway involves the formation of 1-pyrazoline. The subsequent elimination of a nitrogen molecule affords the cyclopropane ring. However in the case of (4-diethoxyphosphorylphenyl)diazomethane containing a strong electron-acceptor substituent in the ring,[14] the major reaction product is 2-pyrazoline, which is resistant to nitrogen extrusion. It was also shown that the aromatization of 1- and 2-pyrazolines in acidic media is accompanied by the elimination of formamide to give in 3-pyrazolylphosphonates.



Scheme 1 Summary of our previous results on 1,3-dipolar cycloaddition reaction of vinylphosphonate **1** with diazo compounds.

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[a] *Department of Chemistry, Moscow State University, Leninskie Gory, GSP-1, 119991 Moscow, Russian Federation.* E-mail: *goulioukina@org.chem.msu.ru*
[b] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr. 31, 119071 Moscow, Russian Federation*

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In the present work, the possibility to give a new turn to the general reaction scheme and to adapt it for the target one-pot synthesis of 3(5)-phosphonylated pyrazoles was demonstrated. All one has to do is to provide conditions for the fast isomerization of the initially formed 1-pyrazoline to 2-pyrazoline (thus suppressing the possibility of nitrogen extrusion with cyclopropane formation) and the elimination of formamide. Both steps would be expected to be catalyzed by base.[15,16] Therefore the preliminary optimization of the reaction conditions included the variation of bases and solvents.

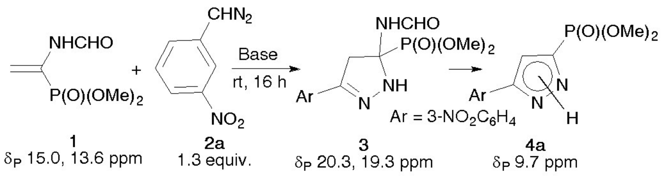
Results and discussion

Reasonably stable and, hence, easy to handle (3-nitrophenyl)diazomethane (**2a**) was chosen as a model diazo compound. The reaction course was monitored using the ^{31}P NMR method by the disappearance of signals from two rotamers of vinylphosphonate **1** at δ_P 15.0 and 13.6 ppm[17] and accumulation of signals from the products. The obtained results presented in Table 1 show that the reaction of **1** with 1.3 equiv. of **2a** in ether in the presence of 10 mol% K_2CO_3 is completed in 16 h and affords almost exclusively 2-pyrazoline **3** (two rotamers in a ratio of 86 : 14; δ_P 20.3 and 19.3 ppm), which precipitates (entry 1). The yield of pyrazolylphosphonate **4a** (δ_P 9.7 ppm) was only 3% and increased to 25% when the experiment was repeated in CH_2Cl_2 in which all reaction products are soluble (entry 2). The use of MeOH turned out to be the most productive: in this case, the yield of target pyrazole **4a** was 89% (entry 3). Note that in all experiments the conversion of vinylphosphonate **1** was close to quantitative, which is consistent with the known fact that the rate of 1,3-dipolar cycloaddition is almost insensitive to the polarity of the medium.[18] In all experiments the formation of dimethyl 1-formamido-2-(3-nitrophenyl)cyclopropylphosphonates (δ_P 23.3 and 22.7 ppm for the *cis*-isomer and δ_P 25.7 and 24.9 ppm for the *trans*-isomer) was detected, but their total yield did not exceed 2%.

The variation of bases showed that the replacement of K_2CO_3 by Cs_2CO_3 (entry 4), K_3PO_4 (entry 5), or MeONa (entry 6) exerted almost no effect on the yield of the target product **4a** and, therefore, cheaper potash was used in further experiments.

The absence of noticeable effect of the nature of the base and a rather strong solvent effect are consistent with the proposed reaction mechanism (Scheme 2), according to which the rate determining stage of 1,3-dipolar cycloaddition leads to 1-pyrazoline formation. The base initiates the fast isomerization of 1-pyrazoline to thermodynamically more stable conjugated 2-pyrazoline. The role of alcohol is more probably the protonation of the leaving group at the next step of formamide elimination rather than an increase in the solubility of an inorganic base.[19]

Table 1 Optimization of the reaction conditions for preparation of pyrazolylphosphonate **4a**[a]

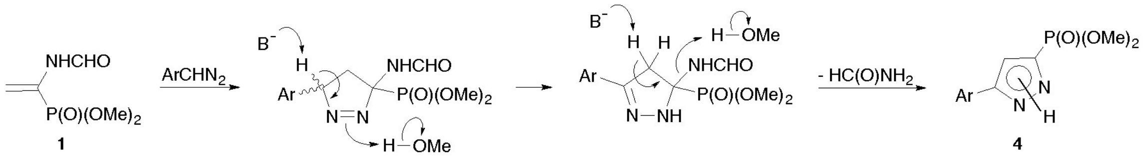


Entry	Solvent	Base	Conversion of **1**[b] (%)	Yield[b,c] (%)	
				3	4a
1	Et_2O	K_2CO_3	96	87(79)	3
2	CH_2Cl_2	K_2CO_3	98	68	25
3	MeOH	K_2CO_3	98	1	89(76)
4	MeOH	Cs_2CO_3	99	5	84
5	MeOH	K_3PO_4	99	5	86
6	MeOH	MeONa	99	3	89

[a] Reaction conditions: **1** (0.25 mmol), **2a** (0.325 mmol), base (10 mol%), solvent (0.65 ml), rt, 16 h. [b] Determined by ^{31}P NMR analysis of the crude reaction mixture. [c] Isolated yields are given in the parentheses.

Under the optimal conditions found, a large series of aryldiazomethanes **2a-p** containing both acceptor and donor substituents in the ring were introduced into the reaction with vinylphosphonate **1**, and the corresponding 5-aryl-substituted dimethyl (1*H*-pyrazol-3-yl)phosphonates **4a-p** were obtained in high yields after chromatographic purification (Table 2). Commenting on the obtained results, two points should be mentioned. First, the reaction time, required for quantitative conversion of vinylphosphonate **1**, is noticeably longer in case of aryldiazomethanes containing strong electron-acceptor substituents in the ring, especially **2b**.[20] The same concerns the sterically hindered aryldiazomethanes **2e,f** containing *ortho*-substituents. These two factors are combined in (2,4-dinitrophenyl)diazomethane, which turned out to be completely inert under the reaction conditions. The second point is the necessity to use a substantial excess of aryldiazomethanes with electron-donor substituents in the ring (e.g., 4-EtO (**2p**), 4-MeO (**2o**), and 4-*i*-Pr (**2n**)), since these diazo compounds are noticeably decomposed during the reaction to form substituted *cis*- and *trans*-stilbenes and dibenzylidenehydrazines.[21] Not unexpectedly, the amount of cyclopropanes increases to 9-10% of total yield, since the donor substituents should impede the proton transfer and isomerization of 1-pyrazoline to 2-pyrazoline.

The structure of pyrazolylphosphonate **4c** was unambiguously proved by the X-ray diffraction analysis data (Fig. 1).[13,22] In the ^{1}H NMR spectra of pyrazolylphosphonates **4**



Scheme 2 Proposed pathway for pyrazolylphosphonates **4** formation.

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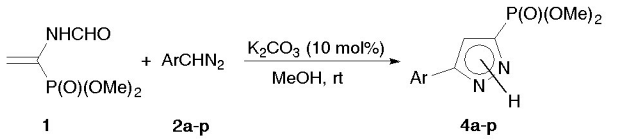
Table 2 Preparation of 5-aryl substituted dimethyl (1*H*-pyrazol-3-yl)phosphonates **4**[a]



Entry	**2** (equiv.)	Ar	Product	Reaction time (h)[b]	Yield of **4** (%)[c]
1	**2a** (1.3)	3-$NO_2C_6H_4$	**4a**	16	76
2	**2b** (1.3)	4-$NO_2C_6H_4$	**4b**	30	72
3	**2c** (1.5)	4-$(EtO)_2P(O)C_6H_4$	**4c**	24	79
4	**2d** (1.5)	4-$MeO_2CC_6H_4$	**4d**	18	78
5	**2e** (1.4)	2-ClC_6H_4	**4e**	17	63
6	**2f** (1.3)	2-BrC_6H_4	**4f**	16	54
7	**2g** (1.3)	3-ClC_6H_4	**4g**	12	78
8	**2h** (1.3)	4-ClC_6H_4	**4h**	4	87
9	**2i** (1.4)	4-BrC_6H_4	**4i**	3	87
10	**2j** (3)	4-$MeSC_6H_4$	**4j**	3	86
11	**2k** (3)	3-$MeOC_6H_4$	**4k**	3	71
12	**2l** (1.3)	Ph	**4l**	3	85(91)[d]
13	**2m** (1.5)	4-FC_6H_4	**4m**	3	67
14	**2n** (4)	4-i-PrC_6H_4	**4n**	3	80
15	**2o** (2)	4-$MeOC_6H_4$	**4o**	3	76
16	**2p** (1.6)	4-$EtOC_6H_4$	**4p**	2	63

[a] Reaction conditions: **1** (0.25 mmol), **2** (equiv., 0.5 M solution in MeOH), K_2CO_3 (10 mol%), rt, 16 h. [b] Time to completion, estimated by ^{31}P MNR. [c] Isolated yield. [d] The yield in the reaction performed on a 2.5 mmol scale is given in the parentheses.

the doublet of the C(4)H proton of the pyrazole ring at δ_H 6.8–7.3 ppm ($^3J_{PH}$ = 1.8–2.4 Hz) is characteristic. The analysis of the ^{13}C NMR spectra is complicated by the fact that the signals of the carbon atoms of the pyrazole ring and *ipso*-carbon of the aryl fragment are broadened, which is explained by prototropic ring tautomerism in the solution.[11b,c,15,23] The detection of a doublet of the quaternary carbon atom bound to phosphorus and lying at δ_C 132.7–138.0 ppm ($^1J_{PC}$ = 220–229 Hz) was particularly difficult. The unambiguous assignment was made on the basis of 2D NMR spectroscopy HMBC experiments, which makes it possible to observe cross peaks arising from the $^2J_{CH}$ coupling constants between the C(4)H proton and the carbon atoms C(3) and C(5).

Ethyl diazoacetate reacts with vinylphosphonate **1** only at elevated temperatures. At 80 °C without solvent, the main reaction product was 2-pyrazoline **5**, which was isolated chromatographically in 80% yield (Table 3, entry 1). The temperature decrease to 50 °C results in a decrease in the reaction rate (entry 2), and the use of the solvent (EtOH in the presence of 10 mol% K_2CO_3 (entry 3) or PhMe (entry 4)) induces the dramatic decrease in the selectivity of the process.

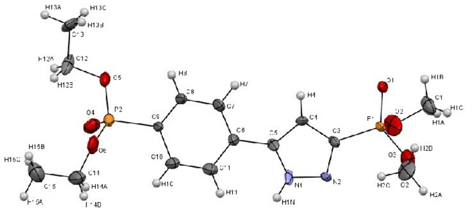
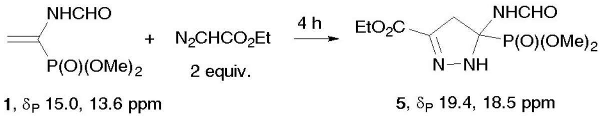


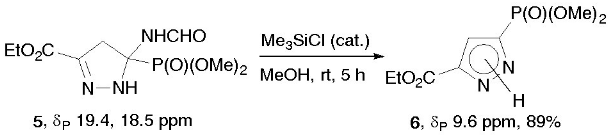
Fig. 1 Single X-ray crystal structure of **4c** (CCDC 959780). Thermal ellipsoids are drawn at a 50% probability.

Table 3 Optimization studies on the reaction of vinylphosphonate **1** with ethyl diazoacetate[a]



Entry	Solvent	T (°C)	Conversion of **1** (%)[b]	Yield of **5** (%)[b,c]
1	None	**80**	100	85(80)
2	None	50	64	59
3	EtOH[d]	80	66	20
4	PhMe	80	59	12

[a] Reaction conditions: **1** (0.28 mmol), N_2CHCO_2Et (0.56 mmol), 4 h. [b] Determined by ^{31}P NMR analysis of the crude reaction mixture. [c] Isolated yield after column chromatography is given in the parentheses. [d] In the presence of K_2CO_3 (10 mol%).



Scheme 3 Aromatization of 2-pyrazoline **5** with pyrazolylphosphonate **6** formation.

An attempt to aromatize 2-pyrazoline **5** under the conditions used in the synthesis of pyrazolylphosphonates **4** (MeOH, K_2CO_3, 20 °C) was unsuccessful: the reaction proceeded very slowly and was accompanied by the transesterification of the ester fragment. Pyrazolylphosphonate **6**[5c] was obtained in high yield when the reaction was carried out in methanol with addition of a catalytic amount of Me_3SiCl (Scheme 3).

It is worthy of note that no elimination of diethyl phosphite was observed in the reactions of vinyl phosphonate **1** with diazo compounds. Meanwhile, rare examples for the aromatization of phosphonylated pyrazolines with the formation of pyrazole due to the C-P bond cleavage are briefly mentioned in literature.[24] We employed this possibility in the synthesis of 3-aryl-substituted 1*H*-pyrazole-5-carboxylates,[25,26] viz., carboxyl analogs of pyrazolylphosphonates **4**. Diethyl 1-arylvinylphosphonates **7** available by the Conant reaction served as the starting dipolarophiles.[27]

The synthesis conditions were optimized for the model diethyl 1-phenylvinylphosphonate (**7a**). The reaction course was monitored by ^{31}P and ^1H NMR spectroscopy. On heating at 50 °C of a solution of vinylphosphonate **7a** and ethyl diazoacetate (2 equiv.) in THF in presence of NaH (2.5 equiv.), the reaction took 18 h for completion. After neutralization of the reaction mixture with a solution of HCl in ether followed by treatment with triethylamine, the target pyrazolecarboxylate **9a** was isolated chromatographically in 82% yield (Table 4, entry 1).

The reaction mechanism (Scheme 4), assuming the deprotonation of 1-pyrazoline formed at the first step, followed by the elimination of the diethyl phosphite anion *via* the E1cB mechanism, and repeated deprotonation to form an

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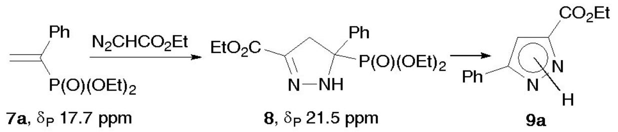
Table 4 Optimization studies on the reaction of vinylphosphonate **7a** with ethyl diazoacetate[a]



Entry	Solvent	Base	T (^{o}C)	Reaction time (h)	Conv. of **7a** (%)[b]	Yield (%)	
						8[b,c]	**9a**
1	THF	NaH (2.5 equiv.)	50	18	97	0	82[d,e]
2	THF	K_2CO_3 (5 mol%)	50	48	97	92(43)	0[f]
3	EtOH	K_2CO_3 (5 mol%)	60	24	92	86	0[f]
4	dioxane	K_2CO_3 (5 mol%)	80	20	92	63	0[f]

[a] Reaction conditions: **7a** (0.4 mmol), N_2CHCO_2Et (0.8 mmol), base, solvent (2 ml). [b] Determined by ^{31}P NMR analysis of the crude reaction mixture. [c] Isolated yield is given in the parentheses. [d] Isolated yield after column chromatography. [e] Formation of tetraethyl (1-phenylethane-1,2-diyl)bis(phosphonate) (11%; δ_P 27.7 and 29.2 ppm ($^3J_{P\text{-}P}$=82.9 Hz)) was also detected by NMR analysis of the crude reaction mixture. [f] Determined by ^{1}H NMR analysis of the crude reaction mixture; doublets due to *orto*-protons are observed at 7.51, 7.45, and 7.72 ppm for compounds **7a, 8**, and **9a**, respectively.

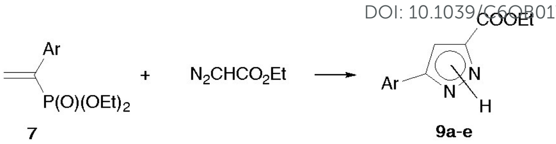
aromatic structure, explains the necessity to use two equivalents of sodium hydride.

The replacement of NaH by K_2CO_3 results in the termination of the reaction at the step of formation of 2-pyrazoline **8** when using THF (entry 2) or ethanol (entry 3) as solvent. No formation of target pyrazolecarboxylate **9a** was observed even on increasing the reaction temperature to 80 ^{o}C (in dioxane), but the selectivity of the process decreased noticeably because of the formation of by-products (entry 4).

2-Pyrazoline **8** was isolated and characterized. The aromatization of 2-pyrazoline **8** occurs smoothly in the presence of 2 equiv. NaH in THF, an increase of temperature from ambient to 50 ^{o}C shortens the reaction time from 24 to 5 h. The aromatization can be carried out both for individual pyrazoline **8** and *in situ*, adding 2 equiv. NaH to the reaction mixture in THF after the reaction of vinylphosphonate **7a** with ethyl diazoacetate in the presence of K_2CO_3 ceased. In both cases, pyrazolecarboxylate **9a** was isolated in a yield of 66%

A series of vinylphosphonates **7b-e** containing 4-chlorophenyl, 4-isobutylphenyl, 4-diphenyl, and 2-naphthyl substituents in the α-position was introduced into the reaction with ethyl diazoacetate to extend the scope of the method. Since the yields of product **9a** were comparable when using both the one-step (method A) and two-step (method B) protocols, we checked both procedures for each substrate of **7b-e**. The obtained results (Table 5) showed that both protocols made it possible to obtain products **9b-e** in good yields. The use of the longer method B is justified in the case of substrates **7b,d** because it gave better yields of the corresponding products **9b,d**.

Table 5 Preparation of 3-aryl substituted ethyl 1*H*-pyrazol-5-carboxylates **9**



Entry	**7**	Ar	Product	Isolated yield (%)	
				Method A[a]	Method B[b]
1	**7a**	Ph	**9a**	82	66
2	**7b**	4-ClC_6H_4	**9b**	57	62
3	**7c**	4-*i*-BuC_6H_4	**9c**	60	56
4	**7d**	4-PhC_6H_4	**9d**	76	83
5	**7e**	2-Napth	**9e**	74	68

[a] Reaction conditions: **7** (0.4 mmol), N_2CHCO_2Et (0.8 mmol), NaH (1.0 mmol), THF (2 ml), 50°C, 18 h. [b] Reaction conditions: 1) **7** (0.4 mmol), N_2CHCO_2Et (0.6-0.8 mmol), K_2CO_3 (5 mol%), THF (2 ml), 50°C, 48-55 h (^{31}P NMR monitoring); 2) NaH (0.8 mmol), 50°C, 5 h.

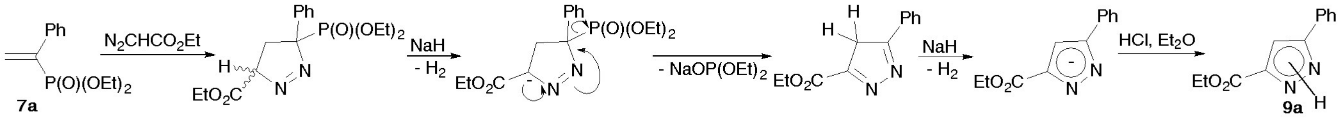
Products **9** were characterized by all relevant methods. The spectral characteristics of substrates **9a,b,e** are consistent with those described in the literature.[25d,l] Note that the published X-ray diffraction data for the 4-methoxyphenyl analog of products **9** show that in the crystalline state pyrazolecarboxylates **9**, unlike pyrazolylphosphonates **4**, exist as an alternative tautomer ethyl 3-aryl-1*H*-pyrazole-5-carboxylate.[25d]

Conclusions

In conclusion, 1,3-dipolar cycloaddition of aryldiazomethanes with dimethyl 1-formamidovinylphosphonate (**1**) features a condition-controlled product-selectivity. Under K_2CO_3/MeOH conditions nitrogen extrusion with cyclopropane ring formation is suppressed and the reaction affords 5-aryl substituted dimethyl (1*H*-pyrazol-3-yl)phosphonates **4** in high yields. Mild reaction conditions and broad functional group tolerance make this strategy synthetically useful. In much the same way, 1,3-dipolar cycloaddition of ethyl diazoacetate with diethyl 1-arylvinylphosphonates **7** under NaH/THF conditions provides regioisomerically pure 3-aryl substituted ethyl 1*H*-pyrazol-5-carboxylates **9**, the reaction being accompanied with the elimination of diethoxylphosphoryl moiety.

Experimental

Reactions were routinely performed under dry conditions in oven-dried glassware and under an air atmosphere unless otherwise specified. Methanol was distilled from magnesium methoxide, THF and Et_2O were distilled from sodium benzophenon ketyl prior to use. The starting material vinylphosphonate **1** was prepared according to the known method.[17,28] Vinylphosphonates **7** were obtained as previously



Scheme 4 Proposed pathway for pyrazolcarboxylate **9a** formation.

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reported.[27] Ethyl diazoacetate was purchased from Aldrich and used as received. Aryldiazomethanes **2** were generated from sodium salts of tosylhydrazones of corresponding aromatic aldehydes by the vacuum pyrolysis method[29] (for **2d,o,p**) or by the pyrolysis in ethylene glycol procedure[30] (for **2a-c,e-n**). (CAUTION! Although we did not experience any problems in handling aryldiazomethanes, full safety precautions should be taken due to their potential explosive nature).

NMR data were recorded on Bruker Avance-300, 400 or Agilent 400-MR spectrometers at ambient temperature. ^{13}C and ^{31}P NMR spectra were ^{1}H decoupled. Chemical shifts are reported in δ-scale in parts per million relative to solvent ($CDCl_3$: δ_C 77.0; Acetone-d$_6$: δ_C 29.8; CD_3OD: δ_C 49.0; DMSO-d$_6$: δ_C 39.5) or the residual solvent peak ($CHCl_3$: δ_H 7.25; Acetone-d$_6$: δ_H 2.04; CD_3OD: δ_H 3.30) as internal standards, or to external 85% H_3PO_4 (δ_P 0). The IR spectra were taken on a SPECORD 75 IR instrument in KBr pellets. High resolution mass spectra (HRMS) were measured on a Bruker maXis spectrometer using electrospray ionization (ESI). Elemental analyses were carried out on an Elementar Vario MICRO Cube analyzer. Melting points were measured with Electrothermal 9100 apparatus and are uncorrected. Column chromatography was carried out using Macherey-Nagel silica gel 60 (0.015–0.04 mm). Preparative thin-layer chromatography (TLS) was performed using 20 × 20 cm pre-coated glass plates SIL G-100 UV254 (Macherey-Nagel) and visualized by UV (254 nm).

Dimethyl [5-(formamido)-3-(3-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-5-yl]phosphonate (3). A foil-covered 4 ml vial was charged with vinylphosphonate **1** (45 mg, 0.25 mmol), 0.5M solution of diazo compound **2a** in Et_2O (0.65 ml, 0.325 mmol), and K_2CO_3 (3.5 mg, 0.025 mmol). The reaction mixture was stirred at rt for 16 h. The resultant precipitate was collected by filtration, washed with Et_2O, acetone, and water and dried in vacuum desiccator over P_2O_5 to give 2-pyrazoline **3** as yellowish solid (68 mg) in 79% yield; a 86:14 mixture of two rotamers in $CDCl_3$. ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.3 (major), 19.3 (minor). ^{1}H NMR (400 MHz, $CDCl_3$) (only for the major rotamer): δ 3.53–3.67 m (2H, CH_2), 3.91 (d, $^3J_{H\text{-}P}$=10.6 Hz, 3H, OCH_3), 3.93 (d, $^3J_{H\text{-}P}$=10.4 Hz, 3H, OCH_3), 6.36 (br. s, 1H, NHC=O), 7.07 (br. s, 1H, NNH), 7.56 (dd, $^3J_{H\text{-}H}$=$^3J_{H\text{-}H}$=8.0 Hz, 1H, ArH), 8.04 (m, $^3J_{H\text{-}H}$=8.0 Hz, 1H, ArH), 8.18 (s, 1H, CHO), 8.20 (m, $^3J_{H\text{-}H}$=8.0 Hz, 1H, ArH), 8.40 (dd, $^4J_{H\text{-}H}$=$^4J_{H\text{-}H}$=1.7 Hz, 1H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) (only for the major rotamer): δ 42.2 (d, $^2J_{C\text{-}P}$=3.1 Hz, CH_2), 54.3 (d, $^2J_{C\text{-}P}$=7.5 Hz, OCH_3), 55.2 (d, $^2J_{C\text{-}P}$=6.7 Hz, OCH_3), 76.1 (d, $^1J_{C\text{-}P}$=197.7 Hz, PC), 121.0 (CH), 123.8 (CH), 129.7 (CH), 131.7 (CH), 133.4 (C_{Ar}), 148.5 (d, $J_{C\text{-}P}$=14.4 Hz, C=N), 148.7 (CNO_2), 161.1 (d, $^3J_{C\text{-}P}$=5.2 Hz, C=O). Anal. calcd for $C_{12}H_{15}N_3O_5P\cdot 2H_2O$: C, 38.10; H, 5.06; N, 14.81. Found: C, 38.61; H, 4.55; N, 14.41.

Representative synthesis: Dimethyl [5-(3-nitrophenyl)-1*H*-pyrazol-3-yl]phosphonate (4a). A foil-covered 4 ml vial was charged with vinylphosphonate **1** (45 mg, 0.25 mmol), 0.5M solution of diazo compound **2a** in MeOH (0.65 ml, 0.325 mmol), and K_2CO_3 (3.5 mg, 0.025 mmol). The reaction mixture was stirred at rt for 16 h. Volatile components were removed on a rotary evaporator and the residue was purified by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.4) to afford pyrazolylphosphonate **4a** as colorless solid (56.5 mg) in 76% yield. Mp 185 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (d, $^3J_{H\text{-}P}$=11.6 Hz, 6H, OCH_3), 7.09 (d, $^3J_{H\text{-}P}$=2.4 Hz, 1H, C(4)H), 7.61 (dd, $^3J_{H\text{-}H}$=$^3J_{H\text{-}H}$=8.0 Hz, 1H, ArH), 8.17-8.22 (m, 2H, ArH), 8.67 (dd, $^4J_{H\text{-}H}$=$^4J_{H\text{-}H}$=1.9 Hz, 1H, ArH), 12.86 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.6 (d, $^2J_{C\text{-}P}$=5.5 Hz, OCH_3), 109.1 (d, $^2J_{C\text{-}P}$=19.1 Hz, C(4)), 120.7 (CH), 122.9 (CH), 129.8 (CH), 131.6 (CH), 132.7 (d, $^1J_{C\text{-}P}$=223 Hz, CP),133.6 (C_{Ar}), 148.7 (CNO_2), 149.3 (d, $^3J_{C\text{-}P}$=14.3 Hz, C(5)). IR (KBr): *v* 3400, 1550, 1529, 1344, 1248, 1184, 1063, 1032, 1003, 843, 781, 741 cm^{-1}. Anal. calcd for $C_{11}H_{12}N_3O_5P$: C, 44.45; H, 4.07; N, 14.14. Found: C, 44.40; H, 4.31; N, 13.84.

Dimethyl [5-(4-nitrophenyl)-1*H*-pyrazol-3-yl]phosphonate (4b). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2b** in MeOH (0.65 ml, 0.325 mmol); reaction time was 30 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.3) gave pyrazolylphosphonate **4b** as white solid (53.5 mg) in 72% yield. Mp 198 °C. ^{31}P NMR (162 MHz, acetone-*d*$_6$): δ 7.4 (major tautomer), 11.7 (minor tautomer) in 83:17 ratio. ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 3.80 (d, $^3J_{H\text{-}P}$=11.4 Hz, 6H, OCH_3), 7.38 (d, $^3J_{H\text{-}P}$=1.9 Hz, 1H, C(4)H), 8.18 (br. d, $^3J_{H\text{-}H}$=8.8 Hz, 2H, ArH), 8.31 (br. d, 2H, ArH), 13.59 (br. s, 1H, NH). ^{13}C NMR (101 MHz, acetone-*d*$_6$): δ 53.5 (d, $^2J_{C\text{-}P}$=5.6 Hz, OCH_3), 111.2 (d, $^2J_{C\text{-}P}$=20.1 Hz, C(4)), 124.9 (2CH), 127.2 (2CH), 139.0 (br., C(5)), 148.3 (CNO_2). IR (KBr): *v* 3420, 1518, 1346, 1236, 1184, 1 061, 1030, 854, 600 cm^{-1}. Anal. calcd for $C_{11}H_{12}N_3O_5P$: C, 44.45; H, 4.07; N, 14.14. Found: C, 44.29; H, 4.12; N, 13.

Dimethyl [5-(4-(diethoxyphosphoryl)phenyl)-1*H*-pyrazol-3-yl]phosphonate (4c). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2c** in MeOH (0.75 ml, 0.375 mmol); reaction time was 24 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.17) gave pyrazolylphosphonate **4c** as pale yellow oil (77 mg) in 79% yield. ^{31}P NMR (121 MHz, CD_3OD): δ 11.6, 18.4. ^{1}H NMR (300 MHz, CD_3OD): δ 1.33 (dt, $^3J_{H\text{-}H}$=7.1 Hz, $^4J_{H\text{-}P}$=0.5 Hz, 6H, CCH_3), 3.84 (d, $^3J_{H\text{-}P}$=11.4 Hz, 6H, OCH_3), 4.13 (m, 4H, OCH_2), 7.24 (d, $^3J_{H\text{-}P}$=1.9 Hz, 1H, C(4)H), 7.85 (dd, $^3J_{H\text{-}P}$=12.9 Hz, $^3J_{H\text{-}H}$=8.6 Hz, 2H, ArH), 7.96 (dd, $^4J_{H\text{-}P}$=4.0 Hz, $^3J_{H\text{-}H}$=8.6 Hz, 2H, ArH). ^{13}C NMR (75 MHz, CD_3OD): δ 16.5 (d, $^3J_{C\text{-}P}$=6.2 Гц, CCH_3), 54.1 (d, $^2J_{C\text{-}P}$=5.9 Hz, OCH_3), 64.0 (d, $^2J_{C\text{-}P}$=5.9 Hz, CH_2), 111.0 (d, $^2J_{C\text{-}P}$=22.3 Hz, C(4)), 127.0 (d, $^3J_{C\text{-}P}$=15.3 Hz, 2CH), 128.7 (d, $^1J_{C\text{-}P}$=191.5 Гц, CP), 133.4 (d, $^2J_{C\text{-}P}$=10.3 Hz, 2CH), 135.5 (d, $^4J_{C\text{-}P}$=3.3 Hz, C), 138.0 (d, $^1J_{C\text{-}P}$=228.3 Hz, CP), 147.8 (dd, $^3J_{C\text{-}P}$=13.3 Hz, $^5J_{C\text{-}P}$=1.0 Hz, C(5)). IR (KBr): *v* 3433, 1480, 1238, 1186, 1130, 1051, 1028, 970 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_{24}N_2O_6P_2$: 389.1025. Found 389.1020.

Dimethyl [5-(4-(methoxycarbonyl)phenyl)-1*H*-pyrazol-3-yl]phosphonate (4d). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2d** in MeOH (0.75 ml, 0.375 mmol); reaction time was 18 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.19) gave pyrazolylphosphonate **4d** as pale yellow solid (61 mg) in 78% yield. Mp 184 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 10.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (d, $^{3}J_{H-P}$=11.5 Hz, 6H, $POCH_3$), 3.92 (s, 3H, $COCH_3$), 7.06 (d, $^{3}J_{H-P}$=2.1 Hz, 1H, C(4)H), 7.88 (pseudo d, $^{3}J_{H-H}$=8.4 Hz, 2H, ArH), 8.09 (pseudo d, $^{3}J_{H-H}$=8.4 Hz, 2H, ArH), 13.04 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 52.1 ($COCH_3$), 53.5 (d, $^{2}J_{C-P}$=5.5 Hz, $POCH_3$), 109.4 (d, $^{2}J_{C-P}$=19.8 Hz, C(4)), 125.6 (2CH), 129.8, 130.2 (2CH), 133.7 (d, $^{1}J_{C-P}$=223.4 Hz, CP), 135.5 (C_{Ar}), 149.5 (br., C(5)), 166.7 (C=O). IR (KBr): *v* 3400, 1724, 1457, 1284, 1240, 1188, 1161, 1103, 1057, 1026, 787 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{15}N_2O_5PNa$: 333.0611. Found 333.0602.

Dimethyl [5-(2-chlorophenyl)-1*H*-pyrazol-3-yl]phosphonate (4e). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2e** in MeOH (0.70 ml, 0.35 mmol); reaction time was 17 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.21) gave pyrazolylphosphonate **4e** as pale yellow solid (45 mg) in 63% yield. Mp 89 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (d, $^{3}J_{H-P}$=11.5 Hz, 6H, OCH_3), 7.15 (d, $^{3}J_{H-P}$=1.8 Hz, 1H, C(4)H), 7.25-7.31 (m, 2H, ArH), 7.44 (m, 1H, ArH), 7.71 (m, 1H, ArH), 8.94 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.3 (d, $^{2}J_{C-P}$=5.5 Hz, OCH_3), 112.2 (d, $^{2}J_{C-P}$=21.5 Hz, C(4)), 127.2 (CH), 129.2, 129.7 (CH), 130.48 (CH), 130.53 (CH), 131.9 (CCl), 135.4 (d, $^{1}J_{C-P}$=226.4 Hz, CP), 145.6 (d, $^{3}J_{C-P}$=14.3 Hz, C(5)). IR (KBr): *v* 3420, 1479, 1244, 1188, 1030, 837, 787, 758 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{11}H_{12}ClN_2O_3PNa$: 309.0166. Found 309.0166.

Dimethyl [5-(2-bromophenyl)-1*H*-pyrazol-3-yl]phosphonate (4f). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2f** in MeOH (0.65 ml, 0.325 mmol); reaction time was 16 h. Purification by preparative TLC (EtOAc/hexane: 20/1, R_f 0.21) using EtOAc/hexane as the eluent gave pyrazolylphosphonate **4f** as white solid (45 mg) in 54% yield. Mp 125 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (d, $^{3}J_{H-P}$=11.5 Hz, 6H, OCH_3), 7.13 (d, $^{3}J_{H-P}$=1.9 Hz, 1H, C(4)H), 7.20 (ddd, $^{3}J_{H-H}$=8.0 Hz, $^{3}J_{H-H}$=7.5 Hz, $^{4}J_{H-H}$=1.6 Hz, 1H, ArH), 7.35 (ddd, $^{3}J_{H-H}$=7.6 Hz, $^{3}J_{H-H}$=7.5 Hz, $^{4}J_{H-H}$=1.2 Hz, 1H, ArH), 7.63 (dd, $^{3}J_{H-H}$=7.6 Hz, $^{4}J_{H-H}$=1.6 Hz, 1H, ArH), 7.65 (dd, $^{3}J_{H-H}$=8.0 Hz, $^{4}J_{H-H}$=1.2 Hz, 1H, ArH), 12.77 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.4 (d, $^{2}J_{C-P}$=5.6 Hz, OCH_3), 112.5 (d, $^{2}J_{C-P}$=21.2 Hz, C(4)), 121.8 (CBr), 127.6 (CH), 129.9 (CH), 131.1 (CH), 131.7, 133.7 (CH), 134.7 (d, $^{1}J_{C-P}$=224 Hz, CP), 147.3 (br., C(5)). IR (KBr): *v* 3471, 1475, 1242, 1180, 1157, 1055, 1030, 987, 958, 860, 845, 835, 766 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{11}H_{12}BrN_2O_3PNa$: 352.9661. Found 352.9659.

Dimethyl [5-(3-chlorophenyl)-1*H*-pyrazol-3-yl]phosphonate (4g). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2g** in MeOH (0.65 ml, 0.325 mmol); reaction time was 12 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.29) gave pyrazolylphosphonate **4g** as white solid (56 mg) in 78% yield. Mp 81 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (d, $^{3}J_{H-P}$=11.5 Hz, 6H, OCH_3), 6.97 (d, $^{3}J_{H-P}$=2.0 Hz, 1H, C(4)H), 7.28 (m, 1H, ArH), 7.31 (m, 1H, ArH), 7.67 (m, 1H, ArH), 7.82 (m, 1H, ArH), 10.26 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.4 (d, $^{2}J_{C-P}$=5.5 Hz, OCH_3), 108.8 (d, $^{2}J_{C-P}$=20.2 Hz, C(4)), 123.9 (CH), 125.9 (CH), 128.4 (CH), 130.1 (CH), 132.8, 134.8 (CCl), 134.1 (d, $^{1}J_{C-P}$=223.4 Hz, CP), 148.6 (d, $^{3}J_{C-P}$=14.4 Hz, C(5)). IR (KBr): *v* 3369, 1479, 1246, 1182, 1032, 839, 787, 775 cm^{-1}. Anal. calcd for $C_{11}H_{12}N_2ClO_3P$: C, 46.09; H, 4.22; N 9.77. Found: C, 46.07; H, 4.64; N, 9.34.

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Dimethyl [5-(4-chlorophenyl)-1*H*-pyrazol-3-yl]phosphonate (4h). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2h** in MeOH (0.65 ml, 0.325 mmol); reaction time was 4 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.2) gave pyrazolylphosphonate **4h** as white solid (62 mg) in 87% yield. Mp 143 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.0. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (d, $^{3}J_{H-P}$=11.5 Hz, 6H, OCH_3), 6.98 (d, $^{3}J_{H-P}$=2.1 Hz, 1H, C(4)H), 7.38 (pseudo d, $^{3}J_{H-H}$=8.5 Hz, 2H, ArH), 7.74 (pseudo d, $^{3}J_{H-H}$=8.5 Hz, 2H, ArH), 13.22 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.4 (d, $^{2}J_{C-P}$=5.5 Hz, OCH_3), 108.8 (d, $^{2}J_{C-P}$=20.4 Hz, C(4)), 127.1 (2CH), 129.0 (2CH), 129.6, 134.2 (CCl), 134.1 (d, $^{1}J_{C-P}$=223.3 Hz, CP), 148.8 (d, $^{3}J_{C-P}$=14.4 Hz, C(5)). IR (KBr): *v* 3388, 1495, 1246, 1178, 1059, 1018, 833, 771 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{11}H_{12}ClN_2O_3PNa$: 309.0166. Found 309.0167.

Dimethyl [5-(4-bromophenyl)-1*H*-pyrazol-3-yl]phosphonate (4i). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2i** in MeOH (0.70 ml, 0.35 mmol); reaction time was 3 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.2) gave pyrazolylphosphonate **4i** as white solid (72 mg) in 87% yield. Mp 159 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 10.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (d, $^{3}J_{H-P}$=11.5 Hz, 6H, OCH_3), 6.98 (d, $^{3}J_{H-P}$=2.1 Hz, 1H, C(4)H), 7.54 (pseudo d, $^{3}J_{H-H}$=8.5 Hz, 2H, ArH), 7.68 (pseudo d, $^{3}J_{H-H}$=8.5 Hz, 2H, ArH), 11.90 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.5 (d, $^{2}J_{C-P}$=5.5 Hz, OCH_3), 108.9 (d, $^{2}J_{C-P}$=19.9 Hz, C(4)), 122.4 (CBr), 127.4 (2CH), 130.2, 132.0 (2CH), 133.6 (d, $^{1}J_{C-P}$=222.6 Hz, CP), 149.4 (d, $^{3}J_{C-P}$=14.8 Hz, C(5)). IR (Nujol): *v* 1492, 1385, 1240, 1175, 1080, 1050, 998, 845, 795 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{11}H_{12}BrN_2O_3PNa$: 352.9661. Found 352.9660.

Dimethyl [5-(4-(methylthio)phenyl)-1*H*-pyrazol-3-yl]phosphonate (4j). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2j** in MeOH (1.5 ml, 0.75 mmol); reaction time was 3 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.17) gave pyrazolylphosphonate **4j** as white solid (64 mg) in 86% yield. Mp 138 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H, SCH_3), 3.84 (d, $^{3}J_{H-P}$=11.5 Hz, 6H, OCH_3), 6.98 (d, $^{3}J_{H-P}$=1.9 Hz, 1H, C(4)H), 7.28 (pseudo d, $^{3}J_{H-H}$=8.3 Hz, 2H, ArH), 7.69 (pseudo d, $^{3}J_{H-H}$=8.3 Hz, 2H, ArH), 13.04 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 15.6 (SCH_3), 53.3 (d, $^{2}J_{C-P}$=5.5 Hz, OCH_3), 108.3 (d, $^{2}J_{C-P}$=20.8 Hz, C(4)), 126.1 (2CH), 126.7 (2CH), 127.4, 139.2 (CSMe), 135.0 (d, $^{1}J_{C-P}$=225.6 Hz, CP), 148.8 (d, $^{3}J_{C-P}$=13.2 Hz, C(5)). IR (KBr): *v* 3383, 1242, 1493, 1171, 1068, 1038, 985, 841, 779 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{12}H_{15}N_2O_3PSNa$: 321.0433. Found 321.0429.

Dimethyl [5-(3-methoxyphenyl)-1*H*-pyrazol-3-yl]phosphonate (4k). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2k** in MeOH (1.5 ml, 0.75

mmol); reaction time was 3 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.25) gave pyrazolylphosphonate **4k** as white solid (50 mg) in 71% yield. Mp 113 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (d, $^3J_{H\text{-}P}$=11.5 Hz, 6H, $POCH_3$), 3.85 (s, 3H, $COCH_3$), 6.99 (d, $^3J_{H\text{-}P}$=2.0 Hz, 1H, C(4)H), 6.90 (m, 1H, ArH), 7.30-7.38 (m, 3H, ArH), 12.69 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.3 (d, $^2J_{C\text{-}P}$=5.5 Hz, $POCH_3$), 55.3 (OMe), 108.8 (d, $^2J_{C\text{-}P}$=20.8 Hz, C(4)), 111.1 (CH), 114.4 (CH), 118.3 (CH), 130.0 (CH), 132.0, 135.0 (d, $^1J_{C\text{-}P}$=222.0 Hz, CP), 149.2 (d, $^3J_{C\text{-}P}$=14.4 Hz, C(5)), 160.0 (COMe). IR (KBr): *v* 3369, 1493, 1248, 1188, 1034, 841, 787 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{12}H_{15}N_2O_4PNa$: 305.0662. Found 305.0654.

Dimethyl (5-phenyl-1*H*-pyrazol-3-yl)phosphonate (4l). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2l** in MeOH (0.65 ml, 0.325 mmol); reaction time was 3 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.24) gave pyrazolylphosphonate **4l** as white solid (54 mg) in 85% yield. Mp 79 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.85. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (d, $^3J_{H\text{-}P}$=11.5 Hz, 6H, OCH_3), 7.01 (d, $^3J_{H\text{-}P}$=2.0 Hz, 1H, C(4)H), 7.33 (t, $^3J_{HH}$=7.4 Гц, 1H, ArH), 7.41 (dd, $^3J_{HH}$=$^3J_{HH}$=7.4 Гц, 2H, ArH), 7.78 (d, $^3J_{HH}$=7.4 Гц, 2H, ArH), 11.52 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.3 (d, $^2J_{C\text{-}P}$=5.5 Hz, OCH_3), 108.6 (d, $^2J_{C\text{-}P}$=21.2 Hz, C(4)), 125.8 (2CH), 128.5 (CH), 128.9 (2CH), 130.5, 135.4 (d, $^1J_{C\text{-}P}$=225.6 Hz, CP), 148.7 (d, $^3J_{C\text{-}P}$=13.8 Hz, C(5)). IR (KBr): *v* 3406, 1495, 1250, 1180, 1038, 787 cm^{-1}. Anal. calcd for $C_{11}H_{13}N_2O_3P$: C, 52.39; H, 5.20; N, 11.11. Found: C, 52.03; H, 5.36; N, 11.20.

This reaction was also repeated using vinylphosphonate **1** (448 mg, 2.5 mmol), 0.5M solution of diazo compound **2l** in MeOH (6.5 ml, 3.25 mmol), and K_2CO_3 (35 mg, 0.25 mmol). The product **4l** was isolated by column chromatography in 91% yield (574 mg).

Dimethyl [5-(4-fluorophenyl)-1*H*-pyrazol-3-yl]phosphonate (4m). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2m** in MeOH (0.75 ml, 0.375 mmol); reaction time was 3 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.38) gave pyrazolylphosphonate **4m** as colorless solid (45 mg) in 67% yield. Mp 117 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (d, $^3J_{H\text{-}P}$=11.5 Hz, 6H, OCH_3), 6.96 (d, $^3J_{H\text{-}P}$=2.0 Hz, 1H, C(4)H), 7.09 (dd, $^3J_{H\text{-}H}$=8.7 Hz, $^3J_{H\text{-}F}$=8.7 Hz, 2H, ArH), 7.76 (dd, $^3J_{H\text{-}H}$=8.7 Hz, $^4J_{H\text{-}F}$=5.3 Hz, 2H, ArH), 13.16 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.4 (d, $^2J_{C\text{-}P}$=5.5 Hz, OCH_3), 108.7 (d, $^2J_{C\text{-}P}$=20.4 Hz, C(4)), 115.8 (d, $^2J_{C\text{-}F}$=21.8 Hz, 2CH), 127.3 (d, $^4J_{C\text{-}F}$=2.7 Hz), 127.6 (d, $^3J_{C\text{-}F}$=8.2 Hz, 2CH), 134.1 (d, $^1J_{C\text{-}P}$=223.1 Hz, CP), 149.0 (d, $^3J_{C\text{-}P}$=14.2 Hz, C(5)), 162.8 (d, $^1J_{C\text{-}F}$=248.0 Hz, CF). IR (KBr): *v* 3400, 1508, 1246, 1178, 1066, 1034, 837, 785 cm^{-1}. Anal. calcd for $C_{11}H_{12}FN_2O_3P$: C, 48.90; H, 4.48; N, 10.37. Found: C, 48.98; H, 4.70; N, 10.07.

Dimethyl [5-(4-isopropylphenyl)-1*H*-pyrazol-3-yl]phosphonate (4n). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2n** in MeOH (2 ml, 1 mmol); reaction time was 3 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.3) gave pyrazolylphosphonate **4n** as white solid (59 mg) in 80% yield. Mp 142 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.9. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (d, $^3J_{H\text{-}H}$=6.9 Hz, 6H, CCH_3), 2.92 (septet, $^3J_{H\text{-}H}$=6.9 Hz, 1H, CH_{iPr}), 3.83 (d, $^3J_{H\text{-}P}$=11.4 Hz, 6H, OCH_3), 6.96 (d, $^3J_{H\text{-}P}$=1.9 Hz, 1H, C(4)H), 7.28 (pseudo d, $^3J_{H\text{-}H}$=8.2 Hz, 2H, ArH), 7.66 (pseudo d, $^3J_{H\text{-}H}$=8.2 Hz, 2H, ArH), 12.97 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.8 (CCH_3), 33.9 (CH_{iPr}), 53.3 (d, $^2J_{C\text{-}P}$=5.6 Hz, OCH_3), 108.6 (d, $^2J_{C\text{-}P}$=21.5 Hz, C(4)), 125.8 (2CH), 127.0 (2CH), 128.0, 135.7 (d, $^1J_{C\text{-}P}$=226.4 Hz, CP), 148.5 (d, $^3J_{C\text{-}P}$=12.9 Hz, C(5)), 149.4 (CPr^i). IR (KBr): *v* 3400, 1502, 1236, 1178, 1043, 787 cm^{-1}. Anal. calcd for $C_{14}H_{19}N_2O_3P$: C, 57.14; H, 6.51; N, 9.52. Found: C, 57.35; H, 6.80; N, 9.20.

Dimethyl [5-(4-methoxyphenyl)-1*H*-pyrazol-3-yl]phosphonate (4o). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2o** in MeOH (1 ml, 0.5 mmol); reaction time was 3 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.24) gave pyrazolylphosphonate **4o** as white solid (64 mg) in 86% yield. Mp 184 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 12.0. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H, $COCH_3$), 3.82 (d, $^3J_{H\text{-}P}$=11.5 Hz, 6H, $POCH_3$), 6.91 (d, $^3J_{H\text{-}P}$=1.8 Hz, 1H, C(4)H), 6.92 (pseudo d, $^3J_{H\text{-}H}$=8.7 Hz, 2H, ArH), 7.68 (pseudo d, $^3J_{H\text{-}H}$=8.7 Hz, 2H, ArH), 10.72 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 53.3 (d, $^2J_{C\text{-}P}$=5.5 Hz, $POCH_3$), 55.3 ($COCH_3$), 108.0 (d, $^2J_{C\text{-}P}$=21.4 Hz, C(4)), 114.3 (2CH), 123.1, 127.1 (2CH), 135.5 (d, $^1J_{C\text{-}P}$=223.8 Hz, CP), 148.4 (d, $^3J_{C\text{-}P}$=11.5 Hz, C(5)), 159.9 (COMe). IR (KBr): *v* 3452, 1618, 1510, 1252, 1230, 1178, 1049, 1028, 841, 827, 785 cm^{-1}. Anal. calcd for $C_{12}H_{15}N_2O_4P$: C, 51.07; H, 5.36; N, 9.93. Found: C, 50.81; H, 5.33; N, 9.79.

Dimethyl [5-(4-ethoxyphenyl)-1*H*-pyrazol-3-yl]phosphonate (4p). The reaction was carried out as described for **4a** using 0.5M solution of diazo compound **2p** in MeOH (0.8 ml, 0.4 mmol); reaction time was 2 h. Purification by preparative TLC (CH_2Cl_2/MeOH: 20/1, R_f 0.26) gave pyrazolylphosphonate **4p** as yellowish solid (47 mg) in 63% yield. Mp 165 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 12.5. ^{1}H NMR (400 MHz, $CDCl_3$): 1.40 (t, $^3J_{H\text{-}H}$=7.0 Hz, 3H, CCH_3), 3.80 (d, $^3J_{H\text{-}P}$=11.4 Hz, 6H, OCH_3), 4.02 (q, $^3J_{H\text{-}H}$=7.0 Hz, 2H, CH_2), 6.88 (d, $^3J_{H\text{-}P}$=1.8 Hz, 1H, C(4)H), 6.90 (pseudo d, $^3J_{H\text{-}H}$=8.8 Hz, 2H, ArH), 7.66 (pseudo d, $^3J_{H\text{-}H}$=8.8 Hz, 2H, ArH), 12.98 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.8 (CCH_3), 53.3 (d, $^2J_{C\text{-}P}$=5.5 Hz, OCH_3), 63.5 (CH_2), 107.8 (d, $^2J_{C\text{-}P}$=21.6 Hz, C(4)), 114.8 (2CH), 122.8, 127.1 (2CH), 135.9 (d, $^1J_{C\text{-}P}$=229.1 Hz, CP), 148.2 (br., C(5)), 159.3 (COEt). IR (KBr): *v* 3369, 1508, 1250, 1178, 1030, 985, 841, 781 cm^{-1}. Anal. calcd for $C_{13}H_{17}N_2O_4P$: C, 52.70; H, 5.78; N, 9.46. Found: C, 52.17; H, 5.64; N, 8.94.

Ethyl 5-(dimethoxyphosphoryl)-5-(formamido)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (5). A foil-covered 4 ml vial was charged with vinylphosphonate **1** (50 mg, 0.28 mmol) and ethyl diazoacetate (60 µl, 0.56 mmol). The reaction mixture was stirred at 80 °C for 4 h. Purification by column chromatography (CH_2Cl_2/MeOH: 20/1, R_f 0.32) afforded 2-pyrazoline **5** as colorless oil (66 mg) in 80% yield; a 84:16 mixture of two rotamers in $CDCl_3$. ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.4 (major), 18.5 (minor). ^{1}H NMR (400 MHz, $CDCl_3$) (only for the major rotamer): δ 1.29 (t, $^3J_{H\text{-}H}$=7.1 Hz, 3H, CCH_3), 3.31 (dd, $^3J_{H\text{-}P}$=18.2 Hz, $^2J_{H\text{-}H}$=18.2 Hz, 1H, C(4)H), 3.43 (dd, $^3J_{H\text{-}P}$=7.2 Hz,

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$^{2}J_{H-H}$=18.2 Hz, 1H, C(4)H), 3.80 (d, $^{3}J_{H-P}$=10.6 Hz, 3H, OCH_3), 3.83 (d,$^{3}J_{H-P}$=10.4 Hz, 3H, OCH_3), 4.25 (q,$^{3}J_{H-H}$=7.1 Hz, 2H, OCH_2) 7.77 (br. s, 1H, NHC=O), 7.93 (br. s, 1H, NNH), 8.09 (s, 1H, CHO). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.1 (C*C*H_3, major), 14.0 (C*C*H_3, minor), 41.1 ($^{2}J_{C-P}$=3.2 Hz, C(4), major), 41.8 ($^{2}J_{C-P}$=2.9 Hz, C(4), minor), 54.0 ($^{2}J_{C-P}$=7.3 Hz, OCH_3, minor), 54.2 ($^{2}J_{C-P}$=7.3 Hz, OCH_3, major), 55.1 ($^{2}J_{C-P}$=6.6 Hz, OCH_3, major), 55.3 ($^{2}J_{C-P}$=6.3 Hz, OCH_3, minor), 61.5 (OCH_2, major), 61.6 (OCH_2, minor), 75.1 ($^{1}J_{C-P}$=198.1 Hz, CP, minor), 76.2 ($^{1}J_{C-P}$=199.8 Hz, CP, major), 141.5 ($^{3}J_{C-P}$=12.2 Hz, C(3), minor), 142.3 ($^{3}J_{C-P}$=11.4 Hz, C(3), major), 161.7 (CHO, minor), 161.8 ($^{3}J_{C-P}$=3.1 Hz, CHO, major), 163.4 (C(O)O, minor), 163.6 (C(O), major). IR (KBr): *v* 3192, 1697, 1666, 1460, 1379, 1263, 1213, 1178, 1037, 1022 cm^{-1}. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_9H_{16}N_3O_6PNa$: 316.0669. Found 316.0672.

Ethyl 3-(dimethoxyphosphoryl)-1*H*-pyrazole-5-carboxylate (6). To a solution of 2-pyrazoline **5** (52 mg, 0.18 mmol) in anhydrous methanol (2 mL) two drops of Me_3SiCl were added. After stirring at rt for 4 h under an argon atmosphere, the mixture was evaporated under vacuum 2 mmHg. The residue was suspended in CH_2Cl_2 and filtered. The filtrate was evaporated under vacuum to provide the pure pyrazole **6** as colorless solid (39 mg) in 89% yield. Mp 109 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, $^{3}J_{H-H}$=7.1 Hz, 3H, CCH_3), 3.79 (d,$^{3}J_{H-P}$=11.5 Hz, 6H, $2OCH_3$), 4.38 (q,$^{3}J_{H-H}$=7.1 Hz, 2H, CH_2), 7.21 (d,$^{3}J_{H-P}$=11.5 Hz, 1H, C(4)H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.17 (C*C*H_3), 53.5 (d, $^{2}J_{C-P}$=5.6 Hz, OCH_3), 61.4 (CH_2), 114.6 (d, $^{2}J_{C-P}$=19.9 Hz, C(4)), 134.6 ($^{1}J_{PC}$=224.2 Hz, CP), 141.5 (d, $^{3}J_{PC}$=13.6 Hz, C(5)), 160.8 (CO). IR (KBr): *v* 3442, 1734, 1730, 1462, 1257, 1242, 1176, 1047 cm^{-1}. Anal. calcd for $C_8H_{13}N_2O_5P$: C, 38.72; H, 5.28; N, 11.29. Found: C, 38.87; H, 5.40; N, 10.99.

Ethyl 5-(diethoxyphosphoryl)-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (8). To a solution of vinylphosphonate **7a** (96 mg, 0.4 mmol) in THF (2 ml) ethyl diazoacetate (63 µl, 0.6 mmol) and K_2CO_3 (3 mg, 0.02 mmol) were added. After stirring at 50 °C for 48 h, the mixture was evaporated under vacuum. The viscous residue was solidified by vigorous stirring with hexane. The resultant precipitate was collected by filtration, washed with Et_2O, hexane and dried under vacuum to give 2-pyrazoline **8** as yellow solid (61 mg) in 43% yield. ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, $^{3}J_{H-H}$=7.1 Hz, 3H, CH_3), 1.23 (t, $^{3}J_{H-H}$=7.1 Hz, 3H, CH_3), 1.32 (t, $^{3}J_{H-H}$=7.1 Hz, 3H, CH_3), 3.33 (dd, $^{3}J_{H-P}$=24.2 Hz, $^{2}J_{H-H}$=17.6 Hz, 1H,C(4)H), 3.81 (dd, $^{3}J_{H-P}$=26.2 Hz, $^{2}J_{H-H}$=17.6 Hz, 1H, C(4)H), 3.86 – 4.09 м (m, 4H, $POCH_2$), 4.28 (q, $^{3}J_{H-H}$=7.1 Hz, 2H, $COCH_2$), 6.98 (br. d, $^{3}J_{H-P}$=4.5 Hz, 1H, NH), 7.30 (m, 1H, ArH), 7.37 (m, 2H, ArH), 7.45 (m, 2H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.2 ($COCH_2$*C*H_3), 16.27 ($POCH_2$*C*H_3), 16.31 ($POCH_2$*C*H_3), 41.7 (C(4)), 61.3 (CO*C*H_2), 63.4 (d, $^{2}J_{C-P}$=7.4 Hz, $POCH_2$), 64.0 (d, $^{2}J_{C-P}$=6.8 Hz, $POCH_2$), 70.5 (d, $^{1}J_{C-P}$=152.6 Hz, CP), 126.6 (d, $^{3}J_{C-P}$=4.0 Hz, 2CH), 128.1 (CH), 128.6 (2CH), 138.7, 142.1 (C(3)), 162.0 (C=O). Anal. calcd for $C_{16}H_{23}N_2O_5P$: C, 54.23; H, 6.54; N, 7.91. Found: C, 53.99; H, 6.31; N, 7.75.

Representative synthesis: Ethyl 3-phenyl-1*H*-pyrazole-5-carboxylate (9a).

Method A. To a solution of vinylphosphonate **7a** (96 mg, 0.4 mmol) and ethyl diazoacetate (84 µl, 0.8 mmol) in THF (2 ml) sodium hydride (60% dispersion in mineral oil, Aldrich; 40 mg, 1 mmol) was added in argon atmosphere. The reaction mixture was stirred at 50 °C for 18 h, cooled to rt, and neutralized by the slow dropwise addition of the satd. ethereal solution of HCl (300 µl), followed by the addition of NEt_3 (130 µl). Volatile components were removed on a rotary evaporator and the residue was purified by column chromatography (EtOAc/hexane: 1/2, R_f 0.8) afforded pyrazolecarboxylate **9a** as white solid (71 mg) in 82% yield.

Method B. A mixture of vinylphosphonate **7a** (96 mg, 0.4 mmol), ethyl diazoacetate (84 µl, 0.8 mmol), K_2CO_3 (3 mg, 0.8 mmol, and THF (2 ml) was stirred at 50 °C for 48 h and cooled to rt in argon atmosphere. After the addition of sodium hydride (60% dispersion in mineral oil, Aldrich; 32 mg, 0.8 mmol), the reaction mixture was further stirred at 50 °C for 5 h, cooled, and worked up as described in Method A. Column chromatography afforded pyrazolecarboxylate **9a** (57 mg) in 66% yield.

Mp 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (t, $^{3}J_{H-H}$=7.1 Hz, 3H, CH_3), 4.25 (q, $^{3}J_{H-H}$=7.1 Hz, 2H, CH_2), 7.02 (s, 1H, C(4)H), 7.32 (t, $^{3}J_{H-H}$=7.4 Hz, 1H, ArH), 7.38 (dd, $^{3}J_{H-H}$=$^{3}J_{H-H}$=7.4 Hz, 2H, ArH), 7.72 (d, $^{3}J_{H-H}$=7.4 Hz, 2H, ArH), 11.40 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.0 (CH_3), 61.0 (CH_2), 105.1 (C(4)), 125.6 (2CH), 128.5 (CH), 128.8 (2CH), 130.3, 140.1 (br., C(5)), 148.1 (br., C(3)), 160.9 (C=O). IR (KBr): *v* 3435, 1726, 1493, 1241, 1194, 1138, 762 cm^{-1}. Anal. calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.56; H, 5.78; N, 12.85.

Ethyl 3-(4-chlorophenyl)-1*H*-pyrazole-5-carboxylate (9b).

Method A. The reaction was carried out as described for **9a** using vinylphosphonate **7b** (110 mg, 0.4 mmol). Purification by column chromatography (EtOAc/hexane: 1/2, R_f 0.8) gave pyrazolecarboxylate **9b** as yellow solid (57 mg) in 57% yield.

Method B. The reaction was carried out as described for **9a** using vinylphosphonate **7b** (110 mg, 0.4 mmol). Column chromatography afforded pyrazolecarboxylate **9b** (62 mg) in 62% yield.

Mp 141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, $^{3}J_{H-H}$=7.1 Hz, 3H, CH_3), 4.35 (q, $^{3}J_{H-H}$=7.1 Hz, 2H, CH_2), 7.04 (s, 1H, C(4)H), 7.37 (pseudo d, $^{3}J_{H-H}$=8.5 Hz, 2H, ArH), 7.69 (pseudo d, $^{3}J_{H-H}$=8.5 Hz, 2H, ArH), 10.24 (br. s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.2 (CH_3), 61.4 (CH_2), 105.4 (C(4)), 126.9 (2CH), 129.0 (2CH), 129.5, 134.3 (CCl), 138.4 (br., C(5)), 148.8 (br., C(3)), 160.3 (C=O). IR (KBr): *v* 3292, 1697, 1473, 1444, 1304, 1277, 1192, 1093, 1028, 957, 833, 773 cm^{-1}. Anal. calcd for $C_{12}H_{11}ClN_2O_2$: C, 57.49; H, 4.42; N, 11.17. Found: C, 57.62; H, 4.57; N, 11.01.

Ethyl 3-(4-isobutylphenyl)-1*H*-pyrazole-5-carboxylate (9c).

Method A. The reaction was carried out as described for **9a** using vinylphosphonate **7c** (119 mg, 0.4 mmol). Purification by column chromatography (EtOAc/hexane: 1/2, R_f 0.5) gave pyrazolecarboxylate **9c** as yellowish solid (65 mg) in 60% yield.

Method B. The reaction was carried out as described for **9a** using vinylphosphonate **7c** (110 mg, 0.4 mmol); reaction time at the first stage was 53 h. Column chromatography afforded pyrazolecarboxylate **9c** (61 mg) in 56% yield.

Mp 168 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.90 (d, $^{3}J_{H\text{-}H}$=6.6 Hz, 6H, CH$_{3\ iBu}$), 1.23 (t, $^{3}J_{H\text{-}H}$=7.1 Hz, 3H, OCH$_2$CH_3), 1.86 (m, 1H, CH$_{iBu}$), 2.47 (d, $^{3}J_{H\text{-}H}$=7.2 Hz, 2H, CH$_{2\ iBu}$), 4.21 (q, $^{3}J_{H\text{-}H}$=7.1 Hz, 2H, OCH$_2$), 6.98 (s, 1H, C(4)H), 7.15 (pseudo d, $^{3}J_{H\text{-}H}$=8.1 Hz, 2H, ArH), 7.61 (pseudo d, $^{3}J_{H\text{-}H}$=8.1 Hz, 2H, ArH), 11.81 (br. s, 1H, NH). ^{13}C NMR (101 MHz, CDCl$_3$): δ 14.1 (OCH$_2$CH$_3$), 22.3 (CH$_{3\ iBu}$), 30.2 (CH $_{iBu}$), 45.2 (CH$_{2\ iBu}$), 61.0 (OCH$_2$), 105.0 (C(4)), 125.4 (2CH), 127.8, 129.6 (2CH), 140.2 (br., C(5)), 142.3 (CBu^{i}), 148.4 (br., C(3)), 161.0 (C=O). IR (KBr): *v* 3159, 1730, 1464, 1379, 1242, 1130, 985 cm^{-1}. Anal. calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. $C_{16}H_{20}N_2O_2$. Found: C, 70.34; H, 7.34; N, 10.19.

Ethyl 3-(biphenyl-4-yl)-1*H*-pyrazole-5-carboxylate (9d). Method A. The reaction was carried out as described for **9a** using vinylphosphonate **7d** (127 mg, 0.4 mmol). Purification by column chromatography (EtOAc/hexane: 1/2, R_f 0.7) gave pyrazolecarboxylate **9d** as yellowish solid (89 mg) in 76% yield. Method B. The reaction was carried out as described for **9a** using vinylphosphonate **7d** (127 mg, 0.4 mmol); reaction time at the first stage was 55 h. Column chromatography afforded pyrazolecarboxylate **9d** (93 mg) in 83% yield.

Mp 192 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.42 (t, $^{3}J_{H\text{-}H}$=7.1 Hz, 3H, CH$_3$), 3.51 (br. s, 1H, NH), 4.42 (q, $^{3}J_{H\text{-}H}$=7.1 Hz, 2H, CH$_2$), 7.15 (s, 1H, C(4)H), 7.36 (t, $^{3}J_{H\text{-}H}$=7.3 Hz, 1H, ArH), 7.45 (dd, $^{3}J_{H\text{-}H}$=7.3 Hz , $^{3}J_{H\text{-}H}$=7.9 Hz , 2H, ArH), 7.63 (d, $^{3}J_{H\text{-}H}$=7.9 Hz , 2H, ArH), 7.67 (d, $^{3}J_{H\text{-}H}$=8.3 Hz , 2H, ArH), 7.84 (d, $^{3}J_{H\text{-}H}$=8.3 Hz , 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d$_6$): δ 14.2 (CH$_3$), 60.5 (CH$_2$), 105.3 (C(4)), 125.9 (2CH), 126.6 (2CH), 127.1 (2CH), 127.7 (CH), 129.0 (2CH), 129.3, 139.4, 139.9, 141.6 (br., C(5)), 146.6 (br., C(3)), 160.8 (C=O). IR (KBr): *v* 3288, 1697, 1472, 1442, 1267, 1186, 1024, 835, 762 cm^{-1}. Anal. calcd for $C_{16}H_{20}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. $C_{18}H_{16}N_2O_2$. Found: C, 74.14; H, 5.86; N, 9.41.

Ethyl 3-(2-naphthyl)-1*H*-pyrazole-5-carboxylate (9e). Method A. The reaction was carried out as described for **9a** using vinylphosphonate **7e** (116 mg, 0.4 mmol). Purification by column chromatography (EtOAc/hexane: 1/2, R_f 0.75) gave pyrazolecarboxylate **9e** as yellowish solid (79 mg) in 74% yield. Method B. The reaction was carried out as described for **9a** using vinylphosphonate **7e** (116 mg, 0.4 mmol); reaction time at the first stage was 53 h. Column chromatography afforded pyrazolecarboxylate **9e** (73 mg) in 68% yield.

Mp 187 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.39 (t, $^{3}J_{H\text{-}H}$=7.1 Hz, 3H, CH$_3$), 4.38 (q, $^{3}J_{H\text{-}H}$=7.1 Hz, 2H, CH$_2$), 7.23 (s, 1H, C(4)H), 7.46-7.51 (m, 2H, ArH), 7.82-7.92 (m, 4H, ArH), 8,23 (s, 1H), 11.70 (br. s, 1H, NH). ^{13}C NMR (101 MHz, CDCl$_3$): δ 14.2 (CH$_3$), 61.4 (CH$_2$), 105.8 (C(4)), 123.6 (CH), 124.6 (CH), 126.4 (CH), 126.5 (CH), 127.7 (CH), 128.22 (CH), 128.27, 128.7 (CH), 133.3, 133.4, 138.9 (br., C(5)), 149.8 (br., C(3)), 160.6 (C=O). IR (KBr): *v* 3261, 1711, 1469, 1257, 1184, 1144, 1024, 820, 779 cm^{-1}. Anal. calcd for $C_{16}H_{14}N_2O_{22}$: C, 72.16; H, 5.30; N, 10.52. $C_{18}H_{16}N_2O_2$. Found: C, 72.29; H, 5.41; N, 10.29.

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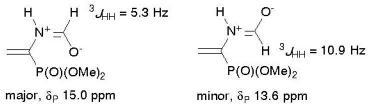

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