ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 2, pp. 184–192. © Pleiades Publishing, Ltd., 2012.
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Asymmetric Synthesis of New Optically Active Sulfinamides of Menthane Series and Their Derivatives

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Received July 20, 2011

Abstract—Asymmetric syntheses were performed of neomenthanesulfinamide in the yield of 60% and *de* 74%, of neomenthanesulfinaldimines and N-substituted neomenthanesulfinamides in 22–80 and 40–90% yields respectively.

DOI: 10.1134/S1070428012020066

Sulfinamides and their derivatives are known to exhibit a pronounced antisclerosis effect, potential antineurotic and antimetastasis action [1], they are widely used in the organic synthesis of chiral amines [2], as reagents for amino group introduction in the preparation of α- and β-amino acids [2, 3], they are employed in the synthesis of drugs, e.g., of sibutramine [4]. Besides, sulfinimines are good ligands in the reactions of asymmetric synthesis [2], and *N*-substituted amides are used as catalysts in the enantioselective reduction of chiral Schiff bases [5].

It was shown in [2, 6–9] that chiral inducers were catalysts based on ligands of salen type used in the oxidation of prochiral disulfides to enantiomerically enriched thiosulfinates which at the amidation and subsequent crystallization provided finally optically pure sulfinamides.

Although the sulfinamides and their derivatives are extensively utilized, the terpene nitrogen-containing sulfinyl derivatives have not been described in the literature up till now, yet natural optically pure monoterpenoids are commercially available. They are labile in the chemical transformations. In this approach the chiral inducer of the sulfinyl group is the substrate molecule itself. Therefore the studies in the chemistry of terpene sulfinamides and their derivatives are now timely.

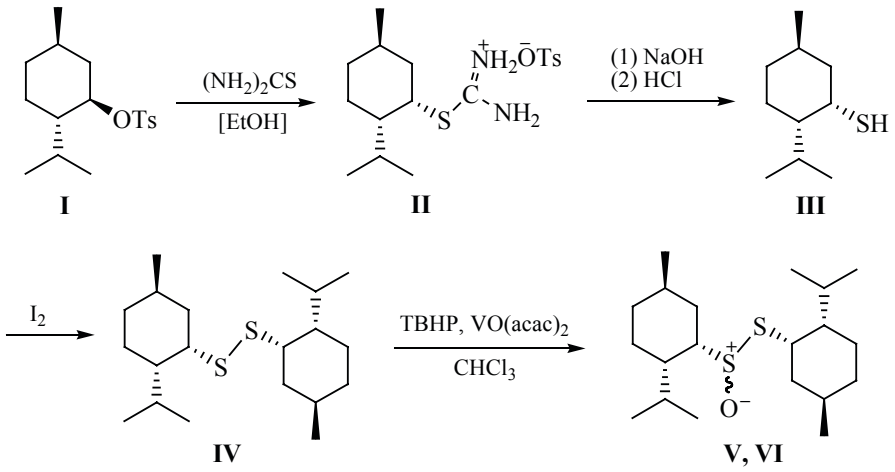
In this study we synthesized a number of sulfinyl derivatives proceeding from neomenthanethiol: sulfinamide, sulfinaldimines, and *N*-substituted sulfinamides.

Initial neomenthanethiol (**III**) was synthesized by the reaction of *L*- menthol *p*-toluenesulfonate (**I**) and thiourea followed by alkaline hydrolysis of the formed isothiouronium salt **II** in 60% yield calculated on compound **I**. In the oxidative dimerization of thiol **III** with iodine dineomenthyl disulfide **IV** was obtained that was oxidized in the system *tert*-butyl hydroperoxide (TBHP)–vanadyl acetylacetonate [$VO(acac)_2$] to give diastereomeric thiosulfinates (**V, VI**) in 67% yield with respect to compound **IV** with *de* 45% (Scheme 1).

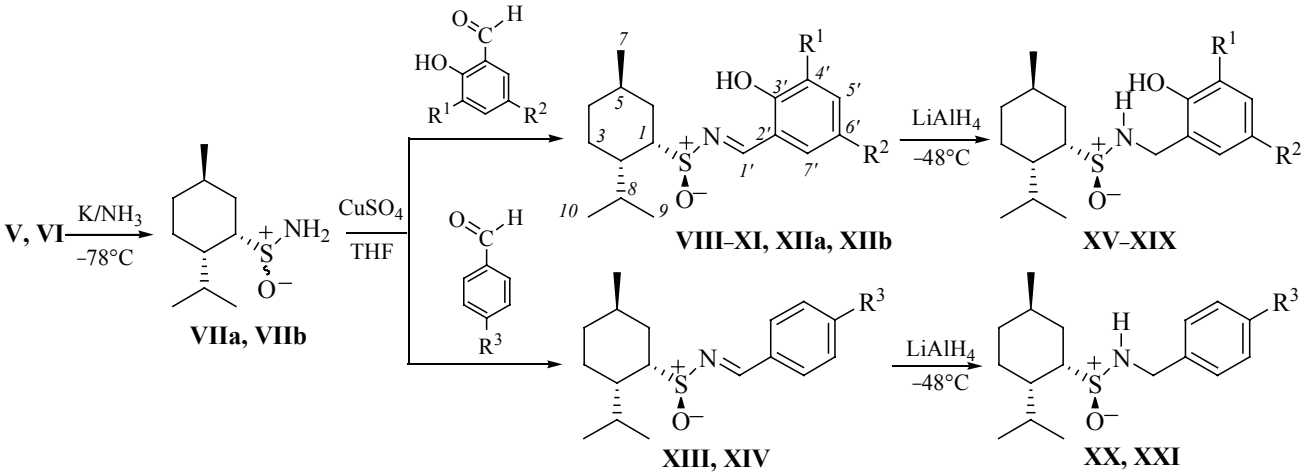
Thiol **III**, disulfide **IV**, and thiosulfinates **V, VI** we have described in [10]. Disulfide **IV** was oxidized with *m*-CPBA to obtain diastereomeric thiosulfinates **V, VI** (*de* 28%). It was presumed that in the course of the reaction formed a sterically less hindered thiosulfinate, where the oxygen of the sulfinyl group and the isopropyl group are oriented in the opposite directions [10].

In this study the diastereomeric mixture **V, VI** of *de* 45% was subjected to amidation. In [2, 8, 9] the amidation of *tert*-butyl-containing thiosulfinates was performed using lithium in liquid ammonia, but with dineomenthyl thiosulfinates this system was inactive. Yet in the reaction of compounds **V, VI** with potassium in liquid ammonia we succeeded in obtaining diastereomeric mixture of neomenthanesulfinamides **VIIa, VIIb** with *de* 74% (Scheme 2). At the amidation for 2 h only the prevailing isomer **V** entered the reaction. The prevailing sulfinamide

Scheme 1.



Scheme 2.



$R^1 = R^2 = H$ (**VIII, XV**), *t*-Bu (**X, XVII**), Br (**XI, XVIII**), I (**XII, XIX**); $R^1 = H$, $R^2 = Cl$ (**IX, XVI**); $R^3 = NO_2$ (**XIII, XX**), $N(CH_3)_2$ (**XIV, XXI**).

VIIa we succeeded to isolate in the individual state by crystallization from methanol and to characterize it. The second diastereomer **VIIb** we failed to isolate in the pure state. The ^1H NMR spectrum of compound **VIIa** contains all characteristic signals of the neomenthane fragment and a broadened singlet of the NH_2 group at 4.12 ppm. In the ^{13}C NMR spectrum the characteristic signal of the atom C^1 of the neomenthane fragment adjacent to the sulfinyl group appears at 65.45 ppm. In the IR spectrum absorption bands of the sulfinyl (1034 cm^{-1}) and amino (3233 cm^{-1}) groups are observed.

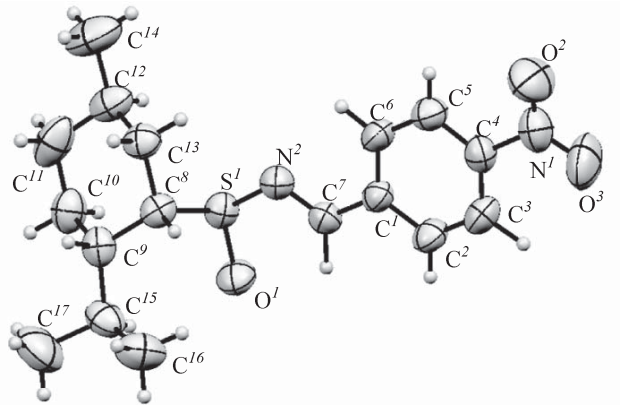
As carbonyl compounds for the condensation with diastereomers **VIIa, VIIb** we selected salicylaldehyde and its derivatives: 5-chlorosalicylic, 3,5-di-*tert*-butylsalicylic, 3,5-dibromo- and 3,5-diiodosalicylic aldehydes, and also *para*-nitro and *para*-dimethylamino derivatives of benzaldehyde. The condensation was carried out in the presence of dehydrating agent $CuSO_4$ and acid catalysts. Individual diastereomer **VIIa** was not used in the pure state for the condensation with aldehydes because of its low yield. The reaction of aldehydes with the diastereomerically enriched mixture **VIIa, VIIb** afforded sulfinylaldimines **VIII–XIV** (Scheme 2). In all cases save compound **XII** it was possible to separate by column chromatography on silica gel in individual state and to characterize only one of the stereoisomeric sulfinimines. At the use of the

3,5-diiodosalicylaldehyde we isolated both sulfinimines (*S*)-(**XIIa)** and (*R*)-(**XIIb)** in the individual state.

In the ^{1}H NMR spectra of sulfinimines the signal of the NH_2 group of the initial sulfinamide is absent, and the characteristic signals of the methine group C$^{1'}$H at the double bond appear in the region 8.5–8.8 ppm, and also the proton signals of the aromatic ring are observed. The ^{13}C NMR spectra contain the signals of the carbon atom of the methine group C$^{1'}$H in the region 159.6–165.4 ppm. In the IR spectra absorption bands characteristic of the C=N bond are observed in the region 1610–1650 cm^{-1}, and also the bands of the sulfinyl group appear. The difference in the absolute configuration of the diiodo-substituted diastereomers (*S*)-(**XIIa)** and (*R*)-(**XIIb)** is observed in the dissimilar location of the corresponding signals of the atoms of neomenthane fragment in the ^{1}H and ^{13}C NMR spectra, but no displacement of the signals of the aromatic atoms occurs for the benzene ring and the sulfinyl group are at a large distance.

The majority of the obtained sulfinimines are liquid or amorphous substances. We succeeded in growing a single crystal of sulfinimine **XIII** suitable for XRD analysis. The sulfur atom of the sulfinyl group has the *S*-configuration where the oxygen atom is oriented in the same direction as the isopropyl group (see the figure). It was described in [2] that sulfinimines with bulky substituents possessed the *E*-configuration of the –N=CH–C group. The XRD data of compound **XIII** agree with this statement. Compounds **VIII–XIV** did not form *Z*-isomers.

Structure **XIII** is characterized by bond lengths and bond angles close to the standard values (see the table). The sulfur atom is located in the trigonal-pyramidal surrounding, therewith the atoms S^1 and O^1 lie virtually in the plane of the nitrophenyl ring. Molecular packing is by layers, the layers are oriented parallel to the [0 1 0] plane. No shortened intermolecular contacts between the layers are observed, inside the layers several shortened contacts are present, the most pronounced between them is the contact between the oxygen of the sulfoxide fragment and the proton in the *ortho*-position to the nitro group of the phenyl ring O^1···H^{5A} [–1 + *x*, *y*, *z*] ~2.32 Å, the distance comparable to that of an intermolecular hydrogen bond.



Spatial arrangement of (*S*,1*S*,2*S*,5*R*,*E*)-2-isopropyl-5-methyl-*N*-(4-nitrobenzylidene)cyclohexanesulfinamide (**XIII**) by XRD data.

It was shown in [2] that the amidation of thiosulfinates proceeded by the mechanism of bimolecular nucleophilic substitution with a complete configuration reversion at the sulfur atom. Consequently, the prevailing in the mixture (*S*)-sulfinamide (**VIIa)** forms from the predominant (*S*)-thiosulfinate (**V)** whose oxygen atom is directed oppositely to the isopropyl group as has been presumed in [10].

Compounds **VIII–XIV,** except for compound **XIIb**, were reduced with $LiAlH_4$ to the corresponding *N*-substituted sulfinamides (**XV–XXI)** obtained in 40–90% yields. All obtained compounds **XV–XXI** were characterized by NMR and IR spectra and by elemental analyses. In the ^{1}H NMR spectra of the reaction products the signals of the methine protons of sulfinimines disappear, and the overlapping multiplets arise of protons H$^{1a'}$, H$^{1b'}$ and NH in the region 4.35–5.70 ppm. In the ^{13}C NMR spectra an additional signal of a methylene group is observed at 40.02–46.24 ppm. In the IR spectra a characteristic absorption band of NH group appears in the region 3200–3400 cm^{-1}.

Hence we synthesized sulfinyl derivatives of menthane series where the sulfinyl group is linked directly to the nitrogen atom. Previously such compounds based on the natural terpenoids were not known. By the XRD analysis of compound **XIII** the absolute configuration of all

Selected bond lengths and bond distances of compound **XIII**

Bond	Å	Angle	deg
S^1–O^1	1.4789(18)	O^{1}S^{1}N^2	110.07(12)
S^1–N^2	1.695(2)	O^{1}S^{1}C^8	108.81(12)
S^1–C^8	1.841(2)	N^{2}S^{1}C^8	93.27(12)
N^2–C^7	1.269(3)	C^{7}N^{2}S^1	116.5(2)
N^1–O^2	1.202(3)	C^{9}C^{8}S^1	112.36(17)
N^1–O^3	1.216(3)	C^{13}C^{8}S^1	108.48(18)
N^1–C^4	1.476(4)	N^{2}C^{7}C^1	120.6(3)

sulfinyl-containing substances obtained in this study was established, and also that of dineomenthylthiosulfinates described in [10].

EXPERIMENTAL

IR spectra were recorded on an IR Fourier spectrophotometer Shimadzu IR Prestige 21 from thin films or pellets with KBr. Melting points were measured on an instrument Gallencamp-Sanyo. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-300 at operating frequencies 300.17 and 75.48 MHz respectively) in $CDCl_3$, as internal reference chloroform signals were used. Complete assignment of the signals in the ^{1}H and ^{13}C NMR spectra was carried out with the help of 2D homo- (^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY) and heteronuclear experiments (^{1}H–^{13}C HSQC, HMBC). The values of the diastereomeric excess was calculated by the ratios of the integral intensities in the ^{1}H NMR spectra of the signals of protons at the C^1 atom, linked to the sulfinyl group. The angle of the optical rotation was measured on an automated digital polarimeter P3002RS Kruss. TLC was performed on Sorbfil plates. Elemental analysis was carried out on an automatic analyzer EA 1110 CHNS-O. The column chromatography was performed on silica gel Alfa Aesar (0.06–0.2 mm).

The XRD analysis of compound **XIII** was performed on a fraction of a light yellow crystal of dimensions 0.25 × 0.20 × 0.15 mm. $C_{17}H_{24}N_2O_3S$. Crystal rhombic, space group $P2_12_12_1$, *a* 8.4679(7), *b* 14.0746(18), *c* 15.3817(13) E, *V* 1833.2(3)5.6(5) E^3, *M* 336.44, d_{calc} 1.219 g cm^{-3}, *Z* 4. Parameters of the unit cell and the measurement of experimental reflections at 295(2) K was carried out on an automatic four-circle diffractometer Xcalibur 3 (OXFORD DIFFRACTION) equipped with a CCD-detector along the standard procedure [11] of ω-2θ-scanning on the monochromated MoK_α-radiation in the angles range $2.75 < \theta < 28.29$. Overall number of measured reflections 8351, among them 4031 independent (R_{int} 0.031), 1882 with $I > 2\sigma(I)$. The completeness of the experiment was 96.5% for the angle θ 26.00°. No correction for extinction was done (μ 0.192 mm^{-1}). The structure was solved by the direct statistical method and refined by the full-matrix least-squares procedure with respect to F^2 in the anisotropic approximation for all nonhydrogen atoms. Hydrogen atoms were placed in the geometrically calculated positions and were refined in the isotropic approximation. All calculations were carried out using SHELX 97 software [12]. The final results of refining are as follows: R_1 0.0364, wR_2 0.0828 for reflections with $I > 2\sigma(I)$, R_1 0.0982, wR_2 0.0875 for all reflections, *S* 1.000. Maximal and minimal peaks of the residual density are 0.133 и –0.129 ē Å^{-3}.

The results of the XRD analysis are deposited in the Cambridge Christallographic Data Center (CCDC no. 851810). These data are in free access at the address www.ccdc.cam.ac.uk/data_request/cif.

***L*-Menthol *para*-toluenesulfonate (I)** was prepared by procedure [13] from the commercial *L*-menthol (Alfa Aesar), $[\alpha]_D^{20}$ –50° (*c* 10, EtOH)**.**

Neomenthanethiol (III). A solution of 0.31 g (1 mmol) of menthol tosylate (**I**) and 0.33 g (4.3 mmol) of thiourea in 5 ml of EtOH was boiled over 4 days. The obtained isothiouronium salt was used without isolation. To the solution of the isothiouronium salt containing the residue of thiourea was added dropwise at cooling under argon 40% NaOH solution till the complete dissolution of the white precipitate of isothiouronium salt. At the repeated precipitation of the isothiouronium salt new portions of NaOH were added till complete dissolution. The mixture was stirred under the inert atmosphere over 3–4 days, then thereto was slowly added dropwise at vigorous stirring 10% solution of HCl. On the acid addition the reaction mixture lost the transparency and got green-brown color. The addition of the acid was stopped when the solution became again transparent and colorless, or the pH of the medium should be controlled: The acid addition was finished at pH 5–6. The solution was stirred for another 5 min, extracted with petroleum ether (3 × 10 ml), dried with Na_2SO_4, the solvent was removed in a vacuum, the residue was subjected to chromatography on silica gel (eluent petroleum ether, developer $KMnO_4$). Yield 60%. Characteristics of thiol **III** are given in [10].

Dineomenthyl disulfide (IV). To a solution of 0.172 g (1 mmol) of neomenthanethiol (**III)** in 4 ml of ethanol was very slowly added dropwise at vigorous stirring a solution of 0.127 g (0.5 mmol) of I_2 in 6 ml of ethanol. The mixture was stirred for 5 h, and thereafter a double excess of I_2 was added, and the stirring was continued for 48 h. Water (5 ml) was added, the product was extracted into petroleum ether (3 × 10 ml). The extract was washed with 10% $Na_2S_2O_3$ solution till the discoloration of the organic phase. The upper layer was separated on a separation funnel, dried with anhydrous Na_2SO_4, the solvent was distilled off in a vacuum, the residue was separated by column chromatography (eluent petroleum ether, developer $KMnO_4$). Yield 98%. Characteristics of disulfide **IV** are given in [10].

Oxidation of disulfides in the system TBHP–$VO(acac)_2$. General procedure. In 5 ml of chloroform was dissolved 1 mmol (0.342 g) of disulfide and 0.01 mmol (2.7 mg) of $VO(acac)_2$. At stirring the solution in chloroform of 1 mmol of TBHP was added. After stirring for 1 h at room temperature 10 ml of water solution containing 0.5 g of $FeSO_4$ and 0.1 g of citric acid was added to the reaction mixture. The reaction product was extracted into ethyl ether (3 × 15 ml). The exract was washed with saturated solutions of $NaHCO_3$ and NaCl, dried with Na_2SO_4. On distilling off the solvent the reaction products were isolated by column chromatography on silica gel (eluent chloroform, developer $KMnO_4$). Yield 67%, *de* 45%. The characteristics of individual thiosulfinates **V, VI** are given in [10].

(*S*,1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexanesulfinamide (VIIa). Into 3 ml of liquid ammonia cooled to –78°C was slowly charged 93 mg (2.32 mmol) of metal potassium, several crystals of $FeCl_3$ was added, and the mixture was stirred for 15–20 min. To this mixture was added slowly dropwise 0.36 g (1 mmol) of the mixture of thiosulfinates **V, VI** in 5 ml of anhydrous THF. The reaction mixture was stirred for 1.5 h, then 0.4 g of NH_4Cl was added, and the stirring was continued for 15 min. The mixture was slowly warmed to room temperature, after evaporation of ammonia the residue was washed with water and extracted with ethyl acetate (3 × 10 ml), the combined organic solutions were dried with Na_2SO_4. The solvent was removed in a vacuum, the reaction products were isolated by column chromatography on silica gel (eluents chloroform, next ethyl acetate). Yield of the diastereomers **VIIa, VIIb** mixture 0.12 g (60% calculated on the mixture **V, VI)**. On recrystallization from methanol yield of **VIIa** 0.05 g (24% calculated on the mixture **V, VI)**, R_f 0.25 (ethyl acetate). White amorphous powder, $[\alpha]_D^{20}$ –6.4° (*c* 0.40, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3233 (NH_2), 2953, 2914, 1449, 1381, 1034 (S=O), 903 (S–N), 716. ^{1}H NMR spectrum, δ, ppm: 0.88 d (3H, C^7H_3, *J* 6.2 Hz), 0.94 d (3H, $C^{10}H_3$, *J* 6.7 Hz), 0.94–1.07 m (1H, H^{4a}), 1.06 d (3H, C^9H_3, *J* 6.2 Hz), 1.18–1.28 m (1H, H^{6a}), 1.29–1.41 m (1H, H^2), 1.60 q.d (1H, H^{3a}, *J* 13.2, *J* 3.5 Hz), 1.65–1.79 m (1H, H^5), 1.84–1.99 m (2H, $H^{3e,4e}$), 2.08 d.d.t (1H, H^8, *J* 12.9, *J* 10.3, *J* 6.5 Hz), 2.31 d.d.t (1H, H^{6e}, *J* 14.4, *J* 3.2, *J* 2.5 Hz), 3.09–3.15 m (1H, H^1), 4.12 br.s (2H, NH_2). ^{13}C NMR spectrum, δ, ppm: 21.88 (C^9), 21.96 (C^{10}), 22.57 (C^7), 26.03 (C^3), 27.79 (C^5), 29.00 (C^8), 35.53 (C^4), 37.66 (C^6), 49.11 (C^2), 65.45 (C^1). Found, %: C 59.07; H 10.41; N 6.89; S 15.77. $C_{10}H_{21}NOS$. Calculated, %: C 58.96; H 10.38; N 6.90; S 16.01.

Sulfinimines VIII–XIV. *General procedure.* To 1 mmol (0.20 g) of a mixture of compounds **VIIa, VIIb** in 20 ml of anhydrous THF was added 1.1 mmol of aldehyde and 0.3 g (2 mmol) of calcined $CuSO_4$ and 5 mol% of *p*-toluenesulfonic acid as catalyst. The mixture was stirred at room temperature over 24–48 h, afterwards the solid residue was filtered off, the filtrate was evaporated in a vacuum, the residue was subjected to column chromatography on silica gel (eluents ethyl acetate, benzene, or CCl_4–EtOAc, 2 : 1). Yields of all obtained sulfinimines are calculated with respect to the mixture of initial sulfinamides **VIIa**, **VIIb**.

(*S*,1*S*,2*S*,5*R*,*E*)-*N*-(2-Hydroxybenzylidene)-2-isopropyl-5-methylcyclohexanesulfinamide (VIII). Yellowish oily fluid, $[\alpha]_D^{20}$ –6.5° (*c* 0.50, $CHCl_3$). Yield 0.11 g (38%), R_f 0.19 (ethyl acetate). IR spectrum, ν, cm^{-1}: 3136 (OH), 2953, 2922, 1643 (C=N), 1620, 1597, 1562, 1458, 1354, 1273, 1200, 1089 (S=O), 897 (S–N), 758. ^{1}H NMR spectrum, δ, ppm: 0.95 d (3H, C^7H_3, *J* 6.4 Hz), 0.98–1.11 m (1H, H^{4a}), 1.02 d (3H, $C^{10}H_3$, *J* 6.6 Hz), 1.08 d (3H, C^9H_3, *J* 6.4 Hz), 1.30 d.d.d (1H, H^{6a}, *J* 14.4, *J* 12.7, *J* 3.6 Hz), 1.42–1.51 m (1H, H^2), 1.74 q.d (1H, H^{3a}, *J* 12.9, *J* 3.3 Hz), 1.73–1.87 m (1H, H^5), 1.90–2.22 m (3H, $H^{3e,4e,8}$), 2.39 d.d.t (1H, H^{6e}, *J* 14.4, *J* 3.1, *J* 2.7 Hz), 3.21–3.24 m (1H, H^1), 7.00–7.08 m (2H, $H^{4',6'}$), 7.45–7.52 m (2H, $H^{5',7'}$), 8.80 s (1H, $H^{1'}$), 11.18 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.73 (C^9), 21.73 (C^{10}), 22.53 (C^7), 26.52 (C^3), 28.37 (C^5), 29.52 (C^8), 35.41 (C^4), 36.98 (C^6), 49.16 (C^2), 68.21 (C^1), 117.31 ($C^{4'}$), 118.58 ($C^{2'}$), 119.85 ($C^{6'}$), 133.20 ($C^{7'}$), 134.63 ($C^{5'}$), 160.15 ($C^{3'}$), 164.59 ($C^{1'}$). Found, %: C 66.44; H 8.15; N 4.59; S 10.39. $C_{17}H_{25}NO_2S$. Calculated, %: C 66.41; H 8.20; N 4.56; S 10.43.

***(S,1S,2S,5R,E)-N*-(5-Chloro-2-hydroxybenzylidene)-2-isopropyl-5-methylcyclohexanesulfinamide (IX).** Yellowish oily fluid, $[\alpha]_D^{22}$ +3.8° (*c* 0.32, $CHCl_3$). Yield 0.13 g (38%), R_f 0.13 (benzene). IR spectrum, ν, cm^{-1}: 3115 (OH), 2953, 1618 (C=N), 1599, 1560, 1476, 1482, 1344, 1271, 1180 (S=O), 1091, 825, 768. ^{1}H NMR spectrum, δ, ppm: 0.94 d (3H, C^7H_3, *J* 6.5 Hz), 0.97–1.11 m (1H, H^{4a}), 1.01 d (3H, $C^{10}H_3$, *J* 6.5 Hz), 1.06 d (3H, C^9H_3, *J* 6.4 Hz), 1.30 d.d.d (1H, H^{6a}, *J* 14.4, *J* 12.6, *J* 3.9 Hz), 1.46 d.d.t (1H, H^2, *J* 12.7, *J* 10.1, *J* 3.0 Hz), 1.71 q.d (1H, H^{3a}, *J* 13.0, *J* 3.3 Hz), 1.71–1.83 m (1H, H^5), 1.88–2.17 m (3H, $H^{3e,4e,8}$), 2.35 d.d.t (1H, H^{6e}, *J* 14.4, *J* 3.0, *J* 2.7 Hz), 3.21–3.25 m (1H, H^1), 7.00 d (1H, $H^{4'}$, *J* 8.8 Hz), 7.40 d.d (1H, $H^{5'}$, *J* 8.8, *J* 2.5 Hz),

7.46 d (1H, H$^{7'}$, *J* 2.5 Hz), 8.72 s (1H, H$^{1'}$), 11.16 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.71 (C^{9}), 21.74 (C^{10}), 22.51 (C^{7}), 26.52 (C^{3}), 28.40 (C^{5}), 29.51 (C^{8}), 35.35 (C^{4}), 37.00 (C^{6}), 49.15 (C^{2}), 68.30 (C^{1}), 118.91 (C$^{4'}$), 119.26 (C$^{2'}$), 124.56 (C$^{6'}$), 132.01 (C$^{7'}$), 134.37 (C$^{5'}$), 158.65 (C$^{3'}$), 163.57 (C$^{1'}$). Found, %: C 59.78; H 7.00; N 3.96; S 9.60. $C_{17}H_{24}ClNO_2S$. Calculated, %: C 59.72; H 7.08; N 4.10; S 9.38.

(*S*,1*S*,2*S*,5*R*,*E*)-*N*-(3,5-Di-*tert*-butyl-2-hydroxybenzylidene)-2-isopropyl-5-methylcyclohexanesulfinamide (X). Colorless oily fluid, $[\alpha]_D^{22}$ –9.6° (*c* 0.32, $CHCl_3$). Yield 0.09 g (22%), R_f 0.28 (benzene). IR spectrum, ν, cm^{-1}: 2964, 2932, 2880, 1614 (C=N), 1578, 1460, 1366, 1252, 1174, 1084 (S=O), 836 (S–N), 762. ^{1}H NMR spectrum, δ, ppm: 0.98 d (3H, C^{7}H$_3$, *J* 6.4 Hz), 1.00–1.14 m (1H, H^{4a}), 1.04 d (3H, C^{10}H$_3$, *J* 6.5 Hz), 1.09 d (3H, C^{9}H$_3$, *J* 6.5 Hz), 1.20–1.32 m (1H, H^{6a}), 1.36 s (9H, C$^{13'}$H$_3$, C$^{14'}$H$_3$, C$^{15'}$H$_3$), 1.38–1.50 m (1H, H^{2}), 1.50 s (9H, C$^{9'}$H$_3$, C$^{10'}$H$_3$, C$^{11'}$H$_3$), 1.76 q.d (1H, H^{3a}, *J* 12.9, *J* 3.4 Hz), 1.80–1.92 m (1H, H^{5}), 1.90–2.11 m (2H, H^{3e,4e}), 2.20 d.d.t (1H, H^{8}, *J* 12.9, *J* 10.3, *J* 6.5 Hz), 2.41 d.d.t (1H, H^{6e}, *J* 14.4, *J* 2.5, *J* 2.3 Hz), 3.18–3.24 m (1H, H^{1}), 7.36 d (1H, H$^{7'}$, *J* 2.4 Hz), 7.56 d (1H, H$^{5'}$, *J* 2.3 Hz), 8.80 s (1H, H$^{1'}$), 11.58 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.76 (C^{9}), 21.80 (C^{10}), 22.56 (C^{7}), 26.60 (C^{3}), 28.43 (C^{5}), 29.43 (C$^{9',10',11'}$), 29.48 (C^{8}), 29.72 (C$^{12'}$), 31.40 (C$^{13',14',15'}$), 34.25 (C$^{8'}$), 35.44 (C^{4}), 37.19 (C^{6}), 49.29 (C^{2}), 68.54 (C^{1}), 117.98 (C$^{2'}$), 127.88 (C$^{7'}$), 129.56 (C$^{5'}$), 137.14 (C$^{4'}$), 141.46 (C$^{6'}$), 157.28 (C$^{3'}$), 165.40 (C$^{1'}$). Found, %: C 71.50; H 9.89; N 3.42; S 7.61. $C_{25}H_{41}NO_2S$. Calculated, %: C 71.55; H 9.85; N 3.34; S 7.64.

(*S*,1*S*,2*S*,5*R*,*E*)-*N*-(3,5-Dibromo-2-hydroxybenzylidene)-2-isopropyl-5-methylcyclohexanesulfinamide (XI). Yellowish oily fluid, $[\alpha]_D^{22}$ +3.7° (*c* 0.87, $CHCl_3$). Yield 0.23 g (50%), R_f 0.23 (benzene). IR spectrum, ν, cm^{-1}: 3428 (OH), 2964, 1612 (C=N), 1592, 1556, 1444, 1370, 1344, 1276, 1220, 1170, 1094 (S=O), 903 (S–N), 764, 744, 692, 624, 564. ^{1}H NMR spectrum, δ, ppm: 0.96 d (3H, C^{7}H$_3$, *J* 6.4 Hz), 0.97–1.14 m (1H, H^{4a}), 1.01 d (3H, C^{10}H$_3$, *J* 6.5 Hz), 1.04 d (3H, C^{9}H$_3$, *J* 6.4 Hz), 1.33 d.d.d (1H, H^{6a}, *J* 14.4, *J* 12.7, *J* 3.6 Hz), 1.42–1.51 m (1H, H^{2}), 1.71 q.d (1H, H^{3a}, *J* 12.9, *J* 3.3 Hz), 1.74–1.87 m (1H, H^{5}), 1.90–2.19 m (3H, H^{3e,4e,8}), 2.50 d.d.t (1H, H^{6e}, *J*14.4, *J* 2.5, *J* 2.3 Hz), 3.23–3.29 m (1H, H^{1}), 7.59 d (1H, H$^{7'}$, *J* 2.2 Hz), 7.84 d (1H, H$^{5'}$, *J* 2.2 Hz), 8.70 s (1H, H$^{1'}$), 11.87 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.74 (C^{9}), 21.80 (C^{10}), 22.57 (C^{7}), 26.50 (C^{3}), 28.40 (C^{5}), 29.46 (C^{8}), 35.37 (C^{4}), 36.87 (C^{6}), 49.33 (C^{2}), 68.13 (C^{1}), 111.41 (C$^{6'}$), 112.09 (C$^{4'}$), 120.19 (C$^{2'}$), 134.34 (C$^{7'}$), 139.51 (C$^{5'}$), 155.85 (C$^{3'}$), 162.99 (C$^{1'}$). Found, %: C 44.01; H 4.95; N 3.08; S 6.73. $C_{17}H_{23}Br_2NO_2S$. Calculated, %: C 43.89; H 4.98; N 3.01; S 6.89.

(*S*,1*S*,2*S*,5*R*,*E*)-*N*-(2-Hydroxy-3,5-diiodobenzylidene)-2-isopropyl-5-methylcyclohexanesulfinamide (XIIa). Yellowish oily fluid, $[\alpha]_D^{20}$ +4.0° (*c* 0.70, $CHCl_3$). Yield 0.21 g (38%), R_f 0.25 (benzene). IR spectrum, ν, cm^{-1}: 3072 (OH), 2916, 1670 (C=N), 1586, 1546, 1458, 1430, 1344, 1306, 1276, 1226, 1154, 1086 (S=O), 900 (S–N), 760, 700, 666, 622, 478. ^{1}H NMR spectrum, δ, ppm: 0.97 d (3H, C^{7}H$_3$, *J* 6.4 Hz), 0.98–1.15 m (1H, H^{4a}), 1.01 d (3H, C^{10}H$_3$, *J* 6.6 Hz), 1.04 d (3H, C^{9}H$_3$, *J* 6.5 Hz), 1.33 d.d.d (1H, H^{6a}, *J* 14.4, *J* 12.7, *J* 3.8 Hz), 1.41–1.51 m (1H, H^{2}), 1.71 q.d (1H, H^{3a}, *J* 12.9, *J* 3.3 Hz), 1.71–1.89 m (1H, H^{5}), 1.95–2.22 m (3H, H^{3e,4e,8}), 2.34 d.d.t (1H, H^{6e}, *J* 14.6, *J* 2.6, *J* 2.3 Hz), 3.23–3.27 m (1H, H^{1}), 7.78 d (1H, H$^{7'}$, *J* 2.0 Hz), 8.19 d (1H, H$^{5'}$, *J* 2.0 Hz), 8.63 s (1H, H$^{1'}$), 12.07 c (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.76 (C^{9}), 21.81 (C^{10}), 22.57 (C^{7}), 26.50 (C^{3}), 28.39 (C^{5}), 29.43 (C^{8}), 35.39 (C^{4}), 36.89 (C^{6}), 49.39 (C^{2}), 68.11 (C^{1}), 81.14 (C$^{4'}$), 86.74 (C$^{6'}$), 120.06 (C$^{2'}$), 141.40 (C$^{7'}$), 150.59 (C$^{5'}$), 158.76 (C$^{3'}$), 162.74 (C$^{1'}$). Found, %: C 36.48; H 4.20; N 2.61; S 5.70. $C_{17}H_{23}I_2NO_2S$. Calculated, %: C 36.51; H 4.15; N 2.50; S 5.73.

(*R*,1*S*,2*S*,5*R*,*E*)-*N*-(2-Hydroxy-3,5-diiodobenzylidene)-2-isopropyl-5-methylcyclohexanesulfinamide (XIIб). Yellowish oily liquid, $[\alpha]_D^{22}$ +65.0° (*c* 0.12, $CHCl_3$). Yield 0.033 r (6%), R_f 0.26 (benzene). IR spectrum, ν, cm^{-1}: 3072 (OH), 2932, 1668 (C=N), 1590, 1546, 1444, 1424, 1346, 1300, 1276, 1218, 1158, 1084 (S=O), 904 (S–N), 760, 700, 666, 622, 478. ^{1}H NMR spectrum, δ, ppm: 0.84 d (3H, C^{7}H$_3$, *J* 6.2 Hz), 0.88–0.98 m (1H, H^{4a}), 0.84 d (3H, C^{10}H$_3$, *J* 6.4 Hz), 1.10 d (3H, C^{9}H$_3$, *J* 6.4 Hz), 1.05–1.21 m (1H, H^{6a}), 1.45–1.55 m (1H, H^{2}), 1.71 d.q (1H, H^{3a}, *J* 12.3, *J* 3.4 Hz), 1.95–2.22 m (5H, H^{3e,4e,5,8,6e}), 3.27–3.32 m (1H, H^{1}), 7.80 d (1H, H$^{7'}$, *J* 2.0 Hz), 8.20 d (1H, H$^{5'}$, *J* 2.0 Hz), 8.57 s (1H, H$^{1'}$), 12.02 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.41 (C^{9}), 21.54 (C^{10}), 22.75 (C^{7}), 26.21 (C^{3}), 27.84 (C^{5}), 29.97 (C^{8}), 33.06 (C^{6}), 34.94 (C^{4}), 47.12 (C^{2}), 62.42 (C^{1}), 81.13 (C$^{4'}$), 86.78 (C$^{6'}$), 119.85 (C$^{2'}$), 141.31 (C$^{7'}$), 150.52 (C$^{5'}$), 158.77 (C$^{3'}$), 162.80 (C$^{1'}$). Found, %: C 36.50; H 4.13; N 2.64; S 5.72. $C_{17}H_{23}I_2NO_2S$. Calculated, %: C 36.51; H 4.15; N 2.50; S 5.73.

(*S*,1*S*,2*S*,5*R*,*E*)-2-Isopropyl-5-methyl-*N*-(4-nitrobenzylidene)cyclohexanesulfinamide (XIII). Yellow crystals, mp 107.5°C, $[\alpha]_D^{22}$ +28° (*c* 0.53, $CHCl_3$). Yield

0.26 g (80%), R_f 0.24 (benzene). IR spectrum, ν, cm^{-1}: 3420, 3120, 3084, 2952, 1618 (C=N), 1590, 1522 (NO_2), 1484, 1453, 1346 (NO_2), 1300, 1088 (S=O), 865 (S–N), 838, 756, 692, 660. ^{1}H NMR spectrum, δ, ppm: 0.89 d (3H, C^{7}H$_3$, *J* 6.4 Hz), 0.96–1.09 m (1H, H^{4a}), 1.02 d (3H, C^{10}H$_3$, *J* 6.5 Hz), 1.08 d (3H, C^{9}H$_3$, *J* 6.5 Hz), 1.16–1.29 m (1H, H^{6a}), 1.42–1.51 m (1H, H^2), 1.68–1.84 m (2H, H^{3a,5}), 1.85–2.04 m (2H, H^{3e,4e}), 2.14 d.d.t (1H, H^8, *J* 12.9, *J* 10.3, *J* 6.5 Hz), 2.49 d.d.t (1H, H^{6e}, *J* 14.4, *J* 3.2, *J* 2.5 Hz), 3.32–3.38 m (1H, H^1), 8.05 d (2H, H$^{3',7'}$, *J* 8.7 Hz), 8.38 d (2H, H$^{4',6'}$, *J* 8.7 Hz), 8.76 s (1H, H$^{1'}$). ^{13}C NMR spectrum, δ, ppm: 21.73 (C^9), 21.76 (C^{10}), 22.62 (C^7), 26.28 (C^3), 28.06 (C^5), 29.41 (C^8), 35.36 (C^4), 35.59 (C^6), 48.92 (C^2), 67.25 (C^1), 124.27 (C$^{4',6'}$), 129.99 (C$^{3',7'}$), 139.06 (C$^{5'}$), 149.79 (C$^{2'}$), 159.59 (C$^{1'}$). Found, %: C 60.65; H 7.20; N 7.92; S 10.01. $C_{17}H_{24}N_2O_3S$. Calculated, %: C 60.69; H 7.19; N 8.33; S 9.53.

(*S*,1*S*,2*S*,5*R*,*E*)-*N*-[4-(Dimethylamino) benzylidene]-2-isopropyl-5-menthylcyclohexanesulfinamide (XIV). Yellow powder, mp 103.7°C, $[\alpha]_D^{22}$ +16° (*c* 0.26, $CHCl_3$). Yield 0.12 g (35%), R_f 0.30 (CCl_4–EtOAc, 1:1). IR spectrum, ν, cm^{-1}: 3424 [$(NCH_3)_2$], 2949, 2845, 1611 (C=N), 1584, 1530, 1450, 1373, 1179, 1086 (S=O), 945 (S–N), 818, 708. ^{1}H NMR spectrum, δ, ppm: 0.89 d (3H, C^{7}H$_3$, *J* 6.5 Hz), 0.94–1.05 m (1H, H^{4a}), 0.95 d (3H, C^{10}H$_3$, *J* 6.6 Hz), 1.10 d (3H, C^{9}H$_3$, *J* 6.5 Hz), 1.21 t.d (1H, H^{6a}, *J* 13.5, *J* 3.6 Hz), 1.32 d.d.t (1H, H^2, *J* 12.8, *J* 9.8, *J* 2.9 Hz), 1.71–1.98 m (4H, H^{3a,3e,4e,5}), 2.17 d.d.t (1H, H^8, *J* 12.9, *J* 10.3, *J* 6.5 Hz), 2.50 d.d.t (1H, H^{6e}, *J* 14.2, *J* 2.5, *J* 2.2 Hz), 3.09 s (6H, H$^{8',9'}$), 3.18–3.23 m (1H, H^1), 6.74 d (2H, H$^{4',6'}$, *J* 8.8 Hz), 7.34 d (2H, H$^{3',7'}$, *J* 8.8 Hz), 8.50 s (1H, H$^{1'}$). ^{13}C NMR spectrum, δ, ppm: 21.82 (C^9), 21.82 (C^{10}), 22.78 (C^7), 26.19 (C^3), 27.79 (C^5), 29.37 (C^8), 34.96 (C^6), 35.55 (C^4), 40.10 (C$^{8',9'}$), 48.67 (C^2), 66.50 (C^1), 111.44 (C$^{4',6'}$), 122.85 (C$^{2'}$), 131.17 (C$^{3',7'}$), 152.95 (C$^{5'}$), 160.52 (C$^{1'}$). Found, %: C 68.30; H 8.56; N 8.82; S 9.62. $C_{19}H_{30}NO_2S$. Calculated, %: C 68.22; H 9.04; N 8.37; S 9.59.

N-Substituted sulfinamides XV–XXI. *General procedure.* To a solution of 1 mmol of an appropriate sulfinimine **VIII–XIV** in 20 ml of anhydrous THF cooled to –48°C was slowly added 0.11 g (3 mmol) of $LiAlH_4$. The mixture was stirred for 10–20 min, then it was filtered under a reduced pressure, the filtrate was washed with 5 ml of water and extracted with ethyl acetate (3 × 10 ml). The extract was dried with Na_2SO_4, the solvent was removed in a vacuum, the residue was subjected to column chromatography on silica gel (eluent ethyl acetate).

(*S*,1*S*,2*S*,5*R*)-*N*-(2-Hydroxybenzyl)-2-isopropyl-5-methylcyclohexanesulfinamide (XV). Colorless oily fluid, $[\alpha]_D^{22}$ +55° (*c* 0.30, EtOH). Yield 0.28 g (90%), R_f 0.56 (EtOAc–hexane, 5 : 1). IR spectrum, ν, cm^{-1}: 3256 (OH), 3145 (NH), 2951, 1600, 1454, 1373, 1265, 1032 (S=O), 854 (S–N), 746, 677. ^{1}H NMR spectrum, δ, ppm: 0.90 d (3H, C^{7}H$_3$, *J* 6.5 Hz), 0.97–1.10 m (1H, H^{4a}), 0.97 d (3H, C^{10}H$_3$, *J* 6.6 Hz), 1.09 d (3H, C^{9}H$_3$, *J* 6.5 Hz), 1.22–1.32 m (1H, H^{6a}), 1.39 d.d.t (1H, H^2, *J* 12.6, *J* 10.2, *J* 2.8 Hz), 1.60 q.d (1H, H^{3a}, *J* 12.9, *J* 3.3 Hz), 1.60–1.72 m (1H, H^5), 1.68–1.89 m (2H, H^{3e,4e}), 2.08 d.d.t (1H, H^8, *J* 2.9, *J* 10.3, *J* 6.5 Hz), 2.19 d.d.t (1H, H^{6e}, *J* 14.3, *J* 3.0, *J* 2.2 Hz), 3.40–3.44 m (1H, H^1), 4.11 d.d (1H, H$^{1a'}$, *J* 13.1, *J* 2.7 Hz), 4.18 d.d (1H, NH, *J* 7.0, *J* 2.7 Hz), 4.48 d.d (1H, H$^{1b'}$, *J* 13.1, *J* 7.0 Hz), 6.87 d.d.d (1H, H$^{6'}$, *J* 7.8, *J* 7.4, *J* 1.3 Hz), 6.95 d.d (1H, H$^{4'}$, *J* 7.8, *J* 1.3 Hz), 7.17 d (1H, H$^{7'}$, *J* 7.4, *J* 1.6 Hz), 7.26 t.d (1H, H$^{5'}$, *J* 7.8, *J* 1.6 Hz), 8.64 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.87 (C^9), 21.97 (C^{10}), 22.57 (C^7), 26.15 (C^3), 27.89 (C^5), 29.30 (C^8), 35.57 (C^4), 38.45 (C^6), 41.20 (C$^{1'}$), 48.85 (C^2), 62.47 (C^1), 118.24 (C$^{4'}$), 120.05 (C$^{6'}$), 124.03 (C$^{2'}$), 130.17 (C$^{5'}$), 130.37 (C$^{7'}$), 155.72 (C$^{3'}$). Found, %: C 66.02; H 8.82; N 4.49; S 10.30. $C_{19}H_{30}NO_2S$. Calculated, %: C 65.98; H 8.79; N 4.53; S 10.36.

(*S*,1*S*,2*S*,5*R*)-*N*-(5-Chloro-2-hydroxybenzyl)-2-isopropyl-5-methylcyclohexanesulfinamide (XVI). Colorless oily fluid, $[\alpha]_D^{22}$ +40.0° (*c* 0.17, $CHCl_3$). Yield 0.30 g (86%), R_f 0.28 (EtOAc). IR spectrum, ν, cm^{-1}: 3258 (OH), 3135 (NH), 2930, 1621, 1445, 1371, 1271, 1034 (S=O), 856 (S–N), 733, 684. ^{1}H NMR spectrum, δ, ppm: 0.90 d (3H, C^{7}H$_3$, *J* 6.4 Hz), 0.95–1.09 m (1H, H^{4a}), 0.96 d (3H, C^{10}H$_3$, *J* 6.5 Hz), 1.07 d (3H, C^{9}H$_3$, *J* 6.4 Hz), 1.27 t.d (1H, H^{6a}, *J* 13.1, *J* 3.5 Hz), 1.39 d.d.t (1H, H^2, *J* 12.5, *J* 10.2, *J* 2.6 Hz), 1.59 q.d (1H, H^{3a}, *J* 12.8, *J* 3.2 Hz), 1.58–1.70 m (1H, H^5), 1.98–2.10 m (3H, H^{3e,4e,8}), 1.18 d.t.d (1H, H^{6e}, *J* 14.1, *J* 2.8, *J* 2.3 Hz), 3.37–3.41 m (1H, H^1), 4.07 d.d (1H, H$^{1a'}$, *J* 12.2, *J* 1.8 Hz), 4.35 br.d (1H, NH, *J* 7.0 Hz), 4.40 d.d (1H, H$^{1b'}$, *J* 12.2, *J* 7.0 Hz), 6.83 d (1H, H$^{4'}$, *J* 9.3 Hz), 7.15 d (1H, H$^{7'}$, *J* 2.6 Hz), 7.6 d.d (1H, H$^{5'}$, *J* 9.3, *J* 2.6 Hz), 8.97 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.86 (C^9), 21.92 (C^{10}), 22.58 (C^7), 26.12 (C^3), 27.91 (C^5), 29.30 (C^8), 35.51 (C^4), 38.33 (C^6), 41.49 (C$^{1'}$), 48.79 (C^2), 62.73 (C^1), 119.19 (C$^{4'}$), 124.31 (C$^{6'}$), 125.73 (C$^{2'}$), 129.68 (C$^{7'}$), 129.75 (C$^{5'}$), 154.31 (C$^{3'}$). Found, %: C 59.35; H 7.65; N 4.26; S 9.25. $C_{17}H_{25}ClNO_2S$. Calculated, %: C 59.37; H 7.62; N 4.07; S 9.32.

(*S*,1*S*,2*S*,5*R*)-*N*-(3,5-Di-*tert*-butyl-2-hydroxybenzyl)-2-isopropyl-5-methylcyclohexanesulfinamide (XVII). Colorless oily fluid, $[\alpha]_D^{22}$ +46.0° (*c* 0.20, $CHCl_3$). Yield 0.31 g (75%), R_f 0.53 (EtOAc–petroleum ether, 1:6). IR spectrum, ν, cm^{-1}: 3280 (NH, OH), 2928, 1740, 1486, 1460, 1366, 1204, 1128, 1038 (S=O), 884 (S–N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.93 d (3H, C^7H_3, *J* 6.4 Hz), 0.97–1.12 m (1H, H^{4a}), 0.98 d (3H, $C^{10}H_3$, *J* 6.6 Hz), 1.11 d (3H, C^9H_3, *J* 6.4 Hz), 1.21–1.33 m (1H, H^{6a}), 1.33 s (9H, $C^{13'}H_3$, $C^{14'}H_3$, $C^{15'}H_3$), 1.32–1.43 m (1H, H^2), 1.46 s (9H, $C^{9'}H_3$, $C^{10'}H_3$, $C^{11'}H_3$), 1.61 q.d (1H, H^{3a}, *J* 12.9, *J* 3.4 Hz), 1.62–1.73 m (1H, H^5), 1.89–2.15 m (3H, $H^{3e,4e,8}$), 2.19 d.d.t (1H, H^{6e}, *J* 14.0, *J* 2.3, *J* 1.9 Hz), 3.40–3.44 m (1H, H^1), 3.99 br.d (1H, NH, *J* 7.7 Hz), 4.12 d.d (1H, $H^{1a'}$, *J* 13.2, *J* 1.9 Hz), 4.52 d.d (1H, $H^{1b'}$, *J* 13.2, *J* 7.7 Hz), 7.06 (1H, $H^{7'}$, *J* 2.3 Hz), 7.36 d (1H, $H^{5'}$, *J* 2.3 Hz), 8.13 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.83 (C^9), 22.03 (C^{10}), 22.56 (C^7), 26.23 (C^3), 27.95 (C^5), 29.37 (C^8), 29.79 ($C^{9',10',11'}$), 31.62 ($C^{13',14',15'}$), 34.23 ($C^{12'}$), 35.22 ($C^{8'}$), 35.56 (C^4), 38.62 (C^6), 41.75 ($C^{1'}$), 48.88 (C^2), 62.79 (C^1), 123.40 ($C^{2'}$), 124.68 ($C^{7'}$), 124.97 ($C^{5'}$), 138.01 ($C^{4'}$), 141.85 ($C^{6'}$), 152.17 ($C^{3'}$). Found, %: C 71.19; H 10.25; N 3.39; S 7.54. $C_{25}H_{43}NO_2S$. Calculated, %: C 71.21; H 10.28; N 3.32; S 7.60.

(*S*,1*S*,2*S*,5*R*)-*N*-(3,5-Dibromo-2-hydroxybenzyl)-2-isopropyl-5-methylcyclohexanesulfinamide (XVIII). Yellowish powder, mp 98.4°C, $[\alpha]_D^{22}$ +67.3° (*c* 0.30, $CHCl_3$). Yield 0.33 g (72%), R_f 0.33 (CCl_4–EtOAc, 2:1). IR spectrum, ν, cm^{-1}: 3280 (NH, OH), 2929, 1742, 1490, 1455, 1334, 1206, 1132, 1038 (S=O), 854 (S–N). ^{1}H NMR spectrum, δ, ppm: 0.90 d (3H, C^7H_3, *J* 6.4 Hz), 0.95–1.08 m (1H, H^{4a}), 0.96 d (3H, $C^{10}H_3$, *J* 6.6 Hz), 1.07 d (3H, C^9H_3, *J* 6.3 Hz), 1.28 t.d (1H, H^{6a}, *J* 13.2, *J* 3.5 Hz), 1.39 d.d.t (1H, H^2, *J* 12.7, *J* 10.1, *J* 3.0 Hz), 1.57 q.d (1H, H^{3a}, *J* 12.9, *J* 3.3 Hz), 1.55–1.68 m (1H, H^5), 1.83–2.06m (3H, $H^{3e,4e,8}$), 2.13 d.d.t (1H, H^{6e}, *J* 14.7, *J* 2.7, *J* 2.3 Hz), 3.37–3.41 m (1H, H^1), 4.11 d.d (1H, $H^{1a'}$, *J* 14.0, *J* 1.9 Hz), 4.25 br.d (1H, NH, *J* 7.4 Hz), 4.44 d.d (1H, $H^{1b'}$, *J* 14.0, *J* 7.4 Hz), 7.29 d (1H, $H^{7'}$, *J* 2.4 Hz), 7.64 d (1H, $H^{5'}$, *J* 2.4 Hz), 8.91s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.84 (C^9), 21.97 (C^{10}), 22.57 (C^7), 26.18 (C^3), 27.90 (C^5), 29.32 (C^8), 35.53 (C^4), 38.54 (C^6), 40.65 ($C^{1'}$), 48.77 (C^2), 62.65 (C^1), 111.14 ($C^{4'}$), 113.54 ($C^{6'}$), 127.27 ($C^{2'}$), 132.19 ($C^{7'}$), 135.25 ($C^{5'}$), 151.42 ($C^{3'}$). Found, %: C 44.01; H 5.36; N 2.82; S 6.83. $C_{17}H_{25}Br_2NO_2S$. Calculated, %: C 43.70; H 5.39; N 3.00; S 6.86.

(*S*,1*S*,2*S*,5*R*)-*N*-(2-Hydroxy-3,5-diiodobenzyl)-2-isopropyl-5-methylcyclohexanesulfinamide (XIX). Yellowish powder, mp 101.3°C, $[\alpha]_D^{22}$ +72.6° (*c* 0.22, $CHCl_3$). Yield 0.22 g (40%), R_f 0.34 (EtOAc–hexane, 1:2). IR spectrum, ν, cm^{-1}: 3246 (NH, OH), 2949, 1440, 1357, 1286, 1224, 1034 (S=O), 997, 864 (S–N). ^{1}H NMR spectrum, δ, ppm: 0.71 d (3H, C^7H_3, *J* 6.4 Hz), 0.76–0.89 m (1H, H^{4a}), 0.78 d (3H, $C^{10}H_3$, *J* 6.6 Hz), 0.90 d (3H, C^9H_3, *J* 6.5 Hz), 1.08 t.d (1H, H^{6a}, *J* 12.9, *J* 3.3 Hz), 1.21 d.d.t (1H, H^2, *J* 12.5, *J* 10.2, *J* 2.5 Hz), 1.40 q.d (1H, H^{3a}, *J* 12.9, *J* 3.3 Hz), 1.38–1.52 m (1H, H^5), 1.68–1.89 m (3H, $H^{3e,4e,8}$), 1.93 d.d.t (1H, H^{6e}, *J* 14.6, *J* 2.6, *J* 2.3 Hz), 3.21–3.26 m (1H, H^1), 3.87 d.d (1H, $H^{1a'}$, *J* 14.2, *J* 1.8 Hz), 4.21 d.d (1H, $H^{1b'}$, *J* 14.2, *J* 7.6 Hz), 5.69 br.d (1H, NH, *J* 7.6 Hz), 7.32 d (1H, $H^{7'}$, *J* 2.1 Hz), 7.82 (1H, $H^{5'}$, *J* 2.1 Hz), 9.83 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 21.74 (C^9), 21.91 (C^{10}), 22.52 (C^7), 26.05 (C^3), 27.61 (C^5), 29.27 (C^8), 35.39 (C^4), 38.53 (C^6), 40.02 ($C^{1'}$), 48.40 (C^2), 61.85 (C^1), 81.68 ($C^{4'}$), 89.23 ($C^{6'}$), 127.43 ($C^{2'}$), 139.54 ($C^{7'}$), 146.24 ($C^{5'}$), 158.80 ($C^{3'}$). Found, %: C 36.35; H 4.41; N 2.67; S 5.73. $C_{17}H_{25}I_2NO_2S$. Calculated, %: C 36.38; H 4.49; N 2.50; S 5.71.

***(S,1S,2S,5R)*-*N*-(4-Nitrobenzyl)-2-isopropyl-5-methylcyclohexanesulfinamide (XX).** Yellow powder, mp 92.7°C, $[\alpha]_D^{22}$ +34.4° (*c* 0.45, $CHCl_3$). Yield 0.32 g (94%), R_f 0.45 (EtOAc). IR spectrum, ν, cm^{-1}: 3177 (NH), 2949, 1603, 1517 (NO_2), 1344 (NO_2), 1036 (S=O), 853 (S–N). ^{1}H NMR spectrum, δ, ppm: 0.87 d (3H, C^7H_3, *J* 6.5 Hz), 0.91–1.02 m (1H, H^{4a}), 0.92 d (3H, $C^{10}H_3$, *J* 6.6 Hz), 1.04 d (3H, C^9H_3, *J* 6.4 Hz), 1.19–1.29 m (1H, H^{6a}), 1.35 d.d.t (1H, H^2, *J* 12.5, *J* 9.8, *J* 2.7 Hz), 1.56 q.d (1H, H^{3a}, *J* 13.0, *J* 3.5 Hz), 1.56–1.66 m (1H, H^5), 1.79–2.07 m (3H, $H^{3e,4e,8}$), 2.23 d.d.t (1H, H^{6e}, *J* 13.8, *J* 2.5, *J* 2.2 Hz), 3.26–3.30 m (1H, H^1), 4.35–4.45 m (3H, $H^{1a',1b'}$, NH), 7.55 d (2H, $H^{3',7'}$, *J* 8.5 Hz), 8.21 d (2H, $H^{4',6'}$, *J* 8.5 Hz). ^{13}C NMR spectrum, δ, ppm: 21.88 (C^9), 21.96 (C^{10}), 22.56 (C^7), 26.13 (C^3), 27.96 (C^5), 29.10 (C^8), 35.47 (C^4), 38.13 (C^6), 46.24 ($C^{1'}$), 49.11 (C^2), 63.49 (C^1), 123.84 ($C^{4',6'}$), 128.82 ($C^{3',7'}$), 146.16 ($C^{2'}$), 147.50 ($C^{5'}$). Found, %: C 60.29; H 7.77; N 8.33; S 9.51. $C_{17}H_{26}N_2O_3S$. Calculated, %: C 60.33; H 7.74; N 8.28; S 9.47.

***(S,1S,2S,5R)*-*N*-[4-(Dimethylamino)benzyl]-2-isopropyl-5-methylcyclohexanesulfinamide (XXI).** Yellowish powder, mp 84.3°C, $[\alpha]_D^{22}$ +49.1° (*c* 0.27, $CHCl_3$). Yield 0.30 g (88%), R_f 0.48 (EtOAc). IR spectrum, ν, cm^{-1}: 3184 (NH), 2951, 1614, 1524, 1450, 1348, 1049 (S=O), 947 (S–N), 810, 754. ^{1}H NMR spectrum, δ, ppm: 0.90 d (3H, C^7H_3, *J* 6.4 Hz), 0.95–1.08 m (1H, H^{4a}), 0.96 d (3H,

$C^{10}H_3$, *J* 6.6 Hz), 1.07 d (3H, C^9H_3, *J* 6.3 Hz), 1.28 t.d (1H, H^{6a}, *J* 13.2, *J* 3.5 Hz), 1.39 d.d.t (1H, H^2, *J* 12.7, *J* 10.1, *J* 3.0 Hz), 1.57 q.d (1H, H^{3a}, *J* 13.0, *J* 3.5 Hz), 1.62–1.75 m (1H, H^5), 1.82–1.98 m (2H, $H^{3e,4e}$), 2.13 d.d.t (1H, H^8, *J* 12.9, *J* 10.4, *J* 6.5 Hz), 2.28 d.d.t (1H, H^{6e}, *J* 14.0, *J* 2.8, *J* 2.5 Hz), 2.97 s (6H, $H^{8',9'}$), 3.26–3.30 m (1H, H^1), 4.25 t (1H, NH, *J* 6.0 Hz), 4.22 t (2H, $H^{1a',1b'}$, *J* 6.0 Hz), 6.74 d (2H, $H^{4',6'}$, *J* 8.6 Hz), 7.24 d (2H, $H^{3',7'}$, *J* 8.6 Hz). ^{13}C NMR spectrum, δ, ppm: 21.92 (C^9), 22.03 (C^{10}), 22.63 (C^7), 26.08 (C^3), 27.90 (C^5), 29.09 (C^8), 35.63 (C^4), 38.09 (C^6), 40.63 ($C^{8',9'}$), 46.07 ($C^{1'}$), 49.15 (C^2), 62.87 (C^1), 112.65 ($C^{4',6'}$), 126.00 ($C^{2'}$), 129.30 ($C^{3',7'}$), 150.20 ($C^{5'}$). Found, %: C 67.84; H 9.50; N 8.38; S 9.49. $C_{19}H_{32}N_2OS$. Calculated, %: C 67.81; H 9.58; N 8.32; S 9.53.

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Russian Foundation for Basic Research (grant no.10-03-00969) and of the Federal Agency for Science and Innovations in the framework of the Federal Targeted program "Scientific and Pedagogical Staff of Innovation Russia" (State Contract no. 02.740.11.0081).

Authors express their gratitude to the researchers of the Laboratory of the physicochemical investigation methods of the Institute of Chemistry, Komi Scientific Center, Ural Division, Russian Academy of Sciences E.N. Zainullina, S.P. Kuznetsov, and A.N. Alekseev for registering NMR spectra sand to E.U. Ipatova for registering IR spectra.

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