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Reactions of Dimethyl 2-Chloroethynylphosphonate with 1-Substituted 5-Oxo-1*H*-1,2,3,4-tetrazoles

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Abstract—Addition of 1-substituted tetrazol-5-ones to dimethyl 2-chloroethynylphosphonate occurred regioselectively to form new geminally substituted bis(4-*R*-5-oxo-4,5-dihydro-1*H*-tetrazol-1-yl)ethenylphosphonates with 65–92% yield.

Keywords: alkenylphosphonate, 5-oxo-1*H*-1,2,3,4-tetrazole, 2-chloroethynylphosphonate, nucleophilic addition, *N*,*O*-binucleophile, X-ray diffraction

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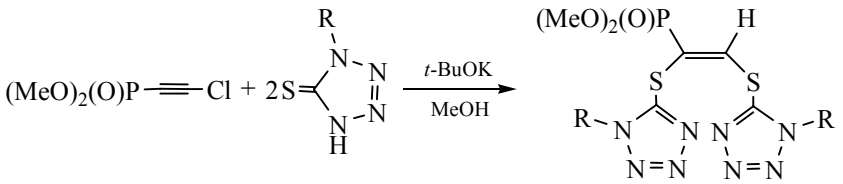
Alkenylphosphonates have been widely used to produce biologically active compounds [1–4], flame retardants [5], polymer additives [6]; they have found interesting applications as reagents in organic synthesis [7–9]. One of the most convenient approaches to synthesize compounds of this class is nucleophilic addition to the double bond. 2-Chloroethynylphosphonate has revealed high reactivity towards different mono- and binucleophiles [10]. Nature of the nucleophiles defines regiochemistry of nucleophilic addition to chloroacetylenephosphonate. In particular, reaction with mononucleophilic reactants occurred via replacement of the chlorine atom followed by addition of the second nucleophile molecule to form geminally disubstituted alkenylphosphonates [11]. The reaction with bifunctional nucleophiles such as 1,2-alkanediols, ethanolamine, *o*-aminophenol, and *o*-phenylenediamine proceeded via substitution of chlorine atom followed by nucleophilic attack of the second nucleophilic site at the same carbon atom to give phosphorylated 1,3-oxalanes, 4,5-dihydrooxazoles, benzoxazoles, and benzimidazoles, respectively [12].

Another direction of the reaction was observed in the case of reacting 2-chloroethynylphosphonate with 1-substituted 5-thio-1,2,3,4-tetrazole under base catalysis in a protic solvent. The reaction resulted in formation of vicinally disubstituted alkenylphosphonates with yields of 80–90% [13] (Scheme 1).

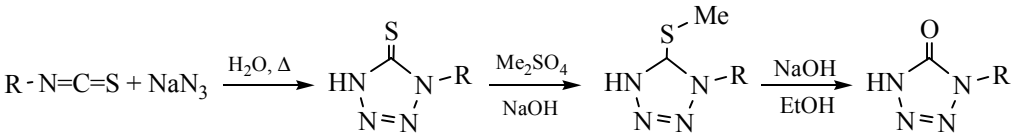
Some of the prepared dimethyl *Z*-1,2-bis[(1*H*-1,2,3,4-tetrazol-5-yl)sulfanyl]ethenylphosphonates showed high antifungal activity comparable to that of fluconazole, the latter being widely used in medical practice for treatment of various fungal infections.

It was of interest to introduce structural analogs of 5-thio-1,2,3,4-tetrazoles, 1-substituted 5-oxo-1,2,3,4-tetrazoles, into the reaction with 2-chloroethynylphosphonate. 1-Phenyl- (**Ia**), 1-benzyl- (**Ib**), 1-(2-chlorophenyl)- (**Ic**), 1-(4-nitrophenyl)- (**Id**), and 1-(2,4-dinitrophenyl)-4,5-dihydro-1*H*-1,2,3,4-tetrazol-5-ones

Scheme 1.



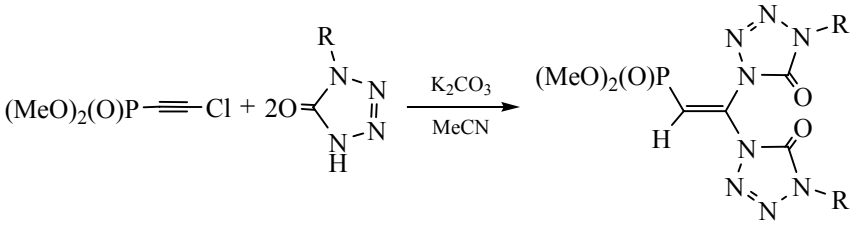
Scheme 2.



Ia–Ie

R = Ph (**Ia**), Bn (**Ib**), 2-Cl-C_6H_4 (**Ic**), 4-NO_2-C_6H_4 (**Id**), 2,4-NO_2-C_6H_3 (**Ie**).

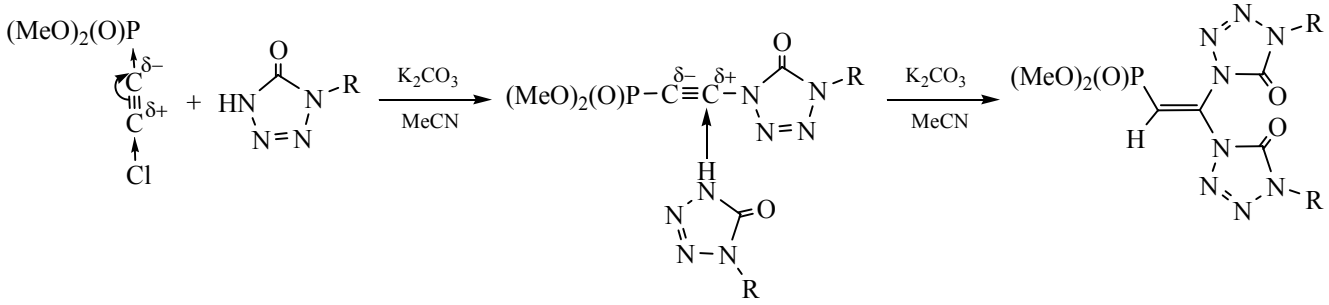
Scheme 3.



IIa–IIe

R = Ph (**IIa**), Bn (**IIb**), 2-Cl-C_6H_4 (**IIc**), 4-NO_2-C_6H_4 (**IId**), 2,4-NO_2-C_6H_3 (**IIe**).

Scheme 4.



(**Ie**) were used as binucleophilic reagents. They were obtained starting from isothiocyanate according to the procedure adopted from [14–16] (Scheme 2).

The reaction of dimethyl 2-chloroethynylphosphonate with the substituted NH-tetrazol-5-ones was found to proceed regioselectively to afford the geminally disubstituted alkenylphosphonates **IIa**–**IIe** with 65–87% yield. The reactions were carried out in anhydrous acetonitrile using two-fold molar excess of 1-R-NH-tetrazol-5-one by stirring the reaction mixture during 16–20 h at room temperature in the presence of K_2CO_3 as acceptor of evolving hydrogen chloride.

According to [17], under those reaction conditions the 1-substituted 5-oxo-1*H*-1,2,3,4-tetrazoles reacted exclusively as non-dissociated (neutral) molecules (Scheme 3).

The reaction progress was monitored by ^{31}P NMR spectroscopy. Completion of the reaction was recognized by disappearance of the signal of starting chloroacetylenephosphonate at –6 ppm and by appearance of the signal of tetrazolyl-substituted alkenylphosphonates **IIa**–**IIe** at 10–12 ppm.

The proposed reaction pathway includes two stages. The first step involves nucleophilic attack of NH group of the 1-R-tetrazol-5-one molecule at the C^2 carbon atom, leading to substitution of the labile chlorine atom and to formation of the corresponding dimethyl-(4-R-5-oxo-4,5-dihydro-1*H*-teterazol-1-yl)ethynylphosphonate (Scheme 4).

At the next step, addition of the second molecule of 1-R-tetrazol-5-one occurs to produce geminally disubstituted bis(4-R-5-oxo-4,5-dihydro-1*H*-tetrazol-1-yl)-ethenylphosphonates.

Table 1. NMR spectral data of compounds **IIa**–**IIe**

Comp. no.	δ_H, ppm (J_{HP}, Hz)		δ_C, ppm (J_{HP}, Hz)			δ_P, ppm	*m*/*z* $[M + Na]^+$
	CH_3OP ($^3J_{HP}$)	PCH= ($^2J_{HP}$)	CH_3OP ($^2J_{CP}$)	PCH= ($^1J_{CP}$)	=CCl ($^2J_{CP}$)		
IIa	3.79 d (12.0)	6.94 d (4.0)	53.35 d (6.0)	109.58 d (189.2)	133.21 d (8.8)	11.98	479.5487
IIb	3.63 d (11.5)	6.78 d (3.5)	53.20 d (5.4)	106.53 d (190.5)	132.98 d (9.0)	12.17	507.3924
IIc	3.83 d (11.5)	6.97 d (4.0)	53.44 d (5.4)	107.49 d (189.8)	133.33 d (9.4)	11.98	547.9891
IId	3.85 d (12.0)	6.98 d (4.7)	53.52 d (5.4)	108.88 d (189.2)	132.52 d (9.1)	11.20	569.0637
IIe	3.72 d (12.0)	6.89 d (4.0)	52.72 d (5.7)	107.84 d (188.7)	131.91 d (9.0)	10.98	659.3368

Noteworthily, reaction of chloroacetylenephosphonate with 1-substituted 5-thio-1,2,3,4-tetrazoles under similar conditions led to preferential formation of the cyclization products; only traces of linear vicinally disubstituted alkenylphosphonates were detected by spectroscopy [13]. In the latter case, unlike the reaction of tetrazol-5-ones, the nucleophilic attack occurred exclusively via the sulfur atom, and the nitrogen atom was not involved into the reaction.

Structure of compounds **IIa**–**IIe** was confirmed by IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, and X-ray diffraction data. Main parameters of ^1H, ^{13}C, and ^{31}P NMR spectra are summarized in Table 1.

In ^1H NMR spectra of alkenylphosphonates **IIa**–**IIe**, the protons of $POCH_3$ fragment resonated as a doublet in the range of 3.63–3.85 ppm, $^3J_{HP}$ 11.5 Hz. The methine proton of PCH moiety manifested as a characteristic doublet signal in weak field (6.78–6.98 ppm, $^2J_{HP}$ 3.0–3.5).

In ^{13}C NMR spectra of **IIa**–**IIe**, a signal of the C^1 carbon atom adjacent to the phosphorus atom appeared as a doublet at δ_C 106.53–108.88 ppm split at phosphorus nucleus with coupling constants of $^1J_{CP}$ 189.2–190.5 Hz, typical of phosphonates with sp^2-hybridized carbon atom. The C^2 carbon atom resonated as a weak doublet signal in the range of 132.52–133.33 ppm, $^2J_{CP}$ 8.8–9.4 Hz. An upfield doublet at about 53 ppm ($^2J_{CP}$ 4.7–5.4 Hz) corresponded to carbon atoms of $POCH_3$ groups.

The chemical shifts of phosphorus were found at δ_P 11.20–12.17 in the spectra of adducts **IIa**–**IIe**. IR spectra of compounds **IIa**–**IIe** contained strong absorption bands assigned to stretching of phosphoryl group (1247–1257 cm^{-1}), of double carbon–carbon bond (1630–1640 cm^{-1}), and of double C=O bond (1686–1696 cm^{-1}). In the mass spectra (HRMS-ESI) of phosphonates **IIa**–**IIe**, the molecular ions $[M + Na]^+$ peaks were found (Table 1).

X-Ray diffraction data of isolated dimethyl {2,2-bis-[4-(2-chlorophenyl)-5-oxo-4,5-dihydro-1*H*-tetrazol-1-yl]ethenyl}phosphonate **IIc** unambiguously confirmed the formation of geminally disubstituted alkenephosphonates (see figure). The compound crystallized in the triclinic (*P*-1) space group with two molecules in the asymmetric unit cell (Table 2). The bond lengths and angles coincided with those typically found in similar compounds and are listed in Tables 3–5.

In conclusion, nucleophilic addition of 1-substituted NH-tetrazol-5-ones to dimethyl ester of 2-chloroethynylphosphonic acid proceeds via regioselective attack of NH site of the tetrazole at the C^2 carbon atom to form geminal bis(4-R-5-oxo-4,5-dihydro-1*H*-tetrazol-1-yl)ethenylphosphonates. The obtained tetrazolyl-substituted alkenylphosphonates are promising synthons for preparation of tetrazolyl-containing phosphonates with potentially wide range of biological activity.

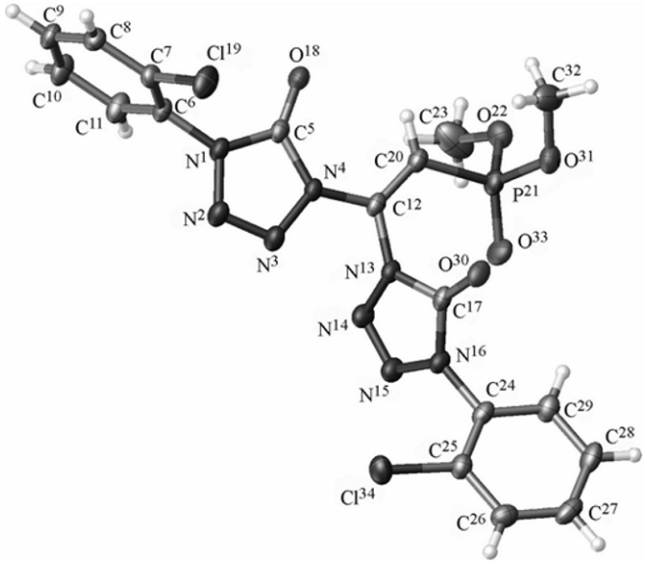
EXPERIMENTAL

NMR spectra of the solutions in $CDCl_3$ were recorded with a Bruker Avance 400 spectrometer [400.13 (^1H), 100.61 (^{13}C), 161.98 MHz (^{31}P)] relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P) reference. IR spectra were recorded using a Shimadzu FTIR-8400S spectrometer (KBr pellets). Mass spectra (HRMS-ESI) were recorded with a Bruker MicrOTOF spectrometer. Melting points were determined on a Kofler bench (VEB Wдgetechnik Rapido, PHMK 81/2969). X-Ray diffraction analysis was performed using a Bruker APEX II CCD diffractometer. TLC analysis was carried out on Merck Kieselgel $60F_{254}$ plates with a UV light developing.

Synthesis of 1-substituted NH-tetrazol-5-ones *(general procedure)*. 0.058 mol of substituted isothiocyanate and about 60 mL of water were added upon stirring to a solution of 0.087 mol of sodium azide in 50 mL of water. The reaction mixture was refluxed during 1.5 h. The reaction progress was monitored with TLC (hexane–EtOAc, 8 : 2). After the reaction was complete, the reaction mixture was acidified with conc. hydrochloric acid to pH ≈ 1. The formed precipitate was filtered off, dried in air, and recrystallized from a large amount of water with the hot filtration.

Dimethylsulfate (0.024 mol) was added dropwise to a solution of 0.015 mol of the so obtained 1-R-tetrazole-5-thione in 50 mL of 5% sodium hydroxide solution. The reaction mixture was stirred at room temperature during 2 h. The reaction progress was monitored with TLC (hexane–EtOAc, 1 : 1). After the reaction was complete, the reaction mixture was extracted three times with ethyl acetate, the extract was washed sequentially with water, saturated sodium chloride solution, and water; then it was dried over Na_2SO_4 and evaporated. Crude 5-methylsulfanyl-1-R-tetrazole was used without further purification.

A solution of 40 mL of ethanol and 0.066 mol of sodium hydroxide was added to 0.0125 mol of 5-methylsulfanyl-1-R-tetrazole upon stirring. The reaction mixture was refluxed during 2 h. The reaction progress was monitored with TLC (hexane–ethyl acetate 1 : 1). After the reaction was complete, the reaction mixture was acidified with conc. hydrochloric acid to pH ≈ 1. The formed precipitate was filtered off. The filtrate was extracted with ethyl acetate, dried over Na_2SO_4, and evaporated. The residue was recrystallized from ethyl acetate.



General view of the molecule of dimethyl {2,2-bis[4-(2-chlorophenyl)-5-oxo-4,5-dihydro-1*H*-tetrazol-1-yl]ethenyl}-phosphonate **IIc**

Synthesis of bis(4-R-5-oxo-4,5-dihydro-1*H*-tetrazol-1-yl)ethenylphosphonate *(general procedure)*. 2.8 mmol of potassium carbonate and 5 mmol of 1-R-

Table 2. Crystallographic data of adduct **IIc**

Parameter	Value	Parameter	Value
Formula	$C_{18}H_{15}Cl_2N_8O_5P_2$	Z	2
M	525.25	d_{calc}, g/cm	1.549
T, K	100(2)	$F(000)$	536
Crystal system	Triclinic	μ, mm^{-1}	3.711
Space group	P-1	$2\theta_{max}$, deg	7.04–153.44
a, Å	9.5300(3)	Reflections collected	23553
b, Å	9.7408(3)	Independent reflections (R_{int})	4711 (0.0513)
c, Å	12.8595(3)	Parameters	309
α, deg	94.011(2)	$R_1[I > 2\sigma(I)]$	0.0438
β, deg	100.164(2)	wR_2 (all data)	0.1095
γ, deg	105.086(3)	GOF	1.198
V, $Å^3$	1126.05(6)		

Table 3. Bond lengths (Å) in the molecule of compound **IIc**

Bond	*d*	Bond	*d*	Bond	*d*
Cl^{19}–C^{7}	1.726(3)	O^{18}–C^{5}	1.205(3)	C^{20}–C^{12}	1.325(4)
P^{21}–O^{33}	1.463(2)	N^{15}–N^{14}	1.270(3)	C^{7}–C^{6}	1.385(4)
P^{21}–O^{31}	1.564(2)	N^{13}–C^{17}	1.389(3)	C^{7}–C^{8}	1.388(4)
P^{21}–O^{22}	1.573(2)	N^{13}–N^{14}	1.375(3)	C^{6}–C^{11}	1.382(4)
P^{21}–C^{20}	1.792(3)	N^{13}–C^{12}	1.409(3)	C^{24}–C^{24}	1.383(4)
Cl^{34}–C^{25}	1.733(3)	N^{3}–N^{2}	1.274(3)	C^{24}–C^{29}	1.388(4)
O^{30}–C^{17}	1.209(3)	N^{1}–C^{5}	1.379(3)	C^{8}–C^{9}	1.388(4)
N^{4}–N^{3}	1.367(3)	N^{1}–N^{2}	1.368(3)	C^{10}–C^{11}	1.390(4)
N^{4}–C^{5}	1.393(3)	N^{1}–C^{6}	1.429(3)	C^{10}–C^{9}	1.383(4)
N^{4}–C^{12}	1.412(3)	O^{31}–C^{32}	1.448(4)	O^{29}–C^{28}	1.386(4)
N^{16}–N^{15}	1.371(3)	O^{22}–C^{23}	1.448(4)	C^{27}–C^{28}	1.384(4)
N^{16}–C^{17}	1.378(3)	C^{26}–C^{25}	1.390(4)		
N^{16}–C^{24}	1.424(3)	C^{26}–C^{27}	1.384(4)		

Table 4. Bond angles (deg) in the molecule of compound **IIc**

Angle	ω	Angle	ω	Angle	ω
$O^{33}P^{21}O^{31}$	111.51(12)	$N^{2}N^{1}N^{5}$	111.8(2)	$C^{11}C^{6}N^{1}$	119.5(2)
$O^{33}P^{21}O^{22}$	115.97(12)	$N^{2}N^{1}C^{6}$	120.6(2)	$C^{11}C^{6}C^{7}$	120.4(2)
$O^{33}P^{21}C^{20}$	113.97(12)	$C^{32}O^{31}P^{21}$	122.74(18)	$C^{26}C^{25}Cl^{34}$	120.1(2)
$O^{31}P^{21}O^{22}$	102.76(12)	$C^{23}O^{22}P^{21}$	119.3(2)	$C^{24}C^{25}Cl^{34}$	119.8(2)
$O^{31}P^{21}C^{20}$	107.90(12)	$O^{18}C^{5}N^{4}$	129.7(2)	$C^{24}C^{25}C^{26}$	120.1(3)
$O^{22}P^{21}C^{20}$	103.75(12)	$O^{18}C^{5}N^{1}$	129.9(2)	$C^{25}C^{24}N^{16}$	120.5(2)
$N^{3}N^{4}C^{5}$	111.49(19)	$N^{1}C^{5}N^{4}$	100.4(2)	$C^{25}C^{24}C^{29}$	120.7(2)
$N^{3}N^{4}C^{12}$	120.4(2)	$N^{3}N^{2}N^{1}$	108.6(2)	$C^{29}C^{24}N^{16}$	118.8(2)
$C^{5}N^{4}C^{l2}$	127.8(2)	$O^{30}C^{17}N^{16}$	129.8(2)	$N^{13}C^{12}N^{4}$	112.1(2)
$N^{15}N^{16}C^{17}$	111.7(2)	$O^{30}C^{17}N^{13}$	129.8(2)	$C^{20}C^{12}N^{4}$	124.4(2)
$N^{15}N^{16}C^{24}$	121.5(2)	$N^{16}C^{17}N^{13}$	100.4(2)	$C^{20}C^{12}N^{13}$	123.5(2)
$C^{17}N^{16}C^{24}$	126.6(2)	$N^{15}N^{14}N^{13}$	107.8(2)	$C^{7}C^{8}C^{9}$	118.9(2)
$N^{14}N^{15}N^{16}$	108.5(2)	$C^{27}C^{26}C^{25}$	119.0(3)	$C^{9}C^{10}C^{11}$	119.8(3)
$C^{17}N^{13}C^{12}$	125.8(2)	$C^{12}C^{20}P^{21}$	122.5(2)	$C^{6}C^{11}C^{10}$	119.6(3)
$N^{14}N^{13}C^{17}$	111.5(2)	$C^{6}C^{7}Cl^{19}$	119.50(19)	$C^{28}C^{29}C^{24}$	119.3(3)
$N^{14}N^{13}C^{17}$	121.2(2)	$C^{6}C^{7}C^{8}$	120.4(2)	$C^{28}C^{27}C^{26}$	121.1(2)
$N^{2}N^{3}N^{4}$	107.7(2)	$C^{8}C^{7}Cl^{19}$	120.1(2)	$C^{10}C^{9}C^{8}$	120.8(2)
$C^{5}N^{1}C^{6}$	127.6(2)	$C^{7}C^{6}N^{1}$	120.0(2)	$C^{27}C^{28}C^{29}$	119.9(3)

tetrazol-5-one were added to a solution of 2.5 mmol of 2-chloroacetylenephosphonic acid dimethyl ester in 7 mL of acetonitrile. The reaction mixture was stirred during 16–20 h at room temperature. Then the inorganic salt was filtered off, and the solvent was removed. The residue was recrystallized from isopropyl alcohol.

Dimethyl [2,2-bis(5-oxo-4-phenyl-4,5-dihydro-1*H*-1,2,3,4-tetrazol-1-yl)ethenyl]phosphonate (IIa).

Table 5. Torsion angles (τ) in the molecule of the compound **IIc**

Angle	τ	Angle	τ	Angle	τ
$Cl^{19}C^{7}C^{6}N^{1}$	0.0(4)	$O^{22}P^{21}C^{20}C^{12}$	139.7(2)	$C^{20}P^{21}O^{22}C^{23}$	–66.5(3)
$Cl^{19}C^{7}C^{6}C^{11}$	178.0(2)	$C^{5}N^{4}N^{3}N^{2}$	0.4(3)	$C^{7}C^{6}C^{11}C^{10}$	1.4(5)
$Cl^{19}C^{7}C^{8}C^{9}$	–178.8(2)	$C^{5}N^{4}C^{12}N^{13}$	–171.6(2)	$C^{7}C^{8}C^{9}C^{10}$	0.3(4)
$P^{21}C^{20}C^{12}N^{4}$	–173.29(19)	$C^{5}N^{4}C^{12}C^{20}$	9.1(4)	$C^{6}N^{1}C^{5}N^{4}$	–178.4(2)
$P^{21}C^{20}C^{12}N^{13}$	7.5(4)	$C^{5}N^{1}N^{2}N^{3}$	–0.7(3)	$C^{6}N^{1}C^{5}O^{18}$	2.9(4)
$Cl^{34}C^{25}C^{24}N^{16}$	–0.7(4)	$C^{5}N^{1}C^{6}C^{7}$	–90.3(3)	$C^{6}N^{1}N^{2}N^{3}$	178.6(2)
$Cl^{34}C^{25}C^{24}C^{29}$	177.4(2)	$C^{5}N^{1}C^{6}C^{11}$	91.7(3)	$C^{6}C^{7}C^{8}C^{9}$	–0.4(4)
$N^{4}N^{3}N^{2}N^{1}$	–0.2(3)	$N^{2}N^{1}C^{5}N^{4}$	0.9(3)	$C^{25}C^{26}C^{27}C^{28}$	0.4(4)
$N^{16}N^{15}N^{14}N^{13}$	0.2(3)	$N^{2}N^{1}C^{5}O^{18}$	–177.8(3)	$C^{25}C^{24}C^{29}C^{28}$	1.0(4)
$N^{16}C^{24}C^{29}C^{28}$	179.1(2)	$N^{2}N^{1}C^{6}C^{7}$	90.5(3)	$C^{24}N^{16}N^{15}N^{14}$	–176.5(2)
$N^{15}N^{16}C^{17}O^{30}$	–178.2(3)	$N^{2}N^{1}C^{6}C^{11}$	–87.5(3)	$C^{24}N^{16}C^{17}O^{30}$	–4.0(4)
$N^{15}N^{16}C^{17}N^{13}$	3.2(3)	$C^{17}N^{16}N^{15}N^{14}$	–2.0(3)	$C^{24}N^{16}C^{17}N^{13}$	177.4(2)
$N^{15}N^{16}C^{24}C^{25}$	–72.4(3)	$C^{17}N^{16}C^{24}C^{25}$	114.0(3)	$C^{24}C^{29}C^{28}C^{27}$	–0.2(4)
$N^{15}N^{16}C^{24}C^{29}$	109.5(3)	$C^{17}N^{16}C^{24}C^{29}$	–64.2(3)	$C^{2}N^{4}N^{3}N^{2}$	–173.6(2)
$N^{3}N^{4}C^{5}O^{18}$	177.9(3)	$C^{17}N^{13}N^{14}N^{15}$	2.4(3)	$C^{12}N^{4}C^{5}O^{18}$	–8.6(4)
$N^{3}N^{4}C^{5}N^{1}$	–0.8(3)	$C^{17}N^{13}C^{12}N^{4}$	–121.4(3)	$C^{12}N^{4}C^{5}N^{1}$	172.7(2)
$N^{3}N^{4}C^{12}N^{13}$	1.3(3)	$C^{17}N^{13}C^{12}C^{20}$	57.9(4)	$C^{12}N^{13}C^{17}O^{30}$	11.9(4)
$N^{3}N^{4}C^{12}C^{20}$	–178.0(2)	$N^{14}N^{13}C^{17}O^{30}$	178.0(3)	$C^{12}N^{13}C^{17}N^{16}$	–169.5(2)
$O^{33}P^{21}O^{31}C^{32}$	–165.1(2)	$N^{14}N^{13}C^{17}N^{16}$	–3.4(3)	$C^{12}N^{13}N^{14}N^{15}$	169.3(2)
$O^{33}P^{21}O^{22}C^{23}$	59.3(3)	$N^{14}N^{13}C^{12}N^{4}$	73.8(3)	$C^{8}C^{7}C^{6}N^{1}$	–178.5(2)
$O^{33}P^{21}C^{20}C^{12}$	12.6(3)	$N^{14}N^{13}C^{12}C^{20}$	–107.0(3)	$C^{8}C^{7}C^{6}C^{11}$	–0.5(4)
$N^{1}C^{6}C^{11}C^{10}$	179.4(3)	$C^{26}C^{25}C^{24}N^{16}$	–179.2(2)	$C^{11}C^{10}C^{9}C^{8}$	0.6(5)
$O^{31}P^{21}O^{22}C^{23}$	–178.8(3)	$C^{26}C^{25}C^{24}C^{29}$	–1.1(4)	$C^{27}C^{26}C^{25}Cl^{34}$	–178.0(2)
$O^{31}P^{21}O^{20}C^{12}$	–111.8(2)	$C^{26}C^{27}C^{28}C^{29}$	–0.5(4)	$C^{27}C^{26}C^{25}C^{24}$	0.4(4)
$O^{22}P^{21}O^{31}C^{32}$	70.0(3)	$C^{20}P^{21}O^{31}C^{32}$	–39.2(3)	$C^{9}C^{10}C^{11}C^{6}$	–1.4(5)

Yield 87%, white crystals, mp 158°C. ^{1}H NMR spectrum, δ, ppm: 3.79 d (6H, OCH_3, $^3J_{HP}$ 12.0 Hz), 6.94 d (1H, =CH, $^2J_{HP}$ 4.0 Hz), 7.39 t and 7.46 t (4H, CH^m, $^3J_{HH}$ 8.0 Hz), 7.48 t (2H, CH^n, $^3J_{HH}$ 8.0 Hz), 7.82 d and 7.91 d (4H, CH^o, $^3J_{HH}$ 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 53.35 d (OCH_3, $^2J_{CP}$ 6.0 Hz), 109.58 d (=CH, $^1J_{CP}$ 189.8 Hz), 128.16 and 128.65 (CH^m, C_6H_4), 129.42 and 129.58 ($CH^{o,p}$, C_6H_4), 133.21 d (=C, $^2J_{CP}$ 8.8 Hz), 133.53 and 134.14 (C^{ipso}, C_6H_4), 146.05 and 147.66 (C=O). ^{31}P NMR spectrum, ($CDCl_3$): δ_P 11.98 ppm.

Dimethyl [2,2-bis(4-benzyl-5-oxo-4,5-dihydro-1*H*-1,2,3,4-tetrazol-1-yl)ethenyl]phosphonate (IIb). Yield 65%, yellowish oil. ^{1}H NMR spectrum, δ, ppm: 3.63 d (6H, OCH_3, $^3J_{HP}$ 11.5 Hz), 4.97 s and 5.06 s (4H, CH_2), 6.78 d (1H, =CH, $^2J_{HP}$ 3.5 Hz), 7.27 m (10H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 48.73 and 48.96 (CH_2), 53.20 d (OCH_3, $^2J_{CP}$ 5.4 Hz), 106.53 d (=CH, $^1J_{CP}$ 190.5 Hz), 127.84 and 128.44 (CH^m, C_6H_4), 128.42 and 128.83 (CH^p, C_6H_4), 128.88 and 129.01 (CH^o, C_6H_4), 133.21d (=C, $^2J_{CP}$ 8.8 Hz), 133.43 and 134.08 (C^{ipso}, C_6H_4), 132.98 d (=C, $^2J_{CP}$ 9.0 Hz), 147.52 and 149.22 (C=O). ^{31}P NMR spectrum, ($CDCl_3$): δ_P 12.17 ppm.

Dimethyl {2,2-bis[4-(2-chlorophenyl)-5-oxo-4,5-dihydro-1*H*-1,2,3,4-tetrazol-1-yl]ethenyl}phosphonate (IIc). Yield 85%, white crystals, mp 154°C. ^{1}H NMR spectrum, δ, ppm: 3.83 d (6H, OCH_3, $^3J_{HP}$ 11.5 Hz), 6.97 d (1H, =CH, $^2J_{HP}$ 4.0 Hz), 7.49 m (8H, C_6H_4Cl). ^{13}C NMR spectrum, δ_C, ppm: 53.44 d (OCH_3, $^2J_{CP}$ 5.4 Hz), 107.49 d (=CH, $^1J_{CP}$ 189.8 Hz), 127.94 and 128.06 (C^5, C_6H_4Cl), 128.98 and 129.38 (C^3, C_6H_4Cl), 129.72 and 130.38 (C^2, C_6H_4Cl), 130.81 and 131.00

(C^6, C_6H_4Cl), 131.85 and 132.27 (C^4, C_6H_4Cl), 132.04 and 132.14 (C^1, C_6H_4Cl), 133.33 d (=C, $^2J_{CP}$ 9.4 Hz), 146.46 and 148.35 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 11.98 ppm.

Dimethyl {2,2-bis[4-(4-nitrophenyl)-5-oxo-4,5-dihydro-1*H*-1,2,3,4-tetrazol-1-yl]ethenyl}phosphonate (IId). Yield 84%, white crystals, mp 173°C. ^1H NMR spectrum, δ, ppm: 3.85 d (6H, OCH_3, $^3J_{HP}$ 12.0 Hz), 6.98 d (1H, =CH, $^2J_{HP}$ 4.7 Hz), 8.22 d and 8.27 d (4H, CH^m, $^3J_{HH}$ 8.0 Hz), 8.41 d and 8.43 d (4H, CH^o, $^3J_{HH}$ 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 53.52 d (OCH_3, $^2J_{CP}$ 5.4 Hz), 108.88 d (=CH, $^1J_{CP}$ 189.2 Hz), 119.17 and 119.32 (CH^m, $C_6H_4NO_2$), 125.19 and 125.37 (CH^o, $C_6H_4NO_2$), 132.52 d (=C, $^2J_{CP}$ 9.1 Hz), 138.22 and 138.90 (C^{ipso}, $C_6H_4NO_2$), 145.55 and 146.55 (CH^p, $C_6H_4NO_2$), 146.91 and 147.22 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 11.20 ppm.

Dimethyl {2,2-bis[4-(2,4-dinitrophenyl)-5-oxo-4,5-dihydro-1*H*-1,2,3,4-tetrazol-1-yl]ethenyl}phosphonate (IIe). Yield 74%; white crystals, mp 185°C. ^1H NMR spectrum, δ, ppm: 3.72 d (6H, OCH_3, $^3J_{HP}$ 12.0 Hz), 6.89 d (1H, =CH, $^2J_{HP}$ 4.0 Hz), 8.15 d (2H, C_6H_3, $^3J_{HH}$ 8.0 Hz), 8.80 d (2H, C_6H_3, $^3J_{HH}$ 8.0 Hz), 8.89 s (2H, C_6H_3). ^{13}C NMR spectrum, δ_C, ppm: 52.72 d (OCH_3, $^2J_{CP}$ 5.7 Hz), 107.84 d (=CH, $^1J_{CP}$ 188.7 Hz), 122.71 and 123.25 (C^6, C_6H_3), 125.67 and 125.79 (C^5, C_6H_3), 131.91 d (=C, $^2J_{CP}$ 9.0 Hz), 139.67 and 139.99 (C^1, C_6H_3), 140.86 and 141.24 (C^3, C_6H_3), 142.17 and 142.77 (C^2, C_6H_3), 145.63 and 146.77 (C^4, C_6H_3), 146.94 and 147.75 (C=O).

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