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Preparation and characterization of selenopheno[2,3-*b*]pyridine *N*-oxides

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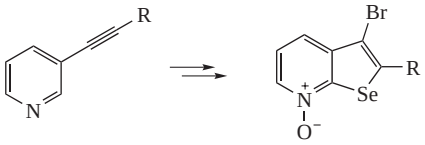
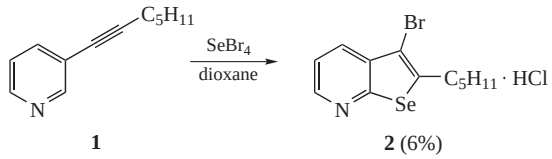
Treatment of 3-alkynylpyridine *N*-oxides with $SeBr_4$ affords 2-R-3-bromoselenopheno[2,3-*b*]pyridine *N*-oxides, whose structures were confirmed by ^1H, ^{13}C, ^{77}Se and ^{15}N NMR spectroscopy and X-ray diffraction.



In the last decade, the synthesis of fused selenophenes has begun to play an important role in the design and synthesis of conducting, superconducting and magnetic materials.[1] The main interest in the synthesis of selenium-containing compounds is growing fast with the discovery of derivatives exhibiting various biological activities.[2] The cyclization of aryl(thienyl)alkynes in the presence of selenium(I), (II), and (IV) halides has become one of the most straightforward synthetic pathways for the preparation of a wide variety of benzo[*b*]selenophenes and selenophenothiophenes.[3] Nevertheless, no studies on the cyclization of 3-ethynyl substituted pyridines have been reported to date.

Based on our experience in selenophene chemistry,[4] we focused on the reaction of substituted 3-ethynylpyridines with various selenium halides ($SeCl_2$, $SeCl_4$, $SeOCl_2$, $SeBr_2$, $SeBr_4$) to develop simple methods for the preparation of selenopheno[2,3-*b*]pyridines (Scheme 1). Our investigation started with the reaction of 3-heptynylpyridine **1** with selenium chlorides, unfortunately, all our attempts failed. Moreover, $SeBr_4$ *in situ* prepared by dissolving SeO_2 in conc. HBr was found as unique reagent for the electrophilic reaction. Thus, desired 3-bromo-2-pentylselenopheno[2,3-*b*]pyridin-7-ium chloride **2**† was isolated in miserable 6% yield (Scheme 1). Molecular structure of **2** was unambiguously confirmed by X-ray analysis (Figure 1).‡ The crystal structure of **2** is characterized by strong hydrogen bond of NH···Cl type between molecular cation and chlorine anion. The length of this bond is 2.948(3) Å [Cl(16)···H(7) 2.04 Å,



1 **2** (6%)

Scheme 1

† *3-Bromo-2-pentylselenopheno[2,3-*b*]pyridinium hydrochloride* **2**. 2-Heptynylpyridine **1** (1.00 mmol) in dioxane (10 ml) was added to the solution of selenium dioxide (0.444 g, 4.00 mmol) in HBr (0.45 ml) and the mixture was stirred at room temperature for 48 h. After the consumption of substrate (LC-MS), ethyl acetate (100 ml) and aqueous $NaHCO_3$ were added (to pH 9). Organic phase was separated, washed with water (2×50 ml) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, crude product was purified by column chromatography on silica gel using CH_2Cl_2–EtOAc (gradient elution 1:0 to 10:1) as eluent. Salt **2** was precipitated as yellowish crystals after addition of HCl to the solution in CH_2Cl_2. Yield 6%, mp 102–103 °C. ^1H NMR (400 MHz, DMSO-d_6) δ: 0.87 (t, 3H, Me, *J* 7.2 Hz), 1.30–1.40 (m, 4H, CH_2), 1.65–1.72 (m, 2H, CH_2), 2.99 (t, 2H, CH_2, *J* 7.2 Hz), 7.56 (dd, 1H, C^5H, *J* 4.5 Hz, *J* 8.0 Hz), 8.04 (dd, 1H, C^4H, *J* 1.5 Hz, *J* 8.0 Hz), 8.55 (dd, 1H, C^6H, *J* 1.5 Hz, *J* 4.5 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 13.7, 21.7, 30.1, 30.5, 31.6, 104.2, 121.1, 131.9, 134.5, 145.9, 146.7, 160.1. LC-MS, *m*/*z*: 333 [M]. Found (%): C, 38.96; H, 3.92; N, 3.67. Calc. for $C_{12}H_{15}ClBrNSe$ (%): C, 39.07; H, 4.07; N, 3.80.

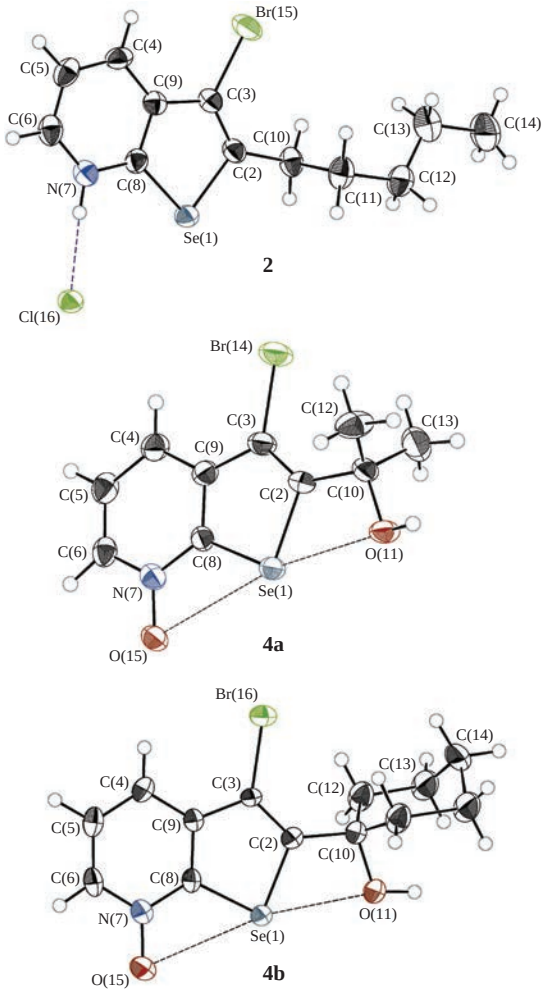
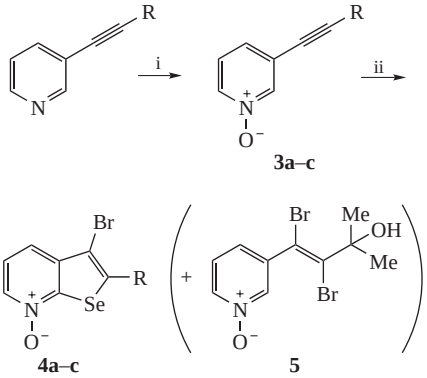


Figure 1 ORTEP molecular structures of **2**, **4a**, and **4b**.

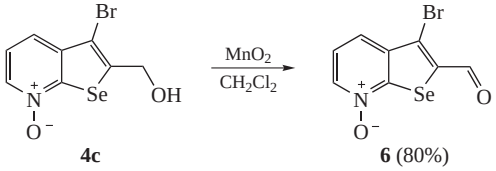
∠Cl(16)···H(7)–N(7) 167°]. The lengths of Se(1)–C(2) and Se(1)−C(8) bonds are 1.908(2) and 1.857(2) Å, respectively. Note that in selenolopyridines Se−C bonds are diverse, unlike selenophenes.[5]

Disappointed with the current result we have decided to oxidize the pyridine nitrogen atom in hope to increase molecule reactivity. The corresponding *N*-oxides **3a**–**c** has been obtained in acceptable yields using *m*-CPBA as an oxidizing agent. Unfortunately, selenium(II) and (IV) chlorides were completely useless for selenohalogenation even under harsh reaction conditions such as large excess of the reagent and heating for 3 days. Luckily, *in situ* prepared selenium(IV) bromide readily reacted with oxide **3a** yielding a mixture of selenopheno[2,3-*b*]pyridine 7-oxide **4a** and dibromo derivative **5** in almost equal amounts (Scheme 2). The cyclization reaction is considered as a two-step process. The first step consists of *anti* addition of $SeBr_4$ to a triple-bond-containing selenobrominated intermediate, which is followed by intramolecular cyclization through an S_EAr mechanism, during which 1 equiv. of HBr and Br_2 is expelled. As a result, a mixture of two products was obtained because the bromine molecule also reacts with the triple bond of the starting alkyne **3a**. Therefore, as previously reported,[4(b)] we performed the reaction in the presence of cyclohexene as a scavenger of the deleterious bromine molecule. In fact, 0.6 equiv. of cyclohexene is the optimal amount related to $SeBr_4$ reducing thus the yield of undesired dibromo derivative **5** to 5%. Raising cyclohexene amount completely prevents the formation of **5** but simultaneously decreases yield of the target **4a**. Similarly, analogues **4b**,**c**[§] were prepared in 15 and 28% yields, respectively.



Scheme 2 *Reagents and conditions*: i, *m*-CPBA (2 equiv.), CH_2Cl_2 (50–77%); ii, SeO_2/HBr (1.2 equiv.), cyclohexene (0.6 equiv.), dioxane.

In compound **4c**, hydroxymethyl group was successfully oxidized to aldehyde with manganese(IV) oxide in 80% yield (Scheme 3). Notably, 3-bromo-2-formylselenopheno[2,3-*b*]pyridine *N*-oxide **6**[¶] can serve as a powerful precursor for the synthesis of various more complicated compounds. Wide range of possible modifications can be envisioned for new compounds **4a**–**c** and **6**,



4c **6** (80%)

Scheme 3

‡ *Crystal data for* **2**, **4a**,**b** *and* **5**. A single crystal diffractometer Bruker–Nonius KappaCCD (MoKα radiation, λ = 0.71073 Å) was used for data collection. The structures were solved using direct method. The SHELXS and SHELXL programs were used for calculations.[7]

Crystals of **2** are monoclinic, space group $P2_1/c$, a = 9.7243(3), b = = 14.2070(5) and c = 10.0777(2) Å, β = 95.427(2)°, V = 1386.02(7) Å^3, Z = 4, F(000) = 720, μ = 5.76 mm^{-1}, d_{calc} = 1.762 g cm^{-3}, T = –100 °C; $2\theta_{max}$ = 60.0°, R = 0.048 for 2524 reflections with $I > 3\sigma(I)$.

Crystals of **4a** (modification I) are tetragonal, space group $P4_32_12$, a = 10.2586(3) and c = 22.2449(4) Å, V = 2341.0(1) Å^3, Z = 8, F(000) = = 1296, μ = 6.60 mm^{-1}, d_{calc} = 1.901 g cm^{-3}, T = –90 °C; $2\theta_{max}$ = 60.0°, R = 0.035 for 2990 reflections with $I > 2\sigma(I)$.

Crystals of **4a** (modification II) are monoclinic, space group $P2_1/n$, a = 11.6017(6), b = 6.9479(3) and c = 13.8354(9) Å, β = 102.831(2)°, V = 1087.4(1) Å^3, Z = 4, F(000) = 648, μ = 7.11 mm^{-1}, d_{calc} = 2.047 g cm^{-3}, T = –100 °C; $2\theta_{max}$ = 56.0°, R = 0.039 for 1913 reflections with $I > 3\sigma(I)$.

Crystals of **4b** are orthorhombic, space group *Pmcn*, a = 6.7658(2), b = 11.5194(4) and c = 16.5195(6) Å, V = 1287.50(8) Å^3, Z = 4, F(000) = = 736, μ = 6.01 mm^{-1}, d_{calc} = 1.935 g cm^{-3}, T = –100 °C; $2\theta_{max}$ = 58.0°, R = 0.034 for 1788 reflections with $I > 2\sigma(I)$.

Crystals of **5** are monoclinic, space group $P2_1/n$, a = 11.7671(4), b = = 7.0872(3) and c = 14.8307(5) Å, β = 106.398(2)°, V = 1186.51(8) Å^3, Z = 4, F(000) = 656, μ = 6.81 mm^{-1}, d_{calc} = 1.887 g cm^{-3}, T = –100 °C; $2\theta_{max}$ = 58.0°, R = 0.053 for 2186 reflections with $I > 3\sigma(I)$.

CCDC 980443–980447 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

§ *General procedure for the preparation of selenopheno[2,3-*b*]pyridine* N*-oxides* **4a**–**c**. Ethynylpyridine *N*-oxide **3** (1.00 mmol) and cyclohexene (0.05 g, 0.60 mmol) in dioxane (10 ml) were added dropwise to the mixture of SeO_2 (0.133 g, 1.20 mmol) in HBr (0.6 ml). The mixture was stirred at room temperature for 24–48 h (TLC control). After disappearing the starting material, ethyl acetate (100 ml) and aqueous $NaHCO_3$ were added (to pH 9). The organic phase was separated, washed with water (2×50 ml) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel using CH_2Cl_2–EtOAc (gradient elution 1:0 to 20:1) as eluent. Dibromo derivative **5** was isolated and characterized from the experiment depriving cyclohexene.

*3-Bromo-2-(2-hydroxy-2-methylethyl)selenopheno[2,3-*b*]pyridine* N*-oxide* **4a**: yield 52%, mp > 200 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.82 (s, 6H, Me), 3.56 (br. s, 1H, OH), 7.38 (dd, 1H, C^{6}H, J 6.2 Hz, J 8.0 Hz), 7.64 (dd, 1H, C^{5}H, J 0.8 Hz, J 8.0 Hz), 8.26 (dd, 1H, C^{4}H, J 0.8 Hz, J 6.2 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 28.4, 74.4, 98.6, 122.3, 130.1, 135.9, 141.8, 150.2, 161.1. LC-MS, *m*/*z*: 335 [M]. Found (%): C, 35.74; H, 2.97; N, 4.17. Calc. for $C_{10}H_{10}BrNO_2Se$ (%): C, 35.85; H, 3.01; N, 4.18.

*3-Bromo-2-(1-hydroxycyclohexyl)selenopheno[2,3-*b*]pyridine* N*-oxide* **4b**: yield 28%, mp > 200 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.21–1.33 (m, 1H, cyclohexane), 1.57–1.75 (m, 7H, cyclohexane), 2.34–2.42 (m, 2H, cyclohexane), 7.53 (dd, 1H, C^{6}H, J 4.6 Hz, J 8.0 Hz), 8.04 (dd, 1H, C^{5}H, J 1.4 Hz, J 8.0 Hz), 8.55 (dd, 1H, C^{4}H, J 1.4 Hz, J 4.6 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 21.0, 24.6, 34.1, 73.7, 96.9, 120.7, 131.7, 136.8, 146.5, 159.3, 159.9. LC-MS, *m*/*z*: 375 [M]. Found (%): C, 41.43; H, 3.67; N, 3.76. Calc. for $C_{13}H_{14}BrNO_2Se$ (%): C, 41.62; H, 3.76; N, 3.73.

*3-Bromo-2-(hydroxymethyl)selenopheno[2,3-*b*]pyridine* N*-oxide* **4c**: yield 15%, mp 147–149 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.74 (d, 2H, CH_2, J 5.5 Hz), 6.40 (t, 1H, OH, J 5.5 Hz), 7.58–7.62 (m, 1H, C^{6}H), 7.66 (dd, 1H, C^{5}H, J 1.0 Hz, J 8.2 Hz), 8.42 (dd, 1H, C^{4}H, J 1.0 Hz, J 6.1 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 60.1, 99.6, 120.9, 123.6, 134.0, 138.0, 147.0, 151.7. LC-MS, *m*/*z*: 333 [M]. Found (%): C, 31.19; H, 1.78; N, 4.47. Calc. for $C_8H_6BrNO_2Se$ (%): C, 31.30; H, 1.97; N, 4.56.

¶ *3-Bromoselenopheno[2,3-*b*]pyridine-2-carbaldehyde* N*-oxide* **6**. Solution of compound **4c** (0.10 g, 0.32 mmol) in dry CH_2Cl_2 (10 ml) was added to the suspension of MnO_2 (0.11 g, 1.30 mmol) in dry CH_2Cl_2 (20 ml) at 0 °C. Then the mixture was left warmed to room temperature and stirred for 12 h. After the consumption of **4c** (TLC control), the mixture was filtered through the short pad of silica gel. The solvent was evaporated to give a pure product as green-yellow needles. Yield 80%, mp 147–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (dd, 1H, C^{6}H, J 4.6 Hz, J 8.0 Hz), 8.30 (dd, 1H, C^{5}H, J 1.7 Hz, J 8.0 Hz), 8.68 (dd, 1H, C^{4}H, J 1.7 Hz, J 4.6 Hz), 10.21 (s, 1H, CHO). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 117.3, 121.1, 134.4, 135.2, 140.4, 150.7, 163.6, 186.0. ^{77}Se NMR (76.36 MHz, $CDCl_3$) δ: 575.9. LC-MS, *m*/*z*: 305 [M]. Found (%): C, 31.42; H, 1.27; N, 4.42. Calc. for $C_8H_4BrNO_2Se$ (%): C, 31.51; H, 1.32; N, 4.59.

Table 1 Chemical shifts of ^{13}C, ^{15}N and ^{77}Se (DMSO-d_6, δ/ppm) and $^{n}J_{^{77}Se,^{13}C}$ and $^{n}J_{^{77}Se,^{1}H}$ coupling constants[a] (Hz) for **4a**, **4b** and **6** and Se−C and Se···O bond distances in Å for **4a**,**b**.

Atom	Compound		
	4a	**4b**	**6**
Se^1	555.7	549.2	552.9
C^2	161.2	152.3	142.9
C^3	98.1	100.2	117.2
C^4	140.0	138.6	138.8
C^5	122.1	121.5	124.3
C^6	123.9	121.1	123.5
C^7	134.6	134.6	137.1
N^8	285.8	285.5	286.8
C^9	147.2	147.6	152.3
C_R	72.7	60.7	185.8
Coupling constant	**4a**	**4b**	**6**
$^{1}J_{Se,C^9}$	105.5	100.6	n.m.[b]
$^{1}J_{Se,C^2}$	94.9	105.1	102.9/*106.5*[c]
$^{2}J_{Se,C_R}$	9.9	11.7	14.8/*14.9*[c]
$^{2}J_{Se,C^3}$	2.6	2.4	n.m.[b]
$^{3}J_{Se,C^7}$	3.9	3.0	n.m.[b]
$^{3}J_{Se,H}$	–	3.6	6.1
$^{3}J_{Se,C^4}$	3.9	3.0	4.7/*5.2*[c]
Bond distance	**4a** (tetragonal)	**4a** (monoclinic)	**4b**
Se(1)−C(2)	1.890(3)	1.894(3)	1.893(4)
Se(1)−C(8)	1.852(4)	1.858(3)	1.859(3)
Se(1)···O(11)	2.684(3)	2.748(3)	2.722(3)
Se(1)···O(15)	3.004(3)	3.019(3)	3.029(3)

[a] The ^{77}Se–^{13}C and ^{77}Se–^{1}H spin–spin coupling constants were obtained from ^{77}Se satellites in ^{13}C and ^{1}H spectra, respectively. Assignment of the ^{13}C signals were obtained from ^{1}H, ^{13}C HSQC and ^{1}H, ^{13}C HMBC spectra. [b] n.m. – not measured. [c] In italic – $CDCl_3$.

as C–Br bond is available for different types of transition metal catalyzed processes.

The formation of Se···O hypervalent bonding is a common feature in selenophenopyridine *N*-oxides **4a**,**b** (Se–C and Se···O distances are given in Table 1). For compound **4a** two crystal modifications have been found, namely, monoclinic and tetragonal forms. In the both crystal structures strong intermolecular hydrogen bonds of OH···O type exist between hydroxy group and oxygen O(15). For the monoclinic form the parameters of this bond are the following: O(11)···O(15), 2.722(3) Å; H(11)···O(15), 1.77 Å; ∠O(11)–H(11)···O(15), 168°. In the tetragonal form this bond is stronger: O(11)···O(15), 2.651(3) Å; H(11)···O(15), 1.89(5) Å, ∠O(11)–H(11)···O(15), 178(4)°. It promotes decreasing the hypervalent Se(1)···O(11) bond distance in the tetragonal modification. In the crystal structure of **4b** (space group *Pmcn*) the symmetric molecules lie in the special position (in mirror plane *m*). Thus, the crystal structure is formed from parallel molecular layers, which are perpendicular to the crystallographic parameter *a*. Inside these layers the molecules are connected by the OH···O hydrogen bonds with the length of 2.810(3) Å [H(11)···O(15), 1.89 Å; ∠O(11)–H(11)···O(15), 163°].

The ^{13}C, ^{77}Se and ^{15}N chemical shifts and the $^{n}J_{^{77}Se,^{13}C}$ and $^{n}J_{^{77}Se,^{1}H}$ coupling constants of **4a**,**b**, and **6** are given in Table 1. The substitution at C^2 atom has slight influence on the ^{1}H, ^{13}C, ^{77}Se, ^{15}N chemical shifts and spin–spin coupling constants. The ^{77}Se signals of **4a**,**b**, and **6** are located in the interval of 549–555 ppm, which is in agreement with literature data.[6] The shielding effect in the sequence **4a**–**4b**–**6** was only observed for the C^2 atom. The ^{15}N signals of **4a**,**b**, and **6** manifest themselves in the range of 285.0–286.8 ppm.

The one bond coupling constants $^{1}J_{C,Se}$ are negative and strongly dependent on hybridization and the *s*-character of the carbon atom. The $^{1}J_{Se,C}$ values for **4a**,**b** and **6** are in a typical range of 100–105 Hz. The two- and three-bond coupling constants $^{n}J_{Se,C}$ and $^{3}J_{Se,H}$ have also been determined, they are positive and much smaller than $^{1}J_{Se,C}$ ones. In contrast to the $^{1}J_{Se,C}$ couplings, the $^{2}J_{Se,R}$, $^{3}J_{Se,C^4}$ and $^{3}J_{Se,H}$ values were found to increase on going from **4a**,**b** to **6**. Interestingly, no cross-peak from aldehyde proton to C^3 carbon was found in ^{1}H-^{13}C HMBC spectra due to the small value of $^{3}J_{^{13}C,^{1}H}$ constant. This may point to the conformation where C(O)H proton is in *cis* position to Br substituent, but oxygen is stretched to Se, indicating some interaction between oxygen and selenium atom C=O···Se.

In summary, simple method for the synthesis of selenophenopyridine *N*-oxides was developed. Pyridine oxidation to *N*-oxides led to considerable increase in ethynyl pyridine reactivity. Product structures were confirmed by X-ray and fully characterized by NMR study.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.07.017.

References

1 (*a*) E. R. Biehl, *Prog. Heterocycl. Chem*., 2015, **27**, 117; (*b*) J. Hollinger, D. Gao and D. S. Seferos, *Isr. J. Chem*., 2014, **54**, 440; (*c*) L. I. Belen'kii and Yu. B. Evdokimenkova, *Adv. Heterocycl. Chem*., 2015, **116**, 193; (*d*) E. Vasiljeva and P. Arsenyan, *Chem. Heterocycl. Compd.*, 2012, **48**, 981 (*Khim. Geterotsikl. Soedin*., 2012, 1057); (*e*) I. Yu. Bagryanskaya, Y. V. Gatilov, N. P. Gritsan, V. N. Ikorskii, I. G. Irtegova, A. V. Lonchakov, E. Lork, R. Mews, V. I. Ovcharenko, N. A. Semenov, N. V. Vasilieva and A. V. Zibarev, *Eur. J. Inorg. Chem.*, 2007, 4751; (*f*) K. Awaga, T. Tanaka, T. Shirai, M. Fujimori, Y. Suzuki, H. Yoshikava and W. Fujita, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 25; (*g*) K. Okamoto, T. Tanaka, W. Fujita, K. Awaga and T. Inabe, *Angew. Chem. Int. Ed*., 2006, **45**, 4516.

2 (*a*) G. Mugesh and H. B. Singh, *Chem. Soc. Rev*., 2000, **29**, 347; (*b*) G. Mugesh, A. Panda, H. B. Singh, N. S. Punekar and R. J. Butcher, *J. Am. Chem. Soc.*, 2001, **123**, 839; (*c*) M. Parnham and H. Sies, *Expert Opin. Investig. Drugs*, 2000, **9**, 607; (*d*) E. E. Alberto, V. do Nascimento and A. L. Braga, *J. Braz. Chem. Soc.*, 2010, **21**, 2032; (*e*) V. Nascimento, N. L. Ferreira, R. F. Canto, K. L. Schott, E. P. Waczuk, L. Sancineto, C. Santi, J. B. Rocha and A. L. Braga, *Eur. J. Med. Chem*., 2014, **87**, 131; (*f*) J. Yan, Y. Guo, Y. Wang, F. Mao, L. Huang and X. Li, *Eur. J. Med. Chem.*, 2015, **95**, 220; (*g*) P. Arsenyan, J. Vasiljeva, I. Shestakova, I. Domracheva and S. Belyakov, *Chem. Heterocycl. Compd*., 2014, **49**, 1674 (*Khim. Geterotsikl. Soedin*., 2014, 1804); (*h*) P. Arsenyan, E. Paegle, S. Belyakov, I. Shestakova, E. Jaschenko, I. Domracheva and J. Popelis, *Eur. J. Med. Chem.*, 2011, **46**, 3434; (*i*) S. H. Abdel-Hafez, *Russ. J. Bioorg. Chem*., 2010, **36**, 370.

3 (*a*) P. Arsenyan, J. Vasiljeva, I. Shestakova, I. Domracheva, E. Jaschenko, N. Romanchikova, A. Leonchiks, Z. Rudevica and S. Belyakov, *C.R. Chim.*, 2015, **18**, 399; (*b*) J. Vasiljeva, I. Domracheva and P. Arsenyan, *Tetrahedron Lett*., 2016, **57**, 196; (*c*) P. Arsenyan, E. Paegle, I. Domracheva, A. Gulbe, I. Kanepe-Lapsa and I. Shestakova, *Eur. J. Med. Chem*., 2014, **87**, 471.

4 (*a*) P. Arsenyan, *Tetrahedron Lett*., 2014, **55**, 2527; (*b*) E. Paegle, S. Belyakov and P. Arsenyan, *Eur. J. Org. Chem*., 2014, 3831; (*c*) P. Arsenyan, J. Vasiljeva and S. Belyakov, *Mendeleev Commun*., 2014, **24**, 32; (*d*) P. Arsenyan, A. Petrenko and S. Belyakov, *Tetrahedron*, 2015, **71**, 2226; (*e*) P. Arsenyan, J. Vasiljeva, S. Belyakov, E. Liepinsh and M. Petrova, *Eur. J. Org. Chem*., 2015, 5842.

5 E. Lukevics, P. Arsenyan, S. Belyakov and O. Pudova, *Chem. Heterocycl. Compd.*, 2002, **38**, 763 (*Khim. Geterotsikl. Soedin.*, 2002, 867).

6 (*a*) H. Duddeck, *Prog. Nucl. Magn. Reson. Spectrosc*., 1995, **27**, 1; (*b*) M. Elsherbini, W. S. Hamama and H. H. Zoorob, *Coord. Chem. Rev*., 2016, **312**, 149.

7 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

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