ISSN 1070-4280, Russian Journal of Organic Chemistry, 2017, Vol. 53, No. 6, pp. 860–868. © Pleiades Publishing, Ltd., 2017.
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Synthesis of New Monoterpene Sulfonic Acids and Their Derivatives

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Received March 17, 2017

Abstract—The oxidation of monoterpene thiols with chlorine dioxide afforded new water-soluble sulfonic acids and their derivatives (sulfonothioates and sulfonyl chlorides). The reaction of terpene thiols with ClO_2 gave the corresponding trisulfides. Sulfonothioates with a pinane skeleton showed antibacterial and antifungal activity.

DOI: 10.1134/S1070428017060082

Alkane- and arenesulfonic acids and -sulfonyl chlorides are intermediate products in organic synthesis and in the manufacture of some pharmaceuticals. The presence of a sulfo group in a drug molecule endows it with somewhat different biological activity and higher solubility in water, which reduces the toxicity and facilitates design of injection dosage forms. Sulfonothiates are known to exhibit bactericidal and fungicidal activity [1].

Physiological activity of terpenes includes bactericidal, analgesic, and expectorant effects, as well as fungicidal and antiviral properties. Introduction of a sulfo group into terpene molecule extends the spectrum of its biological activity [1] and the scope of its application due to improved solubility in water. For example, camphorsulfonic acid is used in the manufacture of coronary vasodilator drugs, antibacterial agents, and analgesics (sulfocamphocaine, semisynthetic penicillins and cephalosporins) [2].

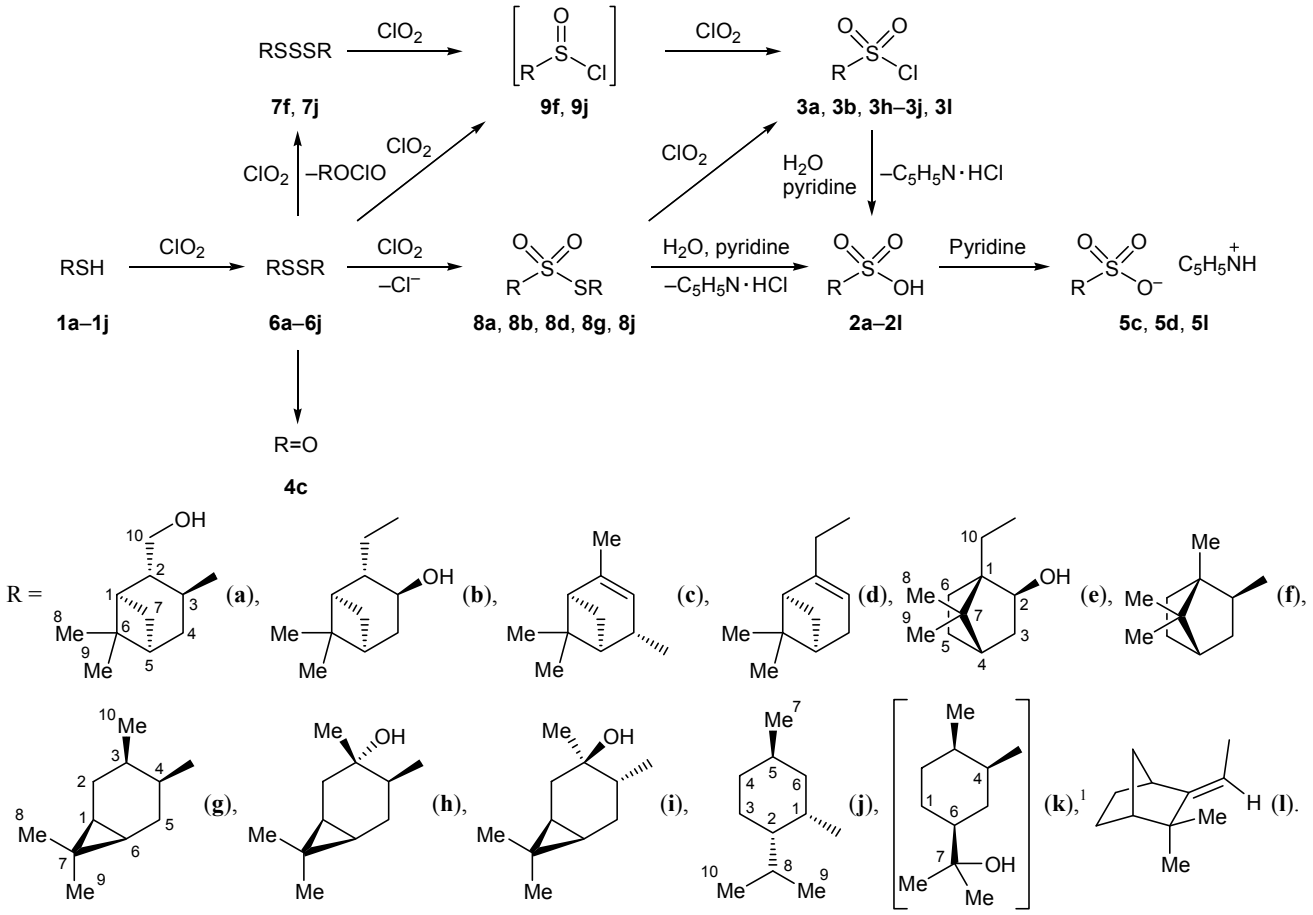
Functionalization of terpene compounds according to known sulfonation methods (reaction with concentrated sulfuric acid, oleum, or chlorosulfonic acid) is complicated due to high lability of the terpene fragment. Under these conditions, most terpenes undergo numerous rearrangements and tarring. Therefore, only a few terpene sulfonic acids have been reported. Camphorsulfonic acid was synthesized in 27–42% yield by reaction of camphor with acetic anhydride and concentrated sulfuric acid [2, 3]. Sodium *p*-menth-1-ene-7-sulfonate was obtained by reaction of β-pinene with sodium hydrogen sulfite and potassium nitrate [4]. The reaction was carried out on heating to 110°C under reduced pressure (4 h), and it involved transformation of the pinane skeleton to menthane.

We have proposed a procedure for the synthesis of new water-soluble monoterpene sulfonic acids and their derivatives via oxidation of the corresponding thiols with chlorine dioxide (ClO_2). Depending on the conditions, several concurrent reaction pathways are possible. Chlorine dioxide is a large-scale product used for bleaching of cellulose and disinfection of water, and its application as oxidant seems to be promising and economically reasonable. Unlike other oxidants, chlorine dioxide molecule possesses an unpaired electron and two reaction centers, chlorine and oxygen atoms. It works well in different media due to good solubility in water and organic solvents.

The product structure in the reactions of ClO_2 with various thiols and disulfides is determined mainly by the substrate structure, and the yields depend on the reactant ratio, solvent nature, and order of addition of the reactants [5–11]. Reactions of ClO_2 with thiols generally produce disulfides, sulfonothioates, sulfonyl chlorides, and sulfonic acids; trisulfides, sulfinyl chlorides, ketones, and esters are formed less frequently [5–11].

As starting compounds we used optically pure thiols with pinane (**1a**–**1d**), bornane (**1e**, **1f**), carane

Scheme 1.



(**1g**–**1i**), and *p*-menthane structures (**1j**), which were prepared according to known procedures, namely 3-sulfanylmyrtanol (**1a**) [12], 10-sulfanylisopinocampheol (**1b**) [13], *trans*-thioverbenol (**1c**) [14], thiomyrtenol (**1d**) [15], 10-sulfanylisoborneol (**1e**) [16], thioisoborneol (**1f**) [17], carane-4-thiol (**1g**) [18], (3*S*)- and (3*R*)-4-sulfanylcaran-3-ols **1h** and **1i** [19], and (3*S*)-*p*-menthane-3-thiol (**1j**) [20].

Sulfonic acids **2a**, **2b**, **2e**, **2f**, and **2l** were synthesized in up to 96% yield by oxidation of the corresponding thiols with excess ClO_2 in aqueous pyridine [10, 11] (Scheme 1). Compounds **2c**, **2d**, and **2g**–**2k** were later prepared according to the same procedure in 76–96% yield. Basic pyridine or DMF was used as solvent to bind free protons and reduced reagent species (chloride, chlorate, and chlorite ions, etc.) formed during the reaction, which favored selective formation of sulfonic acids. For example, in the reaction of **1e** with ClO_2 in methylene chloride the major products were sulfonic acid **2l** and sulfonyl chloride **3l** (Scheme 1) due to catalysis of camphene rearrangement by free protons [11]. The oxidation of **1g** in aqueous methanol or methylene chloride was accompanied by opening of the three-membered ring, assumingly with formation of hydroxy sulfonic acid **2k**, as followed from the sharp downfield shift of the C^7 signal (δ_C 73.45 ppm) relative to the corresponding signals of initial thiol **1g** and sulfonic acid **2g** (δ_C 17.71 and 17.80 ppm, respectively, downfield shift of the C^6 signal (δ_C 48.01 against 31.59 ppm for **1g**), appearance of an additional methylene carbon signal (C^1H_2) in the ^{13}C JMOD spectrum, and disappearance of C^1H signal. Conservation of the cyclohexane ring in structure **2k** was confirmed by the presence of ion peaks with *m*/*z* 97 and 111 due to C_7H_{13} and C_8H_{15} fragments in the mass spectrum. Pyridine as solvent favored formation of acids **2e** (57%) and **2g** (95%).

In the reactions of **1c** with ClO_2, pyridine stabilized final product **2c**, while the reaction in methylene chloride or methanol gave verbenone **4c** as a result of desulfurization. The yields of sulfonic acids in the oxidation of the other thiols in the system methylene chloride–water did not exceed 40%.

[1] The atom numbering of the precursor (**1g**) was conserved.

Unsaturated thiols **1c** and **1d** reacted with ClO_2 in aqueous pyridine to give acids **2c** and **2d** together with pyridinium salts **5c** and **5d** with a selectivity of up to 86 and 35%, respectively. Camphenesulfonic acid was isolated as pyridinium salt **5l** [11]. Presumably, the presence of a C=C double bond contiguous to the sulfo group increases the acidity of **2c**, **2d**, and **2l**. In the ^{1}H NMR spectra of **5c** and **5d**, the signal intensity ratio of the pyridine protons and protons of the terpene fragment was 1 : 1. The C^{10} signal in the ^{13}C NMR spectrum of **5d** was observed in a weaker field (δ_C 65.97 ppm) relative to the corresponding signal of **2d** (δ_C 58.37 ppm). The mass spectra of **5c**, **5d**, and **5l** recorded under mild chemical ionization (positive ion detection) displayed the molecular ion peaks $[M + H]^+$ with the maximum intensity (100%); in the negative ion mass spectra of the same compounds, the base peaks were those belonging to anions of the corresponding acids **2c**, **2d**, and **2l** $[M - H]^-$. The yields of pyridinium salts in the oxidation of the other thiols were insignificant (up to 10%).

Conjugation of lone electron pair on the sulfur atom with C=C double bond hampers oxidation of thiols **1c** and **1d** in less polar solvents. In the oxidation of **1b**, **1c**, and **1d** with ClO_2 in hexane–water (substrate-to-oxidant ratio 1 : 0.5), the conversion of **1c** and **1d** in 0.5 h did not exceed 40%, whereas the conversion of **1b** was complete.

In the first stage, regardless of the solvent nature, all thiols are oxidized with ClO_2 to disulfides **6a**–**6j** [11] whose further transformations are determined by the conditions and substrate structure. Increase of the amount of ClO_2 or solvent polarity (e.g., in going to methanol) promoted unexpected transformation of **6f** and **6j** to trisulfides **7f** and **7j** in 56–78% yield. Compounds **7** are likely to be formed according to the scheme proposed in [10] for the formation of **7f**.

Trisulfide **7j** showed in the mass spectrum the molecular ion peak with *m*/*z* 374, as well as fragment ion peaks with *m*/*z* 236 and 171 corresponding to terpene fragments bearing three and one sulfur atom, respectively. The IR spectrum of **7j** was similar to the spectrum of **6j**. In the ^{13}C NMR spectrum of **7j**, the C^1 signal appeared in a weaker field (δ_C 54.97 ppm) relative to the C^1 signal of **6j** (δ_C 52.60 ppm), and the 1-H proton signal also shifted downfield (δ 3.58 against 3.26 ppm for **6j**). The *cis* arrangement of the SH and isopropyl groups was retained, as shown by using two-dimensional NMR techniques (HSQC, COSY, NOESY, HMBC). The elemental composition of **7j** was consistent with the assumed structure.

The yield of **7j** reached 56%, depending on the conditions. The formation of **7j** was favored by gradual addition of the oxidant to excess thiol. If the oxidant was present in excess with respect to thiol, the major products were sulfonothioate **8j**, sulfonyl chloride **3j**, sulfonic acid **2j**, etc.

The reactions of thiol **1j** with ClO_2 were not selective as compared to thiols with pinane (**1a**–**1d**) and bornane skeletons (**1e**–**1f**). The use of $VO(acac)_2$ as catalyst, which showed previously [7] good results in reactions of diphenyl disulfide with ClO_2, did not improve the selectivity. In the oxidation of **1j** with 2 equiv of ClO_2 in methylene chloride, the yield of sulfonothioate **8j** did not exceed 30% (according to the ^{1}H NMR data). We failed to isolate pure compound **8j**, but the presence of SO_2 stretching bands in the IR spectrum (1321 and 1120 cm^{-1}), downfield shift of the C^1 signal (δ_C 71.42 ppm against δ_C 40.20 ppm for thiol **1j**), and the presence of double set of signals in the NMR spectra (indicating unsymmetrical structure) left no doubt concerning its structure.

The oxidation of **1j** in a more polar solvent such as anhydrous acetonitrile afforded sulfonyl chloride **3j** through unstable intermediate diastereoisomeric sulfinyl chlorides **9j** (*de* 54%). The ^{13}C NMR spectrum displayed one set of signals from each diastereoisomer, and the C^1 signals were located at δ_C 70.48 and 72.71 ppm. The S(=O)Cl group gave rise to absorption band at 1128 cm^{-1} in the IR spectrum. The oxidation of **9j** with 2 equiv of ClO_2 gave **3j** which showed one set of signals in the NMR spectra and downfield shift of the C^1 signal in the ^{13}C NMR spectrum (δ_C 77.92 ppm). The IR spectrum of **3j** contained SO_2 stretching bands at 1369 and 1167 cm^{-1}.

Although the reactions in pyridine selectively afforded the corresponding sulfonic acid, their separation from solvates and pyridinium salts (hydrochlorides, chlorates, and chlorites resulting from reaction of pyridine with the reduced oxidant species) is a difficult problem since almost all reaction products are readily soluble both in water and in organic solvents. Therefore, apart from pyridine, aqueous acetonitrile was tested as solvent to find optimal conditions for the synthesis and isolation of sulfonic acid **2j**. In this case, we succeeded in improving the yield of **2j** from 35 to 80% (in comparison with the reaction in methylene chloride) and isolating it in the pure state by extraction (in comparison with the reaction in pyridine). In the ^{13}C NMR spectrum of **2j**, the C^1 signal was observed in a weaker field (δ_C 59.72 ppm) relative

to the corresponding signal of thiol **1j** (δ_C 40.20 ppm), and a new signal appeared in the ^{1}H NMR spectrum at δ 9.35 ppm due to the OH proton. The IR spectrum of **2j** showed SO_2 stretching bands at 1228, 1197, 1172, 1053, and 1022 cm^{-1}. The mass spectrum of **2j** contained ion peak with *m*/*z* 219.22 $[M-1]^-$.

Under analogous conditions, thiol **1d** was selectively oxidized to sulfonothioate **8d**. The ^{13}C NMR spectrum of **8d** contained a double set of signals, and the C^{10} signal was shifted downfield (δ_C 69.95 ppm) relative to the corresponding signals of **6d** (δ_C 45.72 ppm) and **1d** (δ_C 30.56 ppm). The IR spectrum of **8d** showed SO_2 bands at 1325 and 1128 cm^{-1}.

The oxidation of carane thiols **1g–1i** with ClO_2 was accompanied by opening of the cyclopropane ring. Thiol **1i** reacted with 2 equiv of ClO_2 in aqueous acetonitrile in the presence of $VO(acac)_2$ to give sulfonyl chloride **3i** with a selectivity of up to 70%; however, the product was isolated in less than 30% yield due to its instability during chromatographic purification. In the oxidation of **1h**, the corresponding sulfonyl chloride was formed with a selectivity of ~40%. The formation of **3h** and **3i** followed from the position of the C^4 signals in the ^{13}C NMR spectra (δ_C 85.80 and 84.42 ppm, respectively) and the presence of SO_2 stretching bands in the IR spectra (1369 and 1161 cm^{-1}). The oxidation of **1g** under similar conditions gave sulfonothioate **8g** in a poor yield (16%). The NMR spectra of **8g** contained a double set of signals, the C^4 signal was shifted downfield (δ_C 70.48 ppm), and SO_2 stretching bands were observed in the IR spectrum at 1320 and 1122 cm^{-1}.

Hydroxypinane sulfonothioates **8a** and **8b** [11] were tested for antimicrobial activity against five bacterial strains (*Escherichia coli*, *Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*) and antifungal activity against two fungal strains (*Candida albicans*, *Cryptococcus neoformans*). These bacteria showed multiple resistance to antibiotics. Colistin and Vancomycin were used as reference drugs for gram-negative and gram-positive bacteria, respectively, and Fluconazole was used as reference drug for fungi. Bacterial growth inhibition was evaluated by measuring the optical density at λ 530–600 nm, depending on the particular strain. A compound was assumed to be active if the bacterial growth inhibition was higher than 80%. The results showed that sulfonothioates **8a** and **8b** are active against *Candida albicans*, while compound **8a** also showed activity against *Staphylococcus aureus* and *Cryptococcus neoformans*.

In summary, the oxidation of terpene thiols with pinane, *p*-menthane, bornane, and carane structures with chlorine dioxide afforded the corresponding sulfonic acids in high yields (76–96%) and their derivatives (28–85%). Monofunctional thiols of the *p*-menthane and bornane series characteristically gave rise to the corresponding trisulfides as the major products. Nitrogen-containing aprotic solvents favored smooth transformation of thiols to sulfonic acids and prevented acid-catalyzed rearrangements in the reactions with bornane and carane thiols and desulfurization in the oxidation of thioverbenol.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu IR Prestige 21 spectrometer with Fourier transform. The melting points were determined on a Gallenkamp-Sanyo melting point apparatus. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-300 spectrometer at 300.17 and 75.48 MHz, respectively, using $CDCl_3$ as solvent and reference or D_2O as solvent with addition of sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) as internal standard. The ^{1}H and ^{13}C NMR signals were assigned using two-dimensional homo- (^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY) and heteronuclear experiments (^{1}H–^{13}C HSQC, HMBC). The mass spectra were obtained on a Thermo Finnigan LCQ Fleet HPLC/MS instrument using MeOH and MeCN as solvents and on a Thermo Fisher Scientific TRACE DSQ GC/MS system (electrospray ionization, capillary voltage 5 kV) with positive (**3**–**9**) and negative (**2**) ion detection. The optical rotations were measured on a Kruss P3002RS automated digital polarimeter. Thin-layer chromatography was performed on Sorbfil plates with petroleum ether–ethyl acetate (1:1) (**1a**–**1d**) and $CHCl_3$ (**1e**–**1g**) as eluents; spots were visualized by treatment with a solution of phosphomolybdic acid in ethanol, a solution of $KMnO_4$, or a 0.2% solution of Bromocresol Green in ethanol (for sulfinyl and sulfonyl chlorides). The elemental analyses were obtained with an EA 1110 CHNS-O automated analyzer.

All reactions were carried out in freshly distilled solvents. The products were isolated by column chromatography on silica gel (0.06–0.2 mm, Alfa Aesar) using the same solvent systems as in TLC. The yields were determined by ^{1}H NMR from the intensities of 4-H for **1c** and **1g**–**1k** and of 1-H for **1j**.

Aqueous solution of chlorine dioxide is a commercial product; the concentration of ClO_2 was deter-

mined by titration according to the procedure described in [21]. Solutions of ClO_2 in organic solvents were prepared by extraction from an aqueous solution, the extract was dried over, and the concentration of ClO_2 was determined by titration [21].

Samples for biological screening were prepared and applied to microplates with Caliper Zephyr and Biomek NX automated liquid handling systems. Fungal strains were cultivated on yeast extract peptone dextrose (YEPD) agar. The optical densities at λ 600 nm (OD_{600}) were measured with Tecan M1000 Pro (bacteria) and Biotek Synergy HTX (fungi) microplate readers.

Oxidation of thiols with chlorine dioxide (*general procedures*). The overall volume of the reaction mixture was calculated for a thiol concentration of 0.02 M (sample weight 0.05–0.1 g). The progress of reactions was monitored by TLC.

a. A solution of chlorine dioxide in water or organic solvent was added to a solution of thiol **1** in pyridine, DMF, or acetonitrile to a substrate-to-oxidant ratio of 1 : (2–3).[2] The mixture was stirred for 1–3 h and extracted with chloroform or methylene chloride to isolate neutral compounds, and the aqueous phase was additionally treated with benzene or hexane and evaporated. The dry residue contained 76–96% of sulfonic acid **2**.

b. Thiol **1** was dissolved in an organic solvent, 10 mol % of $VO(acac)_2$ was added, and a solution of chlorine dioxide in water or organic solvent was added. The aqueous and organic phases were separated and evaporated on a rotary evaporator. The dry residue from the organic phase was subjected to column chromatography.

Compounds **2a**, **2b**, **2e**, **2l**, **3a**, **3b**, **3l**, **5l**, **6a**, **6b**, **6e**, **8a**, **8b** [11], **2f**, **6f**, **7f**, **9f** [10], **6c**, **6d** [22], and **4c** [23] were described previously.

{(1*S*,5*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl}methanesulfonic acid (2d). Yield 74% (*a*). IR spectrum (KBr), ν, cm^{-1}: 1325, 1128 (SO_2). ^1H NMR spectrum (D_2O), δ, ppm: 0.84 s (3H, 9-H), 1.21–1.34 m (1H, 7-H), 1.26 s (3H, 8-H), 2.11–2.19 m (2H, 1-H, 5-H), 2.27–2.54 m (3H, 4-H, 7-H), 3.53–3.65 m (2H, 10-H), 5.21 s (1H, 3-H), 10.3 br.s (1H, OH). ^{13}C NMR spectrum (D_2O), δ_C, ppm: 20.53 (C^9), 25.67 (C^8), 31.06, 31.34 (C^7, C^4), 38.23 (C^6), 39.85 (C^5), 45.67 (C^1), 58.37 (C^{10}), 124.66 (C^3), 138.79 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 215.29 (100) $[M - H]^-$, 97.00 (48) $[C_7H_{13}]$.

(1*S*,3*R*,4*S*,6*R*)-3,7,7-Trimethylbicyclo[4.1.0]-heptane-4-sulfonic acid (2g). Yield 84% (*a*). IR spectrum (KBr), ν, cm^{-1}: 3437 br (O–H), 2983, 1467, 1386, 1215 s (SO_2), 1153 s (SO_2), 1026 s (SO_2), 990, 885, 664, 619. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.40–0.51 m (1H, 1-H), 0.69 q (1H, 6-H, *J* = 8.4 Hz), 0.79–0.95 m (H, 5-H), 0.91 s and 0.93 s (6H, 8-H, 9-H), 1.02 d (3H, 10-H, *J* = 7.2 Hz), 0.97–1.23 m (1H, 2-H), 1.89–2.04 m (1H, 5-H), 2.05–2.23 m (2H, 2-H, 3-H), 2.73–2.89 m (1H, 4-H), 8.76 s (OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.06 (C^8), 17.60 (C^{10}), 17.73 (C^7), 18.62 (C^2), 19.41 (C^1), 22.33 (C^6), 26.34 (C^3), 26.43 (C^5), 28.11 (C^9), 59.20 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 434.94 (5) $[2M - H]^-$, 217.19 (100) $[M - H]^-$, 97.03 (13) $[C_7H_{13}]$.

(1*S*,3*S*,4*S*,6*R*)-3-Hydroxy-3,7,7-trimethylbicyclo-[4.1.0]heptane-4-sulfonic acid (2h). Yield 92% (*a*). IR spectrum (KBr), ν, cm^{-1}: 3423 br (O–H), 2983, 1485, 1249 s (SO_2, asym.), 1207 s (SO_2, asym.), 1157 s (SO_2, asym.), 1035 s (SO_2, sym.), 999 s (SO_2, sym.), 756, 682. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.61 t (1H, 1-H, *J* = 8.5 Hz), 0.77–0.98 m (2H, 5-H, 6-H), 0.84 s (3H, 8-H), 0.91 s (3H, 9-H), 1.24 d.d (1H, 2-H, *J* = 15.7, 6.3 Hz), 1.38 s (3H, 10-H), 2.00 d.d (1H, 2-H, *J* = 16.0, 8.8 Hz), 2.22–2.35 m (1H, 5-H), 2.95 d.d (1H, 4-H, *J* = 12.0, 2.0 Hz), 10.57 br.s (1H, 11-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.84 (C^8), 17.81 (C^1), 18.59 (C^7), 20.74 (C^5), 23.62 (C^6), 26.47 (C^{10}), 27.85 (C^9), 35.44 (C^2), 67.81 (C^4), 71.15 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 233.21 (100) $[M - H]^-$, 97.03 (8) $[C_7H_{13}]$.

(1*S*,3*R*,4*R*,6*R*)-3-Hydroxy-3,7,7-trimethylbicyclo-[4.1.0]heptane-4-sulfonic acid (2i). Yield 96% (*a*). IR spectrum (KBr), ν, cm^{-1}: 3410 br (O–H), 2933 s, 1487, 1249 s (SO_2), 1211 s (SO_2), 1161 s (SO_2), 1035 (SO_2), 1001 (SO_2), 756, 682 s, 601. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.60 t (1H, 1-H, *J* = 8.5 Hz), 0.75 t.d (1H, 6-H, *J* = 9.2, 5.2 Hz), 0.92 s (3H, 8-H), 0.96 s (3H, 9-H), 1.20 d.d (1H, 2-H, *J* = 14.3, 3.9 Hz), 1.39 s (3H, 10-H), 1.93 d.d (1H, 2-H, *J* = 14.0, 10.2 Hz), 2.10–2.26 m and 2.27–2.43 m (1H each, 5-H), 2.70 d.d (1H, 4-H, *J* = 11.8, 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.33 (C^8), 17.78 (C^7), 18.30 (C^1), 19.77 (C^6), 20.97 (C^5), 22.39 (C^{10}), 28.46 (C^9), 35.53 (C^2), 64.46 (C^4), 70.53 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 233.21 (100) $[M - H]^-$, 97.03 (11) $[C_7H_{13}]$.

(1*S*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexane-1-sulfonic acid (2j). Yield 78% (*a*; MeCN, H_2O).

[2] Variation of the organic solvent-to-water ratio from 5 : 1 to 5 : 2 had no appreciable effect on the results.

IR spectrum (KBr), ν, cm^{-1}: 3410 br (O–H), 2953 s, 1182 s (SO_2), 1070 (SO_2), 1014, 885, 582. ^1H NMR spectrum (D_2O), δ, ppm: 0.83 d (3H, 7-H, J = 6.1 Hz), 0.90 d (3H, 10-H, J = 6.6 Hz), 0.88–0.97 m (1H, 4-H), 0.99 d (3H, 9-H, J = 6.6 Hz), 1.13–1.38 m (2H, 2-H, 6-H), 1.62–1.95 m (5H, 3-H, 4-H, 5-H, 8-H), 2.25 d.d (1H, 6-H, J = 13.8, 2.2 Hz), 3.39–3.45 m (1H, 1-H). ^{13}C NMR spectrum (D_2O), δ_C, ppm: 20.87 (C^{10}), 21.39 (C^9), 21.84 (C^7), 23.74 (C^3), 26.07 (C^5), 29.10 (C^8), 34.90 (C^4), 37.78 (C^6), 47.29 (C^2), 58.82 (C^1). Mass spectrum, m/z (I_{rel}, %): 219.20 (100) $[M - H]^-$, 97.00 (35) $[C_7H_{13}]$. Found, %: C 54.62; H 9.80; S 13.86. $C_{10}H_{20}O_3S$. Calculated, %: C 54.51; H 9.15; S 14.55.

(1*S*,2*R*,5*S*)-5-(2-Hydroxypropan-2-yl)-2-methylcyclohexane-1-sulfonic acid (2k). Selectivity 68% (*a*; MeCN, H_2O). IR spectrum (film), ν, cm^{-1}: 3423 br (O–H), 1172 (SO_2), 1051 (SO_2). ^1H NMR spectrum (D_2O), δ, ppm: 0.78 d (3H, 10-H, J = 7.2 Hz), 0.93–0.97 m (1H, 1-H), 0.96 s (6H, 8-H, 9-H), 1.12–1.39 m (3H, 2-H, 6-H), 1.39–1.61 m (2H, 5-H), 1.64–1.83 m (1H, 1-H), 2.00–2.31 m (1H, 3-H), 2.57–2.90 m (1H, 4-H). ^{13}C NMR spectrum (D_2O), δ_C, ppm: 12.14 (C^{10}), 19.92 (C^2), 21.54 (C^1), 25.29 (C^8, C^9), 28.24 (C^3), 32.53 (C^5), 48.01 (C^6), 62.55 (C^4), 73.45 (C^7). Mass spectrum, m/z (I_{rel}, %): 235.21 (45) $[M - H]^-$, 111.06 (26) $[C_8H_{15}]$, 97.03 (100) $[C_7H_{13}]$.

(1*S*,3*S*,4*S*,6*R*)-3-Hydroxy-3,7,7-trimethylbicyclo[4.1.0]heptane-4-sulfonyl chloride (3h). Reaction time 1 h (*b*; MeCN, H_2O), selectivity 38–44%; viscous liquid. IR spectrum (film), ν, cm^{-1}: 3402 br (O–H), 1373 s (SO_2), 1163 s (SO_2), 1111 s (C–O). The NMR spectra were obtained by subtracting the signals analogous to **3i** from the spectrum of mixture **3h**/**6h**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.67–0.90 m (1H, 1-H), 1.04 s (3H, 8-H), 1.10 s (3H, 9-H), 1.19–1.40 m (1H, 2-H), 1.55 s (3H, 10-H), 1.68–1.83 m (1H, 6-H), 2.15 d.d (1H, 2-H, J = 16.0, 8.3 Hz), 2.30–2.48 d.d (1H, 5-H), 2.64 d.d.d (1H, 5-H, J = 14.3, 7.7, 3.3 Hz), 3.30 s (1H, OH), 3.89 d.d (1H, 4-H, J = 12.4, 3.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.76 (C^8), 17.40 (C^1), 19.69 (C^7), 21.99 (C^5), 22.67 (C^6), 24.05 (C^{10}), 27.00 (C^9), 33.51 (C^2), 73.06 (C^3), 85.80 (C^4). Mass spectrum, m/z (I_{rel}, %): 253.06 (52) $[M + H]^+$, 137.13 (100) $[C_{10}H_{17}]^+$.

(1*S*,3*R*,4*R*,6*R*)-3-Hydroxy-3,7,7-trimethylbicyclo[4.1.0]heptane-4-sulfonyl chloride (3i). Yield 30% (*b*; MeCN, H_2O), viscous liquid. IR spectrum (film), ν, cm^{-1}: 3445 (O–H), 1369 (SO_2), 1161 (SO_2), 1115 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.85–0.99 m (1H, 1-H), 1.01 s (3H, 8-H), 1.09 s (3H, 9-H), 1.30–1.48 m (1H, 2-H), 1.53 s (3H, 10-H), 1.68–1.85 m (1H, 6-H), 2.10 d.d (1H, 2-H, J = 14.9, 9.4 Hz), 2.41 d.d (1H, 5-H, J = 15.1, 8.0 Hz), 2.64 d.d.d (1H, 5-H, J = 15.0, 11.1, 8.5 Hz), 3.28 s (1H, OH), 3.67 d.d (1H, 4-H, J = 11.0, 8.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.28 (C^8), 18.29 (C^1), 18.46 (C^7), 19.29 (C^6), 21.65 (C^5), 23.38 (C^{10}), 27.96 (C^9), 35.97 (C^2), 73.08 (C^3), 84.42 (C^4). Mass spectrum, m/z (I_{rel}, %): 253.06 (65) $[M + H]^+$, 137.13 (100) $[C_{10}H_{17}]^+$. Found, %: C 47.62; H 6.80; S 12.86. $C_{10}H_{17}ClO_3S$. Calculated, %: C 47.52; H 6.78; S 12.68.

(1*S*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexane-1-sulfonyl chloride (3j). Yield 28% (*b*; reaction time 2 h, MeCN, $CHCl_3$; **1j**–ClO_2 1:6), viscous liquid. IR spectrum (film), ν, cm^{-1}: 1369 (SO_2), 1166 (SO_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.51 (C^{10}), 21.80 (C^9), 22.13 (C^7), 24.83 (C^3), 26.02 (C^5), 30.21 (C^8), 34.77 (C^4), 37.86 (C^6), 50.51 (C^2), 77.89 (C^1). Mass spectrum, m/z (I_{rel}, %): 239.04 (49) $[M + H]^+$, 139.17 (100) $[C_{10}H_{19}]^+$. Found, %: C 49.82; H 7.89; S 12.96. $C_{10}H_{19}ClO_2S$. Calculated, %: C 50.30; H 8.02; S 13.43.

Pyridinium (1*R*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene-4-sulfonate (5c). Yield 86% (*a*). IR spectrum (KBr), ν, cm^{-1}: 3431 br (O–H), 3061, 2515 br (N^+–H), 1631, 1537, 1485, 1294 s (SO_2), 1151 s (SO_2), 1051, 1028 s (SO_2), 819, 758, 721, 684. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 s (3H, 8-H), 0.96–1.09 (1H, 7-H), 1.15 s (3H, 9-H), 1.68 s (3H, 10-H), 1.94–2.06 m (2H, 1-H, 7-H), 2.30–2.40 m (1H, 5-H), 5.29–5.35 m (1H, 3-H), 5.49–5.57 m (H, 4-H), 8.02 t (2H, Py, J = 6.87 Hz), 8.44 t (1H, Py, J = 7.97 Hz), 9.00 d (2H, Py, J = 5.5 Hz), 14.64 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.70 (C^8), 22.80 (C^{10}), 25.00 (C^7), 25.49 (C^9), 46.32 (C^1), 46.86 (C^6), 48.15 (C^5), 71.00 (C^4), 109.45 (C^3), 127.82 (C_{Py}), 142.95 (C_{Py}), 145.08 (C_{Py}), 156.70 (C^2). Mass spectrum, m/z (I_{rel}, %): 591 (23) $[2M + H]^+$, 296.24 (100) $[M + H]^-$. Found, %: C 62.01; H 7.30; N 4.84; S 10.66. $C_{10}H_{16}SO_3 \cdot C_5H_5N$. Calculated, %: C 60.99; H 7.17; N 4.74; S 10.85.

Bis[(1*S*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]trisulfane (7j). Yield 56%, white powder. IR spectrum (KBr), ν, cm^{-1}: 2949 s, 2918 s, 2870 s, 1450, 1375, 1278, 1238, 860. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.83–0.97 m (1H, 4-H_{ax}), 0.93 d (3H, 7-H, J = 6.6 Hz), 0.93 d (3H, 9-H, J = 6.6 Hz), 1.03 d (3H, 10-H, J = 6.6 Hz), 1.08–1.28 m (1H, 6-H_{ax}), 1.09–1.28 m (1H, 2-H), 1.15–1.28 m (1H, 3-H_{ax}), 1.59–1.65 m (1H, 8-H), 1.68–1.77 m (1H, 3-H_{eq}), 1.75–1.78 m (1H, 4-H_{eq}), 1.85–1.95 m (1H, 5-H), 2.40–

2.45 m (1H, 6-H$_{eq}$), 3.55–3.60 m (1H, 1-H). ^{13}C NMR spectrum, δ_C, ppm: 20.20 (C^9), 20.71 (C^{10}), 21.29 (C^7), 26.29 (C^5), 26.49 (C^3), 29.94 (C^8), 35.37 (C^4), 39.98 (C^6), 48.94 (C^2), 54.96 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 374 (11) $[M]^+$, 236 (6) $[C_{10}H_{19}S_3H]$, 171 (8) $[C_{10}H_{19}S]$, 139 (68) $[C_{10}H_{19}]$, 83 (100). Found, %: C 64.12; H 10.21; S 25.70. $C_{20}H_{38}S_3$. Calculated, %: C 64.17; H 10.16; S 25.67.

***S*-[(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]methyl (1*R*,5*S*)-6,6-dimethyl(bicyclo[3.1.1]-hept-2-en-2-yl)methanesulfonothioate (8d).** Yield 85% (*a*; MeCN, H_2O), white powder, $[\alpha]_D^{22} = -3.7°$ (*c* = 0.2, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1325, 1128 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 s (3H, 9′-H), 0.91 s (3H, 9-H), 1.15–1.31 m (2H, 7-H, 7′-H), 1.33 s (6H, 8-H, 8′-H), 2.09–2.19 m (2H, 5-H, 5′-H), 2.24 d (1H, 1′-H, *J* = 5.2 Hz), 2.27–2.54 m (7H, 1-H, 4-H, 4′-H, 7-H, 7′-H), 3.70–3.79 m and 3.82–3.91 m (1H each, 10′-H), 3.97 q (2H, 10-H, *J* = 11.5 Hz), 5.65 s (1H, 3′-H), 5.81 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.09 (C$^{9'}$), 21.21 (C^9) 26.05 (C^8, C$^{8'}$), 31.45 (C$^{7'}$), 31.74 (C^7), 31.88 (C$^{4'}$), 32.03 (C^4), 38.23 (C^6), 40.06 (C$^{5'}$), 40.31 (C^5), 42.78 (C$^{10'}$), 45.15 (C$^{1'}$), 46.20 (C^1), 70.20 (C^{10}), 123.33 (C$^{3'}$), 129.76 (C^3), 135.96 (C$^{2'}$), 140.95 (C^2). Found, %: C 64.69; H 8.21; S 17.35. $C_{20}H_{30}O_2S_2$. Calculated, %: C 65.53; H 8.25; S 17.49.

***S*-(1*R*,3*S*,4*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]-hept-3-yl (1*R*,3*S*,4*R*,6*S*)-4,7,7-trimethylbicyclo-[4.1.0]heptane-3-sulfonothioate (8g).** Yield 16% (*a*; MeCN, H_2O; isolated from the organic fraction), viscous liquid. IR spectrum (film), ν, cm^{-1}: 1320 (SO_2), 1122 (SO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.52–0.68 m (4H, 2′-H, 10′-H), 0.68–0.87 m (1H, 6′-H), 0.87–1.33 m (17H, 1′-H, 6-H, 8-H, 8′-H, 9-H, 9′-H, 10-H), 1.45–2.17 m (6H, 1-H, 2′-H, 3′-H, 5-H, 5′-H), 2.20–2.64 m (3H, 2-H, 3-H, 5′-H), 3.43–3.61 m (1H, 4-H), 3.61–3.87 m (1H, 4′-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.49 (C$^{8'}$), 16.37 (C^8), 16.63 (C$^{7'}$), 17.86 (C^7), 18.30 (C$^{10'}$), 18.46 (C^2), 19.46 (C$^{1'}$, C^{10}), 19.65 (C^1), 21.47 (C$^{6'}$), 22.07 (C^6), 25.35 (C$^{2'}$), 27.09 (C$^{5'}$), 27.44 (C$^{9'}$), 27.78 (C^5), 28.37 (C^3), 28.79 (C^9), 31.46 (C$^{3'}$), 52.50 (C$^{4'}$), 70.48 (C^4). Found, %: C 64.82; H 9.25; S 17.30. $C_{20}H_{34}O_2S_2$. Calculated, %: C 65.20; H 9.20; S 17.49.

***S*-[(1*S*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclo-hexyl] (1*S*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclo-hexane-1-sulfonothioate (8j).** Selectivity 30–48% (*b*). IR spectrum (film), ν, cm^{-1}: 1321 (SO_2), 1120 (SO_2). ^{13}C NMR spectrum (from the spectrum of mixture **3j**/**8j**; $CDCl_3$), δ_C, ppm: 20.51 (C$^{10'}$), 20.69 (C^{10}), 21.11 (C^9), 21.51 (C$^{9'}$), 21.86 (C^7), 22.28 (C$^{7'}$), 25.64 (C$^{3'}$), 26.15 (C^3), 26.25 and 26.42 (C^5, C$^{5'}$), 29.87 and 30.03 (C^8, C$^{8'}$), 34.78 and 35.00 (C^4, C$^{4'}$), 35.24 (C$^{6'}$), 37.92 (C^6), 48.87 (C$^{2'}$), 50.40 (C^2), 53.91 (C^1), 71.37 (C$^{1'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 375.16 (49) $[M + H]^+$, 139.15 (100) $[C_{10}H_{19}]^+$.

(1*S*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclo-hexane-1-sulfinyl chloride (9j). Yield 36–45% (*b*; CH_2Cl_2, **1j**–ClO_2 1:4, reaction time 2 h), mixture of diastereoisomers **A** and **B** (77:23). IR spectrum (film): ν 1128 cm^{-1} (S=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.93 d (3H, 10-H, *J* = 6.1 Hz), 0.95 d (3H, 9-H, *J* = 6.6 Hz), 0.97–1.03 m (1H, 4-H), 1.06 d (3H, 7-H, *J* = 6.6 Hz), 1.28–1.48 m (2H, 2-H, 6-H), 1.72–2.49 m (5H, 3-H, 4-H, 5-H, 8-H), 2.96 d.d (1H, 6-H, *J* = 13.8, 2.2 Hz), 3.68–3.74 m (**A**) and 3.97–4.01 m (**B**) (1H, 1-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.55 and 21.10 (C^9), 21.68 and 21.55 (C^8), 22.34 and 22.78 (C^{10}), 26.08 and 26.01 (C^3), 27.68 and 28.06 (C^5), 29.84 and 29.15 (C^7), 34.77 and 35.31 (C^4), 34.81 and 37.42 (C^6), 48.32 and 50.31 (C^2), 70.48 and 72.71 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 223.08 (100) $[M + H]^+$, 139.15 (38) $[C_{10}H_{19}]^+$.

Antimicrobial activity. Compounds **8a** and **8b** were tested for antimicrobial activity at a concentration of 32 μg/mL in duplicate. A sample of **8a** or **8b** was dissolved in DMSO to a concentration of 10 mg/mL. The resulting solution was diluted to a concentration of 320 μg/mL with 7% aqueous DMSO and dispensed over a 384-well polypropylene plate (StorPlate; Perkin Elmer № 6008690). In a duplicate experiment, 5 μL of the same solution was dispensed over a 384-well plate (NBS; Corning № 3640). After addition of biological media, the concentration of test compounds was ~32 μg/mL, and the concentration of DMSO, 1%.

Bacterial cultures were grown on a cation-adjusted Muller–Hinton broth at 37°C. Each culture was then diluted with 40 volumes of a fresh broth and incubated for 1.5–2 h at 37°C, and a 45-μL portion was added to each well containing compounds to be tested; the concentration of bacteria therein was 5×10^5 CFU/mL (determined from OD_{600}). All microplates were capped and incubated for 18 h at 37°C without shaking.

Bacterial growth inhibition was determined by measuring the optical density at λ 600 nm for each well using only broth and bacterial culture without inhibitor as negative and positive controls, respectively. The inhibition percentage was estimated through *Z*-sets with calculation of mean and standard deviations for wells with samples (without control) in

each microplate. Samples with an inhibition value of more than 80% and *Z*-set ~2.5 in each experiment (n = 2 for different plates) were defined as active.

Fungal strains were cultivated for 72 h at 30°C. A suspension of yeasts containing 10^6 to 5×10^6 cells per milliliter was prepared from 5 colonies. These cultures were diluted with yeast nitrogen base (YNB) medium to a final concentration of 2.5×10^3 CFU/mL and dispensed over microplates in an amount of 45 μL per well. The microplates were capped and incubated for 24 h at 35°C without shaking.

Fungal growth inhibition was estimated by measuring the optical density at λ 530 nm for *C. Albicans* or the difference in the optical densities at λ 600 to 570 nm after addition of resazurin (final concentration 0.001%) and additional incubation for 2 h at 35°C. The inhibition percentage was determined for each well using only tested compounds as negative control and fungal culture without inhibitor as positive control in each microplate through *Z*-sets with calculation of mean and standard deviations for wells with samples (without control) in each microplate. Samples with an inhibition value of more than 80% and *Z*-set ~2.5 in each experiment (n = 2 for different plates) were defined as active.

Colistin and Vancomycin were used as reference drugs for gram-negative and gram-positive bacteria, respectively, and Fluconazole was the reference drug for fungi. The reference antibiotics were applied to the first eight wells of the 23th column of a 384-well microplate at four different concentrations, two of which were higher and the other two were lower than the minimum inhibitory concentration. The results for a microplate were qualified as satisfactory when the *Z*-test (for positive and negative controls) was equal to 0.4 and the reference drugs showed the complete activity spectrum, i.e., complete inhibition at the maximum concentration and no inhibition at the minimum concentration.

This study was performed under financial support by the Russian Foundation for Basic Research and by the government of the Komi Republic (project nos. 16-43-110358 r_a, 16-33-00783 mol_a) using the facilities of the Chemistry Joint Center (Institute of Chemistry, Komi Scientific Center, Ural Branch, Russian Academy of Sciences) and Chromatography Joint Center (Institute of Biology, Komi Scientific Center, Ural Branch, Russian Academy of Sciences).

The authors thank the staff of the Physicochemical Methods Laboratory (Institute of Chemistry, Komi Scientific Center, Ural Branch, Russian Academy of Sciences), namely E.N. Zainullina and S.P. Kuznetsov for recording the NMR spectra, E.U. Ipatova for recording the IR spectra, S.A. Patov, V.A. Belyi, and I.V. Gruzdev for recording the mass spectra, S.L. Smoleva for performing elemental analyses, and I.A. Dvornikova for measuring the optical rotations, as well as the Community for Open Antimicrobial Drug Discovery (Australia) for performing biological tests.

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