Vinyltetrazoles: III.* Metal-Catalyzed Arylation, a New Method of Vinyltetrazoles Functionalization

P. A. Aleshunin^a, K. A. Esikov^a, F. M. Dolgushin^b, and V. A. Ostrovskii^a

^aSt. Petersburg State Technological Institute, St. Petersburg, 190013 Russia e-mail: apa-ti@mail.ru ^bNesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow, Russia

Received September 21, 2012

Abstract—New functionalization procedure was developed for *C*- and *N*-vinyltetrazoles based on Heck reaction. Applying this method diverse (*E*)-styryl- and (*E*)-distyryltetrazoles were obtained for the first time in 76–85% yields. *C*-Vinyltetrazoles are more reactive in Heck cross-coupling than *N*-vinyltetrazoles. The arylation of 1-vinyltetrazole along Heck reaction proceeds with a C–H-activation and leads to the formation of 5-phenyl-1-[2-(*E*)-phenylethenyl]tetrazole.

DOI: 10.1134/S1070428012110097

Vinyl derivatives of tetrazole are first of all regarded as monomers for the synthesis of macromolecular compounds [1–5]. Polymers underlain by vinyltetrazoles are included in the composition of promising energy-rich materials, polymer gas-separation membranes, unwoven filter materials for medicine, and the other composite materials [3–5]. Besides the vinyltetrazoles can be utilized as intermediate reagents in the procedures of the total synthesis of new compounds exhibiting the biological action [4, 6–8].

Vinyltetrazoles possess simultaneously several reaction sites: endocyclic nitrogen atoms and a carbon of the heterocycle, and also contain in their structure an exocyclic $CH=CH_2$ group. The reactions involving the nitrogen atoms of the ring are well known [4, 9]. These are the alkylation, the acetylation, quaternization, Mannich condensation, complexing with metals through the donor-acceptor interactions [3]. These processes do not affect the double bond and can be used for the preparation of new tetrazole-containing monomers and polymers.

Unlike that the vinyltetrazole reactions involving the $CH=CH_2$ group attracted less attention. Individual instances are published of the addition of the electrophilic and nucleophilic reagents to the double bond of the vinyltetrazoles, namely, the hydration [10], the addition of trichloroacetonitrile in the presence of copper catalysts [11], the reaction with hypobromous acid [12] and with the elemental bromine [13]. In all these reactions the products are formed as a result of the opening of the double bond.

Lately an interest arose to styryltetrazoles. For instance, some fluoroquinolones containing a styryltetrazole fragment are regarded as bioisosteric analogs of the drug Levofloxacin [7]. Similar bioisosteric tetrazolecontaining analogs were also described for chromones [8]. These compounds possess pronounced antibacterial and antiallergic properties [7, 8]. However the methods of the preparation of styryltetrazoles described in [7, 8] are of particular character and cannot be applied to a targeted functionalization of vinyltetrazoles.

In this connection the development and examination of new method of vinyltetrazoles functionalization at the exocyclic $CH=CH_2$ group with the retention of the double bond leading to styryltetrazoles is an urgent task.

To this end we developed a metal-catalyzed monoarylation of vinyltetrazoles underlain by Heck reaction that provided a possibility to obtain previously unavailable isomeric C- and N-styryltetrazoles. The Heck crosscoupling is an efficient and stereoselective reaction that is widely used for solving similar problems in the alkene chemistry [14–17].

As initial compounds for Heck arylation we selected

^{*} For Communication II, see [1].

5-vinyl-2-methyltetrazole (I), a typical example of *C*-vinyltetrazoles, and also various *N*-vinyltetrazoles. The following reagents were used in the arylation: catalyst $Pd(OAc)_2$, aryl iodides, aryl bromides, and aryl chlorides with electron-donor and electron-acceptor substituents in the aromatic ring, K_2CO_3 as the base, DMF as solvent. The reactions were carried out under an inert atmosphere, in argon.

We showed that the arylation of tetrazole **I** with aryl halides afforded (*E*)-styryltetrazoles **IIa–IIe** in 79–85% yields (Table 1).

At the use of aryl iodides as the arylating agents the reaction time was minimal, 2.5–3 h. The completion of the tetrazole I reaction with aryl bromides containing electron-acceptor substituents required 4–7 h. The aryl bromides lacking the electron-acceptor substituents, and also aryl chlorides did not react in the applied conditions. The results obtained are in agreement with the published data on the reactivity of aryl halides in the Heck reaction [14–17].

In order to obtain the corresponding *N*-styryltetrazoles we extended the conditions of the arylation of the *C*-vinyltetrazole to the *N*-vinyltetrazoles. However in this case the reaction duration was 20–25 h. In this event the arylation of *N*-vinyltetrazoles made it possible to obtain

 Table 1. Arylation by Heck reaction of 5-vinyl-2-methyltetrazole (I)



Ar = Ph (**a**), o-FC₆H₄ (**b**), p-O₂NC₆H₄ (**c**), m-HO₂CC₆H₄ (**d**), m-NCC₆H₄ (**e**).

ArHlg	Time, h	Compound no.	Yield, %
PhI	3	IIa	80
o-FC ₆ H ₄ I	2.5	IIb	81
PhBr	7	IIa	85
p-O ₂ NC ₆ H ₄ Br	4	IIc	79
<i>m</i> -HO ₂ CC ₆ H ₄ Br	6	IId	83
<i>m</i> -NCC ₆ H ₄ Br	5.5	IIe	85
<i>p</i> -BrC ₆ H ₄ Br	15	_	0
<i>p</i> -MeOC ₆ H ₄ Br	15	_	0
$p-O_2NC_6H_4Cl$	15	_	0

N-(E)-styryltetrazoles with yields exceeding 65%.

We believe that the relatively low activity of the *N*-vinyltetrazoles in Heck reaction may be due to the combination of several factors. The data on the study of the electronic structure of vinyltetrazoles show in general that the electron-aceptor effect of the tetrazolyl substituent on the double bond weakens in going from the *C*-vinyl- to the *N*-vinyltetrazoles [3, 5] resulting in the deactivation of the CH=CH₂ group of *N*-vinyltetrazoles in Heck reaction. Besides it is known that tetrazoles are capable of forming complexes with various metals. In this event the metal ion is coordinated to the nitrogen atom in the position 4 of the heterocycle [4]. Hence a possibility exists that in the arylation of *N*-vinyltetrazoles a coordination occurs of the tetrazole ring to Pd(OAc)₂ catalyst thus removing the catalyst from the zone of Heck reaction.

The analysis of the published data on the metal-catalyzed arylation of deactivated alkenes showed that the above mentioned problem might be solved by introducing into the reaction mixture of triphenylphosphine and copper(I) iodide [14, 16, 17]. These reagents stabilize the formed in situ palladium complexes and as we presume screen the nitrogen atom of the ring in the position 4 preventing the side processes of this atom coordination to the catalyst.

On these assumptions we developed the reaction conditions for the preparation of *N*-styryltetrazoles which reduced the arylation time of the initial *N*-vinyltetrazoles to 8 h and raised the yield of the target compounds to 85% (Tables 2 and 3).

The data obtained allow the estimation of the relative reactivity of *N*-vinyl-5-R-tetrazoles **IIIa–IIIg**, **Va–Vd** in Heck reaction. The arylation time of 2-vinyl-5-aryltetrazoles **IIIa–IIId** is shorter (on the average by 2 h) than that of alkylanalogs **IIIe**, **IIIf**. A similar rule was found for 1-vinyl-5-aryl- (Va) and -5-alkyltetrazoles **Vb**, **Vc** (Table 3).

At the arylation of 2-vinyl-5-aryltetrazoles **IIIa–IIId** the duration of the reaction is notably affected by the character of the substituent in the phenyl ring of the azole. For instance, at the introduction of the electron-donor substituent (reagent **IIIb**, $R = p-CH_3C_6H_4$) the reaction completion required more time, on the average, by 5 h (cf. R = Ph, **IIIa**). In contrast, the tetrazoles with the electron-acceptor substituents ($R = p-CF_3C_6H_4$, *o*-NCC₆H₄) reacted faster with the haloarenes.

Besides the completion of the arylation of 1-vinyltetrazoles requires less time (up to 3 h) than that of the

 Table 2. Arylation by Heck reaction of 2-vinyl-5-R-tetrazoles

 IIIa–IIIg



III, R = Ph (a), p-MeC₆H₄ (b), p-F₃CC₆H₄ (c), o-NCC₆H₄ (d), Me (e), Et (f), H₂N (g); IV, R = Ph: Ar = o-FC₆H₄ (a), Ph (b), o-F₃CC₆H₄ (c); R = p-MeC₆H₄: Ar = o-FC₆H₄ (d), Ph (e); R = p-F₃CC₆H₄: Ar = o-FC₆H₄ (f), Ph (g); R = o-NCC₆H₄, Ar = Ph (h); R = Me, Ar = o-FC₆H₄ (i); R = Et, Ar = Ph (j).

Compound no.	ArHlg	Time, h	Reaction product	Yield, %
IIIa	o-FC ₆ H₄I	7	IVa	78
	PhI	7	IVb	82
	o-F ₃ CC ₆ H ₄ Br	9	IVc	81
IIIb	$o ext{-} ext{FC}_6 ext{H}_4 ext{I}$	12	IVd	79
	PhBr	17	IVe	82
IIIc	$o\text{-}\mathrm{FC}_{6}\mathrm{H}_{4}\mathrm{I}$	5.5	IVf	84
	PhBr	10	IVg	81
IIId	PhI	6	IVh	85
	PhBr	14		84
IIIe	<i>o</i> -FC6H4I	8	IVi	78
IIIf	PhI	9	IVj	80
IIIg	PhI	20	_	_

Table 3. Arylation by Heck reaction of 1-vinyl-5-R-tetrazolesVa–Vd



 $R = Ph (a), Me (b), Et (c), H_2N (d).$

Compound no.	Time, h	Reaction product	Yield, %
Va	4	VIa	82
Vb	6	VIb	80
Vc	7	VIc	81
Vd	20	_	0

2-vinyl-5-aryl(alkyl)tetrazoles.

The attempt at performing Heck arylation of 5-amino-*N*-vinyl-tetrazoles **IIIg**, **Vd** failed: no reaction products were detected.

Thus the highest activity in Heck reaction was observed in *C*-vinyltetrazoles, the reaction of *N*-vinyltetrazoles required more severe conditions.

The structure and homogeneity of all compounds obtained were confirmed by a complex of methods: HPLC-MS, ¹H, ¹³C NMR spectroscopy, XRD analysis.

The spin-spin coupling constants of the protons of the CH=CH group in the ¹H NMR spectra of obtained styryltetrazoles **IIa–IIe**, **IVa–IVi**, **VIa–VIc** were in the range 14.6–16.5 Hz characteristic of the disubstituted alkenes of the *E*-configuration [18].

The exhaustive information on the structure of the synthesized compounds was obtained by the XRD anlysis of single crystals of compounds **IIa**, **VIc** (Figs. 1, 2). The crystallographic data and the man parameters of refinement for compounds **IIa**, **VIc** are listed in Table 4. According to the XRD data the styryltetrazoles exist in the *E*-configuration.

At the next stage of the research we used as terminal alkenes in Heck reaction *C*,*N*-divinyltetrazoles **VII**, **VIII** containing in the structure two double bonds providing a possibility of both selective and exhaustive arylation.



Fig. 1. Molecular structure of (*E*)-2-methyl-5-styryltetrazole (**IIa**) according to XRD data.



Fig. 2. Molecular structure of *(E)*-1-styryl-5-ethyltetrazole **(VIc)** according to XRD data.

VII

Data and refinement	Compound no.		
parameters	IIa	VIc	
Empirical formula	C ₁₀ H ₁₀ N ₄	C ₁₁ H ₁₂ N ₄	
Molecular weight	186.22	200.25	
Crystal system	Monoclinic	Rhombic	
Space group	$P2_1/c$	Pbca	
Temperature, K	120(2)	100(2)	
<i>a</i> , Å	6.0310(6)	12.0020(6)	
<i>b</i> , Å	8.5432(8)	6.8047(4)	
<i>c</i> , Å	18.453(2)	25.811(1)	
β, deg	93.967(2)	90	
<i>V</i> , Å ³	948.5(2)	2107.9(2)	
Ζ	4	8	
D_{calc} , g cm ⁻³	1.304	1.262	
$2\theta_{\text{max}}$, deg	58	52	
μ, cm ⁻¹	0.84	0.81	
Number of independent reflections (R_{int})	2524 (0.0340)	2069 (0.0403)	
R_1 [with respect to F for reflections with $I > 2\sigma(I)$]	0.0510 (1939)	0.0355 (1665)	
wR_2 (with respect to F^2 for all reflections)	0.1349	0.0932	
Number of refined parameters	128	136	
GOF	1.064	1.002	

 Table 4. Crystallographic data and refinement parameters for tetrazoles IIa, VIc

The arylation of tetrazoles **VII**, **VIII** under the conditions of the reaction with *N*-vinyltetrazoles furnished the products of the exhaustive arylation, tetrazoles **IX**, **X**, in the yieldes up to 80% (Scheme 1).

The selective arylation of tetrazoles **VII**, **VIII** was possible at the application of an excess of the terminal alkene with respect to the arylating agent.

We detected the formation of the selective arylation product by means of HPLC-MS and NMR spectroscopy; only in the case of tetrazole **XI** we were able to isolate the product from the reaction mixture (Scheme 2).

Styryltetrazole **IX–XI** according to the data of ¹HNMR spectra¹ exist in the *E*-configuration, same as



i: 4.0 mol% Pd(OAc)₂, 12.0 mol% PPh₃, CuI, Cs₂CO₃, DMF, 120°C.

Scheme 1.

PhI

VШ

the above described C- and N-styryltetrazoles.

Interesting results were obtained at Heck arylation of 1(2)-vinyltetrazoles **XII**, **XIII**. The arylation of 1-vinyltetrazole (**XII**) at the double bond under the conditions developed for the reaction with *N*-vinyltetrazoles was accompanied by a C,H-arylation and afforded 1-(E)-styryl-5-phenyltetrazole (**VIa**). The metal-catalyzed C,H-arylation of 1-R-tetrazoles was described by an example of the reaction of aryl and vinyl halides with 1-phenyltetrazole [19].



i: 3.0 mol% Pd(OAc)₂, 9.0 mol% PPh₃, CuI, Cs₂CO₃, DMF, 100°C

Ph

IX

¹ Coupling constants of the protons of group CH=CH in styryltetrazoles **IX–XI** were 14.8–16.1 Hz.

Unlike that the arylation of 2-vinyltetrazole (**XIII**) occurred exclusively at the double bond with the formation of 2-(*E*)-styryltetrazole (**XIV**).



i: 3.0 mol% Pd(OAc)₂, 9.0 mol% PPh₃, CuI, Cs₂CO₃, DMF, 100°C

The obtained styryl tetrazoles **VIa**, **XIV** according to the ¹H NMR data also exist in the *E*-configuration like the above described *C*- and *N*-styryltetrazoles.

Therefore we have developed a new version of the chemical modification of vinyltetrazoles based on the metal-catalyzed arylation of monsubstituted alkenes along Heck reaction providing a possibility to obtain in high yields previously unavailable (*E*)-styryltetrazoles.

EXPERIMENTAL

¹H and ¹³C NMR spectra were registered on a spectrometer Bruker DPX-300 at operating frequencies 300.1 (¹H) and 75.5 MHz (¹³C). The signals of solvents served as internal references: DMSO- d_6 (δ_H 2.50, δ_C 39.52 ppm), CDCl₃ (δ_H 7.26, δ_C 77.16 ppm). Mass spectra were obtained on a spectrometer Waters LCT Premier (ESI, TOF). The melting points were measured on an instrument PTP with the heating rate in the melting range of 1 deg/min. The characteristics of tetrazoles **I**, **IIIa–IIIg**, **Va–Vd**, **VII**, **VIII**, **XII**, **XIII** are consistent with the published data [20].

Al reactions were carried out in an inert atmosphere (argon). The consumption of vinyltetrazoles and the accumulation of the reaction products were monitored by TLC on Merck Kieselgel 60F₂₅₄ plates, visualization of spots under UV irradiation (λ 254 nm). All compounds obtained were isolated and purified by column chromatography on a sorbent Merck Silica Gel 60 for Column Chromatography (0.063–0.200). The eluent for the column chromatography always was the same as used in TLC. After the chromatographic purification the product was recrystallized from ethanol.

XRD analysis of tetrazoles IIa, VIc. The experimental arrays of data were obtained on a diffractometer Bruker Smart Apex II [graphite monochromator, λ (Mo K_{α}) 0.71073 E, ω -scanning] [21]. The structures were solved

by the direct method and were refined by the full-matrix root-mean-square method with respect to F_{hkl}^2 with the anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were placed in the geometrically calculated positions and were included in the refinement in the rider model. All calculations were performed on a PC applying SHELXTL software [22]. The complete tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters are deposited in the Cambridge Crystallographic Data Center, CCDC 906717 (IIa), 906718 (VIc).

5-[2-(*E***)-Arylethenyl]-2-methyltetrazoles IIa–IIe**. To a solution of 9.0 mmol of ArHlg in 2 ml of DMF was added 0.072 mmol of Pd(OAc)₂, and the mixture was stirred for 20 min at 50°C, then 1.8 mmol of tetrazole I and 3.6 mmol of K₂CO₃ was added. The slurry was stirred at 120°C till the completion of the reaction, it was cooled, poured at a vigorous stirring into 20 ml of water, and filtered through celite. The precipitate was washed with water (2 × 5 ml). The filtrate was extracted with ethyl acetate (3 × 10 ml), the combined extract was dried with anhydrous Na₂SO₄ and evaporated to dryness in a vacuum.

2-Methyl-5-[2-(*E***)-phenylethenyl]tetrazole (IIa)**. Yield 0.27 g (80%), colorless crystals, mp 87–88°C. R_f 0.4 (hexane–dichloromethane–ethyl acetate, 7:2.5:0.5). ¹H NMR spectrum (CDCl₃), δ , ppm: 4.36 s (3H, CH₃), 7.14 d (1H, C<u>H</u>=CHPh, *J* 16.5 Hz), 7.34–7.42 m (3H, Ph), 7.54–7.58 m (2H, Ph), 7.73 d (1H, CH=C<u>H</u>Ph, *J* 16.5 Hz). ¹³C NMR spectrum (DMSO- d_6), δ , ppm: 39.48 (CH₃), 113.46 (<u>C</u>H=CHPh), 127.23, 128.93, 129.14, 135.75 (Ph), 136.37 (CH=<u>C</u>HPh), 164.46 (C⁵). Found: *m/z* 187.0921 [*M* + H]⁺. C₁₀H₁₀N₄. Calculated: *M* 186.2132.

2-Methyl-5-[2-(*E***)-(2-fluorophenyl)ethenyl]tetrazole (IIb)**. Yield 0.3 g (81%), colorless crystals, mp 74–75°C. R_f 0.3 (hexane–dichloromethane–ethyl acetate, 9:0.5:0.5). ¹H NMR spectrum (CDCl₃), δ , ppm: 4.36 C (3H, CH₃), 7.07–7.32 m (4H, C<u>H</u>=CHAr, Ar), 7.58–7.62 m (1H, Ar), 7.85 d (1H, CH=C<u>H</u>Ar, *J* 16.5 Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 39.45 (CH₃), 115.92–116.35 m (<u>C</u>H=CHAr, Ar), 123.73 d (Ar, *J* 0.23 Hz), 124.45 d (Ar, *J* 0.04 Hz), 128.26 (Ar), 129.09 (CH=<u>C</u>HAr), 130.39 d (Ar, *J* 0.17 Hz), 160.29 d (Ar, *J* 3.3 Hz), 164.35 (C⁵). Found: *m/z* 205.0831 [*M* + H]⁺. C₁₀H₉FN₄. Calculated: *M* 204.2136.

2-Methyl-5-[2-(*E***)-(4-nitrophenyl)ethenyl]tetrazole** (IIc). Yield 0.33 g (79%), colorless crystals, mp 201–

202°C. R_f 0.2 (hexane–ethyl acetate, 7:3). ¹H NMR spectrum (CDCl₃), δ , ppm: 4.36 s (3H, CH₃), 7.25 d (1H, C<u>H</u>=CHAr, *J* 16.4 Hz), 7.28 d (2H, Ar, *J* 8.6 Hz), 7.74 d (1H, CH=C<u>H</u>Ar, *J* 16.4 Hz), 8.23 d (2H, Ar, *J* 8.6 Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 39.58 (CH₃), 117.85 (<u>C</u>H=CHAr), 124.27, 127.74 (Ar), 133.70 (CH=<u>C</u>HAr), 142.03, 147.80 (Ar), 163.54 (C⁵). Found: *m/z* 232.0801 [*M* + H]⁺. C₁₀H₉N₅O₂. Calculated: *M* 231.2107.

Methyl 3-[2(*E*)-(2-methyltetrazol-5-yl)ethenyl] benzoate (IId). Yield 0.35 g (83%), colorless crystals, mp 148–149°C. R_f 0.2 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (CDCl₃), δ, ppm: 3.93 s (3H, CO₂CH₃), 4.35 s (3H, CH₃), 7.20 d (1H, C<u>H</u>=CHAr, *J* 16.4 Hz), 7.44– 7.48 m (1H, Ar), 7.71–7.75 m (2H, CH=C<u>H</u>Ar, Ar), 7.99 m (1H, Ar), 8.23 C (1H, Ar). ¹³C NMR spectrum (DMSO- d_6), δ, ppm: 39.50 (2-CH₃), 52.36 (CO₂C<u>H₃), 114.81 (CH=CHAr), 128.17, 129.03, 129.96, 130.93, 131.43 (Ar), 135.21 (CH=C<u>C</u>HAr), 136.15 (Ar), 164.13 (C⁵), 166.77 (Ar). Found: *m/z* 245.1123 [*M* + H]⁺. C₁₂H₁₂N₄O₂. Calculated: *M* 244.2492.</u>

3-[2-(*E***)-(2-Methyltetrazol-5-yl)ethenyl] benzonitrile (IIe)**. Yield 0.32 g (85%), colorless crystals, mp 135–136°C. R_f 0.2 (hexane–dichloromethane, 7:3). ¹H NMR spectrum (CDCl₃), δ , ppm: 4.36 s (3H, CH₃), 7.18 d (1H, C<u>H</u>=CHAr, *J* 16.5 Hz), 7.48–7.61 m (2H, Ar), 7.67 d (1H, CH=C<u>H</u>Ar, *J* 16.5 Hz), 7.75–7.80 m (2H, Ar). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 39.54 (CH₃), 113.28 (Ar), 116.17 (C<u>H</u>=CHAr), 118.47, 129.80, 130.55, 131.11, 132.13 (Ar), 133.73 (CH=<u>C</u>HAr), 137.05 (CN), 163.35 (C⁵). Found: *m/z* 212.0919 [*M* + H]⁺. C₁₁H₉N₅. Calculated: *M* 211.2226.

1(2)-[2-(*E*)-Arylethenyl]-5-R-tetrazoles IVa–IVj, VIa–VIc. To a slurry of 1.8 mmol of CuI and 1.8 mmol of tetrazole IIIa–IIIg, Va–Vd in 2 ml of DMF was added 0.072 mmol of Pd(OAc)₂, 0.21 mmol of PPh₃, 9.0 mmol of ArHlg, and 2.7 mmol of Cs₂CO₃, the mixture was stirred at 120°C till the completion of the reaction. On cooling the mixture was poured at vigorous stirring into 20 ml of water, and the slurry was filtered through celite. The precipitate on the filter was washed with water (2 × 5 ml). The filtrate was extracted with ethyl acetate (3 × 15 ml), the combined extract was dried with anhydrous Na₂SO₄ and evaporated to dryness in a vacuum.

5-Phenyl-2-[2-(*E*)-(2-fluorophenyl)ethenyl] tetrazole (IVa). Yield 0.37 g (78%), colorless crystals, mp 139–140°C. R_f 0.1 (hexane–ethyl acetate, 95 : 5). ¹H NMR spectrum (CDCl₃), δ , ppm: 7.12–7.21 m (2H, Ar), 7.33 m (1H, Ar), 7.49–7.52 m (4H, Ph, Ar), 7.72 d (1H, C<u>H</u>=CHHt, *J* 14.7 Hz), 8.14 d (1H, CH=C<u>H</u>Ht, *J* 14.7 Hz), 8.21 d (2H, Ph). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 116.30 d (Ar, *J* 0.3 Hz), 118.46 (<u>C</u>H=CHHt), 121.20 d (Ar, *J* 0.2 Hz), 124.75 (CH=<u>C</u>HHt), 124.80 (Ar), 127.01, 127.22, 129.08 (Ph), 129.30 d (Ar, *J* 0.3 Hz), 130.72 (Ar), 130.81 (Ph), 161.03 d (Ar, *J* 3.3 Hz), 165.11 (C⁵). Found: *m*/*z* 267.1121 [*M* + H]⁺. C₁₅H₁₁FN₄. Calculated: *M* 266.2730.

5-Phenyl-2-[2-(*E***)-phenylethenyl]tetrazole (IVb)**. Yield 0.36 g (82%), colorless crystals, mp 113–114°C. R_f 0.2 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (CDCl₃), δ, ppm: 7.26–7.56 m (8H_{arom}), 7.69 d (1H, CH=CHHt, *J* 14.5 Hz), 7.99 d (1H, CH=C<u>H</u>Ht, *J* 14.5 Hz), 8.21–8.23 m (2H_{arom}). ¹³C NMR spectrum (DMSO-*d*₆), δ, ppm: 122.53 (<u>C</u>H=CHHt), 124.95 (CH=<u>C</u>HHt); 127.13, 127.23, 127.33, 129.10, 129.24, 129.31, 130.77, 133.20 (Ph); 164.96 (C⁵). Found: *m/z* 249.2121 [*M* + H]⁺. C₁₅H₁₂N₄. Calculated: *M* 248.2825.

2-{2-(*E***)-[3-(Trifluoromethyl)phenyl]ethenyl}-5phenyltetrazole (IVc)**. Yield 0.45 g (81%), colorless crystals, mp 160–161°C. R_f 0.2 (hexane–ethyl acetate, 9:1). ¹H NMR spectrum (CDCl₃), δ , ppm: 7.52–7.64 m (5H, Ph, Ar), 7.71–7.75 m (1H, C<u>H</u>=CHHt, 1H, Ar, *J* 13.9 Hz), 7.80 s (1H, Ar), 8.05 d (1H, CH=C<u>H</u>Ht, *J* 13.9 Hz), 8.22–8.24 m (2H, Ph). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 123.28 (CH=CHHt), 123.89 (Ar), 124.10 d (Ar, *J* 0.05 Hz), 125.96 m (Ar), 126.93, 127.28, 129.17 (Ph), 129.81 (CH=<u>C</u>HHt), 130.24 (Ar), 130.96 (Ph), 134.12 (CF₃), 165.19 (C⁵). Found: *m/z* 317.1108 [*M* + H]⁺. C₁₆H₁₁F₃N₄. Calculated: *M* 316.0912.

5-(4-Methylphenyl)-2-[2-(*E***)-(2-fluorophenyl) ethenyl]tetrazole (IVd)**. Yield 0.39 g (79%), colorless crystals, mp 120–121°C. R_f 0.2 (hexane–ethyl acetate, 9:1). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.43 C (3H, CH₃), 7.13–7.22 m (2H, Ar), 7.31–7.35 m (3H, Ar, Tol), 7.53 m (1H, Ar), 7.72 d (1H, C<u>H</u>=CHHt, *J* 14.7 Hz), 8.10–8.16 m (3H, Tol, CH=C<u>H</u>Ht, *J* 14.7 Hz). ¹³C NMR spectrum (DMSO- d_6), δ , ppm: 21.69 (CH₃), 116.41 d (Ar, *J* 0.3 Hz), 118.28 (<u>C</u>H=CHHt), 121.30 d (Ar, *J* 0.2 Hz), 124.24 (Tol), 124.82 (CH=<u>C</u>HHt), 125.10 (Ar), 127.18, 129.39, 129.82 (Tol), 130.75 d (Ar, *J* 0.3 Hz), 141.09 (Ar), 161.23 (Ar, *J* 3.4 Hz), 165.13 (C⁵). Found: *m/z* 281.2151 [*M* + H]⁺. C₁₆H₁₃FN₄. Calculated: *M* 280.2996.

5-(4-Methylphenyl)-2-[2-(E)-phenylethenyl] tetrazole (IVe). Yield 0.38 g (82%), colorless crystals, mp 118–119°C. R_f 0.2 (hexane–ethyl acetate, 8 : 2).

¹H NMR spectrum (CDCl₃), δ , ppm: 2.42 s (3H, CH₃), 7.30–7.43 m (5H, Ph, Tol), 7.54 m (2H, Ph), 7.67 d (1H, CH=CHHt, *J* 14.7 Hz), 7.97 d (1H, CH=C<u>H</u>Ht, *J* 14.7 Hz), 8.10 d (2H, Tol). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 21.68 (CH₃), 122.58, 124.35 (Tol), 124.74 (<u>C</u>H=CHHt), 127.16 (Tol), 127.31, 129.24 (Ph), 129.46 (CH=<u>C</u>HHt), 129.82, 133.29 (Ph), 141.03 (Tol), 165.06 (C⁵). Found: *m*/*z* 263.1301 [*M* + H]⁺. C₁₆H₁₄N₄. Calculated: *M* 262.3091.

5-[4-(Trifluoromethyl)phenyl]-2-[2-(*E***)-(2fluorophenyl)ethenyl]tetrazole (IVf). Yield 0.48 g (84%), colorless crystals, mp 129–130°C. R_f 0.1 (hexane–ethyl acetate, 9:1). ¹H NMR spectrum (CDCl₃), \delta, ppm: 7.16–7.22 m (2H, Ar), 7.36 m (1H, Ar), 7.54 m (1H, Ar), 7.74–7.79 m (3H, Ar, C<u>H</u>=CHHt,** *J* **14.7 Hz), 8.16 d (1H, CH=C<u>H</u>Ht,** *J* **14.7 Hz), 8.35 d (2H, Ar). ¹³C NMR spectrum (DMSO-***d***₆), \delta, ppm: 116.42 d (Ar,** *J* **0.3 Hz), 119.15 (CH=CHHt), 121.10 d (Ar,** *J* **0.2 Hz), 122.18 q (Ar,** *J* **7.1 Hz), 124.71, 124.85 (Ar), 124.90 (CH=<u>C</u>HHt), 126.11 m (Ar), 127.55 (Ar), 129.53 (Ar,** *J* **0.3 Hz), 130.45, 131.05 (Ar), 161.12 (Ar,** *J* **3.3 Hz), 163.84 (C⁵). Found:** *m/z* **335.1101 [***M* **+ H]⁺. C₁₆H₁₀F₄N₄. Calculated:** *M* **334.0711.**

5-[4-(Trifluoromethyl)phenyl]-2-[2-(*E***)-phenylethenyl]tetrazole (IVg)**. Yield 0.46 g (81%), lightyellow crystals, mp 140–141°C. R_f 0.1 (hexane–ethyl acetate, 95:5). ¹H NMR spectrum (CDCl₃), δ , ppm: 7.41–7.46 m (3H, Ph), 7.56 d (2H, Ar), 7.72 d (1H, CH=CHHt, *J* 14.7 Hz), 7.78 d (2H, Ph), 8.01 d (1H, CH=C<u>H</u>Ht, *J* 14.7 Hz), 8.35 d (1H, Ar). ¹³C NMR spectrum (DMSO- d_6), δ , ppm: 122.17 q (Ar, *J* 7.1 Hz), 122.34 (Ar), 125.54 (<u>C</u>H=CHHt), 126.11 m (Ar), 127.39 (Ar), 127.49, 129.28 (Ph), 129.72 (CH=<u>C</u>HHt), 130.47 (Ph), 132.55 (<u>Ar</u>), 132.94 (Ph), 163.72 (C⁵). Found: *m/z* 317.1221 [*M* + H]⁺. C₁₆H₁₁F₃N₄. Calculated: *M* 316.0905.

2-{2-[(*E*)-**2-Phenylethenyl]tetrazol-5-yl}benzonitrile (IVh). Yield 0.42 g (85%), light-yellow crystals, mp 124–125°C. R_f 0.2 (hexane– ethyl acetate, 9:1). ¹H NMR spectrum (CDCl₃), \delta, ppm: 7.38–7.44 m (3H, Ph), 7.55–7.63 m (3H, Ar, Ph), 7.74–7.78 t (2H, Ar, CH=CHHt,** *J* **14.7 Hz), 7.87 m (1H, Ar), 8.04 d (1H, CH=CHHt,** *J* **14.7 Hz), 8.36 m (1H, Ar). ¹³C NMR spectrum (DMSO-***d***₆), \delta, ppm: 110.51 (Ar), 117.60 (CN), 122.46 (CH=CHHt), 125.90 (Ar), 127.49 (Ph), 129.02 (Ar), 129.11 (Ph), 129.50, 129.61 (Ar), 130.88 (CH=CHHt), 132.72, 133.30 (Ph), 134.86 (Ar), 161.98 (C⁵). Found:** *m/z* **275.0912 [***M* **+ H]⁺. C₁₆H₁₁N₅.** Calculated: M 274.1120.

5-Methyl-2-[2-(*E***)-(2-fluorophenyl)ethenyl] tetrazole (IVi)**. Yield 0.29 g (78%), light-yellow crystals, mp 88–89°C. R_f 0.2 (hexane–ethyl acetate, 9:1). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.60 s (3H, CH₃), 7.11–7.20 m (2H, Ar), 7.32 m (1H, Ar), 7.48 m (1H, Ar), 7.61 d (1H, CH=CHHt, *J* 14.7 Hz), 8.05 d (1H, CH=C<u>H</u>Ht, *J* 14.7 Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ, ppm: 11.09 (CH₃), 116.35 d (Ar, *J* 0.3 Hz), 118.08 d (CH=CHHt, *J* 0.2 Hz), 121.23 d (Ar, *J* 0.2 Hz), 124.74, 124.93 (Ar), 129.37 (CH=<u>C</u>HHt), 130.69 d (Ar, *J* 0.1 Hz), 161.14 (Ar, *J* 3.3 Hz), 163.17 (C⁵). Found: *m/z* 205.1103 [*M*+H]⁺. C₁₀H₉FN₄. Calculated: *M* 204.0736.

2-[2-(*E***)-Phenylethenyl]-5-ethyltetrazole (IVj).** Yield 0.28 g (80%), colorless crystals, mp 160–161°C. R_f 0.2 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.41 t (3H, CH₃), 2.96 q (2H, CH₂), 7.33–7.40 m (3H, Ph), 7.48 m (2H, Ph), 7.55 d (1H, CH=CHHt, *J* 14.7 Hz), 7.88 d (1H, CH=C<u>H</u>Ht, *J* 14.7 Hz), 1³C NMR spectrum (DMSO-*d*₆), δ , ppm: 12.41 (CH₃), 19.24 (CH₂), 122.56 (Ph), 124.44 (CH=CHHt), 127.22, 129.19 (Ph), 129.37 (CH=<u>C</u>HHt), 133.26 (Ph), 167.98 (C⁵). Found: *m*/*z* 201.2199 [*M* + H]⁺. C₁₁H₁₂N₄. Calculated: *M* 200.2397.

5-Phenyl-1-[2-(*E***)-phenylethenyl]tetrazole (VIa)**. Yield 0.36 g (82%), colorless crystals, mp 160–161°C. R_f 0.2 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (CDCl₃), δ, ppm: 7.38–7.45 m (6H, Ph, C<u>H</u>=CHHt, *J* 14.5 Hz), 7.58–7.60 m (4H, Ph), 7.77 m (2H, CH=C<u>H</u>Ht, Ph). ¹³C NMR spectrum (DMSO-*d*₆), δ, ppm: 119.81 (<u>C</u>H=CHHt), 123.25, 127.40 (Ph), 127.98 (CH=<u>C</u>HHt), 128.86, 129.19, 129.30, 131.47, 133.13 (Ph), 152.87 (C⁵). Found: *m/z* 249.1911 [*M* + H]⁺. C₁₅H₁₂N₄. Calculated: *M* 248.2825.

5-Methyl-1-[2-(*E***)-phenylethenyl]tetrazole (VIb)**. Yield 0.27 g (80%), colorless crystals, mp 168–169°C. R_f 0.3 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (CDCl₃), δ , ppm: 7.34 d (1H, C<u>H</u>=CHHt, *J* 14.4 Hz), 7.41–7.52 m (7H, Ph, CH=C<u>H</u>Ht). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 9.38 (CH₃), 117.64 (<u>C</u>H=CHHt), 127.00 (CH=<u>C</u>HHt), 127.11, 129.22, 129.57, 133.12 (C₆H₄), 150.52 (C⁵). Found: *m/z* 187.1391 [*M* + H]⁺. C₁₀H₁₀N₄. Calculated: *M* 186.0932.

1-[2-(*E***)-Phenylethenyl]-5-ethyltetrazole (VIc).** Yield 0.27 g (81%), colorless crystals, mp 112–113°C. R_f 0.3 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.47 t (3H, CH₃), 2.99 m (2H, CH₂), 7.30 d (1H, CH=CHHt, *J* 14.5 Hz), 7.39–7.52 m (7H, Ph, CH=C<u>H</u>Ht). ¹³C NMR spectrum (DMSO- d_6), δ , ppm: 11.48 (CH₃), 17.33 (CH₂), 117.51 (<u>C</u>H=CHHt), 127.02 (CH=<u>C</u>HHt), 127.13, 129.23, 129.56, 133.22 (C₆H₄), 154.86 (C⁵). Found: m/z 201.1198 [M + H]⁺. C₁₁H₁₂N₄. Calculated: M 200.0497.

1,2(5)-Bis[2-(*E***)-arylethenyl]tetrazoles IX, X**. To a slurry of 1.8 mmol of CuI and 1.8 mmol of tetrazole **VII, VIII** in 3 ml of DMF was added 0.072 mmol of Pd(OAc)₂, 0.21 mmol of PPh₃, 18.0 mmol of ArHIg, and 5.4 mmol of Cs₂CO₃, the mixture was stirred at 120°C till the completion of the reaction. On cooling the mixture was poured at vigorous stirring into 25 ml of water, and the slurry was filtered through celite. . The precipitate on the filter was washed with water (2 × 7 ml). The filtrate was extracted with ethyl acetate (2 × 20 ml), the combined extract was dried with anhydrous Na₂SO₄ and evaporated to dryness in a vacuum.

1,5-Bis[**2**-(*E*)-phenylethenyl]tetrazole (**IX**). Yield 0.4 g (80%), colorless crystals, mp 118– 119°C. R_f 0.2 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (DMSO- d_6), δ, ppm: 7.38–7.49 m (6H, Ph), 7.55 d (1H, CH=CHHt, J 14.4 Hz), 7.67 d (1H, CH=CHHt, J 16.0 Hz), 7.76–7.86 m (4H, Ph), 7.90 d (1H, CH=CHHt, J 16.1 Hz), 8.27 d (1H, CH=CHHt, J 14.1 Hz). ¹³C NMR spectrum (DMSO- d_6), δ, ppm: 108.34 (CH=CHHt), 119.21 (CH=CHHt), 124.99 (CH=CHHt), 127.45, 128.11, 128.82, 128.89, 129.01, 130.05 (Ph), 133.61 (CH=CHHt), 134.94, 139.83 (Ph), 151.47 (C⁵). Found: *m*/*z* 275.3181 [*M* + H]⁺. C₁₇H₁₄N₄. Calculated: *M* 274.3198.

1,2-Bis[2-(*E***)-(2-fluorophenyl)ethenyl]tetrazole (X)**. Yield 0.42 g (76%), colorless crystals, mp 134–135°C. R_f 0.1 (hexane–ethyl acetate, 9:1). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 7.22–7.29 m (4H, Ar, CH=C<u>H</u>Ht, *J* 15.8 Hz), 7.43 m (3H, Ar), 7.68 d (1H, CH=C<u>H</u>Ht, *J* 14.8 Hz), 7.85–7.95 m (3H, Ar, C<u>H</u>=CHHt, *J* 15.8 Hz), 8.49 d (1H, CH=C<u>H</u>Ht, *J* 14.8 Hz). ¹³C NMR spectrum (CDCl₃), δ , ppm: 116.40 d (CH=<u>C</u>HHt, *J* 0.1 Hz), 116.53, 116.92 (Ar), 117.73 d (<u>C</u>H=CHHt, *J* 0.05 Hz), 125.59–125.81 m (Ar, CH=<u>C</u>HHt), 129.30 d (Ar, *J* 0.05 Hz), 129.69 d (<u>C</u>H=CHHt, *J* 0.05 Hz), 129.73 (Ar), 132.01 d (Ar, *J* 0.1 Hz), 161.03 d (Ar, *J* 3.3 Hz), 163.26 (C⁵). Found: *m/z* 311.3881 [*M*+H]⁺. C₁₇H₁₂F₂N₄. Calculated: *M* 310.3007.

2-Vinyl-5-[2-(E)-(2-fluorophenyl)ethenyl]tetrazole (XI) was obtained from 1.8 mmol of o-FC₆H₄I, 3.5 mmol of tetrazole VIII, 0.072 mmol of Pd(OAc)₂, 0.216 mmol of PPh₃, 1.8 mmol of CuI,

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 48 No. 11 2012

1.9 mmol of Cs₂CO₃. Yield 0.31 g (80%), colorless crystals, mp 69–70°C. R_f 0.2 (hexane–ethyl acetate, 9 : 1). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 5.50 d (1H, CH₂=CHHt, J 7.8 Hz), 6.16 d (1H, CH₂=CHHt, J 14.7 Hz), 7.21–7.27 m (2H, Ar, CH=CHHt, J 15.7 Hz), 7.38–7.42 m (2H, Ar, CH₂=CHHt), 7.77–7.90 m (3H, Ar, CH=CHHt). ¹³C NMR spectrum (DMSO- d_6), δ , ppm: 109.30 (CH₂=CHHt), 115.69 (CH=CHHt), 116.51 (Ar), 122.63 d (Ar, J 0.2 Hz), 124.91 (Ar), 128.36 (CH=CHHt), 128.52 (Ar), 130.11 (CH₂=CHHt), 131.25 d (Ar, J 0.2 Hz), 160.38 d (Ar, J 3.3 Hz), 162.59 (C⁵). Found: m/z 217.1139 [M + H]⁺. C₁₁H₉FN₄. Calculated: M 216.0743.

N-[2-(*E*)-Arylethenyl]tetrazoles VIa, XIV. To a slurry of 1.8 mmol of CuI and 1.8 mmol of tetrazole XII, XIII in 1 ml of DMF was added 0.054 mmol of Pd(OAc)₂, 0.16 mmol of PPh₃, 18.0 mmol of ArHlg, and 5.1 mmol of Cs₂CO₃, the mixture was stirred at 100°C till the completion of the reaction. On cooling the mixture was poured at vigorous stirring into 15 ml of water, and the slurry was filtered through celite. . The precipitate on the filter was washed with water (2 × 5 ml). The filtrate was extracted with ethyl acetate (2 × 15 ml), the combined extract was dried with anhydrous Na₂SO₄ and evaporated to dryness in a vacuum.

2-[2-(*E***)-Phenylethenyl]tetrazole (XIV)**. Yield 0.25 g (80%), light-yellow crystals, mp 40–41°C. R_f 0.3 (hexane–ethyl acetate, 8:2). ¹H NMR spectrum (CDCl₃), δ , ppm: 7.38–7.43 m (3H, Ph), 7.52–7.55 m (2H, Ph), 7.68 d (4H, C<u>H</u>=CHN, *J* 14.7 Hz), 7.99 d (1H, CH=C<u>H</u>CN, *J* 14.7 Hz), 8.58 s (1H, H⁵). ¹³C NMR spectrum, δ , ppm: 122.43 (<u>C</u>H=CHHt); 125.67, 127.39, 129.26, 129.68 (Ph); 132.94 (CH=<u>C</u>HHt), 152.75 (C⁵). Found: *m/z* 173.1211 [*M* + H]⁺. C₉H₈N₄. Calculated: *M* 172.0766.

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Russian Foundation for Basic Research (grant no. 11-08-00483-a).

REFERENCES

- 1. Aleshunin, P.A., Dmitrieva, U.N., and Ostrovskii, V.A., *Zh. Org. Khim.*, 2011, vol. 47, p. 1846.
- Ostrovskii, V.A., Podkameneva, M.E., Poplavskii, V.S., and Trifonov, R.E., *Izv. Akad. Nauk, Ser. Khim.*, 2009, p. 2082.
- Kizhnyaev, V.N. and Vereshchagin, L.I., Usp. Khim., 2003, vol. 72, p. 159.

- Ostrovskii, V.A., Koldobskii, G.I., and Trifonov, R.E., Comprehensive Heterocycl. Chem. III, 2008, vol. 6, p. 257.
- Kizhnyaev, V.N. and Vereshchagin, L.I., *Viniltetrazoly* (Vinyltetrazoles), Irkutsk: Izd. Irkut. Gos. Univ., 2003, p. 41.
- Casey, M., Moody, C.J., and Rees, C.W., J. Chem. Soc., Chem. Commun., 1982, p. 714.
- Nakayama, K., Kuru, N., Ohtsuka, M., Yokomizo, Y., Sakamoto, A., Kawato, H., a, Yoshida, K., Ohta, T., Hoshino, K., Akimoto, K., Itoh, J., Ishida, H., Cho, A., Palme, M.H., Zhang, J.Z., Leeb, V.J., and Watkins, W.J., *Bioorg. Med. Chem. Lett.*, 2004, vol. 14, p. 2496.
- Diwakar, S.D., Bhadwat, S.S., Shingare, M.S., and Gill, C.H., *Bioorg. Med. Chem. Lett.*, 2008, vol. 18, p. 4678.
- 9. Koldobskii, G.I. and Ostrovskii, V.A., *Usp. Khim.*, 1994, vol. 63, p. 847.
- Hermann, S.H., US Patent 3564005, 1971; Chem. Abstr., 1971, vol. 74, 112805.
- Shvekhgeimer, G.A., Kobrakov, K.I., Mityagina, O.G., Korolev, V.K., and Promonenkov, V.K., *Khim. Geterotsikl. Soedin.*, 1986, p. 711.
- 12. Bratilov, S.B., Kovaleva, S.M., Shchetinina, T.V.,

Petrov, V.V., Poplavskii, V.S., and Ostrovskii, V.A., *Zh. Org. Khim.*, 1992, vol. 28, p. 2344.

- 13. Buzilova, S.R., Shul'gina, V.M., Gareev, G.A., and Vereshchagin, L.I., *Khim. Geterotsikl. Soedin.*, 1980, p. 842.
- Metal Catalyzed Cross-Coupling Reactions, Diederich, F. and Stang, P.J., Eds., New York: Wiley Intersci., 1998, p. 99.
- 15. Beletskaya, I.P. and Cheprakov, A.V., *Chem. Rev.*, 2000, vol. 100, p. 3009.
- 16. Handbook of Organopalladium Chemistry for Organic Synthesis, Negishi, E.I., New York: Wiley Intersci., 2002.
- 17. *The Mizoroki–Heck Reaction*, Oestreich, M., Ed., New York: Wiley Intersci., 2009, p. 1.
- Gunther, H., NMR Spectroscopy: an Introduction, Chichester: Wiley, 1980.
- 19. Spulak, M., Lubojacky, R., Senel, P., Kunes, J., and Pour, M., *J. Org. Chem.*, 2010, vol. 75, p. 241.
- Vereshchagin, L.I., Kizhnyaev, V.N., and Pokatilov, F.A., Nekondensirovannye tetrazoly: spravochnoe izdanie, Irkutsk: Izd. Irkut. Gos. Univ., 2007, p. 8.
- 21. APEX II Software Package, Bruker AXS Inc., USA, 2005.
- 22. Sheldrick, G.M., Acta Cryst. A, 2008, vol. 64, p. 112.