Synthesis of α-amino oximes and bis-α-amino oximes from the monoterpene hydrocarbons 3-carene and α-pinene and α,ω-diamines

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The reaction of nitroso chlorides of natural monoterpene hydrocarbons, 3-carene and α-pinene, with simple α,ω-diamines (1,2-diaminoethane, 1,3-diaminopropane, piperazine, 1,6-diaminohexane, diethylenetriamine) results in the formation of α-amino oximes and bis-α-amino oximes. The product structures were proved by spectroscopy. The procedures of separation and purification of diamino oximes and diamino dioximes are described. Detailed analysis of the ^{1}H and ^{13}C NMR spectra of the new chiral nitrogen-containing derivatives was carried out.

Key words: monoterpenoids, 3-carene, α-pinene, nitroso chlorides, α-amino oximes, bis-α-amino oximes, 1,2-diaminoethane, 1,3-diaminopropane, piperazine, 1,6-diaminohexane, diethylenetriamine, ^{1}H and ^{13}C NMR.

Diamino dioximes (bis-α-amino oximes) with various substituents represent a rather interesting class of compound vigorously studied in recent years. Suffice it to mention that diamino dioxime complexes with ^{99}Th are used in radiomedicine[1] and that they can be cross-linked at the oxime groups under phase transfer catalysis conditions to give a new group of polyheteroatomic macrocyclic compounds.[2] In this work, we describe a simple and efficient method for the preparation of a number of α-amino oximes from unsaturated monoterpene hydrocarbons, namely, 3-carene (**1**) and α-pinene (**2**), using the nitroso chlorides obtained from these hydrocarbons as the key intermediates, and give examples of transformation of readily available natural terpenes into new chiral polyfunctional nitrogen derivatives.

The reaction of terpene nitroso chlorides with simple amines resulting in α-amino oximes has been thoroughly studied for a large number of substrates.[3] However, the reactions of terpene nitroso chlorides with diamines have not been studied except for the reactions with aromatic 1,2-diamines giving rise to tetrahydrophenazine derivatives.[4]

It was found that, unlike aromatic diamines, aliphatic and saturated heterocyclic α,ω-diamines such as ethylenediamine, 1,3-diaminopropane, piperazine, hexamethylenediamine, and diethylenetriamine do not undergo intramolecular condensation to give heterocyclic structures when react with terpene nitroso chlorides **3** and **4** but give instead two types of products, diamino monooximes (α-amino oximes) **5—10** and diamino dioximes (dioximes of diamino diketones, bis-α-amino oximes) **11—18** (Scheme 1). Like simple amines,[5] α,ω-diamines always react stereoselectively with terpene nitroso chlorides to give only one stereoisomer with retained configuration of the atom at which the substitution of the amino group for the chlorine atom takes place and with *E*-configuration of the oxime group; this can be readily established by analysis of the ^{1}H and ^{13}C NMR spectra of the products and by comparison of the results with the previously obtained data for compounds of the 3-carene and α-pinene series.[5]

The formation of products with retained configuration of the quaternary carbon atom and with *E*-configuration of the oxime group can be interpreted (Scheme 2) taking into account the mechanism of chlorine replacement in nitroso chlorides;[3] the reaction of nitroso chlorides **3** and **4** prepared from olefins **1** and **2**, respectively, with a base (amine) results in dehydrochlorination to yield nitrosoolefins **19**, **20**, which react with an amine molecule (acting as a nucleophile) giving rise to amino oximes **5—10**. In compounds **5—10**, the configuration of the quaternary carbon atom bound to the amino group is dictated by different steric accessibilities of the *Re* and *Si* sides of the carbon—carbon double

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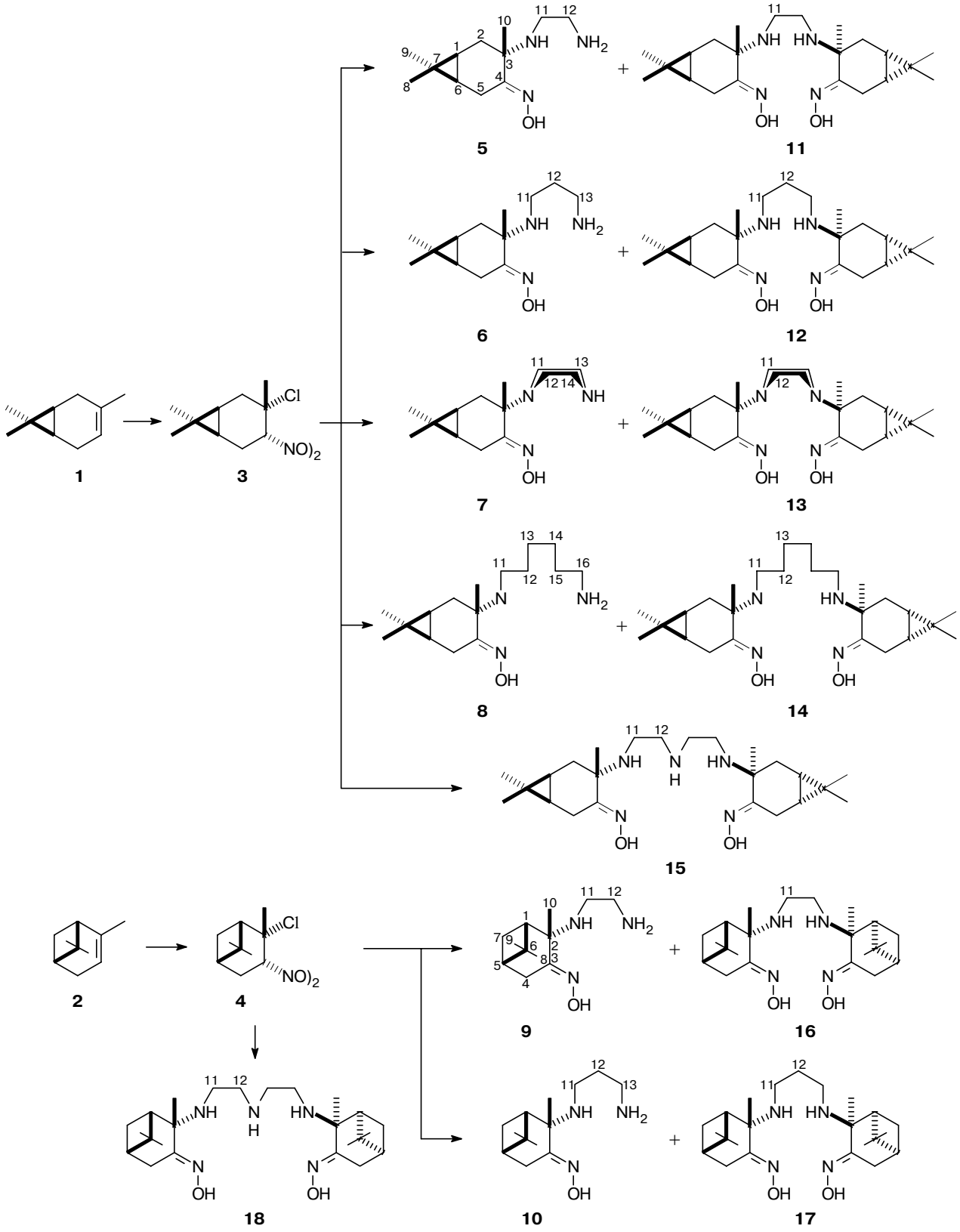
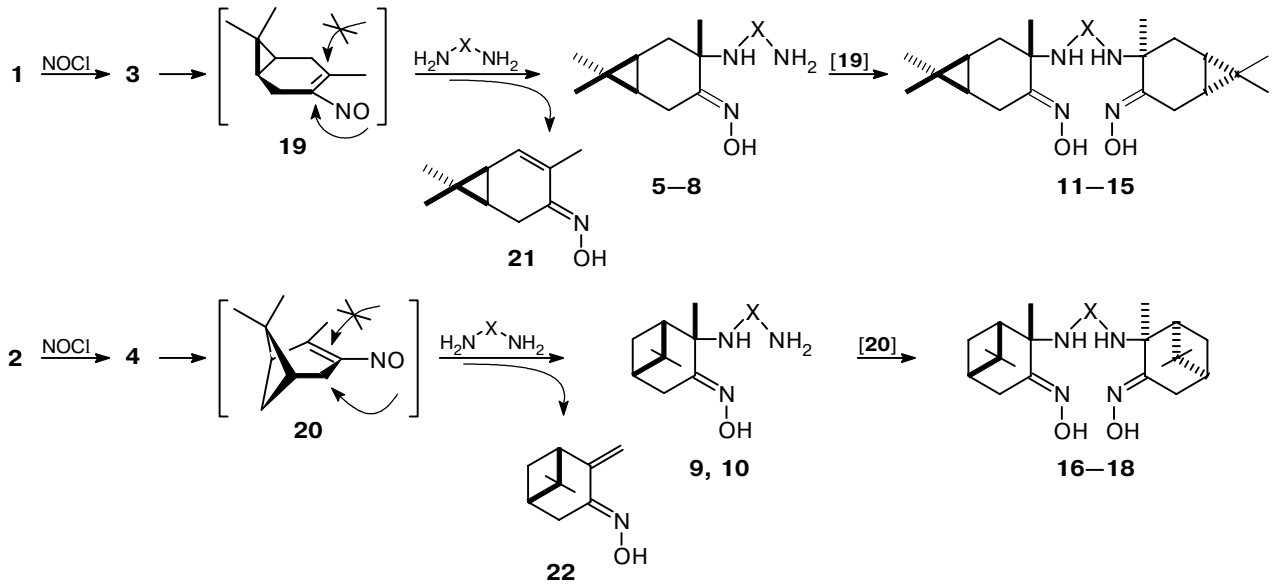
Scheme 1



Scheme 2



bonds in nitrosoolefins **19**, **20**. Stereochemically, the initial olefin **1** or **2** and the nitrosoolefin **19** or **20** produced from it are analogs; therefore, the stereochemistry of the addition of NOCl to **1** or **2** is the same as that for the amine addition to nitrosoolefins **19**, **20**; as a consequence, in the substitution of the amino group for chlorine, the configuration is retained. The *E*-configuration of the oxime group in the products **5—10** is due to the *s-trans*-conformation of the intermediate nitrosoolefin **19**, **20**, which is the most stable form in the case of tetrasubstituted C=C double bond. The side products formed in the reaction of nitroso chlorides with amines are always unsaturated oximes **21**, **22**, resulting from the reaction of nitrosoolefins **19**, **20** with amine (acting as a base), namely, 2-caren-4-one oxime (**21**) in the reactions of 3-carene nitroso chloride (**3**) and pinocarvone oxime (**22**) in the reactions of α-pinene nitroso chloride (**4**).

The reaction of nitroso chlorides with α,ω-diamines can be carried out in two variants at different nitroso chloride : diamine ratios. When a large excess of amines is used, amino oximes **5—10** are the major reaction products. If the reaction is carried out at an equimolar amine to nitroso chloride ratio, in addition to monooximes **5—10**, dioximes **11—18** are formed upon the reaction of diamine with two nitrosoolefin molecules. Monooximes and dioximes can be readily separated because their physicochemical properties are substantially different. All diamino dioximes **11—18** prepared are poorly soluble compounds and, therefore, their finely crystalline precipitates can be easily isolated by filtration from the sum of the reaction products. Conversely, diamino monooximes **5—10** are readily soluble; therefore, they are isolated and purified by extraction with an organic solvent followed by chromatography and transformation into crystalline hydrochlorides. Characteristic features of the diamino oximes **5—10** synthesized include enhanced solubility in water compared to the solubility of simple terpene α-amino oximes, hygroscopicity of their hydrochlorides, and the ability to form hydrates, most likely, due to the large number of polar groups in the molecule. Triamino oximes of this type obtained from diethylenetriamine are expected to be even more water-soluble; in this procedure, they cannot be isolated at all in noticeable amounts.

All the compounds **5—18** were synthesized from natural monoterpenes in an optically active form. The capability of forming complexes with various transition metal ions known for this type of compound opens up good prospects for further investigation of these products as chiral ligands and as the starting compounds for the synthesis of chiral polyheteroatomic macrocycles.

Experimental

All solvents: *tert*-butyl methyl ether, acetonitrile, ethyl acetate, methyl alcohol, isopropyl alcohol, pyridine, petroleum ether (b.p. 40—70 °C), and chloroform, were used freshly distilled. TLC was performed on Silufol with a fixed Silpearl silica gel layer on aluminum foil. The components were detected by spraying the plates with visualizing solutions and subsequent heating to 100—150 °C. The visualizing reagents included solutions of vanillin (1 g of vanillin + 5 mL of conc. H_2SO_4 + 100 mL of 95% EtOH), ferric chloride (10 g of $FeCl_3 \cdot 6H_2O$ + 100 mL of 95% EtOH), ninhydrin (0.5 g of ninhydrin + 3 mL of glacial AcOH + 100 mL of 95% EtOH), and concentrated H_2SO_4. Column chromatography was carried out using KSK silica gel (Russia) with a grain size of

0.10—0.20 mm dried in air and activated by heating at 140 °C for 5 h. IR spectra were measured on a Bruker Vector 22 spectrophotometer for solutions in $CHCl_3$ (*c* 1%) or KBr (*c* 0.25%). Optical rotation was measured on a Polamat A polarimeter. Melting points were determined on a Köffler stage. Microanalyses were carried out on Hewlett Packard 185 and Carlo Erba 1106 analyzers. Mass spectra were recorded on a Finnigan MAT-8200 mass spectrometer (EI, 70 eV). NMR spectra were recorded on Bruker AM-400 (400.13 MHz for ^1H and 100.61 MHz for ^{13}C) and Bruker DRX-500 (500.132 MHz for ^1H and 125.758 MHz for ^{13}C) spectrometers for solutions with a concentration of 40—100 mg mL^{-1} at 25—27 °C. The solvent signals: $CDCl_3$ (δ_C = 76.90, δ_H = 7.24), methanol-d_4 (δ_C = 49.00, δ_H = 3.35), pyridine-d_5 (δ_C = 123.50, δ_H = 7.19), and DMSO-d_6 (δ_C = 39.50, δ_H = 2.50), were used as the internal standard. The signals were assigned using ^{13}C NMR spectra recorded in the *J*-modulation mode (proton noise decoupling, the opposite phases for signals of atoms with even and odd numbers of attached protons with adjustment to the J = 135 Hz constant) using 2D $^1H—^1H$ homonuclear correlation spectra and $^{13}C—^1H$ heteronuclear correlation spectra with direct spin coupling constants (J = 135 Hz), and $^{13}C—^1H$ heteronuclear correlation for long-range spin coupling constants (J = 10 Hz).

(+)-3-Carene (**1**) with $[\alpha]_{578}^{20}$ +16.0 (d_4^{20} 0.863) was prepared by distillation of the turpentine from Scots pine (*Pinus silvestris*). Fluka (1*R*)-(+)-α-pinene (**2**) (*ee* > 96%) was used. Dimeric nitroso chlorides **3** (m.p. 101—102 °C) and **4** (108—109 °C) were prepared from (+)-3-carene (**1**) and α-pinene (**2**), respectively, using a standard procedure[3] on treatment with gaseous nitrosyl chloride in a CH_2Cl_2 solution. Ethylenediamine, 1,3-diaminopropane, piperazine, hexamethylenediamine, and diethylenetriamine (Aldrich) were used as received.

Preparation of diamino monooximes 5—10 (general procedure, reaction with excess amine). A suspension of dimeric nitroso chloride **3** or **4** (1.00 g, 2.48 mmol) in a mixture of diamine (ethylenediamine, 1,3-diaminopropane, piperazine, or hexamethylenediamine, 50 mmol) and methanol (40 mL) was stirred at 50 °C until the starting nitroso chloride dissolved. After evaporation of the solvent *in vacuo*, 3 *M* HCl (30 mL) was added to the residue, and the resulting solution was washed with $MeOBu^t$ (3×10 mL). The organic extracts were rejected and the acidic aqueous solution was treated with concentrated aqueous ammonia (15 mL). The reaction products were extracted with $MeOBu^t$ (3×10 mL) and the aqueous phase was saturated with NaCl and extracted again with $MeOBu^t$ (2×10 mL). The combined organic extract was washed with brine (20 mL) and dried with anhydrous Na_2SO_4, the solvent was removed *in vacuo*, and the residue was chromatographed (elution with EtOAc—petroleum ether) to give diamino monooximes **5—10** as colorless or slightly yellowish viscous materials. The diamino oxime hydrochlorides were prepared by triturating the product with two equivalents of concentrated HCl and the resulting crystalline material was dried *in vacuo* over P_2O_5, washed with EtOAc, and recrystallized. Yield 75—85%.

Preparation of diamino monooximes 5—10 and diamino dioximes 11—14, **16**, **17 (general procedure).** A suspension of Na_2CO_3 (0.88 g, 8.3 mmol) and nitroso chloride dimer **3** or **4** (3.35 g, 8.3 mmol) in a mixture of diamine (ethylenediamine, 1,3-diaminopropane, piperazine, or hexamethylenediamine, 9.0 mmol) and methanol (15 mL) was stirred at 50 °C until the initial nitroso chloride dissolved. After removal of the solvent *in vacuo*, 3 *M* HCl (20 mL) was added to the residue, the resulting solution was extracted with $MeOBu^t$ (3×10 mL), the organic extracts were rejected, and the aqueous phase was treated with concentrated aqueous ammonia (7 mL). The colorless crystals that precipitated were filtered off, washed on the filter with $MeOBu^t$ (3×10 mL), and dried in air to give bis-α-amino oximes **11—14**, **16**, **17** in 20—40% yield (relative to nitroso chloride).

The aqueous-ammonia filtrate was saturated with NaCl and extracted with $MeOBu^t$ (3×10 mL). The extract was washed with brine (20 mL), dried with Na_2SO_4, and concentrated *in vacuo*, and the residue was chromatographed (elution with EtOAc—petroleum ether) to give diamino monooximes **5—10** as colorless or slightly yellowish viscous materials in 30—45% yield.

(1*S*,3*S*,6*R*)-3-(2-Aminoethylamino)-4-caranone (*E*)-oxime (5). Yellow glassy material. IR ($CHCl_3$), ν/cm^{-1}: 3595 (O—H), 3430 (N—H), 3330 (N—H), 930 (=N—OH). ^1H ($CDCl_3$), δ: 0.72 (ddd, 1 H, H(1), J = 9.5, 9.0, 5.4 Hz); 0.77 (s, 3 H, H(8)); 0.86 (ddd, 1 H, H(6), J = 9.0, 8.9, 1.5 Hz); 0.98 (s, 3 H, H(10)); 1.10 (s, 3 H, H(9)); 1.32 (dd, 1 H, *pro*-*R*-H(2), J = 15.1, 5.4 Hz); 2.08 (dd, 1 H, *pro*-*S*-H(2), J = 15.1, 9.5); 2.23 (dd, 1 H, *pro*-*R*-H(5), J = 18.8, 8.9 Hz); 2.30 (m, 2 H, H(12)); 2.52 (m, 2 H, H(11)); 2.91 (dd, 1 H, *pro*-*S*-H(5), J = 18.8, 1.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.37 (C(8)), 16.35 (C(1)), 17.70 (C(7)), 18.88 (C(5)), 18.91 (C(6)), 21.96 (C(10)), 27.86 (C(9)), 34.60 (C(2)), 42.03 (C(11)), 43.05 (C(12)), 54.30 (C(3)), 161.01 (C(4)).

Dihydrochloride of compound 5: white crystals, m.p. 187—189 °C (from water); $[\alpha]_{578}^{22}$ +98.7 (*c* 1.78, MeOH). High-resolution MS, found: m/z 225.18420. $C_{12}H_{23}N_3O$. Calculated: M = 225.18410. MS, m/z (I_{rel} (%)): 225 (19), 208 (11), 195 (77), 177 (10), 166 (100), 156 (20), 143 (71), 124 (23), 107 (53), 85 (31), 55 (16), 44 (47).

***N*,*N*′-Bis-{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl}-1,2-ethylenediamine (11).** White crystals, m.p. 163.0—165.5 °C (from 10% aqueous CH_3OH), $[\alpha]_{578}^{22}$ +169 (*c* 4.63, MeOH). IR ($CHCl_3$), ν/cm^{-1}: 3640 (O—H), 945 (=N—OH). High-resolution MS, found: m/z 390.29974. $C_{22}H_{38}N_4O_2$. Calculated: M = 390.29946. MS, m/z (I_{rel} (%)): 390 $[M]^+$ (9), 373 (8), 321 (9), 308 (6), 208 (13), 195 (40), 179 (10), 166 (100), 150 (9), 55 (10), 44 (13), 43 (12). ^1H NMR (methanol-d_4), δ: 0.80 (ddd, 2 H, H(1), J = 9.5, 9.5, 5.0 Hz); 0.83 (s, 6 H, H(8)); 0.98 (ddd, 2 H, H(6), J = 9.5, 9.0, 1.5 Hz); 1.04 (s, 6 H, H(10)); 1.15 (s, 6 H, H(9)); 1.41 (dd, 2 H, *pro*-*R*-H(2), J = 15.0, 5.0 Hz); 2.14 (dd, 2 H, *pro*-*S*-H(2), J = 15.0, 9.5 Hz); 2.28, 2.67 (both m, each 2 H, H(11)); 2.35 (dd, 2 H, *pro*-*R*-H(5), J = 19.0, 9.0 Hz); 3.03 (dd, 2 H, *pro*-*S*-H(5), J = 19.0, 1.5 Hz). ^{13}C NMR (methanol-d_4), δ: 14.63 (C(8)), 18.19 (C(1)), 18.62 (C(5)), 19.79 (C(7)), 21.00 (C(6)), 22.41 (C(10)), 28.46 (C(9)), 35.89 (C(2)), 43.40 (C(11)), 55.71 (C(3)), 162.34 (C(4)).

(1*S*,3*S*,6*R*)-3-[*N*-(3-Aminopropyl)amino]-4-caranone dihydrochloride hemihydrate (6 · 2 HCl · 0.5 H_2O). Colorless crystals, m.p. 123 °C (from aqueous Pr^iOH, dec.); $[\alpha]_{578}^{26}$ +50.2 (*c* 1.79, H_2O). Found (%): C, 48.3; H, 9.1; Cl, 21.8; N, 12.8. $C_{13}H_{27}N_3O \cdot 2HCl \cdot 0.5H_2O$. Calculated (%): C, 48.60; H, 8.78; Cl, 22.07; N, 13.08. IR (KBr), ν/cm^{-1}: 3424 (O—H), 3380 (N—H), 941 (N—O). High-resolution MS, found: m/z 239.19980. $C_{13}H_{25}N_3O$. Calculated: M = 239.19976. MS, m/z (I_{rel} (%)): 239 (2), 205 (4), 191 (7), 165 (37), 123 (88), 106 (100), 91 (36), 79 (42), 77 (48), 43 (57), 41 (59). ^1H NMR (Py-d_5), δ: 0.79 (s, 3 H, H(8)); 0.99 (s, 3 H, H(9)); 1.21 (ddd, 1 H, H(1), J = 9.0, 9.0, 6.5 Hz); 1.47 (ddd, 1 H, H(6), J = 9.0, 9.0, 2.7 Hz); 1.52 (dd, 1 H, *pro*-*R*-H(2), J = 16.0,

6.0 Hz); 1.82 (s, 3 H, H(10)); 3.00 (m, 2 H, H(12)); 3.01 (dd, 1 H, *pro-S*-H(5), J = 19.0, 2.7 Hz); 3.14 (dd, 1 H, *pro-R*-H(5), J = 8.6, 18.7 Hz); 3.23 (dt, 1 H, *pro-S*-H(2), J = 16.5, 9.0 Hz); 3.51 (m, 2 H, H(11)); 3.63 (m, 2 H, H(13)). ^{13}C NMR (Py-d_5), δ: 14.63 (C(8)), 17.31 (C(1)), 18.16 (C(5)), 19.83 (C(7)), 20.89 (C(6)), 21.55 (C(10)), 25.95 (C(12)), 27,91 (C(9)), 32.52 (C(2)), 38.29 (C(13)), 41.54 (C(11)), 60.70 (C(3)), 155.20 (C(4)).

(1*S*,3*S*,6*R*)-3-[*N*-(3-Aminopropyl)amino]-4-caranone (6). ^{1}H NMR ($CDCl_3$), δ: 0.69 (ddd, 1 H, H(1), J = 9.2, 9.2, 5.1 Hz); 0.75 (s, 3 H, H(8)); 0.96 (ddd, 1 H, H(6), J = 9.2, 9.2, 1.0 Hz); 0.97 (s, 3 H, H(9)); 1.08 (s, 3 H, H(10)); 1.28 (dd, 1 H, *pro-R*-H(2), J = 15.0, 5.0 Hz); 1.60 (AB part of ABXYZ$_2$ system, 2 H, H(12), $\Delta\delta_{AB}$ = 20 Hz, J_{AB} = 13.3, $J_{AX} = J_{AY} = J_{AZ} = J_{BX} = J_{BY} = J_{BZ}$ = 6.7 Hz); 2.07 (dd, 1 H, *pro-S*-H(2), J = 15.0, 9.2 Hz); 2.20 (dd, 1 H, *pro-R*-H(5), J = 18.5, 9.2 Hz); 2.28 and 2.52 (both dt, each 1 H, H(11), J = 11.2, 6.7 Hz); 2.75 (t, 2 H, H(13), J = 6.7 Hz); 2.87 (dd, 1 H, *pro-S*-H(5), J = 18.5, 1.0 Hz); 4.0—5.5 (v.br., 4 H, O—H and N—H). ^{13}C NMR (Py-d_5), δ: 14.30 (C(8)), 16.31 (C(1)), 17.63 (C(5)), 18.85 (C(6)), 18.90 (C(7)), 21.70 (C(10)), 27.81 (C(9)), 32.61 (C(12)), 34.41 (C(2)), 40.15 (C(13)), 40.74 (C(11)), 54.57 (C(3)), 160.76 (C(4)).

***N,N′*-Bis-{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl}-1,3-propylenediamine (12).** Colorless crystals, m.p. 204 °C (from a MeOH—$CHCl_3$ mixture, dec.), $[\alpha]_{578}^{26}$ +278 (c 1.75, Py). Found (%): C, 68.2; H, 9.6; N, 13.8. $C_{23}H_{40}N_4O_2$. Calculated (%): C, 68.28; H, 9.97; N, 13.85. IR (KBr), ν/cm^{-1}: 3407 (O—H), 3302 (N—H), 942 (N—O). High-resolution MS, found: m/z 404.31498. $C_{23}H_{40}N_4O_2$. Calculated: M = 404.31511. MS, m/z (I_{rel} (%)): 404 $[M]^+$ (1), 387 (5), 238 (31), 205 (11), 195 (100), 166 (84), 140 (15), 127 (19), 123 (14), 107 (20), 82 (11), 79 (12), 58 (18), 55 (11), 41 (20), 30 (20). ^{1}H NMR (Py-d_5), δ: 0.77 (ddd, 2 H, H(1), J = 9.5, 9.5, 5.0 Hz); 0.87 (s, 6 H, H(8)); 0.95 (s, 6 H, H(9)); 0.96 (dd, 2 H, H(6), J = 9.5, 9.0 Hz); 1.43 (s, 6 H, H(10)); 1.49 (dd, 1 H, *pro-R*-H(2), J = 14.5, 5.0 Hz); 1.81 (tt, 2 H, H(12), J = 6.5, 6.5 Hz); 2.25 (dd, 2 H, *pro-S*-H(2), J = 14.5, 9.5 Hz); 2.3 (br., 2 H, N—H, $W_{1/2} \approx$ 200 Hz); 2.55 (dd, 2 H, *pro-R*-H(5), J = 18.2, 9.5 Hz); 2.59 and 2.78 (both dt, each 2 H, H(11), J = 11.0, 6.5 Hz); 3.44 (d, 1 H, *pro-S*-H(5), J = 18.2 Hz); 12.48 (br.s, 2 H, O—H). ^{13}C NMR (Py-d_5), δ: 14.61 (C(8)), 17.13 (C(1)), 18.23 (C(5)), 18.94 (C(7)), 20.19 (C(6)), 22.85 (C(10)), 28.16 (C(9)), 32.31 (C(12)), 35.69 (C(2)), 42.61 (C(11)), 54.78 (C(3)), 160.48 (C(4)).

(1*S*,3*S*,6*R*)-3-*N*-Piperazino-4-caranone (*E*)-oxime dihydrochloride (7 · 2 HCl). Yellowish crystals, m.p. 193—195 °C (from $CHCl_3$), $[\alpha]_{578}^{22}$ +177 (c 1.65, $CHCl_3$), $[\alpha]_{578}^{24}$ +116 (c 1.75, CH_3OH). Found (%): C, 52.1; H, 8.5; Cl, 21.4; N, 13.1. $C_{14}H_{25}N_3O \cdot 2HCl$. Calculated (%): C, 51.85; H, 8.39; Cl, 21.86; N, 12.96. IR ($CHCl_3$), ν/cm^{-1}: 3500—3200 (O—H, N—H), 945 (N—O). High-resolution MS, found: m/z 251.20027. $C_{14}H_{25}N_3O$. Calculated: M = 251.19975. MS, m/z (I_{rel} (%)): 251 (9), 234 (24), 209 (4), 195 (4), 193 (7), 180 (4), 169 (30), 152 (100), 138 (7), 123 (14), 106 (11), 87 (45), 85 (48), 70 (9), 56 (45), 44 (29). ^{1}H NMR (DMSO-d_6), δ: 0.63 (ddd, 1 H, H(1), J = 9.4, 9.4, 6.1 Hz); 0.71 (s, 3 H, H(8)); 0.88 (dd, 1 H, H(6), J = 9.4, 9.4 Hz); 0.89 (s, 3 H, H(9)); 0.97 (s, 3 H, H(10)); 1.03 (dd, 1 H, *pro-R*-H(2), J = 15.9, 6.1 Hz); 2.09 (dd, 1 H, *pro-R*-H(5), J = 18.0, 9.4 Hz); 2.29 (dd, 1 H, *pro-S*-H(2), J = 15.9, 9.4 Hz); 2.45 (m, 2 H, H(11) or H(12)); 2.78 (m, 2 H, H(12) or H(11)); 2.81 (d, 1 H, *pro-S*-H(5), J = 18.0 Hz); 2.99 (m, 4 H, H(13) and H(14)). ^{1}H NMR (Py-d_5), δ: 0.58 (ddd, 1 H, H(1), J = 9.2, 9.1, 5.7 Hz); 0.84 (s, 3 H, H(8)); 0.92 (ddd, 1 H, H(6), J = 9.1, 9.0, 0.8 Hz); 0.94 (s, 3 H, H(9)); 1.10 (s, 3 H, H(10)); 1.18 (dd, 1 H, *pro-R*-H(2), J = 15.7, 5.7 Hz); 2.28 (dd, 1 H, *pro-S*-H(2), J = 15.7, 9.2 Hz); 2.35 (dd, 1 H, *pro-R*-H(5), J = 17.3, 9.0 Hz); 2.48 (m, 2 H, H(11) or H(12)); 2.68 (m, 2 H, H(12) or H(11)); 2.95 (m, 4 H, H(13) and H(14)); 3.37 (dd, 1 H, *pro-S*-H(5), J = 17.3, 0.8 Hz). ^{13}C NMR (DMSO-d_6), δ: 14.51 (C(10)), 14.68 (C(8)), 16.38 (C(1)), 17.78 (C(7)), 17.99 (C(5)), 20.28 (C(6)), 27.84 (C(9)), 31.51 (C(2)), 42.27 (C(11 and C12)), 43.74 (C(13) and C(14)), 58.87 (C(3)), 160.93 (C(4). ^{13}C NMR (Py-d_5), δ: 14.72 (C(10)), 14.85 (C(8)), 17.45 (C(1)), 18.31 (C(7)), 18.76 (C(5)), 21.49 (C(6)), 28.19 (C(9)), 32.29 (C(2)), 46.47 and 46.70 (C(11), C(12), C(13) and C(14)), 59.39 (C(3)), 162.37 (C(4)).

***N,N′*-Bis-{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl}piperazine (13).** White crystals, m.p. 202.5—203.5 °C (from a CH_3OH—CH_3CN mixture, 3 : 1), $[\alpha]_{578}^{22}$ +134 (c 0.75, $CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 3600 (O—H), 880 (=N—OH). High-resolution MS, found: m/z 416.31534. $C_{24}H_{40}N_4O_2$. Calculated: M = 416.31511. MS, m/z (I_{rel} (%)): 416 (21), 399 (15), 358 (6), 334 (20), 304 (14), 250 (11), 248 (15), 234 (35), 233 (24), 209 (26), 193 (11), 191 (10), 169 (21), 166 (27), 165 (13), 152 (100), 135 (11), 123 (22), 107 (23), 106 (26), 93 (20), 91 (26), 87 (34), 85 (61), 79 (23), 77 (23), 69 (12), 67 (14), 56 (40), 55 (22), 43 (31), 41 (32). ^{1}H NMR (Py-d_5), δ: 0.76 (ddd, 2 H, H(1), J = 9.0, 8.8, 5.8 Hz); 0.93 (s, 6 H, H(8)); 1.00 (m, 2 H, H(6)); 1.01 (s, 6 H, H(9)); 1.22 (s, 6 H, H(10)); 1.30 (dd, 2 H, *pro-R*-H(2), J = 15.7, 5.8 Hz); 2.43 (dd, 2 H, *pro-S*-H(2), J = 15.7, 9.0 Hz); 2.47 (dd, 2 H, *pro-R*-H(5), J = 17.7, 9.0 Hz); 2.5 and 2.7 (br, each 4 H, H(11), H(12)); 3.47 (dd, 2 H, *pro-S*-H(5), J = 17.7, 1.3 Hz), 12.46 (s, 2 H, N—OH). ^{13}C NMR (Py-d_5), δ: 14.94 (C(10)), 15.031 (C(8)), 17.74 (C(1)), 18.42 (C(7)), 18.88 (C(5)), 21.68 (C(6)), 28.33 (C(9)), 32.57 (C(2)), 46.99 (C(11) and C(12)), 59.05 (C(3)), 162.52 (C(4)).

(1*S*,3*S*,6*R*)-3-(6-Aminohexylamino)-4-caranone (*E*)-oxime dihydrochloride (8 · 2 HCl). Yellowish crystals, m.p. 136.0—138.0 °C (from EtOAc, dec.); $[\alpha]_{578}^{22}$ +211 (c 0.237, Py). Found (%): C, 54.0; H, 8.9; Cl, 20.4; N, 12.1. $C_{16}H_{31}N_3O \cdot 2HCl$. Calculated (%): C, 54.23; H, 9.39; Cl, 20.01; N, 11.86. IR (KBr), ν/cm^{-1}: 910 (N—O). High-resolution MS, found: m/z 281.24652. $C_{16}H_{31}N_3O$. Calculated: M = 281.24671. MS, m/z (I_{rel} (%)): 281 (2), 191 (2), 165 (27), 123 (60), 106 (100), 91 (16), 79 (22), 77 (28), 43 (57), 41 (59). ^{1}H NMR ($CDCl_3$), δ: 0.71 (ddd, 1 H, H(1), J = 9.5, 9.5, 5.0 Hz); 0.81 (s, 3 H, H(10)); 0.85 (ddd, 1 H, H(6), J = 9.5, 9.0, 1.5 Hz); 1.03 (s, 3 H, H(8)); 1.05 (s, 3 H, H(9)); 1.12—1.50 (m, 9 H, *pro-R*-H(2), 2 H(12), 2 H(13), 2 H(14), 2 H(15)); 2.10 (m, 1 H, *pro-S*-H(2)); 2.41 and 2.64 (both m, 5 H, 2 H(11), 2 H(16), *pro-R*-H(5)); 2.89 (dd, 1 H, *pro-S*-H(5), J = 19.0, 1.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.92 (C(8)), 17.21 (C(1)), 18.30 (C(5)), 19.20 (C(7)), 19.79 (C(6)), 23.89 (C(10)), 27.25 (C(13)), 27.35 (C(14)), 28.54 (C(9)), 30.57 (C(12)), 32.12 (C(15)), 35.02 (C(2)), 42.64 (C(11)), 45.64 (C(16)), 55.01 (C(3)), 161.32 (C(4)).

***N,N′*-Bis{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl}-1,6-hexamethylenediamine (14).** White crystals, m.p. 159.0—161.0 °C (from $CHCl_3$), $[\alpha]_{578}^{22}$ +243 (c 0.15, Py). Found (%): C, 69.6; H, 10.5; N, 12.2. $C_{26}H_{46}N_4O_2$. Calculated (%): C, 69.9; H, 10.4; N, 12.5. IR ($CHCl_3$), ν/cm^{-1}: 915 (=N—OH). High-resolution MS, found: m/z 446.36219. $C_{26}H_{46}N_4O_2$. Calculated: M = 446.36208. MS, m/z (I_{rel} (%)): 446 (2), 429 (9), 411(7), 377 (9), 370 (15), 280 (49), 264 (36), 262 (32), 247 (18), 223 (16), 212 (19), 199 (16), 182 (23), 167 (23), 165 (33), 150

(24), 115 (47), 98 (100), 55 (31), 41 (22). ^{1}H NMR (Py-d_5), δ: 0.66 (ddd, 2 H, H(1), *J* = 9.5, 9.5, 5.0 Hz); 0.81 (s, 6 H, H(8)); 0.89 (ddd, 2 H, H(6), *J* = 9.5, 9.0, 1.5 Hz); 0.92 (s, 6 H, H(9)); 1.13 (m, 4 H, H(13)); 1.40 (s, 6 H, H(10)); 1.46 (dd, 2 H, *pro-R*-H(2), *J* = 15.0, 5.0 Hz); 1.64 (m, 4 H, H(12)); 2.28 (dd, 1 H, *pro-S*-H(2), *J* = 15.0, 9.5 Hz); 2.43 and 2.64 (both m, each 2 H, H(11)); 2.49 (dd, 2 H, *pro-R*-H(5), *J* = 19.0, 9.0 Hz); 3.39 (dd, 2 H, *pro-S*-H(5), *J* = 19.0, 1.5 Hz). ^{13}C NMR (Py-d_5), δ: 14.60 (C(8)), 16.60 (C(1)), 17.80 (C(5)), 19.05 (C(7)), 19.14 (C(6)), 21.70 (C(10)), 27.37 (C13)), 28.17 (C(9)), 30.57 (C12)), 34.72 (C(2)), 42.64 (C11)), 54.61 (C3)), 160.14 (C(4)).

(1*S*,2*S*,5*S*)-2-(2-Aminoethylamino)-3-isopinocamphone (*E*)-oxime (9). Yellowish crystals, m.p. 85—86 °C (from EtOAc), $[\alpha]_{578}^{25}$ +77 (*c* 2.24, $CHCl_3$). IR, $CHCl_3$), ν/cm^{-1}: 3580 (O—H), 3330 (N—H), 3380 (N—H), 935 (=N—OH). High-resolution, MS, found: *m/z* 208.18089 ($[M]^+ - OH$). $C_{12}H_{23}N_3O$ Calculated: $[M]^+ - OH$ = 208.18136. MS, *m/z* (I_{rel} (%)): 208 (8), 195 (32), 166 (100), 150 (3), 149 (4), 148 (4), 124 (14), 110 (51), 107 (11), 106 (18), 82 (8), 79 (11), 70 (9), 69 (9), 55 (6), 53 (7), 44 (16). 43 (13), 42 (11), 41 (17). ^{1}H NMR ($CDCl_3$), δ: 0.82 (s, 3 H, H(9)); 1.22 (s, 3 H, H(8)); 1.34 (s, 3 H, H(10)); 1.48 (d, 1 H, *pro-R*-H(7), *J* = 10.2 Hz); 1.88 (m, 2 H, H(1), H(5)); 2.13 (dddd, 1 H, *pro-S*-H(7), *J* = 10.2, 6.2, 6.2, 2.7 Hz); 2.39 (m, 2 H, H(11)); 2.50 (dd, 1 H, *pro-R*-H(4), *J* = 18.2, 2.1 Hz); 2.70 (m, 2 H, H(12)); 2.75 (ddd, 1 H, *pro-S*-H(4), *J* = 18.2, 2.8, 2.7 Hz); 3.0—4.5 (v.br, 4 H, O—H and N—H). ^{13}C NMR ($CDCl_3$), δ: 22.53 (C(9)), 24.03 (C(10)), 27.61 (C(8)), 27.74 (C(7)), 29.64 (C(4)), 37.71 (C(5)), 38.73 (C(6)), 41.94 (C(12)), 43.60 (C(11)), 49.70 (C(1)), 59.57 (C(2)), 160.61 (C(3)).

***N,N′*-Bis-{(1*S*,2*S*,5*R*)-3-[(*E*)-hydroxyimino]-2,6,6-trimethylbicyclo[3.1.1]hept-2-yl}-1,2-ethylenediamine (16).** White crystals, m.p. 155—157 °C (from 10% aqueous CH_3OH); $[\alpha]_{578}^{22}$ +53.2 (*c* 0.87, $CHCl_3$). IR ($CHCl_3$), ν/cm^{-1}: 3590 (O—H), 3350 (N—H), 930 (=N—OH). High-resolution MS, found: *m/z* 390.29860. $C_{22}H_{38}N_4O_2$. Calculated: M = 390.29946. MS, *m/z* (I_{rel} (%)): 390 (5), 373 (2), 208 (10), 195 (26), 178 (8), 165 (100), 149 (6), 124 (10), 110 (41), 106 (12), 79 (10), 69 (10), 55 (6), 43 (12), 41 (15). ^{1}H NMR ($CDCl_3$), δ: 0.87 (s, 6 H, H(9)); 1.26 (s, 6 H, H(8)); 1.41 (s, 6 H, H(10)); 1.47 (d, 2 H, *pro-R*-H(7), *J* = 10.6 Hz); 1.90 (dddd, 2 H, H(5), *J* = 5.5, 5.5, 2.9, 2.6 Hz); 1.94 (dd, 2 H, H(1), *J* = 5.5, 5.5); 2.19 (dddd, 2 H, *pro-S*-H(7), *J* = 10.6, 5.5, 5.5, 1.8 Hz); 2.46 (m, 4 H, H(11)); 2.58 (dd, 2 H, *pro-R*-H(4), *J* = 18.8, 2.9 Hz); 2.72 (ddd, 2 H, *pro-S*-H(4), *J* = 18.8, 2.6, 1.8 Hz); 10—11 (v.br., 2 H, O—H). ^{13}C NMR ($CDCl_3$), δ: 22.86 (C(9)), 24.44 (C(10)), 27.68 (C(8)), 27.88 (C(7)), 29.765 (C(4)), 37.79 (C(5)), 39.08 (C(6)), 41.60 (C11)), 49.57 (C(1)), 60.15 (C(2)), 160.28 (C(3)).

(1*S*,2*S*,5*S*)-2-[*N*-(3-Aminopropyl)amino]-3-isopinocamphone (*E*)-oxime dihydrochloride sesquihydrate (10 · 2 HCl · 0.5 H_2O). Colorless crystals, m.p. 100 °C (from aqueous Pr^iOH, dec.), $[\alpha]_{578}^{21}$ +38.9 (*c* 1.02, H_2O). Found (%): C, 46.4; H, 8.9; Cl, 20.5; N, 12.4. $C_{13}H_{27}Cl_2N_3O \cdot 1.5H_2O$. Calculated (%): C, 46.02; H, 8.91; Cl, 20.90; N, 12.38. IR (KBr), ν/cm^{-1}: 3509 (O—H), 3240 (N—H) 943 (N—O). MS, *m/z* (I_{rel} (%)): 225 (15), 224 (13), 195 (14), 167 (18), 151 (31), 130 (14), 125 (20), 123 (24), 111 (42), 76 (93), 59 (42), 46 (100), 37 (96). ^{1}H NMR (D_2O), δ: 0.91 (s, 3 H, H(8)); 1.30 (d, 1 H, *pro-R*-H(7), *J* = 11.8 Hz); 1.36 (s, 3 H, H(9)); 1.67 (s, 3 H, H(10)); 2.00—2.10 (m, 2 H, 2 H(12)); 2.12 (m, 1 H, H(5)); 2.36 (dd, 1 H, H(1), *J* =5.5, 5.5 Hz); 2.53 (ddd, 1 H, *pro-S*-H(7), *J* = 11.8, 6.0, 5.5, 2.5 Hz); 2.70 (dd, 1 H, *pro-R*-H(4), *J* = 19.0, 2.5 Hz); 2.86 (ddd, 1 H, *pro-S*-H(4), *J* = 19.0, 5.5, 5.5 Hz); 3.02 (dddd, 1 H, H(11a), *J* = 12.5, 11.0, 5.5 Hz); 3.10 (dd, 2 H, 2 H(13), *J* = 7.8, 7.8 Hz); 3.21 (ddd, 1 H, H(11б), *J* = 12.5, 11.5, 5.5 Hz). ^{13}C NMR (D_2O), δ: 21.59 (C(8)), 21.74 (C(10)), 24.28 (C(12)), 26.53 (C(9)), 26.59 (C(7)), 29.71 (C(4)), 36.69 (C(5)), 36.98 (C(13)), 38.96 (C(11)), 39.20 (C(6)), 46.71 (C(1)), 66.54 (C(2)), 158.25 (C(3)).

***N,N′*-Bis{(1*S*,2*S*,5*S*)-3-[(*E*)-hydroxyimino]-2,6,6-trimethylbicyclo[3.1.1]hept-2-yl}-1,3-propylenediamine hemihydrate (17 · 0.5 H_2O).** Colorless crystals, m.p. 125 °C (from aqueous MeOH), $[\alpha]_{578}^{16}$ +100 (*c* 1.44, MeOH). Found (%): C, 66.7; H, 10.2; N, 13.7. $C_{23}H_{40}N_4O_2 \cdot 0.5H_2O$. Calculated (%): C, 66.79; H, 9.99; N, 13.55. IR (KBr), ν/cm^{-1}: 3564 (O—H), 3278 (N—H), 939 (N—O). MS, *m/z* (I_{rel} (%)): 328 (9), 222 (17), 220 (26), 203 (36), 194 (52), 177 (36), 166 (94), 150 (38), 124 (27), 110 (90), 108 (43), 96 (52), 83 (50), 82 (71), 79 (40), 73 (86), 69 (36), 58 (31), 53 (30), 44 (100), 39 (29), 43 (47), 42 (48), 41 (93), 39 (29), 30 (79). ^{1}H NMR (Py-d_5), δ: 0.89 (s, 6 H, H(8)); 1.23 (s, 6 H, H(9)); 1.57 (s, 6 H, H(10)); 1.79 (tt, 2 H, H(12), *J* = 6.1, 6.1 Hz); 1.88 (d, 1 H, *pro-R*-H(7), *J* = 10.3 Hz); 1.91 (dddd, 2 H, H(5), *J* = 5.7, 5.7, 2.8, 2.8 Hz); 2.04 (dd, 2 H, H(1), *J* = 5.7, 5.7 Hz); 2.27 (dddd, 2 H, *pro-S*-H(7), *J* = 10.3, 5.7, 5.7, 2.8 Hz); 2.55 (dt, 2 H, H(11a), *J* = 11.0, 6.1 Hz); 2.85 (dd, 2 H, *pro-R*-H(4), *J* = 18.3, 2.8 Hz); 3.00 (dt, 2 H, H(11b), *J* = 11.0, 6.1 Hz); 3.16 (ddd, 2 H, *pro-S*-H(4), *J* = 18.3, 2.8, 2.8 Hz). ^{13}C NMR (Py-d_5), δ: 22.63 (C(8)), 23.70 (C(10)), 27.88 (C(9)), 28.16 (C(7)), 30.01 (C(12)), 30.43 (C(4)), 38.34 (C(5)), 39.08 (C(6)), 42.04 (C(11)), 50.27 (C(1)), 60.35 (C(2)), 159.49 (C(3)).

Preparation of triaminodioximes 15 and 18 (general procedure). A suspension of Na_2CO_3 (0.88 g, 8.3 mmol) and nitroso chloride dimer **3** or **4** (3.35 g, 8.3 mmol) in a diethylenetriamine (9.0 mmol) and methanol (15 mL) mixture was stirred at 50 °C until the initial nitroso chloride dissolved. After removal of the solvent *in vacuo,* 3 *M* HCl (20 mL) was added to the residue, the resulting solution was extracted with $MeOBu^t$ (3×10 mL), the organic extracts were rejected, and the aqueous phase was treated with concentrated aqueous ammonia (7 mL). The white crystals that precipitated were filtered off, washed on the filter with $MeOBu^t$ (3×10 mL), and dried in air to give bis-α-amino oximes **17** (53%) and **18** (24%).

***N,N*-Di-(2-{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl}-ethylamino)amine (15).** White crystals, m.p. 144—146 °C (from CH_2Cl_2—MeOH), $[\alpha]_{578}^{22}$ +170 (*c* 1.78, Py). Found (%): C, 66.7; H, 10.1; N, 16.0. $C_{24}H_{43}N_5O_2$. Calculated (%):C, 66.48; H, 10.00; N, 16.15. IR (KBr), ν/cm^{-1}: 3600—3300 (O—H, N—H), 940 and 930 (=N—OH). MS, *m/z* (I_{rel} (%)): 251 (10), 238 (31), 220 (28), 205 (20), 195 (24), 166 (51), 165 (26), 150 (37), 123 (61), 106 (68), 73 (100), 44 (66). ^{1}H NMR (Py-d_5), δ: 0.81 (s, 3 H, H(8)); 0.82 (ddd, 1 H; H(1), *J* = 9.1, 9.1, 5.2 Hz); 0.93 (s, 3 H, H(9)); 1.01 (ddd, 1 H, H(6), *J* = 9.1, 9.1, 1.1 Hz); 1.44 (s, 3 H, H(10)); 1.45 (dd, 1 H, *pro-R*-H(2), *J* = 15.1, 5.2 Hz); 2.32 (dd, 1 H, *pro-S*-H(2), *J* = 15.1, 9.1 Hz); 2.69 (dd, 1 H, *pro-R*-H(5), *J* = 18.7, 9.1 Hz); 3.03 (ddd, 1 H, H(11a), *J* = 12.8, 5.2, 5.2 Hz); 3.15 (ddd, 1 H, H(11b), *J* = 12.8, 6.9, 5.2 Hz); 3.27 (m, 2 H, H(12a,b)); 3.33 (d, 1 H, *pro-S*-H(5), *J* = 18.4 Hz). ^{13}C NMr (Py-d_5), δ: 14.63 (C(8)), 17.11 (C(1)), 18.22 (C(5)), 19.00 (C(7)), 19.99 (C(6)), 22.95 (C(10)), 27.99 (C(9)), 34.94 (C(2)), 39.73 (C(11)), 48.34 (C(12)), 55.23 (C3)), 159.63 (C(4)).

***N,N*-Di-(2-{(1*S*,2*S*,5*S*)-3-[(*E*)-hydroxyimino]-2,6,6-trimethylbicyclo[3.1.1]hept-2-yl}ethylamino)amine (18).** White crystals, m.p. 152—154 °C (from a CH_3CN—MeOH mixture),

$[\alpha]_{578}^{22}$ +80 (*c* 1.30, Py). Found (%): C, 66.2; H, 10.1; N, 16.2. $C_{24}H_{43}N_5O_2$. Calculated (%): C, 66.48; H, 10.00; N, 16.15. IR (KBr), ν/cm^{-1}: 3500—3100 (O—H, N—H), 930 and 920 (=N—OH). MS, *m/z* (I_{rel} (%)): 251 (8), 238 (12), 226 (13), 220 (60), 208 (11), 195 (28), 166 (91), 125 (30), 122 (34), 110 (51), 106 (21), 73 (100), 44 (56). ^{1}H NMR (Py-d_5), δ: 0.93 (s, 6 H, H(8)); 1.24 (s, 6 H, H(9)); 1.58 (s, 6 H, H(10)); 1.91 (d, 1 H, *pro-R*-H(7), *J* = 10.5 Hz); 1.91 (m, 2 H, H(5)); 2.00 (dd, 2 H, H(1), *J* = 5.8, 5.8 Hz); 2.21 (dddd, 2 H, *pro-S*-H(7), *J* = 10.5, 5.8, 5.8, 2.8 Hz); 2.61 (dt, 2 H, H(11a), *J* = 11.0, 6.1 Hz); 2.72 (m, 4 H, H(12)); 2.83 (dd, 2 H, *pro-R*-H(4), *J* = 18.3, 2.8 Hz); 2.94 (dt, 2 H, H(11b), *J* = 11.0, 6.1 Hz); 3.18 (ddd, 2 H, *pro-S*-H(4), *J* = 18.3, 2.8, 2.8 Hz). ^{13}C NMR (Py-d_5), δ: 22.72 (C(8)), 24.50 (C(10)), 28.02 (C(9)), 28.52 (C(7)), 30.39 (C(4)), 38.63 (C(5)), 39.07 (C(6)), 41.63 (C(11)), 50.37 (C(12)), 50.68 (C(1)), 59.98 (C(2)), 160.58 (C(3)).

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