ISSN 1070-3632, Russian Journal of General Chemistry, 2018, Vol. 88, No. 7, pp. 1418–1424. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © V.R. Akhmetova, N.S. Akhmadiev, G.M. Nurtdinova, V.M. Yanybin, A.B. Glazyrin, A.G. Ibragimov, 2018, published in Zhurnal Obshchei Khimii, 2018, Vol. 88, No. 7, pp. 1126–1132.

S,S-Complexes of Copper(I) Halides with 1,2-Bis(3,5-dimethyloxazol-4-ylmethylsulfanyl)ethane as New Catalysts for Phenylacetylene Aminomethylation

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Received March 1, 2018

Abstract—New metal–heterocycle S,S-complexes based on Cu(I) binary halides and a polydentate ligand, 1,2-bis(3,5-dimethyloxazol-4-ylmethylsulfanyl)ethane have been prepared. The obtained complexes have demonstrated high catalytic activity in aminomethylation of phenylacetylene with *N,N,N',N'*-tetramethylmethanediamine, bis(oxazolidin-3-yl)methane, or benzaldehyde–piperidine system.

Keywords: Cu(I) dihalide complexes, aminomethylation, phenylacetylene, bis(3,5-dimethylisoxazole), *N,N,N',N'*-tetramethylmethanediamine, bis(1,3-oxazolidin-3-yl)methane, propargylamines

DOI: 10.1134/S1070363218070113

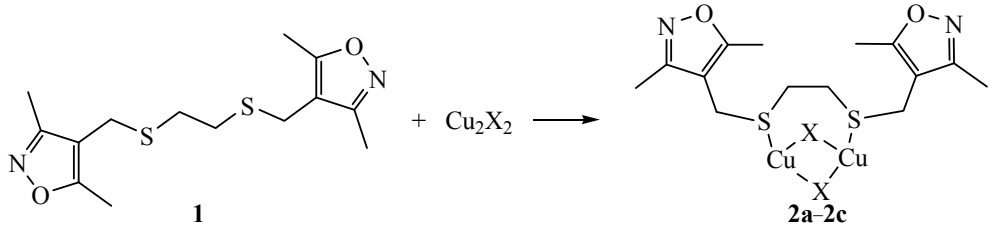
Activation of C–H-bonds with a metal complex catalyst is widely used in organic chemistry. This approach plays a key role in copper(I)-catalyzed synthesis of propargylamines via aminomethylation of terminal acetylenes [1–3]. One of the popular ways to obtain propargylamines is multicomponent condensation of acetylenes, aldehydes, and amines in the presence of various catalytic systems [4]. This method has some disadvantages including the process duration, moderate yield of the target products, formation of side products, and the use of microwave irradiation [5]. The interest to propargylamines is due to their application as universal synthetic units in the preparation of heterocyclic compounds (pyrroles, pyrrolidines, oxazolidinones, phenanthrolines, and indolizines), drugs, and natural compounds exhibiting high biological activity [6–8]. Hence, the development of new efficient catalysts for the propargylamines synthesis is of interest.

According to [9], ligands containing isoxazole and amine (or imine) units demonstrate high catalytic activity in cross-coupling of terminal alkynes (Sonogashira reaction) due to the presence of two different coordination sites in the ligand structure: the electron-withdrawing azole ring and the electron-donator amino group. The said approach preserves the metal ion activity over the catalytic cycle because of the stabilization of inter-mediate complexes.

We have suggested that ligands containing isoxazole cycles and sulfur atoms should also exhibit a similar property of preservation the activity of the metal ion during aminomethylation of terminal alkynes. We have developed a one-pot synthesis of 1,2-bis(3,5-dimethyloxazol-4-yl-methylsulfanyl)ethane **1** via condensation of acetylacetone, formaldehyde, 1,2-ethanedithiol, and hydroxylamine to obtain such ligands [10]. The prepared bis(3,5-dimethyloxazole) **1** containing a sulfide linker is a promising precursor for the synthesis of metal complexes. According to the X-ray diffraction data, isoxazole rings of precursor **1** are in *trans*-position relative to the sulfanylalkyl chain [10].

In this study new complexes with three copper(I) halides were prepared basing on bissulfanyloxazole 1; their catalytic activity in aminomethylation of phenylacetylene was studied. It was shown that the reaction

Scheme 1.



X = Cl (**2a**), Br (**2b**), I (**2c**).

of compound **1** with Cu_2Cl_2, Cu_2Br_2, and Cu_2I_2 occurred in acetonitrile at 60°C with the formation of dicopper(I) *S*,*S*-dihalides 1,2-bis(3,5-dimethyloxazole-4-yl-methylsulfanyl)ethanes **2a–2c** (gray-white powders) (Scheme 1).

Elemental analysis data confirmed the composition of the prepared complexes: the ligand–Cu_2X_2 ratio was 1 : 1. The complexes IR spectra contained absorption bands in the 316–324 cm^{-1} region related to the vibrations of the Cu–S bonds. Hence, Cu(I) ions (soft Lewis acids) were coordinated by the electron-donating S atoms (soft bases). This fact coincided with the HSAB theory [11]. The set of the proton signals in the ^1H NMR spectrum of complex **2a** was identical to that for the precursor **1** with a characteristic upfield shift. Copper content in complex **2a** was 24.78% according to atomic absorption spectroscopy data. Basing on the obtained spectral and analytical data, structures **2a–2c** were assigned to the complexes.

The positive ions $[M - X]^+$ (X = Cl, Br, I) were registered for the *S*,*S*-complexes by means of high-resolution mass spectrometry. The absence of the molecular ion signal of the *S*,*S*-complexes was due to the decomposition of the molecule under laser irradiation during MALDI experiment.

Recrystallization of the *S*,*S*-chelate copper(I) complexes **2a–2c** to obtain monocrystals was failed. Therefore, their geometry was simulated by minimizing the total energy in the framework of the PBE/3z approximation of DFT method using PRIRODA software package. The simulation results for the *S*,*S*-complex **2a** are given in Fig. 1. It was shown that isoxazole units were in *cis*-position with respect to the metallocycle, and the four-membered cycle Cu_2X_2 (X = Cl, Br, I) took a folded conformation in the studied complexes.

Thermal properties. According to the thermogravimetric analysis (TGA), Cu(I) complexes **2a–2c** were relatively thermally stable. Temperature of their decomposition onset was above 180°C. A characteristic step in the 200–300°C range corresponded to the mass loss of 25–27%. It should be assigned to the complexes decomposition with the formation of gaseous products including hydrogen halides.

The corresponding differential thermogravimetry (DTG) curves contained a characteristic peak with a maximum at T_{DTG} corresponding to the fastest complex decomposition. The T_{DTG} value increased in the **2a–2c** series, from 217 (**2a**) to 257°C (**2c**) (Table 1). It should be noted that the differential scanning calorimetry (DSC) curves showed an exothermic peak in the 200–300°C range with the T_{max} value close to the T_{DTG} value (Table 1). That exothermic effect corresponded to the decomposition of compounds **2a–2c**. Apparently, the observed effect was due to the chemical transformation of the complexes under oxidative conditions. The exothermic effect value (ΔH) corresponding to the complexes decomposition increased in the **2a–2c** series, from 172 (**2a**) to 270 J/g (**2c**) (Table 1). Thus, complex **2c** was the most thermally stable, and its decomposition was accompanied by the strongest heat effect.

The study of thermal decomposition of compound **2b** using DSC method revealed the presence of two peaks in the 230–270°C range: a weaker endothermic at T_{m1} 243°C (ΔH = –69 J/g) and a stronger exothermic at T_{m2} 254°C (ΔH = 245 J/g). It should be noted that those peaks were quite close. Apparently, the endothermic peak corresponded to the melting of the substance: the T_{m1} value was close to the melting point (246°C) determined via a standard method using a Kofler apparatus (Table 1). Melting of compound **2b** was followed by its decomposition reflected in the exothermic peak in the thermogram with the T_{m2} value close to the T_{DTG} value in the TGA curve.

Hence, melting points of compounds **2a–2c** were close to their decomposition temperature. In this regard,

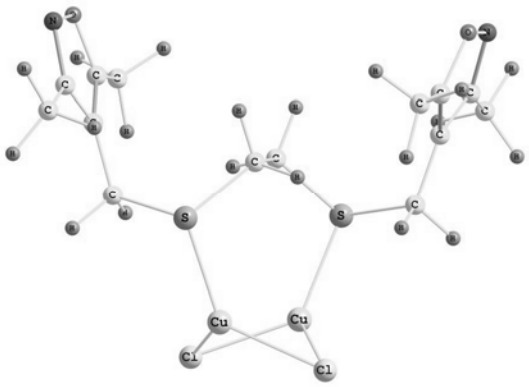


Fig. 1. Optimized structure of the *S*,*S*-complex **2a**.

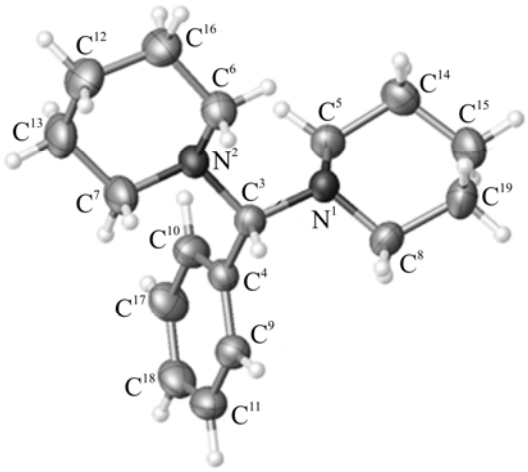


Fig. 2. General view of molecule of compound **8** in a crystal.

the use of complexes **2a–2c** as catalytic systems should be limited to the –70 to 180°C temperature range.

Catalytic properties. Cu(I) salts are known to catalyze the reactions of acetylene compounds [12, 13]. We presumed that copper(I) dihalides complexes **2a–2c** might be efficient catalytic systems for targeted functionalization of terminal alkynes. In view of that, we investigated the catalytic activity of the copper complexes **2a–2c** in a model reaction of phenylacetylene aminomethylation with *N*,*N*,*N*',*N*'-tetramethylmethanediamine **4** [14], bis(1,3-oxazolydin-3-yl)methane **5** [15, 16], and under conventional conditions of the Mannich reaction (condensation with aldehyde and amine).

It was shown that the reaction of phenylacetylene **3** with reagent **4** in the presence of 5 mol % of copper complexes **2a–2c** in toluene occurred with the formation of the target product of aminomethylation **6** and traces of bisphenylacetylene (Table 2). The most efficient catalyst for that reaction was complex **2c** which was active at 2.5 mol % (yield of product **5** 96%) and 0.1 mol % loading (yield of product **5** 94%). As exemplified by aminomethylation of phenylacetylene with benzaldehyde and piperidine, synthesis of propargylamine **7** in the presence of 5 mol % of the catalyst **2b** was carried out in 83% yield, which was comparable to the activity of the nanosized catalyst Cu(I)/TiO_2 obtained via redox method on titanium-oxide carrier [17].

In the absence of a catalyst the condensation of benzaldehyde and piperidine led to the formation of (dipiperidinyl-1)methylbenzene **8** (its structure was confirmed by means of X-ray diffraction) (Table 2).

The reaction of compound **3** with bis(1,3-oxazolidine-3-yl)methane **5** catalyzed by compounds **2a**, **2c** resulted in the formation of the target product 3-(3-phenylprop-2-yne-1-yl)-1,3-oxazolidine **9**, in a high yield and selectivity (Table 3).

Competitive catalytic activity of complexes **2a–2c** and copper(I) chloride catalyst in aminomethylation of phenylacetylene **3** with reagents **4** and **5** is given in the Tables 2 and 3. Catalytic activity of complexes **2a–2c** in this reaction of phenylacetylene **3** could be explained by the presence of donating-withdrawing fragments in a molecule of the complex catalyst. The starting reagents were in the coordination sphere of the catalyst under the reaction conditions: copper(I) cation

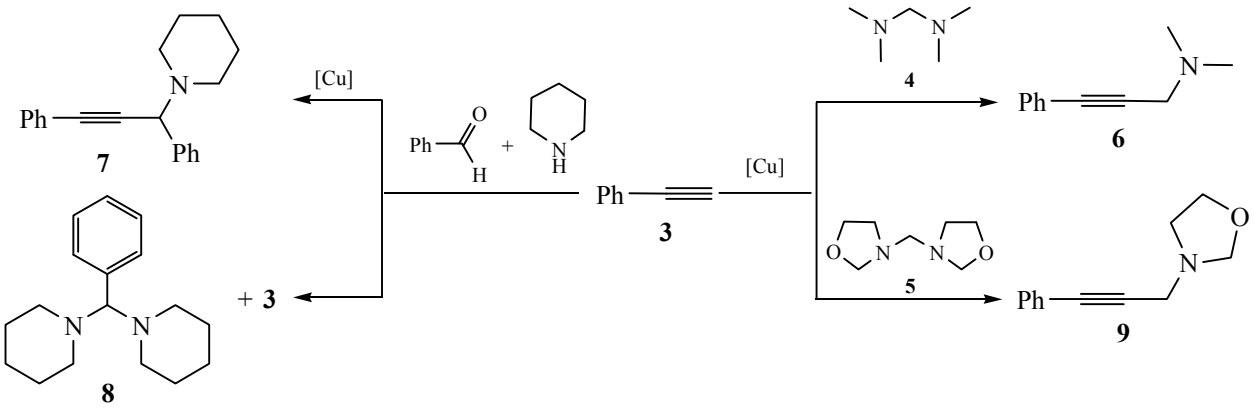
Table 1. Thermal stability and thermal decomposition parameters of complexes **2a–2c**

Comp. no.	mp, °C	TGA-DSC				DSC			
		Δm	T_{DTG}, °C	T_{max}, °C	ΔH, J/g	T_{m1}, °C	ΔH, J/g	T_{m2}, °C	ΔH, J/g
2a	221–223	25.6	217	218	172	213	31	241	223
2b	224–248	27.1	241	242	186	–	–	–	–
2c	246–248	25.3	257	260	270	243	–69	255	245

Table 2. The catalysts influence on the yield of products of aminomethylation of phenylacetylene by *N,N,N',N'*-tetramethylmethanediamine **4**

Catalyst	Total yield, %	Products composition, %			Conversion, %	Selectivity, %
		phenylacetylene	**6**	bisphenylacetylene		
–	6	1.5	78	20.5	8	79
Cu_2Cl_2	94	6.5	70	23.5	98	75
2a	96	6	90	4	99	96
2b	94	41.5	50.5	8	62	86
2c	99	–	99.8	0.2	100	99.8

Scheme 2.



formed π-complex with the triple bond of phenylacetylene [1, 18]; isoxazole electron-withdrawing rings were coordinated with the nitrogen atom of the aminomethylation reagent [9]. This fact led to the activation of CH_2 electrophilic center and its further reaction with acetylene substrate in the inner-sphere part of the catalyst.

The obtained data on aminomethylation of phenylacetylene indicated that the use of complexes **2a** and **2c** as catalysts led to the increase in the yield of the target products (96–100%) and in the conversion of the substrates (86–100%) in comparison to the known copper(I) salts used under the same conditions.

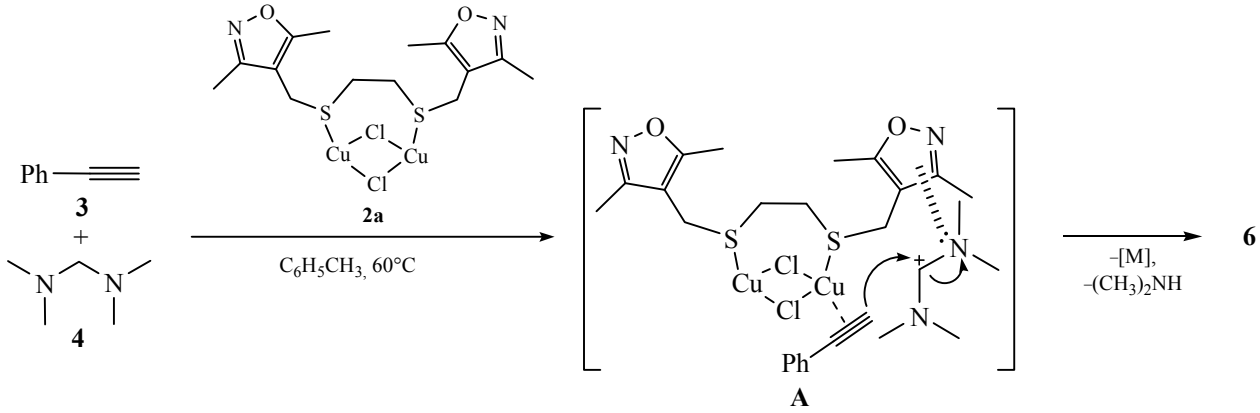
EXPERIMENTAL

The ^{1}H NMR spectra were registered using a Bruker Avance 400 spectrometer (400.13 MHz). The IR spectra were recorded using a Bruker Vertex-70V and a Specord M80 devices in Nujol. Elemental analysis was performed using a Carlo Erba 1106 instrument. Copper content in complexes **2a**–**2c** was determined using atomic absorption spectroscopy (continuous method, in acetylene–air flame) using a Shimadzu AA-6800 spectrometer. Melting points were measured using a RNMK 80/2617 (Kofler hot stage) apparatus. GLC analysis was performed using a Shimadzu GC-9A chromatograph [flame ionization detector, stationary phase SE-30 (5%) on Chromaton N-AW-HMDS carrier, steel column 2000×3 mm, temperature programming 50–270°C, 8 deg/min, carrier gas helium]. GC–MS-analysis was carried out using a Shimadzu GC 2010 chromatograph [mass-spectroscopic detector GCMS-QP2010 Ultra (Shimadzu,

Table 3. Catalyst effect on the yield of products of aminomethylation of phenylacetylene with bis(1,3-oxazolidin-3-yl)methane **5**

Catalyst	Products composition, %	
	phenylacetylene	**9**
–	100	–
Cu_2Cl_2	71	29
2a	–	100
2b	43	57
2c	14	86

Scheme 3.



Japan), capillary column Supelco 5ms (60 m × 0.25 m × 0.25 μm), carrier gas helium]. The reactions course was monitored by TLC (Sorbfil plates, developing with iodine vapor). High resolution mass-spectra (MALDI-TOF) were recorded using a Bruker Autoflex™ III Smartbeam spectrometer (positive ions mode, sinapic acid as the matrix). The specimens were prepared for the analysis using dried drop method [20, 21]. Solid-state UV laser with wavelength 355 nm was used as the radiation source. Thermogravimetric analysis was performed using a TGA–DSC (Mettler Toledo) instrument in a dynamic mode (heating rate 5 deg/min, in air). DSC analysis was performed using a DSC-1 (Mettler Toledo) instrument in the dynamic mode (heating rate 10 deg/min, in air).

Quantum-chemical simulation of the structure of the *S*,*S*-complexes was performed by means of density functional theory (DFT) method in the PBE/3z approximation implemented in PRIRODA software package [22].

The chemicals were of at least 99% purity. Acetylacetone, 1,2-ethanedithiol, hydroxylamine, and copper(I) chloride (bromide, iodide) were commercially available (Acros Organics or Sigma-Aldrich). Benzaldehyde for aminomethylation of phenylacetylene was prepared as described in [19].

1,2-Bis[sulfanylmethyl(3,5-dimethylisoxazol-4-yl)]ethane (1) was prepared as described in [10]. Yield 82%, colorless crystals, mp 154–156°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (6H, CH_3), 2.33 s (6H, CH_3), 2.64 s (4H, SC_2H_4S), 3.59 s (4H, SC_2H_4Iz). Spectral characteristics were identical to those reported in [10].

General procedure for the synthesis of complexes 2a–2c. A mixture of copper(I) salt (0.28 mmol), 0.09 g (0.28 mmol) of 1,2-bis[sulfanylmethyl(3,5-dimethylisoxazol-4-yl)]ethane **1**, and 4 mL of freshly distilled CH_3CN was stirred at 60°C for 3 h. The precipitate was filtered off, washed with CH_3CN (2× 15 mL), and dried.

Chelate *S*,*S*-complex 2a. Yield 0.09 g (63%), white powder, mp 221–223°C (CH_3CN). IR spectrum, ν, cm^{-1}: 1702 (C=C), 1197 (C–O), 886 (C–N), 734 (C–S), 320 (Cu–S), 294 (Cu–Cl). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.10 br.s (6H, CH_3), 2.24 br.s (6H, CH_3), 2.57 br.s (4H, SC_2H_4S), 3.32 br.s (4H, SCH_2Iz). Mass spectrum, *m*/*z* (I_{rel}, %): 487.1006 [M – Cl]$^+$. Found, %: C 32.58; H 3.82; Cl 13.51; Cu 24.78; N 5.43; S 12.87. $C_{14}H_{20}Cl_2Cu_2N_2O_2S_2$. Calculated, %: C 32.94; H 3.95; Cl 13.89; Cu 24.90; N 5.49; S 12.56.

Chelate *S*,*S*-complex 2b. Yield 0.07 g (39%), gray powder, mp 244–248°C (CH_3CN). IR spectrum, ν, cm^{-1}: 1702 (C=C), 1197 (C–O), 886 (C–N), 734 (C–S), 533, 508, 428, 324 (Cu–S), 284 (Cu–Br). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.12 br.s (6H, CH_3), 2.31 br.s (6H, CH_3), 2.59 br.s (4H, SC_2H_4S), 3.41 br.s (4H, SCH_2Iz). Mass spectrum, *m*/*z* (I_{rel}, %): 516.8818 [M – Br]$^+$. Found, %: C 28.31; H 3.39; Br 26.53; Cu 21.17; N 4.76; S 10.94. $C_{14}H_{20}Br_2Cu_2N_2O_2S_2$. Calculated, %: C 28.06; H 3.36; Br 26.66; Cu 21.20; N 4.67; S 10.70.

Chelate *S*,*S*-complex 2c. Yield 0.11 g (57%), gray powder, mp 246–248°C. IR spectrum, ν, cm^{-1}: 1702 (C=C), 1197 (C–O), 886 (C–N), 734 (C–S), 486, 393 (Cu–S), 316 (Cu–S), 281 (Cu–I), 268. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.20 br.s (6H, CH_3), 2.33 br.s (6H, CH_3), 2.54 br.s (4H, SC_2H_4S), 3.34 br.s (4H, SCH_2Iz). Mass spectrum, *m*/*z* (I_{rel}, %): 564.8335 [M – I]$^+$. Found, %: C 24.51; H 2.85; I 36.78; Cu 18.66; N 4.11; S 9.57. $C_{14}H_{20}I_2Cu_2N_2O_2S_2$. Calculated, %: C 24.25; H 2.91; I 36.61; Cu 18.33; N 4.04; S 9.25.

Catalytic properties of complexes 2a–2c. The reactions of aminomethylation of phenylacetylene **3** with *N*,*N*,*N*′,*N*′-tetramethylmethanediamine **4** [14], benzaldehyde, and piperidine [17], or bis(1,3-oxazolidin-3-yl)methane **5** [15] were carried out according to standard procedures.

***N*,*N*-Dimethyl-3-phenylprop-2-yne-1-amine (6).** Light yellow oil. Mass spectrum, *m*/*z* (I_{rel}, %): 158 (65) [*M* – H]$^+$, 144 (10), 116 (20), 115 (100), 89 (22), 82 (47), 42 (36). Spectral characteristics were identical to those reported in [23].

1-(1,3-Diphenylprop-2-yne-1-yl)piperidine (7). Yellow powder, mp 64–65°C (EtOH) (mp 65.9–66.4°C). Mass spectrum, *m*/*z* (I_{rel}, %): 275 (25) [*M*]$^+$, 232 (10), 199 (17), 198 (95), 192 (20) 191 (100), 189 (22), 165 (10), 115 (16). Spectral characteristics were identical to those reported in [17].

(Dipiperidinyl-1)methylbenzene (8). Colorless crystals, mp 76–78°C (EtOH) (mp 78°C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.53 m (12H, CH_2), 2.35 m (8H, CH_2), 3.58 s (1H, CH), 7.21–7.35 m (5H, Ph). Spectral characteristics were identical to those reported in [24].

3-(3-Phenylprop-2-yne-1-yl)-1,3-oxazolidine (9). Yellow oil. Mass spectrum, *m*/*z* (I_{rel}, %): 186 (22) [*M* – H]$^+$, 157 (18), 156 (20), 115 (100), 89 (10), 42 (35). Spectral characteristics were identical to those reported in [15].

X-ray diffraction data for compound **8** were collected using an automated XCalibur Eos diffractometer equipped with a CCD-detector and MoK_α-radiation source (graphite monochromator, λ 0.71073 Å, ω-scanning, $2\theta_{max}$ 62°). Collection and processing of the data were performed using CrysAlis^{Pro} Oxford Diffraction Ltd. software [25]. The structure was solved by the direct method and refined under anisotropic approximation via the full matrix least squares method implemented in SHELX software [26] of OLEX2 software package [27]. Hydrogen atoms were localized using differential Fourier synthesis and included to the refinement with fixed positions and temperature parameters. The complete structural data were deposited at the Cambridge Crystallographic Data Centre (CCDC 1551097).

ACKNOWLEDGMENTS

Authors acknowledge R.A. Khisamutdinov (Chemistry Institute, Ufa Research Center, Russian Academy of Sciences) for performing IR spectroscopy experiments.

This study was partially financially supported by the Russian Foundation for Basic Research and Academy of Sciences of Bashkortostan (project no. 17-43-020292r_a) in the scope of the project part 4.6007.2017/8.9 and performed using the equipment of Regional Center for Joint Usage "Agidel" (governmental State Assignment AAAA-A117012610060-7).

CONFLICT OF INTERESTS

Authors declare no conflict of interests.

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