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PII: S0022-328X(20)30171-6

DOI: <https://doi.org/10.1016/j.jorganchem.2020.121269>

Reference: JOM 121269

To appear in: *Journal of Organometallic Chemistry*

Received Date: 24 December 2019

Revised Date: 27 March 2020

Accepted Date: 29 March 2020

Please cite this article as: O.M. Trofimova, E.A. Grebneva, Y. Bolgova, D.V. Pavlov, T.I. Vakul'skaya, A.I. Emelyanov, A.S. Pozdnyakov, Anti-Markovnikov addition of 2-mercaptobenzoxazole and 2-mercaptobenzothiazole to trimethoxy(vinyl)silane under solvent- and catalyst-free conditions, *Journal of Organometallic Chemistry* (2020), doi: <https://doi.org/10.1016/j.jorganchem.2020.121269>.

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# Anti-Markovnikov addition of 2-mercaptobenzoxazole and 2-mercaptobenzothiazole to trimethoxy(vinyl)silane under solvent- and catalyst-free conditions

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## Abstract

The addition of 2-mercaptobenzoxazole or 2-mercaptobenzothiazole to trimethoxy(vinyl)silane was studied. The thiol-ene reaction leads to previously unknown carbofunctional (trimethoxysilyl)ethyl derivatives of 2-mercaptobenzazoles  $C_6H_4N(Y)CS(CH_2)_2Si(OMe)_3$  ( $Y = O, S$ ) with anti-Markovnikov orientation. The proposed mechanism is confirmed by EPR spectroscopy and quantum chemical calculations.

**Keywords:** 2-mercaptobenzoxazole; 2-mercaptobenzothiazole; trimethoxy(vinyl)silane; thiol-ene reaction; EPR spectroscopy; DFT calculations

## 1. Introduction

The addition of thiols to alkenes has been known for a long time [1–4]. The thiol-ene reaction has recently seen widespread use for the formation of various polymeric organic materials [4]. It is known that the addition to 1-alkenes occurs with high selectivity with anti-Markovnikov orientation [1,2]. The thiyl radical adds to the less substituted end of the C=C bond to form a carbon-centered radical. The addition is initiated photochemically or thermally, with or without the initiators. A radical initiator (peroxide, AIBN, UV irradiation) or an oxidizing agent was used to promote the formation of sulfur-centered radicals and anti-Markovnikov adducts [5–7]. At the present time, the efforts of researchers are focused on the search for alternative conditions for the synthesis of anti-Markovnikov adducts. Solvent- and catalyst-free reactions have attracted increasing interest of synthetic chemists, due to the highly facile, efficient and environmentally benign process. The high reactivity of the thiyl radicals makes them unique for implementation of complex catalyst-free reactions. The active applications of the thiyl radicals for the synthesis and modification of polymers with bulky or highly reactive substituents are based upon their ability to add to carbon-carbon multiple bonds, which allows functional systems with tailor-made properties to be obtained [2].

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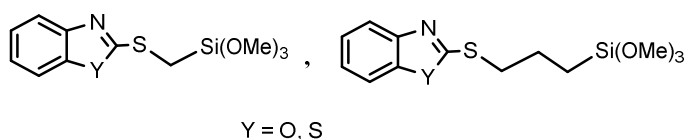
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The addition of different thiols to the double C=C bond of vinylsilanes has been actively studied since the beginning of the sixties of the last century [8,9]. Most sulfur-containing organosilicon monomers were synthesized by photochemical thiylation of unsaturated organosilicon compounds. The free radical addition of thiols to vinylsilanes and vinylsiloxanes occurs with classical anti-Markovnikov regioselectivity. For instance, 2-, 3-, or 4-[(2-(triethoxysilyl)ethyl)thio]aniline is obtained by adding 2-, 3-, or 4-mercaptoaniline to triethoxy(vinyl)silane upon heating in the presence of AIBN [10]. Photoinitiated thiylation of triethoxy(vinyl)silane with hydrogen sulfide gas affords 2-triethoxysilylethanethiol and *bis*(2-triethoxysilylethyl)sulfide [11]. However, photochemical reaction of gaseous H<sub>2</sub>S to dimethyl(chloromethyl)vinylsilane gave 3,3-dimethyl-1-thia-3-silacyclopentane [12]. The photochemical addition of 1,2-ethanedithiol to trichlorovinyl- and triorganylvinylsilanes R<sub>3</sub>SiCH=CH<sub>2</sub> (R = Cl, Et, EtO) leads to the formation of mono- and bisadducts. It is interesting to note that vinylsilanes containing alkyl and alkoxy groups at the silicon atom react much more easily than chlorosubstituted vinylsilanes [13]. The addition of ethanethiol, 1,2-ethanedithiol, or benzenethiol with chlorovinylsilanes H<sub>2</sub>C=CHSiMe<sub>3-n</sub>Cl<sub>n</sub> (n = 1–3) gives the corresponding adducts in quantitative and near quantitative yields [14]. It was found that a reaction with a benzenethiol required a significantly longer reaction time. 2-Aminoethanethiol hydrochloride is also easily added under the action of UV irradiation to R<sub>3</sub>SiCH=CH<sub>2</sub> (R = Me, Et, MeO, EtO, AcO) [15]. The photochemical addition of mercaptoacetic acid to vinyl(trialkoxy)silanes (R = OMe, OEt) gives a mixture of adducts due to intra- and intermolecular condensation of S-trialkoxysilylethyl derivatives of thioglycolic acid [16]. 1-Thioacetoxo-2-[methyl(didecyl)silyl]ethane was prepared by hydrothiolation of didecyl(methyl)vinylsilane with thioacetic acid under photochemical initiation in THF in the presence of benzophenone [17].

The addition of thiols to carbon-carbon double bonds is well studied. However, organosilicon derivatives containing a heterocyclic fragment with various heteroatoms (N, O, and S) in the cycle bonded to the silicon atom by a thioethylene bridge still remains unknown.

Previously, we have synthesized organosilicon derivatives of 2-mercaptobenzoxazole and 2-mercaptobenzothiazole, by nucleophilic substitution of (1-chloroalkyl)trimethoxysilanes with the appropriate 2-mercaptoazoles. Their heterocyclic fragment is bonded to the silicon atom by a thiomethylene or thiopropylene bridge [18–20] (Fig. 1).

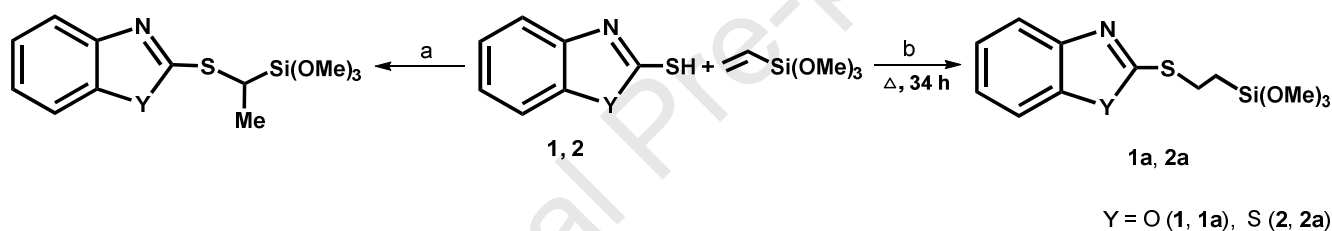


**Fig. 1.** Organosilicon derivatives of 2-mercaptobenzoxazole and 2-mercaptobenzothiazole.

mercaptobenzothiazole have not yet been studied. In the present work, we report on the synthesis of the anti-Markovnikov product by addition of 2-mercaptobenzoxazole and 2-mercaptobenzothiazole to trimethoxy(vinyl)silane in solvent- and catalyst-free conditions.

## 2. Results and discussion

New 2-[[2-(trimethoxysilyl)ethyl]thio]-1,3-benzoxazole **1a** and -1,3-benzothiazole **2a** have been prepared by addition of 2-mercaptobenzoxazole **1** or 2-mercaptobenzothiazole **2** to trimethoxy(vinyl)silane upon heating to 145 °C of any solvent- and catalyst-free. Formally, the reaction can proceed in two directions *a* and *b* (Scheme 1). The thiol-ene reactions with trimethoxy(vinyl)silane can give either of two possible products corresponding to Markovnikov ( $\alpha$ -product) or anti-Markovnikov ( $\beta$ -product) addition (Scheme 1).



**Scheme 1.** The synthesis of compounds **1a** and **2a**.

Additions of 2-mercaptobenzazoles to vinylsilane occur with the classical anti-Markovnikov regioselectivity (way *b*). The presence of electron-withdrawing substituents at the silicon atom in vinylsilane (R = OMe) leads to additional polarization of the C=C multiple bond that enhances its reactivity in H<sub>2</sub>C=CHSi(OMe)<sub>3</sub>. The reaction carried out in the presence of an excess of electron-rich trimethoxy(vinyl)silane as a radical trap allowed the formation of the corresponding compounds **1a** and **2a** in good yield.

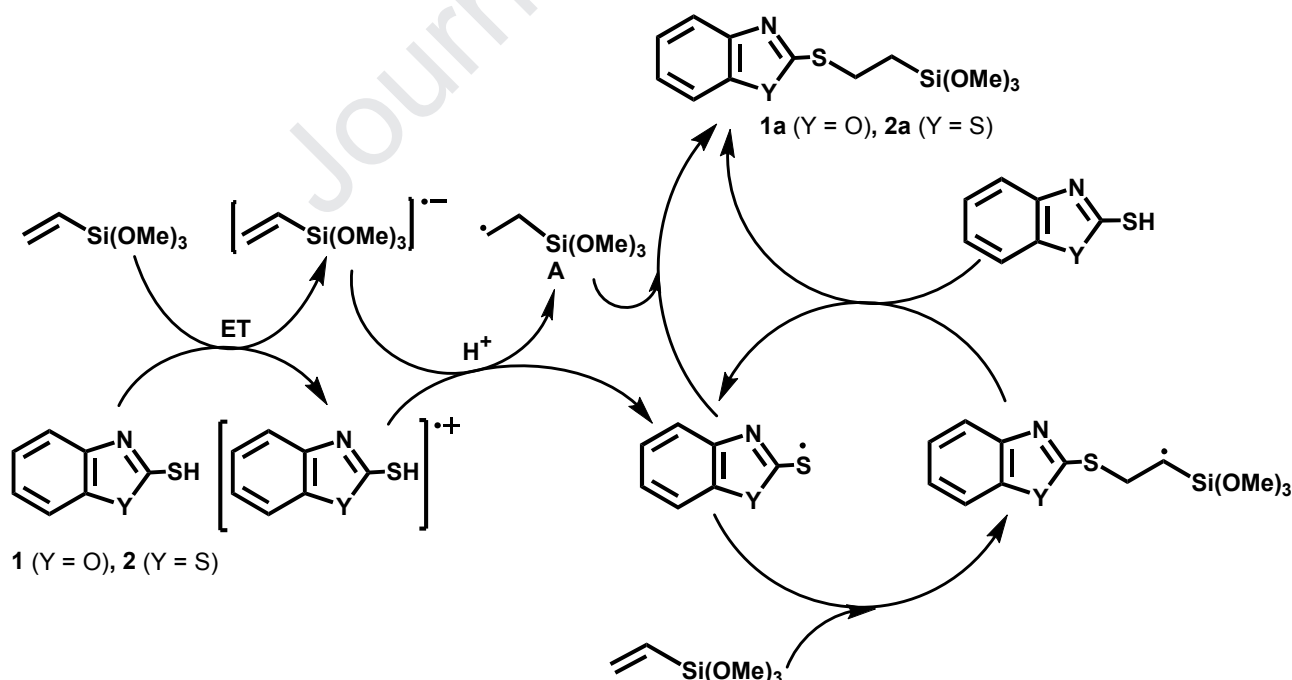
The reaction mixture was boiled upon stirring for 34 h in the absence of any solvent- and catalyst-free. During the reaction, the temperature of the reaction mixture gradually increases to 145 °C, and the thiol-ene reaction is completed. Compounds **1a** and **2a** are light yellow liquids, readily soluble in organic solvents. Their yields are 70 (**1a**) and 80% (**2a**). It should be noted that the reaction of 2-mercaptobenzoxazole with trimethoxy(vinyl)silane in a sealed ampoule without atmospheric oxygen proceeds faster (1 h) to give the target product in 86% yield. The composition and structure of the synthesized silanes **1a** and **2a** are confirmed by elemental analysis, IR and NMR spectroscopy, as well as mass spectrometry.

The FTIR spectra of compounds **1a** and **2a** contains the characteristic frequencies of the absorption bands of the Si(OMe)<sub>3</sub> group, as well as the absorption bands of the corresponding heterocyclic fragments, shifted to the high-frequency region in the range of 1000-1400 cm<sup>-1</sup>. The chemical shifts in the <sup>29</sup>Si NMR spectra of compounds **1a** and **2a** are shifted upfield (-46.1 ppm and -46.0 ppm, respectively). This indicates the presence of a tetracoordinated silicon atom in them. The mass spectra of compounds **1a** and **2a** are characterized by a low intensity of the molecular ion peaks with *m/z* 299 (6%) and 315 (9%), respectively. The peak of the ion [Si(OMe)<sub>3</sub>]<sup>+</sup> with *m/z* 121 has the highest intensity (100%) in the mass spectra of compounds **1a** and **2a**.

The interaction of 2-mercaptobenzoxazole **1** or 2-mercaptobenzothiazole **2** with trimethoxy(vinyl)silane without a photoinitiator, catalyst and solvent most likely occurs under thermal initiation with the formation of the β-isomer, 2-[[2-(trimethoxysilyl)ethyl]thio]-1,3-benzoxazole **1a** or -1,3-benzothiazole **2a**.

The thermal initiation of the S–H bond facilitates the generation of thiyl radicals. After thermal initiation, the thiyl radical C<sub>6</sub>H<sub>4</sub>N(Y)CS<sup>•</sup> (Y = O, S) adds to the less substituted end of the C=C bond to form a carbon-centered thioethyl radical via a reversible process. The resulting radical can then abstract a hydrogen atom from another molecule of thiol to give the thioethyl product and thiyl radical, which propagates the chain (Scheme 2).

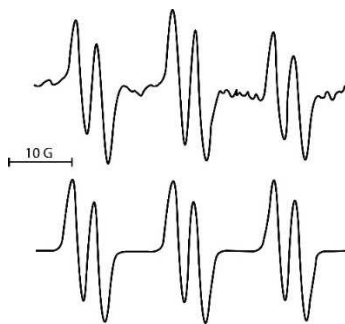
The reaction carried out in the presence of an excess of electron-rich vinylsilane as a radical trap allowed the formation of the corresponding adducts in good yields.



**Scheme 2.** The proposed mechanism for the synthesis of compounds **1a** and **2a** (ET – one electron transfer).

However, direct confirmation of the radical mechanism by EPR detection of radicals involved in the reaction has not yet been obtained. Both thiyl and vinyl radicals of the compounds are unstable and their detection in some cases is possible only in the presence of spin traps [21–23]. An experiment, carried out in resonator EPR spectrometer, with a mixture of 2-mercaptobenzoxazole and trimethoxy(vinyl)silane under the above conditions has shown that silane, thiol and their mixture are EPR-silent. This evidences that the radicals under these conditions either are not formed or are unstable.

C-phenyl-N-tert-butyl nitron (PBN) spin-trap has been used to detect the possible radicals. This was allowed recording a signal of adduct **I** (Fig. 2), the characteristics of which are given in Table.



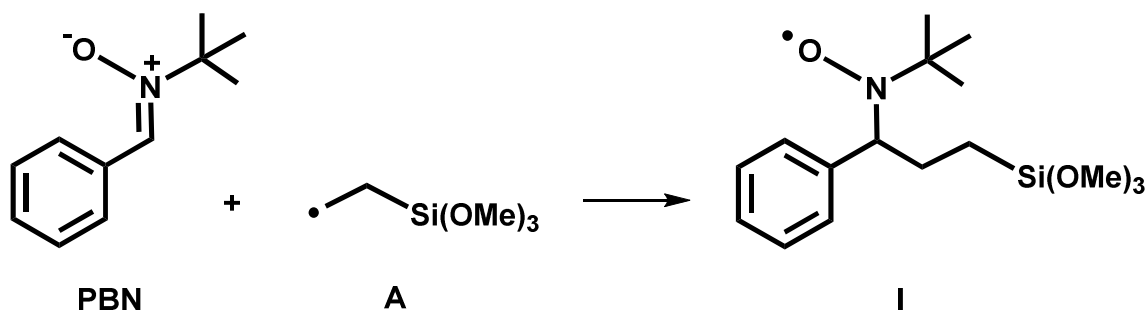
**Fig. 2.** The EPR spectrum of spin adduct **I** recorded in the reaction mixture at 202 °C (experimental above, simulated below).

**Table**

Experimental and calculated characteristics of the EPR of spin adduct **I**.

Value	$a_N$ , G	$a_H$ , G	g-factor
experimental	14.62	2.84	2.0065
calculated	14.23	2.24	2.0078

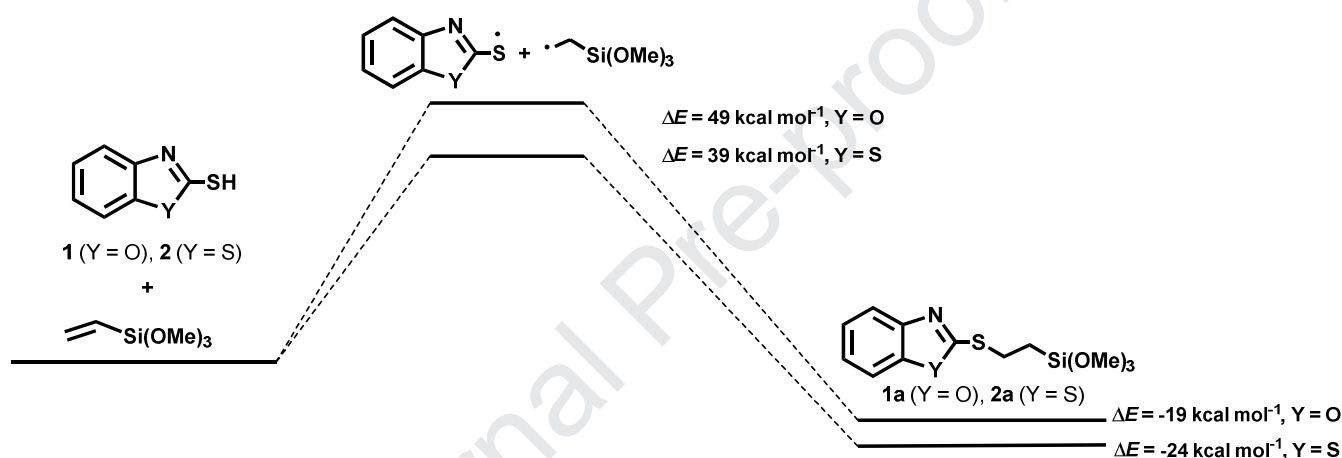
The analysis of EPR data and results of quantum-chemical calculations of the hyperfine structure (HFS) constants of radicals reveals that the spin adduct corresponds to structure **I** (Scheme 3), which is formed upon trapping the radical  $\cdot\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$  (**A**) by PBN trap (Scheme 3).



**Scheme 3.** Formation of adduct **I**.

We have assumed that the radical **A** is the result of outer-sphere one-electron transfer (ET) from thiol [24] to silane to form thiol radical cation and a silane radical anion, respectively. This process is accompanied by a fast deprotonation of the thiol radical cation followed by equally fast protonation of the silane radical anion to deliver a pair of benzazolylthiyl and trimethoxy(ethyl)silyl radicals, which further give the reaction products **1a** or **2a** (Scheme 2).

To confirm the proposed mechanism, quantum-chemical calculations [25], evaluating energy profile of the reaction, have been performed. It turns out that energy of the pair of benzazolylthiyl and trimethoxysilylethyl radicals is by 39 (Y = S) and 49 (Y = O) kcal mol<sup>-1</sup> higher than that of the initial singlet state, while energy of the reaction products is lower by 24 (compound **2a**) and 19 kcal mol<sup>-1</sup> (compound **1a**) (Scheme 4).



**Scheme 4.** Energy profile of the reaction.

The easier addition of 2-mercaptobenzothiazole **1** to trimethoxy(vinyl)silane as compared to 2-mercaptobenzoxazole **2** can be explained by a larger change in total energy (by 5 kcal mol<sup>-1</sup>) and a lower total energy of trimethoxysilylethyl and benzazolylthiyl radical pair (by 10 kcal mol<sup>-1</sup>).

The synthesized compounds **1a** and **2a** are promising biologically active substances. According to the PASS program [26], 2-[[2-(trimethoxysilyl)ethyl]thio]-1,3-benzoxazole **1a** and -1,3-benzothiazole **2a** can be used as medicines that protect the body or improve its functions. Silanes **1a** and **2a** are the starting compounds in the synthesis of new trifluorosilylethyl- and silatranylethyl derivatives of 2-mercaptobenzoxazole and 2-mercaptobenzothiazole.

### 3. Conclusions

In summary, we have developed an efficient protocol for the anti-Markovnikov addition of 2-mercapto-1,3-benzoxazole and 2-mercapto-1,3-benzothiazole to trimethoxy(vinyl)silane in solvent-

and catalyst-free reactions. The thiol-ene addition reaction is effective method for the introduction of the 2-mercaptobenzazoles into unsaturated compounds

## 4. Experimental

### 4.1. General information

2-Mercaptobenzoxazole, 2-mercaptobenzothiazole and trichloro(vinyl)silane were purchased from commercial sources and used as received, without further purification. The trimethoxy(vinyl)silane was synthesized by the alkoxylation of trichloro(vinyl)silane. A mixture of trichloro(vinyl)silane (161.49 g, 1.0 mol) and hexane (171.50 g, 1.99 mol) (volume ratio 1: 1) was added dropwise over 1 h to urea (180.18 g, 3.0 mol) in abs. methanol (96.12 g, 3.0 mol). The reaction mixture was stirred for 2 h. Then the upper layer was separated and distilled at atmospheric pressure. Yield 128.96 g (87%), colorless liquid, bp 123 °C,  $n_D^{25}$  1.3920 and consistent with literature data [27].

All reactions were carried out under argon atmosphere using a typical borosilicate glassware.

FTIR spectra were recorded on a Varian 3100 FTIR spectrometer in the spectral range between 4000–400  $\text{cm}^{-1}$ , using sample as a thin film. The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker DRX-400 spectrometer ( $^1\text{H}$ , 400.13 MHz;  $^{13}\text{C}$ , 100.62 MHz;  $^{15}\text{N}$  40.55 MHz;  $^{29}\text{Si}$  79.50 MHz). The NMR spectra were performed at 297 K in  $\text{CDCl}_3$ . For  $^1\text{H}$  NMR spectra, HMDSO (0.05 ppm) was used as internal standard; in  $^{13}\text{C}$  NMR spectra, chemical shifts were assigned relative to the residual signal of the solvent  $\text{CDCl}_3$  (77.0 ppm), for  $^{15}\text{N}$  NMR spectra, internal standard was  $\text{MeNO}_2$ . The  $^{15}\text{N}$  chemical shifts were obtained using the  $^1\text{H}$ - $^{15}\text{N}$  HMBC-gp method of heteronuclear inverse two-dimensional spectroscopy with a gradient pulse. Standard 5 mm glass NMR tubes were used.  $^{29}\text{Si}$  chemical shifts were measured with respect to internal standard  $\text{Me}_4\text{Si}$ .

EPR spectra were recorded on a FT ELEXSYS E580 Bruker radio spectrometer (9.7 GHz) in sealed quartz capillaries. The accuracy of g-factor measurement is  $\pm 0.0002$ . Spectrum recording conditions: modulation amplitude 1 G, modulation frequency 100 kHz, time constant 0.04 s, conversion time 0.08 s, microwave power 0.6325 mW, gain 60 dB. EPR spectra were simulated using the WINEPR SimFonia 1.25 program (Bruker Inc. 1996). Quantum chemical calculations were performed using the GAUSSIAN 09 program. Geometry optimization and g-factors values were calculated using B3LYP functional in DFT method at the 6-311++G(d,p) basis set. The hyperfine structure constants were calculated using M062X/6-311++G(d,p), due to the calculations in B3LYP functional turned out to be basis-dependent. Thus, addition of diffuse functions to basis set or change of basis set double-zeta to triple-zeta, leads to increase the calculated HFSC values as much as twice that is unsatisfactory [28]. The use of special basis sets such as EPR-II, EPR-III is impossible, since



they do not have functions for silicon atoms. We used the M062X functional of the M06 family, as this functional shows an essentially lower dependence on the basis sets [29].

Mass spectra were recorded on a Shimadzu GCMS-QP5050A mass spectrometer, injector temperature 200–250 °C, helium carrier gas, detector temperature 290 °C, quadrupole mass analyzer, EI ionization (70 eV). Chromatographic separation of the studied compound samples was done on a SPB-5 (60 m × 0.25 mm × 0.25 μm) capillary column, helium carrier gas, 0.7 ml/min flow, evaporator temperature 230 °C, 280 kPa pressure, gradient from 60 to 250 °C at 10 °C/min. Elemental analysis was performed with a Thermo Scientific Flash 2000 CHNS-Analyzer. Gravimetric determination of silicon content was carried out by the literature method [30]. Melting points were determined on a Boetius heating bench.

## 4.2. Synthesis and characterization

### 4.2.1. Synthesis of 2-[[2-(trimethoxysilyl)ethyl]thio]-1,3-benzoxazole (**1a**).

**Method 1.** Trimethoxy(vinyl)silane (11.86 g, 0.08 mol) was added to 2-mercaptobenzoxazole **1** (10.58 g, 0.07 mol) under argon atmosphere. The reaction mixture was heated under reflux for 34 h. A homogeneous reaction mass formed, and its temperature increased from 122 to 145 °C by the end of the experiment. Fractional distillation under reduced pressure afforded the 14.67 g (70%) of compound **1a**. The product obtained was a light yellow liquid, bp 164–167 °C (3 mmHg),  $n_D^{20}$  1.4795.

**Method 2.** In an ampoule previously purged with dry argon, 2-mercaptobenzoxazole **1** (1.06 g, 0.007 mol) and trimethoxy(vinyl)silane (1.19 g, 0.008 mol) are placed. The cooled ampoule with the reaction mixture was sealed in vacuo and placed in an oven (ES-4610). The reaction mixture was kept at 200 °C for 1 h. Fractional distillation under reduced pressure afforded the 1.8 g (86%) of compound **1a**, a light yellow liquid, bp 164–167 °C (3 mmHg),  $n_D^{20}$  1.4795. FTIR (ν, cm<sup>-1</sup>): 805, 1088, 1189 (Si(OMe)<sub>3</sub>), 748, 1011, 1126, 1281, 1499, 1597 (benzoxazole), 2841 (Si(OMe)<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 1.25 (m, 2H, CH<sub>2</sub>Si); 3.38 (m, 2H, SCH<sub>2</sub>); 3.58 (s, 9H, OCH<sub>3</sub>); 7.15 (dd, 1H, H-5, <sup>3</sup>J<sub>5-6</sub> = 7.5 Hz, <sup>3</sup>J<sub>5-4</sub> = 7.6 Hz); 7.20 (dd, 1H, H-6, <sup>3</sup>J<sub>6-5</sub> = 7.4 Hz, <sup>3</sup>J<sub>6-7</sub> = 7.8 Hz); 7.36 (d, 1H, H-7, <sup>3</sup>J<sub>6-7</sub> = 7.8 Hz); 7.54 (d, 1H, H-4, <sup>3</sup>J<sub>4-5</sub> = 7.6 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 10.38 (CH<sub>2</sub>Si); 26.95 (SCH<sub>2</sub>); 50.94 (OCH<sub>3</sub>); 109.40 (C-7); 117.97 (C-4); 123.36 (C-6); 123.81 (C-5); 141.73 (C-3a); 151.43 (C-7a); 164.57 (C-2). <sup>29</sup>Si NMR (CDCl<sub>3</sub>, ppm): δ -46.1. <sup>15</sup>N NMR (CDCl<sub>3</sub>, ppm): δ -146.0. MS *m/z* (*I*<sub>rel</sub>, %): 299 [M]<sup>+</sup> (6), 271 [M-CH<sub>2</sub>CH<sub>2</sub>]<sup>+</sup> (5), 266 [M-S-H]<sup>+</sup> (6), 240 [M-SCH<sub>2</sub>CH<sub>2</sub>+H]<sup>+</sup> (4), 239 [M-SCH<sub>2</sub>CH<sub>2</sub>]<sup>+</sup> (11), 238 [M-SCH<sub>2</sub>CH<sub>2</sub>-H]<sup>+</sup> (18), 208 [M-SCH<sub>2</sub>CH<sub>2</sub>-OMe]<sup>+</sup> (4), 151 [M-CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>+H]<sup>+</sup> (51), 133 [M-SCH<sub>2</sub>Si(OMe)<sub>3</sub>+H]<sup>+</sup> (6), 122 [M-C<sub>6</sub>H<sub>4</sub>NOCSCH<sub>2</sub>CH<sub>2</sub>+H]<sup>+</sup> (18), 121 [Si(OMe)<sub>3</sub>]<sup>+</sup> (100), 118 [M-SCH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>]<sup>+</sup> (8), 107 [Si(OMe)<sub>3</sub>-Me+H]<sup>+</sup> (6), 91 [Si(OMe)<sub>3</sub>-OMe+H]<sup>+</sup> (62), 90 [Si(OMe)<sub>3</sub>-OMe]<sup>+</sup> (8), 75 [Si(OMe)<sub>3</sub>-OMe-Me]<sup>+</sup> (6), 61 [Si(OMe)<sub>3</sub>-OMe-

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 $\text{Me}_2+\text{H}]^+$  (14), 59  $[\text{Si}(\text{OMe})_3-(\text{OMe})_2]^+$  (12). Elemental analysis (%): Calculated for  $\text{C}_{12}\text{H}_{17}\text{NO}_4\text{SiS}$ : C 48.14; H 5.72; N 4.68; Si 9.38; S 10.71. Found: C 47.88; H 5.85; N 4.61; Si 9.60; S 11.07.

#### 4.2.2. Synthesis of 2-[[2-(trimethoxysilyl)ethyl]thio]-benzothiazole (**2a**).

The title compound was prepared following procedure 1, starting from 2-mercaptobenzothiazole (1.0 g, 0.006 mol) and trimethoxy(vinyl)silane (1.19 g, 0.008 mol). The product **2a** was obtained as an a light yellow liquid (1.51 g, 80%), bp 186-190 °C (3 mmHg). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 806, 1085, 1189 ( $\text{Si}(\text{OMe})_3$ ), 672, 761, 999, 1277, 1315, 1427, 1459 (benzoxazole), 2841 ( $\text{Si}(\text{OMe})_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  1.24 (m, 2H,  $\text{CH}_2\text{Si}$ ); 3.41 (m, 2H,  $\text{SCH}_2$ ); 3.57 (s, 9H,  $\text{OCH}_3$ ); 7.20 (t, 1H, H-6,  $^3J_{6-5} \sim ^3J_{6-7} = 8.0$  Hz); 7.32 (t, 1H, H-5,  $^3J_{5-6} \sim ^3J_{5-4} = 8.0$  Hz); 7.66 (d, 1H, H-7,  $^3J_{7-6} = 8.0$  Hz); 7.80 (d, 1H, H-4,  $^3J_{4-5} = 8.0$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  10.33 ( $\text{CH}_2\text{Si}$ ); 28.18 ( $\text{SCH}_2$ ); 50.31 ( $\text{OCH}_3$ ); 120.61 (C-7); 121.05 (C-4); 123.80 (C-5); 125.65 (C-6); 134.81 (C-7a); 152.92 (C-3a); 166.66 (C-2).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  -46.0.  $^{15}\text{N}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  -85.5. MS  $m/z$  ( $I_{\text{rel}}$ , %): 315  $[\text{M}]^+$  (16), 284  $[\text{M}-\text{S}+\text{H}]^+$  (4), 283  $[\text{M}-\text{S}]^+$  (11), 282  $[\text{M}-\text{S}-\text{H}]^+$  (11), 256  $[\text{M}-\text{SCH}_2\text{CH}_2+\text{H}]^+$  (13), 255  $[\text{M}-\text{SCH}_2\text{CH}_2]^+$  (14), 254  $[\text{M}-\text{SCH}_2\text{CH}_2-\text{H}]^+$  (52), 223  $[\text{M}-\text{SCH}_2\text{CH}_2-\text{OMe}-\text{H}]^+$  (9), 193  $[\text{M}-\text{Si}(\text{OMe})_3-\text{H}]^+$  (6), 194  $[\text{M}-\text{Si}(\text{OMe})_3]^+$  (4), 168  $[\text{M}-\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3]^+$  (7), 167  $[\text{M}-\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3+\text{H}]^+$  (44), 165  $[\text{M}-\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3-\text{H}]^+$  (25), 135  $[\text{M}-\text{SCH}_2\text{CH}_2\text{Si}(\text{OMe})_3+\text{H}]^+$  (3), 122  $[\text{M}-\text{C}_6\text{H}_4\text{NSCSCH}_2\text{CH}_2+\text{H}]^+$  (20), 121  $[\text{Si}(\text{OMe})_3]^+$  (100), 91  $[\text{Si}(\text{OMe})_3-\text{OMe}+\text{H}]^+$  (56), 90  $[\text{Si}(\text{OMe})_3-\text{OMe}]^+$  (9), 77  $[\text{Si}(\text{OMe})_3-\text{Me}_3+\text{H}]^+$  (4), 61  $[\text{Si}(\text{OMe})_3-\text{OMe}-\text{Me}_2+\text{H}]^+$  (18), 60  $[\text{Si}(\text{OMe})_3-(\text{OMe})_2+\text{H}]^+$  (5), 59  $[\text{Si}(\text{OMe})_3-(\text{OMe})_2]^+$  (16). Elemental analysis (%): Calculated for  $\text{C}_{12}\text{H}_{17}\text{NO}_3\text{SiS}_2$ : C 45.68; H 5.43; N 4.44; Si 8.90; S 20.33. Found: C 45.31; H 5.10; N 4.72; Si 8.57; S 19.96.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgement

The results were obtained using the equipment of Baikal analytical centre of collective using SB RAS. All calculations of the molecular geometry and HFS constants were performed on the «Akademik V.M. Matrosov» computation cluster (Irkutsk Supercomputer Center of the Siberian Branch of the Russian Academy of Sciences).<sup>2</sup>

<sup>2</sup> The website: Irkutsk: IDSTU SO RAN. URL: <http://hpc.icc.ru> (2019).

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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