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Azabrendanes IV. Synthesis and characterization of *N*-(alkyl- and benzylsulfonyl)-*exo*-2-hydroxy-4-azatricyclo[4.2.1.0^{3,7}]nonanes

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Abstract—*exo*- and *endo*-5-Aminomethylbicyclo[2.2.1]hept-2-enes have been obtained from stereoisomeric *exo*- and *endo*-5-cyanobicyclo[2.2.1]hept-2-enes and the corresponding sulfonamides were obtained through reaction of amines with methyl-, *n*-propyl-, *n*-butyl-, benzyl-, and cyclohexylsulfonyl chlorides. From the stereoisomeric sulfonamides with peroxy acids, various products were obtained: *exo*-sulfonamides were transformed into epoxy derivatives, and, in contrast, most of the *endo*-stereoisomers underwent heterocyclization resulting in substituted *exo*-2-hydroxy-4-azatricyclo[4.2.1.0^{3,7}]nonanes. The type of the products obtained did not depend on the type of peroxy acid used (peroxyacetic, peroxyphthalic, and *m*-chloroperoxybenzoic one). In contrast to other *endo*-sulfonamides, *N*-(cyclohexylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene in reaction with peroxyacetic acid did not undergo heterocyclization, probably, due to steric factors. The structure and stereochemical homogeneity of the sulfonamides and the structure of the products of their oxidation with peroxy acids were confirmed by spectroscopic methods. The molecular structure of *N*-(cyclohexylsulfonyl)-*endo*-5-aminomethyl-*exo*-2,3-epoxybicyclo[2.2.1]heptane was determined by X-ray diffraction analysis. The mechanism of the intramolecular heterocyclization reaction of *N*-substituted *endo*-5-aminomethyl-*exo*-2,3-epoxybicyclo[2.2.1]heptanes was studied at the BHandHLYP/6-31G(d) level of theory.
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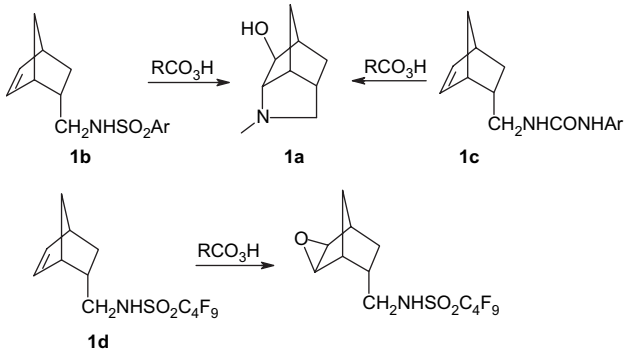
1. Introduction

Azabrendanes **1a** are of interest as potential biologically active systems or as intermediates for the preparation of such compounds.[1] They are easily obtained by epoxidation of the *p*-substituted arylsulfonamides of type **1b** having an *endo*-orientation of the substituent. The ability to heterocyclization decreases when the number of substituents in the benzene ring increases, especially in the case of nitro groups in an *o*-position.[2] Analogous heterocyclization of the ureas **1c** (Ar=C_6H_5, *m*-ClC_6H_4Cl) under oxidation conditions has been described previously.[3] Ring transformations of this kind are attributed to a favorable location of the substituted nitrogen atom in the vicinity of the loosening π*-molecular orbital of the incipient epoxy ring.[4]



On the other hand, a number of cases when the structural analogs of the compounds **1b**, **1c** in reactions with peroxy acids are transformed into epoxy compounds without heterocyclization are well known. For example, the lack of heterocyclization by fluorine-containing sulfonamide **1d**,[5] and by a series of *endo*-carboxamides including methyl, trifluoromethyl, and aryl substituents at nitrogen atom **1e**,[6] has been

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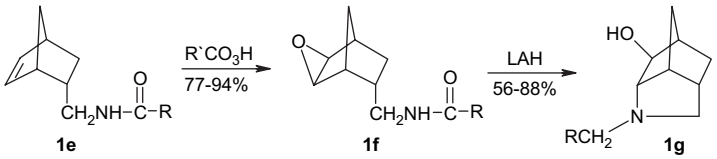


Scheme 1.

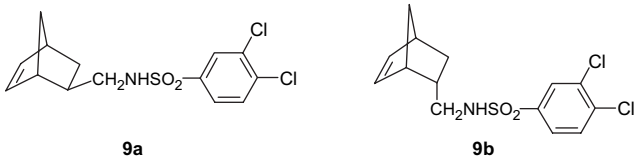
shown. *N*-Alkyl-substituted azabrendanes **1d** have been obtained in the latter case by chemoselective reduction of epoxy amides **1f** and subsequent cyclization of the epoxy amines (Scheme 1).[6]

The reasons determining the behavior of the substituted *endo*-5-aminomethylbicyclo[2.2.1]hept-2-enes in reactions with peroxy acids and formation of two different types of oxidation products have not been stated until recently. In order to obtain new facts, which would help to address this issue, we have investigated in the current work the behavior of stereoisomeric alkyl-, benzyl-, and cyclohexylsulfonamides in reactions with peroxy acids.

2. Results and discussion

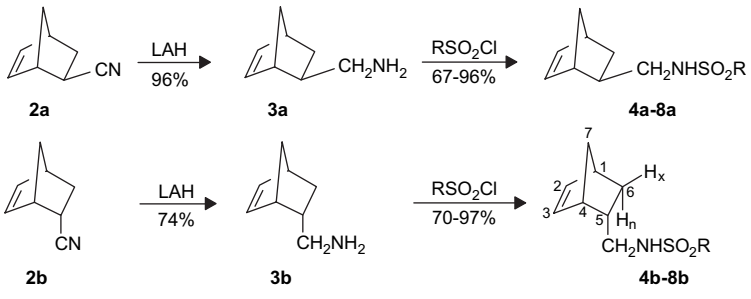
The required stereoisomeric sulfonamides were synthesized using *exo*- and *endo*-cyanobicyclo[2.2.1]hept-2-enes **2a**, **2b** that were obtained by methods described in the literature.[7] These stereoisomeric nitriles were converted into amines **3a**, **3b** by the action of lithium aluminum hydride.[7,8] In accordance with the literature,[9] the reduction of nitrile **2b** was accompanied by epimerization of the product. An impurity (5–10%) of the corresponding *exo*-stereoisomer was revealed by ^{1}H NMR spectroscopy. In contrast, amine **3a** was obtained in a diastereochemically homogeneous state. A number of *exo*-sulfonamides **4a**–**8a** and their *endo*-stereoisomers **4b**–**8b** were prepared from amines **3a**, **3b** by action of the corresponding sulfonyl chlorides (Scheme 2). High product yields were achieved when the reaction was carried out in dry ether with an equimolar ratio of the reagents and triethylamine.

IR spectra of synthesized sulfonamides contain all necessary bands appropriate to absorption of present functional groups. The orientation of the substituent in sulfonamides can be seen distinctly in NMR spectra. The identification of the signals has been carried out by using literature data as well as the results of two-dimensional spectra obtained using correlation spectroscopy (COSY) of amine **3b** and stereoisomeric *N*-(3,4-dichlorophenylsulfonyl)-5-aminomethylbicyclo[2.2.1]hept-2-enes **9a**, **9b**.[10]



The criteria for characterization of the stereoisomeric sulfonamides **4**–**8**, proposed earlier when studying aromatic series of sulfonamides, appeared to be suitable.[11] Essential distinctions have been found in the structure of ^{13}C spectra of stereoisomers **4a**, **4b**, **8a**, **8b**. The assignment of the signals has been made using the published data on the spectra of key amines **3a**, **3b**,[8] the data on selective double resonance ^{13}C–(H) of stereoisomeric substituted norbornenes,[12] and the results of the study of two-dimensional ^{13}C–^{1}H spectra of arylsulfonamides **9a**, **9b**. Position of signals characterizing the resonance of the olefinic fragment nuclei is the principle difference of the stereoisomers spectra—the difference of chemical shifts of the C^2 and C^3 nuclei ($\Delta\delta$) in the case of *endo*-stereoisomers reaches 6–7 ppm, whereas analogous parameter in the spectra of *exo*-stereoisomers does not exceed 0.9 ppm.

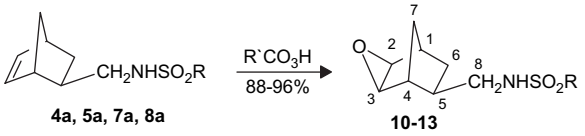
Different oxidants were used for the epoxidation of the sulfonamides, i.e., peroxyphthalic acid generated in situ from phthalic anhydride and 30% aqueous solution of hydrogen peroxide (method A), crystalline peroxyphthalic acid (method B). These methods have been previously used for the epoxidation of the substituted norbornenes.[2,3,6] In addition to these methods, peroxyacetic acid generated in situ from acetic anhydride and 56% aqueous solution of hydrogen peroxide (method C), and *m*-chloroperoxybenzoic acid



R=CH_3 (**4a, b**), n-C_3H_7 (**5a, b**), n-C_4H_9 (**6a, b**), $C_6H_5CH_2$ (**7a, b**), C_6H_{11}-cyclo (**8a, b**)

Scheme 2.

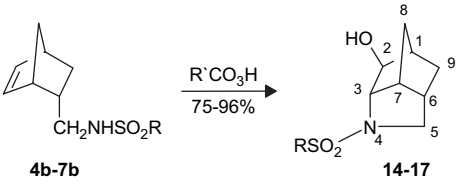
(method D) have also been used. Reactions were carried out in ethyl acetate or chloroform with TLC monitoring. It was shown by spectroscopic investigations that *exo*-sulfonamides **4a**–**8a** were transformed into epoxy derivatives **10**–**13** (Scheme 3).



R=CH_3 (**4a, 10**), n-C_3H_7 (**5a, 11**), $C_6H_5CH_2$ (**7a, 12**), C_6H_{11}-cyclo (**8a, 13**)

Scheme 3.

In contrast, azabrendanes **14**–**17** were obtained from stereoisomeric *endo*-sulfonamides **4b**–**8b** under the action of peroxy acids (Scheme 4). The conclusions about the structure of the products of oxidation have been made based on the analysis of IR and ^1H and ^{13}C NMR spectra.

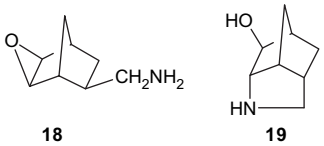


R=CH_3 (**14**), n-C_3H_7 (**15**), n-C_4H_9 (**16**), $C_6H_5CH_2$ (**17**)

Scheme 4.

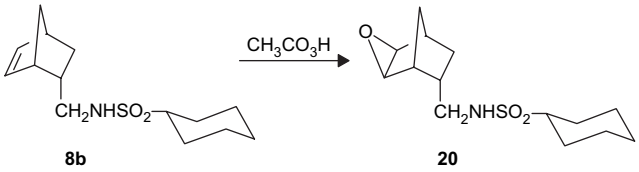
IR spectra of the oxidization products of two types contain all necessary bands characterizing absorption of the present functional groups.

Substantial differences were discovered in the ^1H NMR spectra of the products of the epoxidation of *exo*- and *endo*-sulfonamides. For comparison purposes, we have used the spectral data of parent compounds of the two mentioned groups (epoxyamine **18** and *exo*-2-hydroxy-4-azatricyclo[4.2.1.$0^{3,7}$]nonane **19**), for which two-dimensional spectra (COSY method) have been measured earlier.[13] Similar procedure was also used for epoxide **12**. The latter allowed the assignment of the signals of H^1 and H^4, H^2 and H^3 protons with higher precision.



The signals with negligible difference of chemical shifts in the field of 3.00–3.15 ppm are present in the ^1H NMR spectra of epoxides with the signals of olefin fragment protons being absent. *exo*-Orientation of epoxide cycle follows from significant nonequivalence of the signals of bridge protons (H^{7s} and H^{7a}), as well as considerable strong-field shift of one of them into the field of 0.7–0.8 ppm. Together with the absence of the signals of epoxide ring protons, the ^1H NMR spectra of azabrendanes are mostly characterized by two signals, i.e., one-proton singlet of H^2 proton (3.50–3.70 ppm) and the doublet of H^3 proton (3.20–3.60 ppm). The splitting of the latter derives from its interaction with H^7 proton with vicinal constant of 5.1–5.6 Hz. The ^{13}C NMR spectra of epoxides contain characteristic signals of epoxide ring carbon atoms (C^2, C^3) in a narrow field of 51–52 ppm. Also characteristic is the strong-field shift of the C^7 nucleus signal to the field of 23–24 ppm, which is caused by the emergence of epoxide ring with *exo*-orientation.[12,14] Three key signals corresponding to carbon atoms bonded to oxygen and nitrogen atoms (C^2, C^3, and C^5) have been detected in the ^{13}C NMR spectra of azabrendanes, which are located in the fields of 81.3–81.5, 69.2–69.9, and 54.4–54.6 ppm, respectively.

In contrast to the aforementioned results, one of the *endo*-sulfonamides (*N*-(cyclohexylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene **8b**) was converted into epoxide **20** in the reaction with peroxyacetic acid in chloroform (Scheme 5). The structure of that epoxide was determined by X-ray diffraction analysis. The *exo*-2,3-epoxybicyclo[2.2.1]-heptane fragment is disordered over two positions (conformers **A** and **B**) with equal populations due to rotation around the C(6)–C(8) bond (Fig. 1). The C(5)–C(6A)–C(8)–N(1) and C(5)–C(6B)–C(8)–N(1) torsion angles are 41(1)° and −56.7(7)°, respectively. The oxiran ring has an *exo*-orientation in both conformers; such orientation of oxiran ring was found in related structures.[15–18] Cyclohexane ring has *sc* orientation relative to the N(1)–C(8) bond (the C(9)–S(1)–N(1)–C(8) torsion angle is 70.9(4)°) and it adopts



Scheme 5.

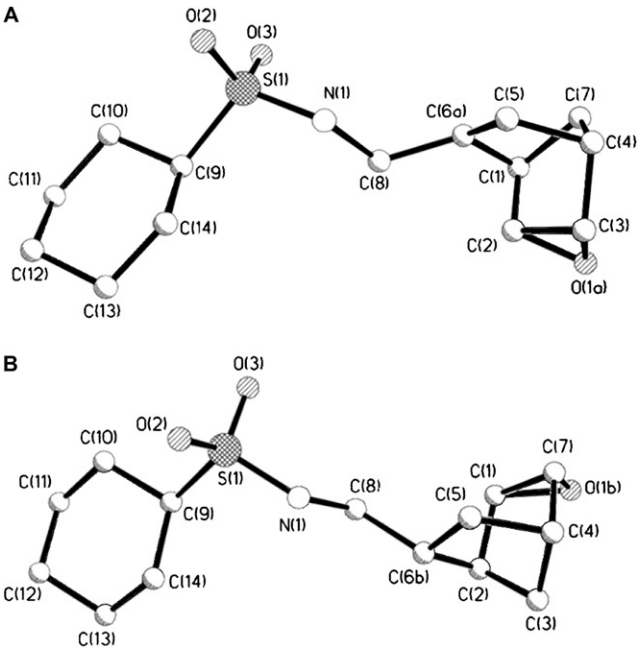
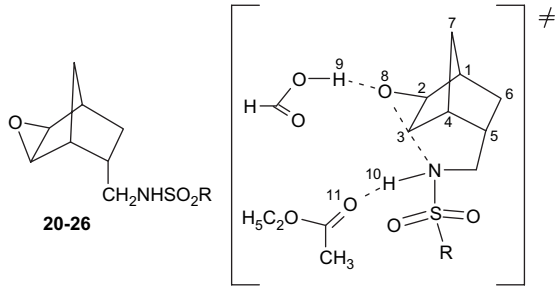


Figure 1. The perspective view of the molecule **20** (conformers **A** and **B**).

a chair conformation. Molecules **20** form dimers in crystal phase due to weak intermolecular hydrogen bonds N(1)–H(1N)···O(2)′ (1−*x*, 0.5+*y*, 0.5+*z*): distance of H···O is 2.99 Å and angle of N–H···O is 137°. This, probably, causes elongation of the S(1)–O(2) bond up to 1.459(3) Å as compared to mean value of 1.428 Å.[19] Atomic coordinates and crystallographic parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 629019).

The compounds **13** and **20**, which were synthesized in the current work, allowed a comparison of the NMR spectra of the epoxy derivatives of sulfonamides with different orientations of the substituent in the bicyclic skeleton. As in the case of unsaturated analogues **8a**, **8b**, the epoxide **20** with *endo*-oriented substituent has a more profound nonequivalence of epoxide ring protons H^2, H^3 (3.22 and 3.13 ppm), a less considerable difference in the resonance of prebridge protons (H^1 and H^4), and a signal of H^{6n} proton significantly shifted to the strong field as compared to isomer **13** (0.80 and 1.10 ppm). The differences in ^{13}C NMR spectra originate mostly from the positions of the signals of C^3, C^6, and C^8 atoms (52.1 and 48.8, 32.2 and 29.5, 48.2 and 44.9 ppm for compound **13** and **20**, respectively), which are closest to the C^5 atom bearing a substituent with sulfonamide group.



R=C_6H_{11} (**20**), CF_3 (**21**), n-C_4F_9 (**22**), CH_3 (**23**), n-C_3H_7 (**24**), n-C_4H_9 (**25**), $CH_2C_6H_5$ (**26**)

3. Quantum-chemical calculations

Formation of azabrendanes during the interaction of *endo*-sulfonamides with peroxy acids may proceed with or without formation of an epoxide as an intermediate compound. Recently, we have shown that the oxygen-transfer step for the reaction of olefins with peroxy acids is followed by very fast proton-transfer and epoxy ring closure step.[20] Detailed analysis of the potential energy surface (PES) of *endo*-amine **3b** interaction with peroxyacetic acid at the UBHandHLYP/6-31G(d) level of theory showed that there is no pathway on the PES, which corresponds to the formation of the azabrendane before epoxy ring closure. Thus, we conclude that formation of azabrendanes is a step-wise process, which includes formation of the corresponding epoxide and its intramolecular opening by a nitrogen-containing substituent.

We have performed quantum-chemical study of the ability to heterocyclization of two groups of epoxides viz., the ones that are unable to form azabrendane systems (compound **20** based on the data from the current study and epoxides **21**, **22** from our recent investigations[4]) and those, for which heterocyclization was revealed to be typical **23**–**26**. Since interaction of peroxy acids with olefins results in the formation of an intermolecular complex 'epoxide–acid', a molecule of formic acid was explicitly considered modeling the electrophilic activation of epoxidic ring. In order to take into account the specific solvation of sulfonamides, one molecule of solvent (ethyl acetate) was considered forming H-bond H_{10}–O_{11}.

Calculations were performed at the BHandHLYP/6-31G(d) level of theory[21] using the Gaussian 03 package.[22] The geometry of transition states and prereaction complexes for the aforedescribed model has been fully optimized in vacuo and the transition states were verified to have only one imaginary frequency vibrational mode that connects the reactant and products. The influence of polar solvent on the activation barrier has been estimated in the framework of the SCRF model[23] at the same level of the theory for optimized in vacuo geometry. A dielectric constant (ε=6.02), which formally corresponds to the bulk of ethyl acetate has been used.

According to the calculations (Table 1), *n*-perfluorobutyl-(**22**) and trifluoromethyl-(**21**) derivatives are characterized by the highest values of activation energy due to high electron withdrawing ability of the substituent, which decreases the nucleophilic ability of the attacking amino group.

Table 1. Selected geometric parameters of transition states for heterocyclization reaction of sulfonamide **20**–**26** (Å, °) and corresponding values of activation energy (ΔE_{act}, kJ/mol), calculated at SCRF-BHandHLYP/6-31G(d)//BHandHLYP/6-31G(d) level of theory

Compound	Bond lengths (Å)				Angles (°)			ΔE_{act}
	O^8H^9	$H^{10}O^{11}$	O^8C^3	C^3N	O^8C^3N	$O^8C^2C^3$	$O^8C^2C^3N$	
20	1.386	1.872	2.083	1.986	151.72	92.77	154.76	140.30
21	1.403	1.763	2.142	1.900	149.92	95.94	152.95	167.20
22	1.347	1.788	2.137	1.929	149.45	95.60	152.98	169.24
23	1.388	1.856	2.079	1.978	151.75	92.58	154.96	133.18
24	1.385	1.854	2.077	1.985	151.74	92.43	154.99	126.63
25	1.386	1.851	2.076	1.985	151.96	92.37	155.12	130.30
26	1.388	1.859	2.076	1.982	151.97	92.43	155.11	130.22

A higher activation barrier for the heterocyclization of cyclohexylsulfonamide **20** compared to compounds **23**–**26** is primarily a result of a steric factor effect. An important role of the latter is determined by the structure of the substrate, in which the attack of the nitrogen atom bearing a bulky cyclohexyl substituent is hindered by a negligible effective size of the rear area of the bicyclic skeleton containing the substituent. Acyclic alkyl derivatives are characterized by rather close values of activation barriers, which prove the closeness of +I-inductive effects for different alkyl substituents.

The calculated values of activation energy for sulfonamides **20**–**26** are in agreement with experimental data, which shows that compounds **20**–**22** are not subjected to the heterocyclization, while derivatives **23**–**26** are easily converted into azabrendanes. Thus, this theoretical model could be used to predict the ability of *endo*-substituted derivatives of epoxynorbornane to heterocyclization.

4. Experimental section

4.1. General

All solvents for reactions were dried and distilled immediately prior to use. Melting points were determined in capillary tubes and are uncorrected. Infrared spectra were recorded on a Specord 75-IR spectrometer using KBr pellets. ^{1}H NMR spectra were recorded at 300 and 400 MHz, and ^{13}C NMR spectra were recorded at 100.6 MHz on Varian and Bruker spectrometers. Chemical shifts are reported in parts per million relative to TMS in $CDCl_3$. For thin-layer chromatographic (TLC) analysis, TLC plates (Silufol UV-254) were used with ether as an eluant and iodine vapor as a developer. Elemental analyses were carried out on a Carlo Erba analyzer.

The synthesis of the unsaturated amines **3a**, **3b** were performed by the methods described in the literature[7] and the yields were 96 and 74%, respectively.

4.2. General procedure for the synthesis of sulfonamides 4a, 4b–8a, 8b

A solution of the corresponding sulfonyl chloride (0.01 mol) in 10 mL of dry ether was added by drops under stirring to the solution of amine **3a** or **3b** (0.01 mol) and triethylamine (0.01 mol) in 10 mL of dry ether. The completion of reaction was monitored by TLC. Formed salt was filtered out, organic layer was washed with water, dried with calcinated magnesium sulfate, solvent was removed, and product was purified by distillation or crystallization from benzene or 2-propanol.

4.2.1. *N*-(Methylsulfonyl)-*exo*-5-aminomethylbicyclo-[2.2.1]hept-2-ene (4a). Colorless liquid; bp 175–176 °C/6 mm Hg; n_D^{20} 1.4986; 1.95 g (97%) yield. Found: C, 53.74; H, 7.55; N, 6.87. $C_9H_{15}NO_2S$ requires: C, 53.73; H, 7.46; N, 6.97%. IR: 3350, 3038, 1658, 1464, 1324, 1138, 704. δ_H 6.07 (2H, m, 2-CH, 3-CH), 4.73 (1H, m, NH), 3.16 (1H, dd, *J* 12.3, 7.3 Hz, 8-CH^a), 3.08 (1H, dd, *J* 12.3, 6.3 Hz, 8-CH^b), 2.94 (3H, s, CH_3), 2.84 (1H, m, 1-CH), 2.67 (1H, m, 4-CH), 1.58 (1H, m, 5-CH), 1.42 (1H, m, 7a-CH_2), 1.29 (1H, d, *J* 11.7 Hz, 6x-CH_2), 1.26 (1H, m, 7s-CH_2), 1.15 (1H, d, *J* 11.7 Hz, 6n-CH_2). δ_C 138.1 (2-CH), 137.3 (3-CH), 49.5 (CH_3), 45.9 (8-CH_2), 45.0 (7-CH_2), 42.7 (4-CH), 41.1 (1-CH), 40.4 (5-CH), 31.8 (6-CH_2).

4.2.2. *N*-(Methylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (4b). White solid; mp 64–65 °C; 1.95 g (97%) yield. Found: C, 53.76; H, 6.91; N, 6.89. $C_9H_{15}NO_2S$ requires: C, 53.73; H, 7.46; N, 6.97%. IR (KBr): 3356, 3038, 1662, 1464, 1326, 1148, 720. δ_H 6.16 (1H, dd, *J* 5.7, 3.1 Hz, 2-CH), 5.93 (1H, dd, *J* 5.7, 2.9 Hz, 3-CH), 4.48 (1H, m, NH), 2.91 (3H, s, CH_3), 2.90 (1H, m, 8-CH^a), 2.87 (1H, m, 1-CH), 2.80 (1H, m, 4-CH), 2.74 (1H, m, 8-CH^b), 2.25 (1H, m, 5-CH), 1.86 (1H, ddd, *J* 11.7, 8.0, 3.9 Hz, 6x-CH_2), 1.46 (1H, d, *J* 8.3 Hz, 7s-CH_2), 1.25 (1H, d, *J* 8.3 Hz, 7a-CH_2), 0.54 (1H, ddd, *J* 11.7, 4.4, 2.9 Hz, 6n-CH_2). δ_C 138.1 (2-CH), 131.6 (3-CH), 49.5 (CH_3), 47.3 (7-CH_2), 44.0 (4-CH), 42.4 (8-CH_2), 40.0 (1-CH), 39.3 (5-CH), 30.1 (6-CH_2).

4.2.3. *N*-(*n*-Propylsulfonyl)-*exo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (5a). White solid; mp 73–75 °C; 1.90 g (83%) yield. Found: C, 57.65; H, 8.40; N, 6.07. $C_{11}H_{19}NO_2S$ requires: C, 57.64; H, 8.30; N, 6.11%. IR (KBr): 3256, 3038, 1464, 1314, 1130, 704. δ_H 6.06 (2H, m, 2-CH, 3-CH), 4.70 (1H, m, NH), 3.14 (1H, dd, *J* 12.3, 7.2 Hz, 8-CH^a), 3.06 (1H, dd, *J* 12.3, 6.3 Hz, 8-CH^b), 2.93 (2H, t, *J* 6.6 Hz, CH_2), 2.83 (1H, m, 1-CH), 2.64 (1H, m, 4-CH), 1.80 (2H, m, CH_2), 1.57 (1H, m, 5-CH), 1.41 (1H, m, 7a-CH_2), 1.28 (1H, d, *J* 11.5 Hz, 6x-CH_2), 1.26 (1H, m, 7s-CH_2), 1.14 (1H, d, *J* 11.5 Hz, 6n-CH_2), 1.01 (3H, t, *J* 7.5 Hz, CH_3).

4.2.4. *N*-(*n*-Propylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (5b). Colorless liquid; bp 155–156 °C/3 mm Hg; n_D^{20} 1.4944; 1.76 g (77%) yield. Found: C, 57.70; H, 8.32; N, 6.10. $C_{11}H_{19}NO_2S$ requires: C, 57.64; H, 8.30; N, 6.11%. IR: 3250, 3042, 1328, 1144, 720. δ_H 6.18 (1H, dd, *J* 5.6, 3.1 Hz, 2-CH), 5.92 (1H, dd, *J* 5.6, 2.9 Hz, 3-CH), 4.56 (1H, m, NH), 2.94 (2H, m, CH_2), 2.93 (1H, m, 8-CH^a), 2.86 (1H, m, 1-CH), 2.80 (1H, m, 4-CH), 2.73 (1H, m, 8-CH^b), 2.22 (1H, m, 5-CH), 1.86 (1H, ddd, *J* 11.7, 8.2, 4.0 Hz, 6x-CH_2), 1.80 (2H, m, CH_2), 1.45 (1H, d, *J* 8.3 Hz, 7s-CH_2), 1.23 (1H, d, *J* 8.3 Hz, 7a-CH_2), 1.04 (3H, t, *J* 7.4 Hz, CH_3), 0.52 (1H, ddd, *J* 11.7, 4.4, 2.7 Hz, 6n-CH_2).

4.2.5. *N*-(*n*-Butylsulfonyl)-*exo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (6a). White solid; mp 64–65 °C; 1.80 g (74%) yield. Found: C, 59.27; H, 8.74; N, 5.71. $C_{12}H_{21}NO_2S$ requires: C, 59.26; H, 8.64; N, 5.76%. IR (KBr): 3256, 3044, 1464, 1304, 1146, 708. δ_H 6.06 (2H, m, 2-CH, 3-CH), 4.67 (1H, m, NH), 3.13 (1H, dd, *J* 12.5, 7.0 Hz, 8-CH^a), 3.06 (1H, dd, *J* 12.5, 6.1 Hz, 8-CH^b), 2.96 (2H, t, *J* 6.4 Hz, CH_2), 2.85 (1H, m, 1-CH), 2.67 (1H, m, 4-CH), 2.28 (2H, m, CH_2), 1.88 (2H, m, CH_2), 1.60 (1H, m, 5-CH), 1.42 (1H, m, 7a-CH_2), 1.29 (1H, d, *J* 11.3 Hz, 6x-CH_2), 1.27 (1H, m, 7s-CH_2), 1.12 (1H, d, *J* 11.3 Hz, 6n-CH_2), 1.08 (3H, t, *J* 7.3 Hz, CH_3).

4.2.6. *N*-(*n*-Butylsulfonyl)-*endo*-5-aminomethylbicyclo-[2.2.1]hept-2-ene (6b). Colorless liquid; bp 163–164 °C/3 mm Hg; n_D^{20} 1.4956; 1.70 g (70%) yield. Found: C, 59.35;

H, 8.68; N, 5.80. $C_{12}H_{21}NO_2S$ requires: C, 59.26; H, 8.64; N, 5.76%. IR: 3256, 3044, 1464, 1312, 1142, 720. δ_H 6.12 (1H, dd, *J* 5.7, 3.0 Hz, 2-CH), 5.91 (1H, dd, *J* 5.7, 2.8 Hz, 3-CH), 4.57 (1H, m, NH), 3.00 (2H, t, *J* 6.5 Hz, CH_2), 2.92 (1H, m, 8-CH[a]), 2.86 (1H, m, 1-CH), 2.80 (1H, m, 4-CH), 2.76 (1H, m, 8-CH[b]), 2.32 (2H, m, CH_2), 2.25 (1H, m, 5-CH), 1.88 (1H, ddd, *J* 11.7, 8.1, 4.0 Hz, 6x-CH_2), 1.80 (2H, m, CH_2), 1.46 (1H, d, *J* 8.0 Hz, 7s-CH_2), 1.23 (1H, d, *J* 8.0 Hz, 7a-CH_2), 1.04 (3H, t, *J* 7.5 Hz, CH_3), 0.52 (1H, ddd, *J* 11.7, 4.2, 2.7 Hz, 6n-CH_2).

4.2.7. *N*-(*n*-Benzylsulfonyl)-*exo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (7a). White solid; mp 103–104 °C; 2.35 g (85%) yield. Found: C, 64.90; H, 6.71; N, 5.13. $C_{15}H_{19}NO_2S$ requires: C, 64.98; H, 6.86; N, 5.05%. IR (KBr): 3336, 3256, 3072, 1608, 1504, 1320, 1171, 696. δ_H 7.37 (5H, m, ArH), 6.03 (2H, m, 2-CH, 3-CH), 4.26 (1H, m, NH), 4.23 (2H, m, CH_2Ph), 3.01 (1H, dd, *J* 12.5, 6.4 Hz, 8-CH[a]), 2.91 (1H, dd, *J* 12.5, 6.0 Hz, 8-CH[b]), 2.79 (1H, m, 1-CH), 2.57 (1H, m, 4-CH), 1.47 (1H, m, 5-CH), 1.32 (1H, d, *J* 8.6 Hz, 7a-CH_2), 1.23 (1H, ddd, *J* 11.7, 8.4, 2.3 Hz, 6x-CH_2), 1.20 (1H, d, *J* 8.6 Hz, 7s-CH_2), 1.05 (1H, dd, *J* 11.7, 3.9 Hz, 6n-CH_2).

4.2.8. *N*-(*n*-Benzylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (7b). White solid; mp 91–92 °C; 2.66 g (96%) yield. Found: C, 64.90; H, 6.79; N, 5.13. $C_{15}H_{19}NO_2S$ requires: C, 64.98; H, 6.86; N, 5.05%. IR (KBr): 3328, 3269, 3050, 1604, 1504, 1320, 1168, 720. δ_H 7.39 (5H, m, ArH), 6.17 (1H, dd, *J* 5.4, 3.0 Hz, 2-CH), 5.88 (1H, dd, *J* 5.4, 2.4 Hz, 3-CH), 4.23 (2H, m, CH_2Ph), 4.11 (1H, m, NH), 2.81 (1H, m, 1-CH), 2.79 (1H, m, 4-CH), 2.71 (1H, dd, *J* 12.3, 6.0 Hz, 8-CH[a]), 2.68 (1H, dd, *J* 12.3, 5.7 Hz, 8-CH[b]), 2.17 (1H, m, 5-CH), 1.82 (1H, dd, *J* 11.7, 9.3, 3.9 Hz, 6x-CH_2), 1.48 (1H, dd, *J* 8.1 Hz, 7s-CH_2), 1.24 (1H, dd, *J* 8.1 Hz, 7a-CH_2), 0.49 (1H, dd, *J* 11.7, 4.2, 2.7 Hz, 6n-CH_2).

4.2.9. *N*-(Cyclohexylsulfonyl)-*exo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (8a). White solid; mp 104–105 °C; 1.80 g (67%) yield. Found: C, 62.44; H, 8.68; N, 5.07. $C_{14}H_{23}NO_2S$ requires: C, 62.45; H, 8.55; N, 5.20%. IR (KBr): 3236, 3038, 1314, 1134, 704. δ_H 6.03 (2H, m, 2-CH, 3-CH), 4.17 (1H, m, NH), 3.15 (1H, dd, *J* 12.7, 7.0 Hz, 8-CH[a]), 3.07 (1H, dd, *J* 12.7, 6.2 Hz, 8-CH[b]), 2.82 (1H, m, 1-CH), 2.66 (1H, m, 4-CH), 1.55 (1H, m, 5-CH), 1.35 (1H, d, *J* 8.3 Hz, 7a-CH_2), 1.27 (1H, d, *J* 11.7 Hz, 6x-CH_2), 1.27 (1H, d, *J* 8.3 Hz, 7s-CH_2), 1.13 (1H, dd, *J* 11.7, 3.9 Hz, 6n-CH_2). δ_C 137.0 (2-CH), 136.1 (3-CH), 61.4 ($CH_{cyclohexyl}$), 48.9 (8-CH_2), 45.0 (7-CH_2), 44.1 (4-CH), 41.7 (1-CH), 40.0 (5-CH), 30.9 (6-CH_2), 26.5 (2×$CH_{2\ cyclohexyl}$), 25.2 (3×$CH_{2\ cyclohexyl}$).

4.2.10. *N*-(Cyclohexylsulfonyl)-*endo*-5-aminomethylbicyclo[2.2.1]hept-2-ene (8b). White solid; mp 95.5–97 °C; 2.04 g (76%) yield. Found: C, 62.32; H, 8.64; N, 5.21. $C_{14}H_{23}NO_2S$ requires: C, 62.45; H, 8.55; N, 5.20%. IR (KBr): 3252, 3034, 1320, 1142, 716. δ_H 6.16 (1H, dd, *J* 5.7, 3.1 Hz, 2-CH), 5.92 (1H, dd, *J* 5.7, 2.7 Hz, 3-CH), 3.97 (1H, m, NH), 2.87 (1H, m, 1-CH), 2.85 (1H, m, 4-CH), 2.84 (1H, m, 8-CH[a]), 2.72 (1H, m, 8-CH[b]), 2.17 (1H, m, 5-CH), 1.84 (1H, dd, *J* 11.5, 3.9 Hz, 6x-CH_2), 1.45 (1H, d, *J* 8.2 Hz, 7s-CH_2), 1.25 (1H, d, *J* 8.2 Hz, 7a-CH_2), 0.53 (1H, ddd, *J* 11.5, 4.3, 2.5 Hz, 6n-CH_2). δ_C 138.2 (2-CH), 131.7 (3-CH), 61.1 ($CH_{cyclohexyl}$), 49.5 (7-CH_2), 47.6 (8-CH_2), 44.0 (4-CH), 42.3 (1-CH), 39.8 (5-CH), 30.0 (6-CH_2), 26.4 (2×$CH_{2\ cyclohexyl}$), 25.1 (3×$CH_{2\ cyclohexyl}$).

4.3. General procedure for epoxidation of stereoisomeric sulfonamides (4a, 4b–8a, 8b)

Method A: to a stirred mixture of olefin (2 mmol), sodium hydrocarbonate (4 mmol), and acetic anhydride (4 mmol) in 25 mL of chloroform a 50% hydrogen peroxide solution (4 mmol) was added gradually. Termination of the reaction was determined by TLC monitoring. Formed acetic acid was neutralized with sodium carbonate saturated aqueous solution till pH 7–8. Organic layer was separated and aqueous layer was extracted with chloroform three times. Combined organic layer was dried with calcinated magnesium sulfate and then solvent was removed.

Method B: a mixture of the olefin (2 mmol), carbamide (1 mmol), and 75% monoperoxyphthalic acid (4 mmol) in ethyl acetate (20 mL) was stirred at room temperature. Termination of the reaction was determined by TLC monitoring. After neutralization of the reaction mixture by a saturated solution of sodium hydrocarbonate, the organic layer was collected and dried with calcinated magnesium sulfate, and the solvent was removed by distillation.

Method C: to a stirred mixture of the olefin (2 mmol), well-grinded phthalic anhydride (4 mmol), and carbamide (1 mmol) in ethyl acetate (20 mL), a 50% hydrogen peroxide solution (4 mmol) was added gradually. Termination of the reaction was determined by TLC monitoring. After the usual treatment, the organic layer was isolated and dried with calcinated magnesium sulfate, and the solvent was removed.

Method D: to a stirred mixture of the olefin (2 mmol) in 20 mL of chloroform, a 75% *m*-chloroperoxybenzoic acid (2 mmol) was added. Termination of the reaction was determined by TLC monitoring. Then, the reaction mixture was treated by the way analogous to method B.

4.3.1. *N*-(Methylsulfonyl)-*exo*-5-aminomethyl-*exo*-2,3-epoxybicyclo[2.2.1]heptane (10). White solid; mp 89–90 °C; 0.40 g (92%) (method A) yield. Found: C, 49.70; H, 6.94; N, 6.40. $C_9H_{15}NO_3S$ requires: C, 49.78; H, 6.91; N, 6.45%. IR (KBr): 3286, 3024, 1447, 1321, 1158, 845. δ_H 5.27 (1H, m, NH), 3.13 (2H, m, 2-CH, 3-CH), 3.00 (1H, m, 8-CH[a]), 2.96 (3H, s, CH_3), 2.94 (1H, m, 8-CH[b]), 2.48 (1H, m, 1-CH), 2.43 (1H, m, 4-CH), 1.75 (1H, m, 5-CH), 1.53 (1H, ddd, *J* 12.2, 5.7, 1.7 Hz, 6x-CH_2), 1.28 (1H, d, *J* 10.0 Hz, 7s-CH_2), 1.14 (1H, dd, *J* 12.2, 4.0 Hz, 6n-CH_2), 0.83 (1H, d, *J* 10.0 Hz, 7a-CH_2).

4.3.2. *N*-(*n*-Propylsulfonyl)-*exo*-5-aminomethyl-*exo*-2,3-epoxybicyclo[2.2.1]heptane (11). White solid; mp 90–91.5 °C; 0.46 g (95%) (method C) yield. Found: C, 53.80; H, 7.94; N, 5.66. $C_{11}H_{19}NO_3S$ requires: C, 53.88; H, 7.76; N, 5.71%. IR (KBr): 3028, 1465, 1323, 1292, 1157, 1072, 848. δ_H 4.58 (1H, m, NH), 3.08 (1H, d, *J* 3.6 Hz, 2-CH), 3.06 (1H, d, *J* 3.6 Hz, 3-CH), 3.02 (1H, m, 8-CH[a]), 3.00 (1H, m, 8-CH[b]), 2.95 (2H, t, *J* 6.7 Hz, CH_2), 2.45 (1H, m,

1-CH), 2.38 (1H, m, 4-CH), 1.81 (2H, m, CH_2), 1.69 (1H, m, 5-CH), 1.50 (1H, ddd, *J* 12.7, 8.3, 2.3 Hz, 6x-CH_2), 1.27 (1H, d, *J* 10.4 Hz, 7s-CH_2), 1.10 (1H, dd, *J* 12.7, 4.1 Hz, 6n-CH_2), 1.04 (3H, t, *J* 7.5 Hz, CH_3), 0.78 (1H, d, *J* 10.4 Hz, 7a-CH_2). δ_C 54.4 (CH_2), 51.6 (2-CH), 51.1 (3-CH), 46.9 (8-CH_2), 39.5 (4-CH), 39.0 (1-CH), 37.0 (5-CH), 31.3 (6-CH_2), 23.3 (7-CH_2), 17.4 (CH_2), 12.9 (CH_3).

4.3.3. *N*-(Benzylsulfonyl)-*exo*-5-aminomethyl-*exo*-2,3-epoxybicyclo[2.2.1]heptane (12). White solid; mp 95.5–96.5 °C; 0.56 g (96%) (method D) yield. Found: C, 61.47; H, 6.49; N, 4.82. $C_{15}H_{19}NO_3S$ requires: C, 61.43; H, 6.48; N, 4.78%. IR (KBr): 3320, 3280, 3030, 1600, 1510, 1450, 1328, 1136, 848. δ_H 7.35 (5H, m, ArH), 4.45 (1H, m, NH), 4.21 (2H, m, CH_2Ph), 3.05 (1H, d, *J* 3.5 Hz, 2-CH), 3.00 (1H, d, *J* 3.5 Hz, 3-CH), 2.79 (1H, m, 8-CH^a), 2.77 (1H, m, 8-CH^b), 2.41 (1H, m, 1-CH), 2.28 (1H, m, 4-CH), 1.57 (1H, m, 5-CH), 1.42 (1H, ddd, *J* 12.7, 8.4, 2.4 Hz, 6x-CH_2), 1.22 (1H, d, *J* 10.4 Hz, 7s-CH_2), 1.00 (1H, dd, *J* 12.7, 4.1 Hz, 6n-CH_2), 0.68 (1H, d, *J* 10.4 Hz, 7a-CH_2). δ_C 131.7, 130.0, 129.9, 129.4 (4×ArCH), 59.8 (CH_2Ph), 52.6 (2-CH), 52.1 (3-CH), 48.2 (8-CH_2), 40.3 (4-CH), 39.9 (1-CH), 37.9 (5-CH), 32.0 (6-CH_2), 24.1 (7-CH_2).

4.3.4. *N*-(Cyclohexylsulfonyl)-*exo*-5-aminomethyl-*exo*-2,3-epoxybicyclo[2.2.1]heptane (13). White solid; mp 98–99.5 °C; 0.50 g (88%) (method C) yield. Found: C, 58.81; H, 8.06; N, 4.85. $C_{14}H_{23}NO_3S$ requires: C, 58.95; H, 8.07; N, 4.91%. IR (KBr): 3315, 3260, 3030, 1512, 1452, 1328, 1136, 846. δ_H 4.31 (1H, m, NH), 3.09 (1H, d, *J* 3.7 Hz, 2-CH), 3.07 (1H, d, *J* 3.7 Hz, 3-CH), 2.98 (1H, m, 8-CH^a), 2.97 (1H, m, 8-CH^b), 2.45 (1H, m, 1-CH), 2.38 (1H, m, 4-CH), 1.70 (1H, m, 5-CH), 1.50 (1H, ddd, *J* 12.5, 8.2, 2.3 Hz, 6x-CH_2), 1.25 (1H, d, *J* 10.3 Hz, 7s-CH_2), 1.10 (1H, dd, *J* 12.5, 4.3 Hz, 6n-CH_2), 0.78 (1H, d, *J* 10.3 Hz, 7a-CH_2). δ_C 62.4 ($CH_{cyclohexyl}$), 52.6 (2-CH), 52.1 (3-CH), 48.2 (8-CH_2), 40.4 (4-CH), 40.3 (1-CH), 38.0 (5-CH), 32.2 (6-CH_2), 27.4 (2×$CH_{2\ cyclohexyl}$), 26.1 (3×$CH_{2\ cyclohexyl}$), 24.2 (7-CH_2).

4.3.5. *N*-(Methylsulfonyl)-*exo*-2-hydroxy-4-azatricyclo-[4.2.1.0^{3,7}]nonane (14). White solid; mp 97–98 °C; 0.33 g (75%) (method A) yield. Found: C, 49.69; H, 6.86; N, 6.41. $C_9H_{15}NO_3S$ requires: C, 49.78; H, 6.91; N, 6.45%. IR (KBr): 3460, 1462, 1318, 1142, 1060. δ_H 3.66 (1H, s, 2-CH), 3.56 (1H, d, *J* 5.6 Hz, 3-CH), 3.32 (1H, dd, *J* 9.3, 4.2 Hz, 5-CH^a), 3.24 (1H, d, *J* 9.3 Hz, 5-CH^b), 2.92 (3H, s, CH_3), 2.60 (1H, m, 7-CH), 2.36 (1H, m, 6-CH), 2.20 (1H, m, 1-CH), 1.97 (1H, d, *J* 10.0 Hz, 8s-CH_2), 1.94 (1H, ddd, *J* 13.5, 9.7, 4.7 Hz, 9x-CH_2), 1.51 (1H, d, *J* 10.0 Hz, 8a-CH_2), 1.00 (1H, dd, *J* 13.5, 4.0 Hz, 9n-CH_2). δ_C 81.3 (2-CH), 69.2 (3-CH), 54.3 (5-CH_2), 44.8 (7-CH), 41.5 (1-CH), 36.4 (6-CH), 33.8 (9-CH_2), 32.6 (8-CH_2).

4.3.6. *N*-(*n*-Propylsulfonyl)-*exo*-2-hydroxy-4-azatricyclo-[4.2.1.0^{3,7}]nonane (15). Colorless liquid; mp 116–118 °C/6 mm Hg; 0.46 g (94%) (method C) yield. Found: C, 53.78; H, 7.85; N, 5.64. $C_{11}H_{19}NO_3S$ requires: C, 53.88; H, 7.76; N, 5.71%. IR: 3462, 1326, 1144, 1064. δ_H 3.65 (1H, s, 2-CH), 3.55 (1H, d, *J* 5.1 Hz, 3-CH), 3.31 (1H, dd, *J* 9.0, 4.5 Hz, 5-CH^a), 3.23 (1H, d, *J* 9.0 Hz, 5-CH^b), 2.95 (2H, t, *J* 6.5 Hz, CH_2), 2.58 (1H, m, 7-CH), 2.34 (1H, m, 6-CH), 2.16 (1H, m, 1-CH), 1.92 (1H, d, *J* 10.7 Hz, 8s-CH_2), 1.90 (1H, ddd, *J* 13.3, 9.7, 4.7 Hz, 9x-CH_2), 1.82 (2H, m, CH_2), 1.43 (1H, d, *J* 10.7 Hz, 8a-CH_2), 1.03 (3H, t, *J* 7.4 Hz, CH_3), 0.97 (1H, dd, *J* 13.3, 2.3 Hz, 9*n*-CH_2). δ_C 81.4 (2-CH), 69.4 (3-CH), 54.3 (CH_2), 52.4 (5-CH_2), 45.0 (7-CH), 41.4 (1-CH), 36.9 (6-CH), 33.7 (9-CH_2), 32.8 (8-CH_2), 17.0 (CH_2), 12.9 (CH_3).

4.3.7. *N*-(*n*-Butylsulfonyl)-*exo*-2-hydroxy-4-azatricyclo-[4.2.1.0^{3,7}]nonane (16). White solid; mp 104–106 °C; 0.48 g (93%) (method C) yield. Found: C, 55.68; H, 8.06; N, 5.42. $C_{12}H_{21}NO_3S$ requires: C, 55.60; H, 8.11; N, 5.40%. IR (KBr): 3460, 1466, 1313, 1148, 1066, 1017. δ_H 3.67 (1H, s, 2-CH), 3.54 (1H, d, *J* 5.3 Hz, 3-CH), 3.29 (1H, dd, *J* 9.2, 4.6 Hz, 5-CH^a), 3.28 (1H, d, *J* 9.2 Hz, 5-CH^b), 2.82 (2H, t, *J* 6.4 Hz, CH_2), 2.57 (1H, m, 7-CH), 2.36 (1H, m, 6-CH), 2.24 (2H, m, CH_2), 2.16 (1H, m, 1-CH), 1.94 (1H, d, *J* 10.7 Hz, 8s-CH_2), 1.90 (1H, ddd, *J* 13.1, 9.7, 4.9 Hz, 9x-CH_2), 1.43 (1H, d, *J* 10.7 Hz, 8a-CH_2), 1.09 (3H, t, *J* 7.3 Hz, CH_3), 0.98 (1H, dd, *J* 13.1, 2.3 Hz, 9n-CH_2). δ_C 81.4 (2-CH), 69.3 (3-CH), 57.8 (CH_2), 54.1 (5-CH_2), 45.0 (7-CH), 41.4 (1-CH), 36.9 (6-CH), 33.7 (9-CH_2), 32.8 (8-CH_2), 29.6 (CH_2), 22.5 (CH_3).

4.3.8. *N*-(Benzylsulfonyl)-*exo*-2-hydroxy-4-azatricyclo-[4.2.1.0^{3,7}]nonane (17). White solid; mp 65–66 °C; 0.56 g (96%) (method C) yield. Found: C, 61.48; H, 6.63; N, 4.81. $C_{15}H_{19}NO_3S$ requires: C, 61.43; H, 6.48; N, 4.78%. IR (KBr): 3460, 1474, 1442, 1340, 1158. δ_H 7.38 (5H, m, ArH), 4.26 (2H, m, CH_2Ph), 3.51 (1H, s, 2-CH), 3.18 (1H, d, *J* 5.3 Hz, 3-CH), 3.12 (1H, dd, *J* 9.0, 4.6 Hz, 5-CH^a), 3.02 (1H, d, *J* 9.0 Hz, 5-CH^b), 2.42 (1H, m, 7-CH), 2.21 (1H, m, 6-CH), 2.09 (1H, m, 1-CH), 1.84 (1H, ddd, *J* 13.4, 8.5, 4.7 Hz, 9x-CH_2), 1.82 (1H, d, *J* 10.5 Hz, 8s-CH_2), 1.34 (1H, d, *J* 10.5 Hz, 8a-CH_2), 0.89 (1H, dd, *J* 13.4, 2.6 Hz, 9n-CH_2). δ_C 130.8, 129.0, 128.8 (4×ArCH), 81.5 (2-CH), 69.9 (3-CH), 54.7 (5-CH_2), 44.9 (7-CH), 41.3 (1-CH), 36.9 (6-CH), 33.6 (9-CH_2), 32.7 (8-CH_2).

4.3.9. *N*-(Cyclohexylsulfonyl)-*endo*-5-aminomethyl-*exo*-2,3-epoxybicyclo[2.2.1]heptane (20). White solid; mp 134–135 °C; 0.56 g (98%) (method A) yield. Found: C, 58.90; H, 8.07; N, 4.88. $C_{14}H_{23}NO_3S$ requires: C, 58.95; H, 8.07; N, 4.91%. IR (KBr): 3298, 3277, 1310, 1140, 1082, 847. δ_H 4.34 (1H, m, NH), 3.22 (1H, d, *J* 3.3 Hz, 2-CH), 3.13 (1H, d, *J* 3.3 Hz, 3-CH), 3.18 (1H, m, 8-CH^a), 3.08 (1H, m, 8-CH^b), 2.53 (1H, m, 1-CH), 2.49 (1H, m, 4-CH), 2.11 (1H, m, 5-CH), 1.76 (1H, ddd, *J* 12.7, 10.2, 4.3 Hz, 6x-CH_2), 1.22 (1H, d, *J* 10.4 Hz, 7s-CH_2), 0.80 (1H, dd, *J* 12.7, 2.5 Hz, 6n-CH_2), 0.78 (1H, d, *J* 10.4 Hz, 7a-CH_2). δ_C 62.04 ($CH_{cyclohexyl}$), 51.0 (2-CH), 48.8 (3-CH), 44.9 (8-CH_2), 41.9 (4-CH), 38.1 (1-CH), 37.2 (5-CH), 29.5 (6-CH_2), 27.2 (2×$CH_{2\ cyclohexyl}$), 26.6 (3×$CH_{2\ cyclohexyl}$), 25.0 (7-CH_2).

Crystal data for **20**: the crystals of $C_{14}H_{23}NO_3S$ are monoclinic. At 293 K a=11.803(3), b=6.292(2), c=20.125(7) Å, β=91.05(3)°, V=1494.3(8) Å^3, space group $P2(1)/c$, Z=4, D_c=1.269 g/cm^3, μ=0.221 mm^{-1}, $F(000)$=616. Intensity of 4533 reflections (4343 independent, R_{int}=0.07) was measured on an automatic four-circles Siemens P3/PC diffractometer (graphite monochromated Mo Kα radiation, $\theta/2\theta$ scanning, $2\theta_{max}$=60°). The structure was solved by direct method using SHELXTL PLUS

package.[24] Position of hydrogen atoms was calculated geometrically and refined using 'riding' model with fixed $U_{iso}=1.2U_{eq}$ of non-hydrogen atoms connected with respective H atom. Disordered part of structure was refined with all the O–C and C–C bonds restrained to 1.410(5) and 1.540(5) Å, respectively. Full-matrix least-squares refinement against F^2 (190 parameters) in anisotropic approximation using 4343 reflections was converted to $wR2=0.250$ ($R1=0.103$ for 1450 reflections with $F>4\sigma(F)$, $S=1.355$). Atomic coordinates and crystallographic parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 629019).

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