ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 4, pp. 505–511. © Pleiades Publishing, Ltd., 2009.
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Reaction of *N*-(2,3-Epoxypropyl)arenesulfonamides with (Bicyclo[2.2.1]hept-5-en-*endo*-2-yl)methanamine

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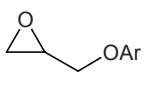
Received July 28, 2008

Abstract—Reactions of bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethanamine with *N*-(2,3-epoxypropyl)arenesulfonamides gave amino alcohols having a norbornene fragment and sulfonamide group. The major products were formed via opening of the oxirane ring according to the Krasuskii rule. The product structure was determined by ^{1}H and ^{13}C NMR spectroscopy using DEPT and two-dimensional COSY, NOESY, HMQC, and HMBC techniques.

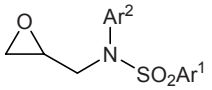
DOI: 10.1134/S107042800904006X

Amino alcohols attract persistent interest as biologically active compounds and intermediate products for the preparation of practically important synthetic and natural products [1]. Apart from alkyl- and aryloxiranes, aryl 2,3-epoxypropyl ethers like **Ia** are used as precursors of amino alcohols. *N*-Aryl-*N*-(2,3-epoxypropyl)arenesulfonamides **Ib** have been studied to a lesser extent. Such compounds were used in the synthesis of various polymeric materials, in particular plasticizers, varnishes, adhesives, and coatings with enhanced strength and heat resistance [2]. Some sulfonamides like **Ib** were found to exhibit herbicidal activity [3]. In the recent years data have been reported on high biological activity of amino alcohols having sulfonamide groups; adrenergics, antihelminthics, antidepressants, β-adrenoreceptor blockers and agonists, antiarrhythmics, and intermediates for asymmetric syntheses of biologically active compounds have been found among sulfonamide derivatives of amino alcohols [4]. Sulfonamides are known to act as enzyme inhibitors (e.g., **Ic**, R = Ar, Alk [5]); for example, compounds like **Id** were reported to inhibit human β-secretase [6].

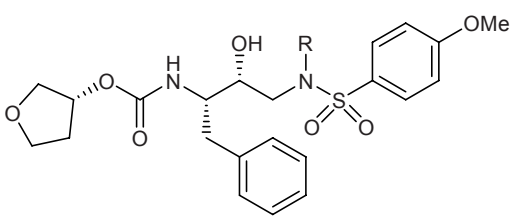
The goal of the present work was to synthesize amino alcohols containing sulfonamide groups and cage-like fragments. We previously found [7] that some sulfonamides of the norbornene and norbornane series exhibit biological (in particular neurotropic)



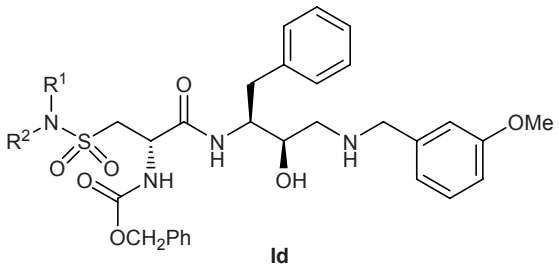
Ia



Ib

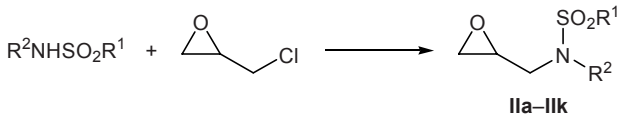


Ic



Id

Scheme 1.



IIa–IIk

$R^1 = R^2 = Ph$ (**a**), $R^1 = Ph$, $R^2 = 2\text{-}MeOC_6H_4$ (**b**), $3\text{-}O_2NC_6H_4$ (**c**), $2\text{-}MeO\text{-}5\text{-}O_2NC_6H_3$ (**d**), $2,5\text{-}Cl_2C_6H_3$ (**e**), 2-naphthyl (**f**); $R^1 = 2\text{-}O_2NC_6H_4$, $R^2 = Ph$ (**g**); $R^1 = 4\text{-}O_2NC_6H_4$, $R^2 = Ph$ (**h**), $4\text{-}MeC_6H_4$ (**i**); $R^1 = 4\text{-}MeC_6H_4$, $R^2 = 2\text{-}MeO\text{-}5\text{-}O_2NC_6H_3$ (**j**), 1-naphthyl (**k**).

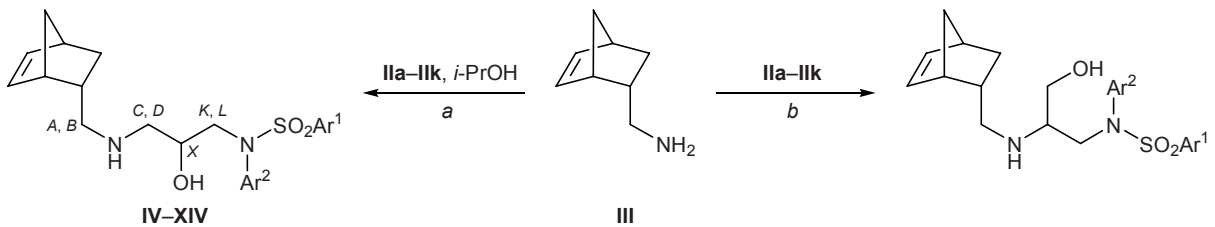
activity. As starting epoxy compounds we used *N*-aryl-*N*-(2,3-epoxypropyl)arenesulfonamides **IIa**–**IIk** which were synthesized by reaction of the corresponding *N*-arylarenesulfonamides with 2-chloromethyloxirane [8] (Scheme 1). The ^1H NMR spectra of sulfonamides **IIb**, **IIf**, **IIh**, and **IIi** contained signals from protons in the CH_2O (δ 2.40–2.45 and 2.70–2.75 ppm) and CHO groups (δ 2.80–3.45 ppm); the geminal and vicinal ^1H–^1H coupling constants for these protons in the spectrum of **IIb** were $^2J = 5.30$ and $^3J = 4.70$, 2.40 Hz. The NCH_2 protons resonated at δ 3.50–3.80 ppm, signals from aromatic protons appeared in the region δ 6.70–8.13 ppm, and methyl and methoxy groups in the aromatic rings gave signals at δ 2.44 and 3.30 ppm, respectively.

The cage-like component was bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethanamine (**III**). The key step in the synthesis of **III** was isolation of stereochemically pure bicyclo[2.2.1]hept-5-ene-*endo*-2-carbonitrile by fractional distillation of a mixture of stereoisomeric *exo*- and *endo*-nitriles obtained by Diels–Alder reaction of cyclopentadiene with acrylonitrile. The *endo* isomer was then reduced with lithium tetrahydridoaluminate [9]. Compounds **IIa**–**IIk** reacted with amine **III** in isopropyl alcohol in the cold or on heating to 50–60°C. According to the TLC data, mixtures of products were formed in all cases. By column chromatography on silica gel we isolated the major products (50–80%) resulting from opening of the oxirane ring. Study on pharmacological properties of one of the obtained amino alcohols revealed its analgesic and tranquilizing effects. Aminolysis of epoxy derivatives **IIa**–**IIk** could follow path *a* or *b* [10] (Scheme 2).

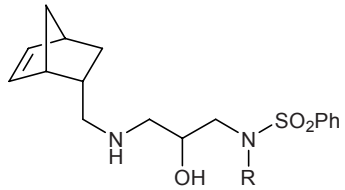
The IR spectra of the products contained absorption bands at 1350–1340 and 1185–1170 cm^{-1} due to symmetric and antisymmetric stretching vibrations of the sulfonyl group, respectively. Absorption bands in the region 3400–3200 cm^{-1} were assigned to vibrations of the hydroxy and amino groups. Also, absorption bands belonging to vibrations of bonds in the aromatic rings were present [11]. The strained double C=C bond in the bicyclic fragment gave rise to a weak absorption band because of fairly symmetric structure of the unsaturated fragment; this band was displaced to 1575–1550 cm^{-1} due to strong steric strain [12] and was usually obscured by the band corresponding to bending vibrations of the amino group. On the other hand, bending vibrations of the =C–H bonds were clearly distinguished (725–720 cm^{-1}) [12]. Compounds having a nitro group in the aromatic ring displayed absorption bands at 1560–1550 and 1350–1340 cm^{-1} (νNO_2); and absorption bands at 2890–2880 cm^{-1} (νC–H) were present in the IR spectra of methoxy-substituted derivatives [11]. The above data convincingly indicate the presence of amino, hydroxy, and sulfonamide groups in molecules of the aminolysis products.

Important information was obtained by analysis of the ^1H NMR spectra of amino alcohols **IV**–**XIV**. Protons at the double bond (5-H and 6-H) in the bicyclic fragment resonated at δ 6.19–6.05 and 6.06–5.82 ppm. Signals from protons in the bridging methylene group (*syn*-7-H and *anti*-7-H) were located at δ 1.43–1.23 and 1.26–1.08 ppm ($^2J = 7.2$–8.4 Hz), and protons at the bridgehead carbon atoms (1-H and 4-H) gave signals in the region δ 2.69–2.96 ppm. The 2-H signal appeared at δ 2.11–2.64 ppm as a complex multiplet due to coupling with 1-H, *exo*-3-H, *endo*-3-H, and two protons in the $2\text{-}CH_2$ group (8-H). The latter are diastereotopic, for they are located in the vicinity of the chiral C^2 center; their chemical shifts range from δ 2.30 to 2.90 ppm. Characteristically, the *exo*-3-H and *endo*-3-H signals appeared at δ 1.74–2.00 and 0.42–0.68 ppm; their position is considered to be the main

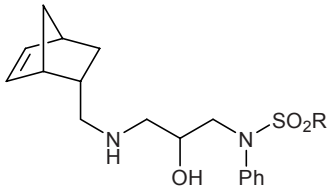
Scheme 2.



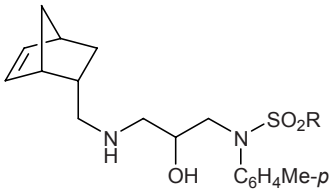
IV–XIV **III**



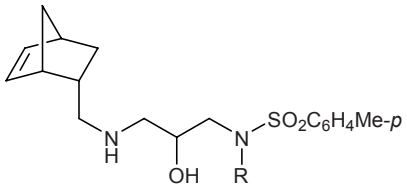
IV–IX



X, **XI**



XII



XIII, **XIV**

IV, R = Ph; **V**, R = 2-$MeOC_6H_4$; **VI**, R = 3-$O_2NC_6H_4$; **VII**, **XIII**, R = 2-MeO-5-$O_2NC_6H_3$; **VIII**, R = 2,5-$Cl_2C_6H_3$; **IX**, R = 2-naphthyl; **X**, R = 2-$O_2NC_6H_4$; **XI**, **XII**, R = 4-$O_2NC_6H_4$; **XIV**, R = 1-naphthyl.

criterion for the determination of spatial orientation of substituent at the neighboring carbon atom [13].

As shown in Scheme 2, aminolysis of epoxy derivatives **IIa**–**IIk** according to paths *a* and *b* could produce two regioisomeric adducts differing by the site of addition of the amino nitrogen atom. The isomer structure can be determined on the basis of the ^{1}H NMR spectral pattern corresponding to the $NCH_2CH(OH)CH_2N$ or $NCH(CH_2OH)CH_2N$ fragment. Signals from these protons are located within the range δ 3.65–4.09 ppm, and the downfield signals in that region belong to protons neighboring to the hydroxy group. Their intensity (1H in C**H**OH or 2H in C**H**$_2$OH) is specific for each structure. The problem is complicated due to nonequivalence of methylene protons and overlap of their signals. For example, the chemical shifts of all protons in the amino alcohol fragment of compound **IV** fall into the range from δ 3.57 to 3.65 ppm. The structure of compounds **V** and **X** was confirmed by analysis of their ^{13}C NMR spectra recorded using DEPT pulse sequence, as well as of two-dimensional COSY, NOESY, HMQC, and HMBC spectra [14]. Figures 1 and 2 show some correlations in the COSY and HMBC spectra of **X**, which allowed us to reliably assign all proton and carbon signals. The complete sets of correlations are given in table.

The ^{1}H NMR spectra of compounds **V** and **X** turned out to be fairly similar, though the methoxy and nitro groups in their molecules are located in different benzene rings (attached to the nitrogen atom or sulfonyl group). The C**H**OH signal appeared as an unresolved multiplet at δ 3.77–3.82 ppm, and signals from the SO_2NCH_2 and NHC**H**$_2$ methylene protons were located at δ 3.44–3.77 and 2.69–3.08 ppm, respectively [15]. The chemical shifts of protons in the amino alcohol fragment change in the following series: $H_X > H_K$, $H_L > H_C$, $H_D > H_A$, H_B. The corresponding carbon chemical shifts change in the same order, δ_C, ppm: **V**: 65.0 (COH), 56.0 (SO_2NCH_2), 52.0 ($NHCH_2$); **X**: 65.1 (COH), 55.9 (SO_2NCH_2), 51.2 ($NHCH_2$). Carbon atoms in the bicyclic skeleton are characterized by the following chemical shifts, δ_C, ppm: **V**: 138.0 (C^5) 131.3 (C^6), 49.8 (C^7); **X**: 138.5 (C^5), 132.7 (C^6), 49.8 (C^7). These data are consistent with the presence of *endo*-oriented substituent in the strained norbornene fragment.

The base peak in the mass spectrum of compound **X** was that with *m*/*z* 136 (100%, $\mathbf{F}_3$; Scheme 3). Its structure provides an additional support to the assumed direction of oxirane ring opening in the reaction of amine **III** with sulfonamides **II** (path *a* in Scheme 2).

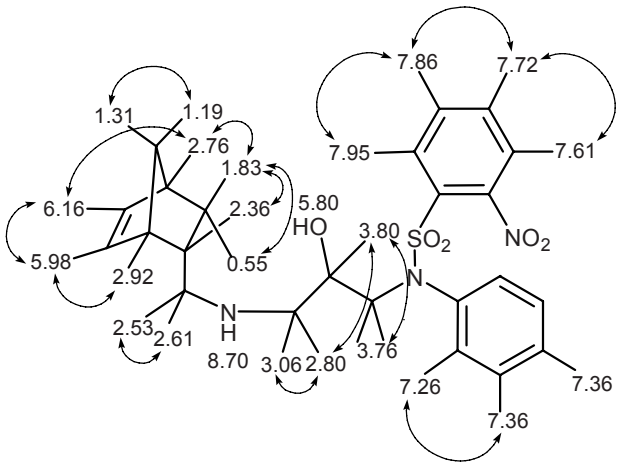
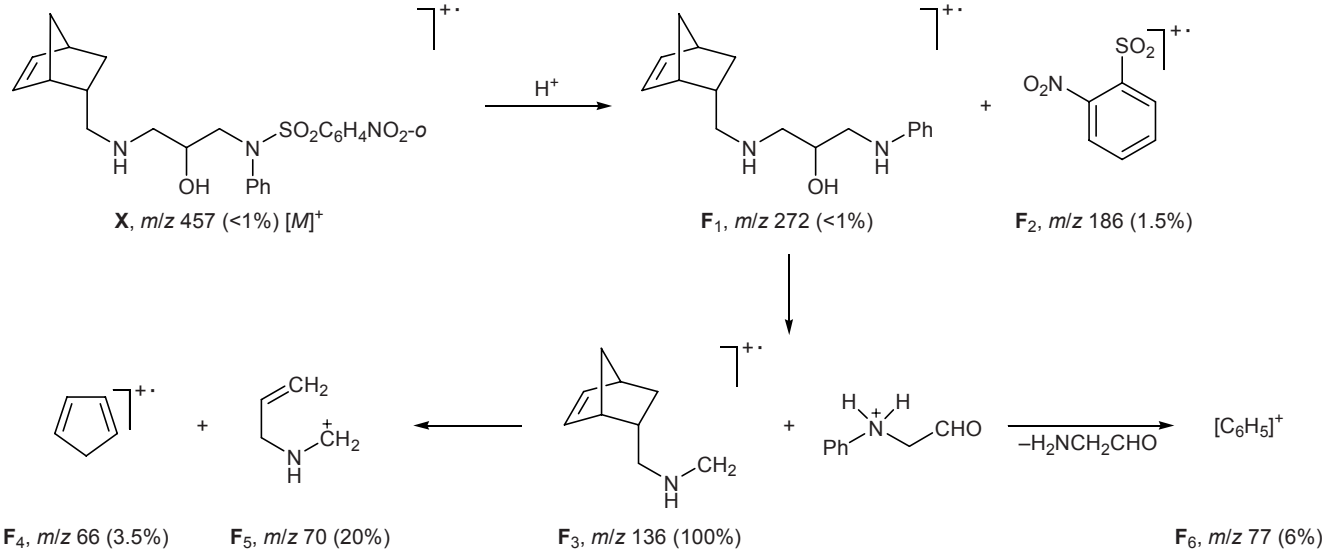


Fig. 1. ^{1}H–^{1}H correlations in the COSY spectrum of compound **X**; ^{1}H chemical shifts are given (δ, ppm).

Scheme 3.



X, *m*/*z* 457 (<1%) $[M]^+$ **F**$_1$, *m*/*z* 272 (<1%) **F**$_2$, *m*/*z* 186 (1.5%)

F$_4$, *m*/*z* 66 (3.5%) **F**$_5$, *m*/*z* 70 (20%) **F**$_3$, *m*/*z* 136 (100%) **F**$_6$, *m*/*z* 77 (6%)

EXPERIMENTAL

The IR spectra were recorded in KBr on a UR-20 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ or DMSO-d_6 on Varian VXR and Varian Mercury-400 instruments at 300 or 400 MHz for ^{1}H and 100 MHz for ^{13}C using tetramethylsilane as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silicagel 60F_{254} plates using diethyl ether as eluent; spots were visualized by treatment with iodine vapor. The elemental compositions were determined on a Carlo Erba analyzer.

Amino alcohols IV–XIV (*generl procedure***).** Compound **IIa**–**IIk**, 1 mmol, was added to a solution of 1 mmol of amine **III** in 10 ml of propan-2-ol, the mixture was stirred until the reaction was complete (TLC), the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel using in succession diethyl ether, diethyl ether–propan-2-ol, and propan-2-ol as eluent. The yield of the main fraction [R_f 0.14–0.56 (diethyl ether)] was 52–84%. Crystalline products were recrystallized from propan-2-ol.

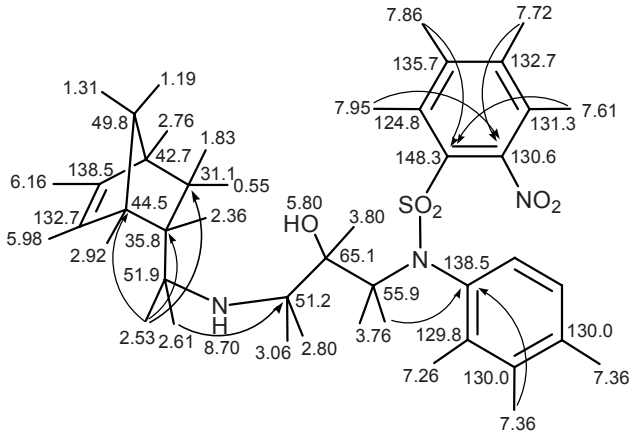


Fig. 2. ^{13}C–^{1}H correlations in the HMBC spectrum of compound **X**; ^{1}H and ^{13}C chemical shifts are given (δ, δ_C, ppm).

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-phenylbenzenesulfonamide (IV).** Yield 52%, mp 129–130°C, R_f 0.56 (diethyl ether). IR spectrum, ν, cm^{-1}: 3325, 3070, 1595, 1355, 1175, 1100, 1080, 1035, 880, 850, 790, 770, 730. ^{1}H NMR spectrum, δ, ppm: 0.49 m (1H, *endo*-3-H), 1.22 d (1H, *anti*-7-H), 1.41 d (1H, *syn*-7-H, ^2J = 8.3 Hz), 1.82 m (1H, *exo*-3-H, ^2J = 11.4, $^3J_{6,5}$ = 10.2, $^3J_{6,1}$ = 3.3 Hz), 2.18 m (1H, 2-H), 2.30–2.33 m (2H, H_A, H_B), 2.75 m (2H, H_C, H_D), 2.76 br.s (1H, 4-H), 2.83 br.s (1H, 1-H), 3.14 s (1H, OH), 3.57 m (2H, H_K, H_L), 3.60 (1H, NH), 3.65 m (1H, H_X), 5.90 (1H, 6-H, $^3J_{6,1}$ = 2.4 Hz), 6.11 (1H, 5-H, $^3J_{5,6}$ = 5.1, $^3J_{5,4}$ = 3.0 Hz), 7.05–7.58 (10H, H_{arom}). Found, %: C 66.83; H 6.91; N 6.87. $C_{23}H_{28}N_2O_3S$. Calculated, %: C 66.96; H 6.84; N 6.79.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-(2-methoxyphenyl)-benzenesulfonamide (V).** Yield 62%, mp 158–160°C, R_f 0.61 (Et_2O–*i*-PrOH, 10:1). IR spectrum, ν, cm^{-1}: 3300, 3075, 1725, 1595, 1500, 1340, 1180, 1100, 850, 780, 750, 725. ^{1}H NMR spectrum, δ, ppm: 0.49 m (1H, *endo*-3-H, $^3J_{3,2}$ = 2.4 Hz), 1.10 d (1H, *anti*-7-H), 1.23 d (1H, *syn*-7-H, ^2J = 8.0 Hz), 1.76 m (1H, *exo*-3-H, ^2J = 11.6, $^3J_{3,2}$ = 10.4, $^3J_{3,4}$ = 2.8 Hz), 2.32 m (1H, 2-H),

2.36 br.s (1H, OH), 2.46–2.48 m (2H, H_A, H_B), 2.69 m (1H, H_C), 2.88 br.s (2H, 1-H, 4-H), 2.93 br.s (1H, NH), 3.04 m (1H, H_D), 3.25 s (3H, OCH_3), 3.45 m (2H, H_K, H_L), 3.77 m (1H, H_X), 5.90 d.d (1H, 6-H, $^3J_{6,1}$ = 2.4 Hz), 6.05 d.d (1H, 5-H, $^3J_{5,6}$ = 5.2, $^3J_{5,4}$ = 3.2 Hz), 6.76–7.52 m (9H, H_{arom}). Found, %: C 64.98; H 6.73; N 6.41. $C_{24}H_{30}N_2O_4S$. Calculated, %: C 65.13; H 6.83; N 6.33.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-(3-nitrohenyl)benzenesulfonamide (VI).** Yield 55%, mp 101–103°C, R_f 0.56 (Et_2O–*i*-PrOH, 10:1). IR spectrum, ν, cm^{-1}: 3400, 3070, 1543, 1520, 1456, 1175, 741. ^1H NMR spectrum, δ, ppm: 0.42 m (1H, *endo*-3-H, $^3J_{3,2}$ = 2.7 Hz), 1.17 d (1H, *anti*-7-H), 1.29 d (1H, *syn*-7-H, ^2J = 7.2 Hz), 1.75 m (1H, *exo*-3-H, ^2J = 11.4, $^3J_{3,2}$ = 10.2, $^3J_{3,4}$ = 3.3 Hz), 2.12 m (1H, 2-H), 2.20–2.22 m (2H, H_A, H_B), 2.52 m (1H, H_C), 2.65 m (1H, H_D), 2.73 br.s (1H, 4-H), 2.79 br.s (1H, 1-H), 3.57 m (1H, H_K), 3.62 m (1H, H_L), 3.66 m (1H, H_X), 5.88 d.d (1H, 6-H, $^3J_{6,1}$ = 2.4 Hz), 6.10 d.d (1H, 5-H, $^3J_{5,6}$ = 5.2, $^3J_{5,4}$ = 3.2 Hz), 7.58–8.31 m (9H, H_{arom}). Found, %: C 60.50; H 6.08; N 9.24. $C_{23}H_{27}N_3O_5S$. Calculated, %: C 60.38; H 5.95; N 9.18.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-(2-methoxy-5-nitrophenyl)benzenesulfonamide (VII).** Yield 73%, mp 138–140°C, R_f 0.52 (Et_2O–*i*-PrOH, 10:1). IR spectrum, ν, cm^{-1}: 3330, 3080, 1590, 1525, 1350, 1175, 880, 845, 770, 735. ^1H NMR spectrum, δ, ppm: 0.61 m (1H, *endo*-3-H), 1.19 d (1H, *anti*-7-H), 1.37 d (1H, *syn*-7-H, *J* = 7.5 Hz), 1.92 m (1H, *exo*-3-H), 2.56 m (1H, 2-H), 2.70–2.80 m (2H, H_A, H_B), 2.75 br.s (2H, 1-H, 4-H), 3.01 m (1H, H_C), 3.03 m (1H, H_D), 3.40 m (1H, H_K), 3.42 s (3H, OCH_3), 3.59 m (1H, H_L), 3.69 m (1H, H_X), 4.21 br.s (1H, OH), 5.15 br.s (1H, NH), 5.99 m (1H, 6-H), 6.11 (1H, 5-H), 6.80–8.08 m (8H, H_{arom}). Found, %: C 59.25; H 6.11; N 8.70. $C_{24}H_{29}N_3O_6S$. Calculated, %: C 59.12; H 6.00; N 8.62.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-(2,5-dichlorophenyl)-benzenesulfonamide (VIII).** Yield 84%, mp 118–119°C, R_f 0.22 (Et_2O). IR spectrum, ν, cm^{-1}: 3370, 3080, 1595, 1500, 1455, 1350, 1175, 765, 735. ^1H NMR spectrum, δ, ppm: 0.68 m (1H, *endo*-3-H), 1.26 d (1H, *anti*-7-H), 1.46 d (1H, *syn*-7-H, ^2J = 8.2 Hz), 2.00 m (1H, *exo*-3-H, ^2J = 11.4, $^3J_{3,2}$ = 9.9, $^3J_{3,4}$ = 3.0 Hz), 2.64 m (1H, 2-H), 2.70–2.90 m (2H, H_A, H_B), 2.83 br.s (2H, 1-H, 4-H), 3.11 m (2H, H_C, H_D), 3.41 m (1H, H_K), 3.51 m (1H, H_L), 3.75 m (1H, H_X), 4.15 br.s (1H, OH), 4.39 br.s (1H, NH), 6.06 d.d (1H, 6-H, $^3J_{6,1}$ = 2.4 Hz), 6.18 d.d (1H, 5-H, $^3J_{5,6}$ = 5.4, $^3J_{5,4}$ = 3.0 Hz), 6.89–7.74 m (8H, H_{arom}). Found, %: C 57.47; H 5.51; N 5.70. $C_{23}H_{26}Cl_2N_2O_3S$. Calculated, %: C 57.38; H 5.44; N 5.82.

Correlations in the ^1H and ^{13}C NMR spectra of compound **X**

δ, ppm	δ_C, ppm		
	HMQC	HMBC	COSY
8.73	–	–	–
7.97	124.8	148.3, 132.7, 130.6	7.88
7.88	135.7	148.3, 131.3, 124.8	7.97, 7.74
7.74	132.7	148.3, 130.6	7.88, 7.62
7.62	131.3	148.3, 135.7	7.74
7.37	130.0	138.5, 131.3, 130.0	7.28
7.28	129.8	138.5, 129.2	7.37
6.18	138.5	49.8, 44.5–44.6, 42.6	6.00, 2.78
6.00	132.7	49.8, 44.5–44.6, 42.6	6.18, 2.94
5.81	–	–	–
3.82	65.1	–	2.80, 3.77
3.77	55.9	138.5, 65.1, 51.2	3.82
3.08	51.2	–	2.80
2.94	44.5–44.6	138.5, 42.7, 31.1	3.00
2.80	51.2	65.1	3.82, 3.08
2.78	42.7	51.9–52.2	6.18, 1.84
2.63	51.9–52.2	51.2, 44.5–44.6, 35.8, 31.1	2.55
2.55	51.9–52.2	51.2, 44.5–44.6, 35.8, 31.1	2.63
2.38	35.8	–	1.84
1.84	31.1	138.5	2.78, 2.38, 0.56
1.33	49.8	42.6, 35.8, 31.1	1.21
1.21	49.8	135.8, 132.7, 42.6, 44.5–44.6, 42.6, 35.8, 31.1	1.33
0.56	31.1	49.8	1.84

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-(2-naphthyl)benzenesulfonamide (IX).** Yield 69%, mp 227–228°C, R_f 0.18 (Et_2O). IR spectrum, ν, cm^{-1}: 3400, 3075, 1595, 1520, 1450, 1360, 1175, 760, 750. ^1H NMR spectrum, δ, ppm: 0.55 m (1H, *endo*-3-H), 1.08 d (1H, *anti*-7-H), 1.32 d (1H, *syn*-7-H, ^2J = 8.1 Hz), 1.82 m (1H, *exo*-3-H, ^2J = 12.0, $^3J_{3,2}$ = 10.2, $^3J_{3,4}$ = 3.6 Hz), 2.49 m (1H, 2-H), 2.60–2.70 m (2H, H_A, H_B), 2.69 br.s (2H, 1-H, 4-H), 2.96 m (1H, H_C), 3.07 m (1H, H_D), 3.43 m (1H, H_K), 3.64 m (1H, H_L), 3.86 m (1H, H_X), 4.16 br.s (1H, OH), 5.26 br.s (1H, NH), 5.94 d.d (1H, 6-H, $^3J_{6,1}$ = 2.7 Hz), 6.09 d.d (1H, 5-H, $^3J_{5,6}$ = 5.7, $^3J_{5,4}$ = 3.0 Hz), 7.04–7.79 m (12H, H_{arom}). Found, %: C 70.22;

H 6.61; N 5.98. $C_{27}H_{30}N_2O_3S$. Calculated, %: C 70.10; H 6.54; N 6.06.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-2-nitro-*N*-phenylbenzenesulfonamide (X).** Yield 74%, mp 132–134°C, R_f 0.65 (Et_2O–*i*-PrOH, 10:1). IR spectrum, ν, cm^{-1}: 3340, 3075, 1595, 1375, 1340, 1175, 1135, 1080, 885, 790, 770, 750, 730. ^1H NMR spectrum, δ, ppm: 0.56 m (1H, *endo*-3-H, $^3J_{3,2}$ = 2.7 Hz), 1.21 d (1H, *anti*-7-H), 1.33 d (1H, *syn*-7-H, ^2J = 8.1 Hz), 1.84 m (1H, *exo*-3-H, ^2J = 11.2, $^3J_{3,2}$ = 9.6, $^3J_{3,4}$ = 3.0 Hz), 2.38 m (1H, 2-H), 2.55 d.d and 2.63 d.d (1H each, H_A, H_B), 2.78 br.s (1H, 4-H), 2.80 d (1H, H_C), 2.94 br.s (1H, 1-H), 3.08 d (1H, H_D), 3.77 m (2H, H_K, H_L), 3.82 m (1H, H_X), 5.81 br.s (1H, OH), 6.00 d.d (1H, 6-H, $^3J_{6,1}$ = 2.8 Hz), 6.18 d.d (1H, 5-H, $^3J_{5,6}$ = 5.4, $^3J_{5,4}$ = 2.8 Hz), 7.27–7.98 m (9H, H_{arom}), 8.73 br.s (1H, NH). Found, %: C 60.30; H 5.87; N 9.30. $C_{23}H_{27}N_3O_5S$. Calculated, %: C 60.38; H 5.95; N 9.18.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-4-nitro-*N*-phenylbenzenesulfonamide (XI).** Yield 80%, mp 154–156°C, R_f 0.63 (Et_2O–*i*-PrOH, 10:1). IR spectrum, ν, cm^{-1}: 3400, 3070, 1600, 1531, 1491, 1452, 1352, 1335, 1167, 1090, 883, 775, 741, 721. ^1H NMR spectrum, δ, ppm: 0.49 m (1H, *endo*-3-H, $^3J_{3,2}$ = 3.0 Hz), 1.23 d (1H, *anti*-7-H), 1.42 d (1H, *syn*-7-H, ^2J = 7.5 Hz), 1.82 m (1H, *exo*-3-H, ^2J = 12.0, $^3J_{3,2}$ = 10.2, $^3J_{3,4}$ = 3.3 Hz), 2.15 m (1H, 2-H), 2.30 m (2H, H_A, H_B), 2.78 br.s (1H, 4-H), 2.83 br.s (1H, 1-H), 2.70 m (2H, H_C, H_D), 3.61 m (2H, H_K, H_L), 3.66 m (1H, H_X), 5.89 d.d (1H, 6-H, $^3J_{6,1}$ = 3.0 Hz), 6.12 d.d (1H, 5-H, $^3J_{5,6}$ = 5.4, $^3J_{5,4}$ = 2.7 Hz), 7.06–8.31 m (9H, H_{arom}). Found, %: C 60.47; H 6.03; N 9.09. $C_{23}H_{27}N_3O_5S$. Calculated, %: C 60.38; H 5.95; N 9.18.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-(4-methylphenyl)-4-nitrobenzenesulfonamide (XII).** Yield 76%, mp 94–96°C, R_f 0.65 (Et_2O–*i*-PrOH, 10:1). IR spectrum, ν, cm^{-1}: 3320, 3075, 1720, 1600, 1530, 1350, 1320, 1175, 1100, 880, 770, 735. ^1H NMR spectrum, δ, ppm: 0.58 m (1H, *endo*-3-H, $^3J_{3,2}$ = 3.0 Hz), 1.18 d (1H, *anti*-7-H), 1.38 d (1H, *syn*-7-H, ^2J = 7.5 Hz), 1.88 m (1H, *exo*-3-H, ^2J = 12.0, $^3J_{3,2}$ = 10.2, $^3J_{3,4}$ = 3.3 Hz), 2.28 s (3H, CH_3), 2.31 br.s (1H, OH), 2.46 m (1H, 2-H), 2.61–2.63 m (2H, H_A, H_B), 2.77 br.s (1H, 4-H), 2.96 br.s (1H, 1-H), 3.01 m (1H, H_C), 3.18 m (1H, H_D), 3.62–3.79 m (2H, H_K, H_L), 4.09 m (1H, H_X), 5.96 d.d (1H, 6-H, $^3J_{6,1}$ = 2.7 Hz), 6.12 d.d (1H, 5-H, $^3J_{5,6}$ = 5.7, $^3J_{5,4}$ = 3.0 Hz), 6.45 br.s (1H, NH), 6.88–8.26 m (8H, H_{arom}). Found, %: C 61.19; H 6.33; N 9.04. $C_{24}H_{29}N_3O_5S$. Calculated, %: C 61.13; H 6.20; N 8.91.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-*N*-(2-methoxy-5-nitrophenyl)-4-methylbenzenesulfonamide (XIII).** Yield 74%, mp 132–134°C, R_f 0.27 (Et_2O). IR spectrum, ν, cm^{-1}: 3340, 3075, 2880, 1595, 1560, 1350, 1505, 1450, 1350, 1180, 760, 740. ^1H NMR spectrum, δ, ppm: 0.66 m (1H, *endo*-3-H), 1.25 d (1H, *anti*-7-H), 1.43 d (1H, *syn*-7-H, ^2J = 8.1 Hz), 1.97 m (1H, *exo*-3-H, ^2J = 12.3, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.3 Hz), 2.41 s (3H, CH_3), 2.41 m (1H, 2-H), 2.60 m and 2.78 m (1H each, H_A, H_B), 2.81 br.s (2H, 1-H, 4-H), 3.06 m (1H, H_C), 3.13 m (1H, H_D), 3.43 m (1H, H_K), 3.55 m (1H, H_L), 3.57 s (3H, OCH_3), 3.71 m (1H, H_X), 4.20 br.s (1H, OH), 5.17 br.s (1H, NH), 6.03 d.d (1H, 6-H, $^3J_{6,1}$ = 3.0 Hz), 6.17 d.d (1H, 5-H, $^3J_{5,6}$ = 5.4, $^3J_{5,4}$ = 3.0 Hz), 6.85–8.16 m (8H, H_{arom}). Found, %: C 59.94; H 6.35; N 8.24. $C_{25}H_{31}N_3O_6S$. Calculated, %: C 59.86; H 6.23; N 8.38.

***N*-{3-[(Bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)-amino]-2-hydroxypropyl}-4-methyl-*N*-(1-naphthyl)-benzenesulfonamide (XIV).** Yield 47%, mp 166–167°C, R_f 0.14 (Et_2O). IR spectrum, ν, cm^{-1}: 3380, 3070, 2970, 2880, 1600, 1510, 1470, 1350, 1180, 880, 845, 780, 740. ^1H NMR spectrum, δ, ppm: 0.42 m (1H, *endo*-3-H, $^3J_{3,2}$ = 2.7 Hz), 1.18 d (1H, *anti*-7-H), 1.38 d (1H, *syn*-7-H, ^2J = 8.1 Hz), 1.74 m (1H, *exo*-3-H, ^2J = 12.0, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.3 Hz), 2.11 m (1H, 2-H), 2.40–2.44 m (2H, H_A, H_B), 2.42 s (3H, CH_3), 2.74 br.s (2H, 1-H, 4-H), 2.78 m (1H, H_C), 2.81 m (1H, H_D), 3.21 br.s (2H, OH, NH), 3.44–3.60 m (2H, H_K, H_L), 3.69 m (1H, H_X), 5.82 d.d (1H, 6-H, $^3J_{6,1}$ = 2.7 Hz), 6.07 d.d (1H, 5-H, $^3J_{5,6}$ = 5.7, $^3J_{5,4}$ = 3.0 Hz), 6.91–8.17 m (8H, H_{arom}). Found, %: C 70.71; H 6.85; N 5.99. $C_{28}H_{32}N_2O_3S$. Calculated, %: C 70.56; H 6.77; N 5.88.

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