Sulfuric acid-promoted rearrangement of 3-(*N*-acylamino)-substituted caran-4-one oximes

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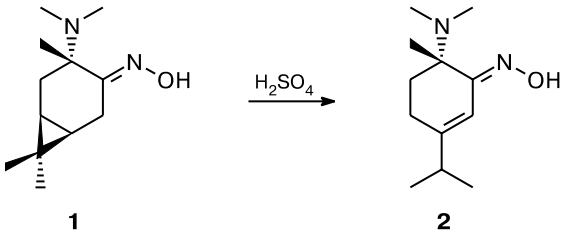
The rearrangement of 3-(*N*-acylamino)-substituted caran-4-one oximes in the presence of sulfuric acid affords 2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one derivatives. 3-Aminocaran-4-one oximes, in which the amino group contains such substituents as acetyl, propionyl, chloroacetyl, 1-adamantylcarbonyl, benzoyl, 2-thienylcarbonyl, or anilinocarbonyl, undergo this reaction. *N*-Acyl derivatives of higher fatty (heptanoic and nonadecanoic) acids do not undergo this reaction. The reaction with D_2SO_4 leads to the replacement of all hydrogen atoms of the isopropyl group by deuterium. The mechanism of this rearrangement is proposed.

Key words: monoterpenoids, 3-carene, oximes, rearrangement, amides, sulfuric acid.

In recent years, the chemistry of α-amino oximes of the terpene series has been extensively studied primarily from the viewpoint of their use in the synthesis of macrocyclic compounds and various heterocyclic derivatives. Until recently, only one example of acid-catalyzed rearrangement of carene-derived α-dimethylamino oxime **1** has been documented. Dissolution of the latter in concentrated sulfuric acid afforded amino oxime of the the *p*-menthane series **2** (Scheme 1)[1] as the only product in virtually quantitative yield.

Scheme 1



1 **2**

This is a very unusual result because, under these conditions, terpenoids generally are either resinified or give complex mixtures of product. Recently,[2] we have found a new rearrangement of a carane-type derivative. In the present study, we describe the investigation of this rearrangement in detail.

The rearrangement was studied using *N*-acyl derivatives **3a—i** as an example. The latter were prepared from amino oxime **4**, which was, in turn, synthesized from (+)-3-carene (**5**) (Scheme 2). Compounds **3a—h** were synthesized by the reaction of amino oxime **4** with an equivalent amount of the corresponding acyl halide,* whereas aminocarbonyl derivative **3i** was prepared with the use of *N*-phenyl-1*H*-imidazole-1-carboxamide generated from imidazole and phenyl isocyanate. The rearrangement of acylated derivatives **3** was carried out in the presence of concentrated sulfuric acid in chloroform at room temperature. Higher fatty acid derivatives (compounds **3c** and **3d**) virtually do not undergo this reaction, and the starting compounds are recovered in 85—90% yield. In other cases, the reaction gives products **6a,b,e—i** in good yields. Analysis of the ^1H and ^{13}C NMR spectra of products **6** showed that all these compounds belong to the same structural type, *viz.*, (*E*)-oximes of 1-isopropyl-5-methyl-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one, which differ by the substituent at the C(3) atom.

The following pathway can be proposed to explain the mechanism of formation of products **6a—i** (Scheme 3). Compounds **3** are protonated at the quaternary carbon atom, which is accompanied by opening of the cyclopropane ring to form carbocation **7** of the *m*-menthane series. The latter undergoes a 1,2-hydride shift followed by an interaction of the carbocationic center with the oxygen atom of the amide group.

To verify this mechanism, we carried out the reaction of compound **3a** with deuterated sulfuric acid. Analysis of the mass spectrum and the ^1H and ^{13}C NMR spectra of

* In the presence of an excess of acyl halide, the reaction yields not only the N-acylation product but also the N,O-acylation product.

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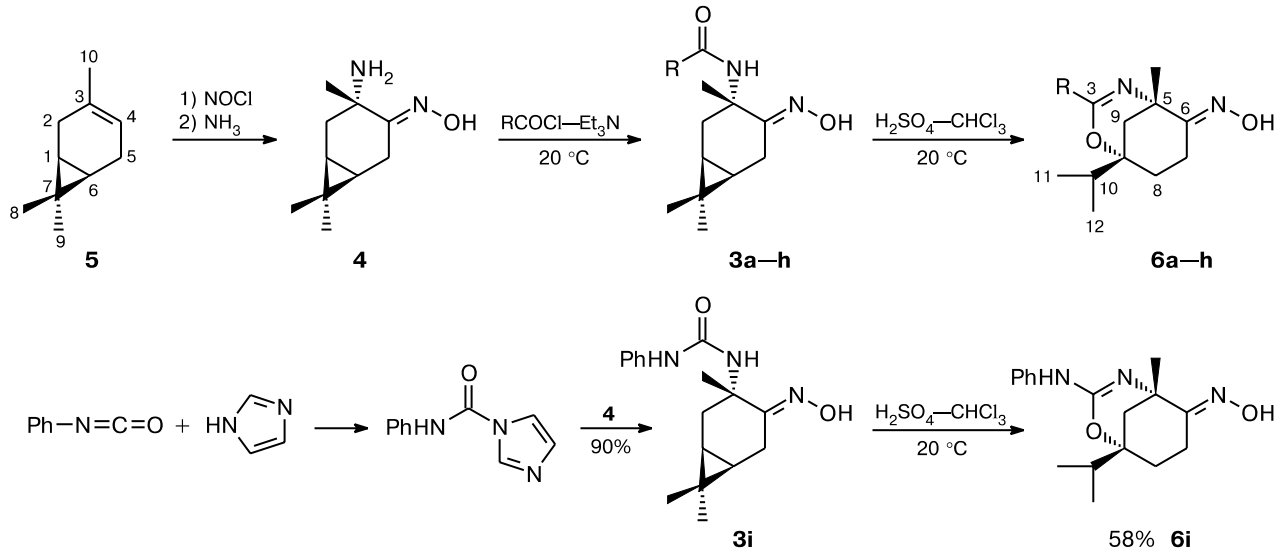
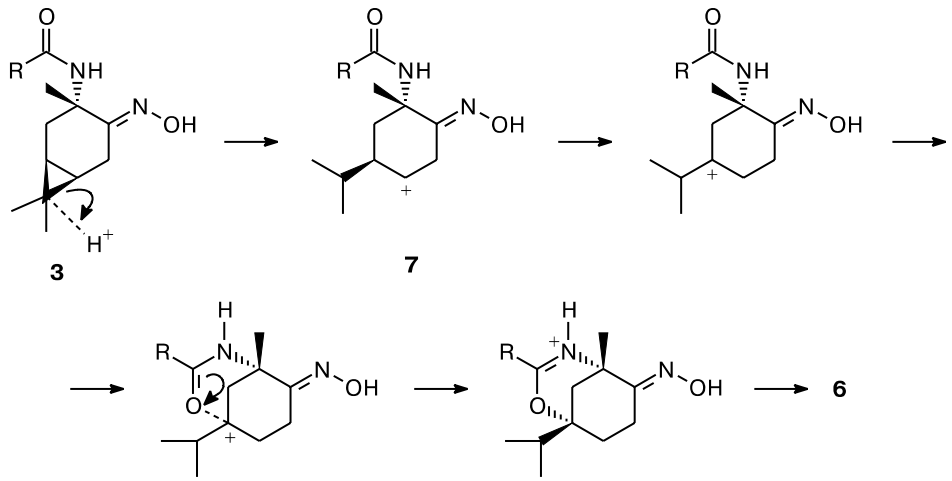
Scheme 2



5 **4** **3a—h** **6a—h** **3i**

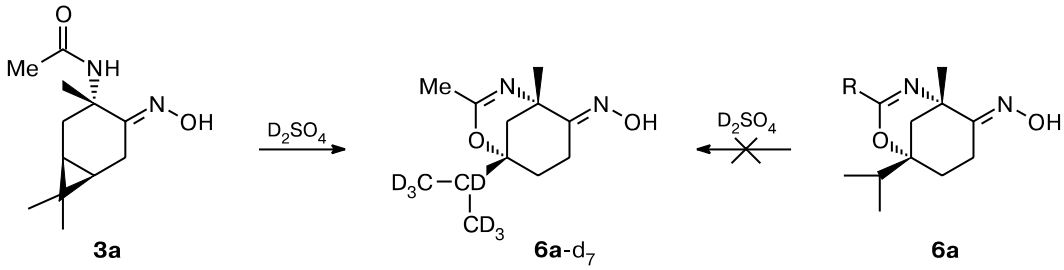
3, 6	R	Yield (%)	
		3	6
a	Me	71	71
b	CH_2Me	85	70
c	$(CH_2)_5Me$	94	—
d	$(CH_2)_{17}Me$	85	—
e	CH_2Cl	94	69
f	1-adamantyl	90	65
g	Ph	78	83
h	2-thienyl	65	78

Scheme 3



3 **7** **6**

Scheme 4

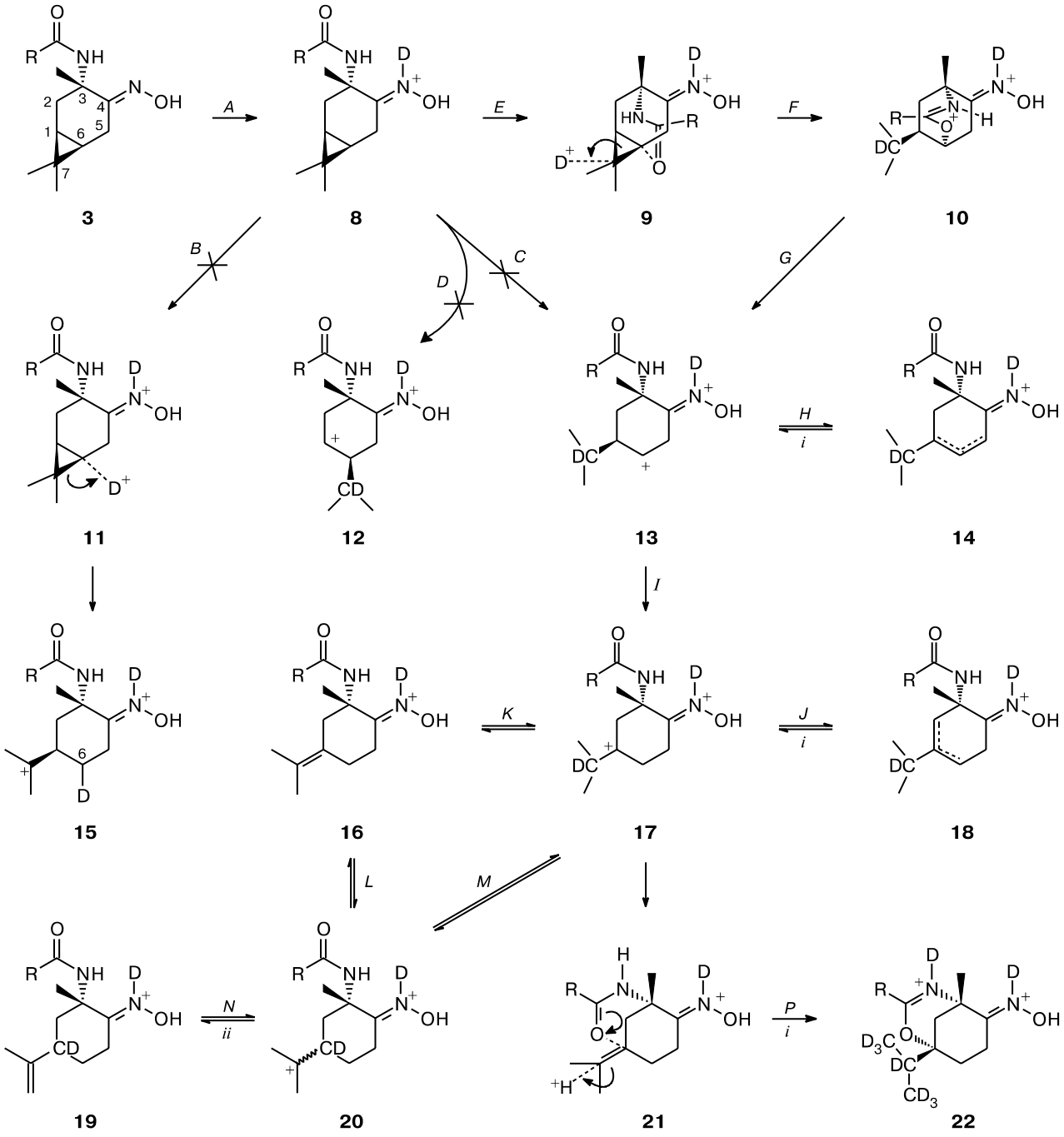


3a **6a**-d_7 **6a**

product **6a**-d_7 demonstrated that seven deuterium atoms were included into the molecule so that the isopropyl group was completely deuterated. At the same time, storage of compound **6a** in D_2SO_4 did not result in the inclusion of deuterium and compound **6a** was recovered (Scheme 4).

Scheme 3 does not explain how the deuterium label is included into the isopropyl group. We analyzed different possible reaction mechanisms, calculated the heats of formation of various probable intermediates, and proposed the pathway (Scheme 5), which accounts for all the observed features of the transformations.

Scheme 5



i. Slowly. *ii*. Rapidly.

A. Since the transformation of compounds **3** occurs in concentrated sulfuric acid, the initial step involves, apparently, protonation of the most basic fragment, *viz.*, the oxime oxygen atom, and all further transformations occur in the presence of the protonated oxime group.

B. Direct cleavage of cyclopropane as a result of the attack of a proton (a deuteron) on the C(6) atom giving rise to a compound of the *m*-menthane series (**8**→**11**→**15**) does not occur; otherwise, deuterium would be detected in the product at the C(6) atom, which was not observed.

C and *D*. Direct cleavage of cyclopropane as a result of the attack of a proton (a deuteron) on the C(7) atom can be rejected because compound **12** of the *p*-menthane series would otherwise be predominantly generated (the calculated heats of formation show that compound **6** should be more stable than **13**).

E, *F*, and *G*. Cleavage of cyclopropane in cation **8** occurs as a result of the attack of a proton on the C(7) atom and anchimeric assistance of the acetamide group. Product **10** containing the bicyclic system of bicyclo[3.2.2]nonane undergoes isomerization to give *m*-menthane derivative **13**.

H. Dication **13** is not in equilibrium with the corresponding alkenes **14**; otherwise, deuterium would be included into the α and β positions with respect to the oxime group, which was not observed.

I. Isomerization **13**→**17** occurs *intramolecularly* through a 1,2-hydride shift. This is the only explanation for the absence of the deuterium label at the C(6) atom.

J. Dication **17** cannot be in equilibrium with the corresponding alkenes **18**, because the existence of this equilibrium would result in the inclusion of deuterium into the cyclohexane fragment of the product.

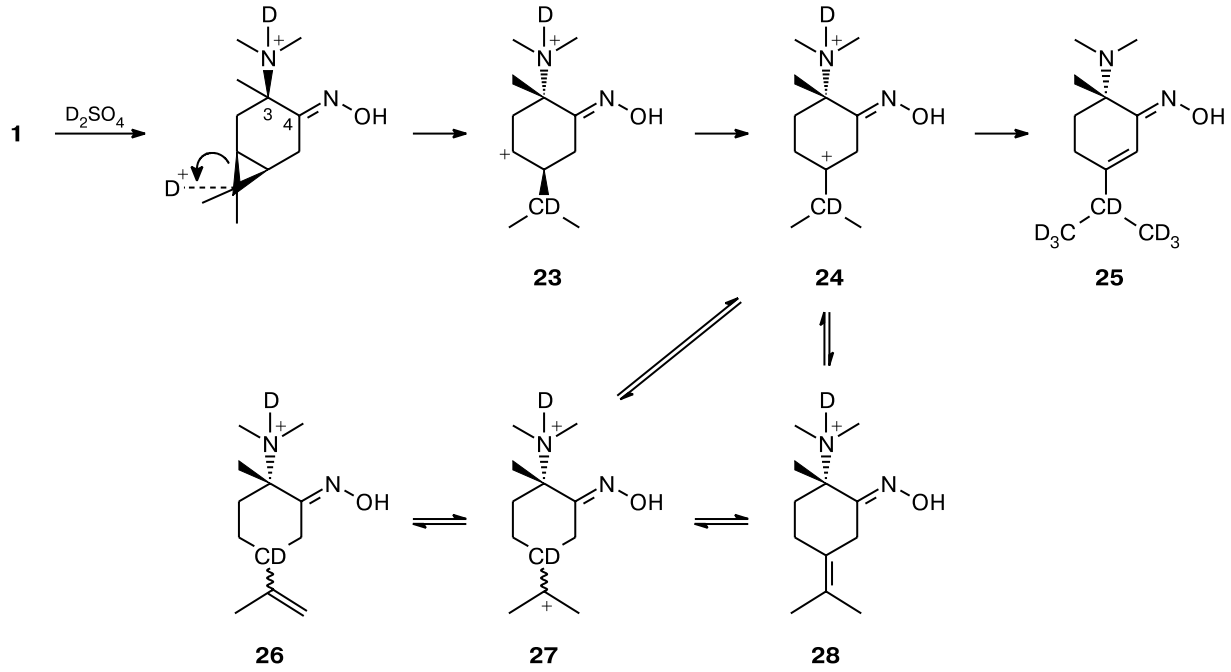
K, *L*, and *M*. Dication **17** is transformed into dication **20** through a 1,2-hydride shift, although the intermolecular transfer (**17** ⇌ **16** ⇌ **20**) cannot be ruled out.

N. Species **20** should occur in equilibrium with the corresponding isopropenyl derivatives **19**. It is this equilibrium that accounts for the presence of deuterium in the methyl groups of the isopropyl fragment.

O. Step **17**→**22** is more slow than transformations **17** ⇌ **16** ⇌ **20** ⇌ **19** and should be irreversible under the reaction conditions.

This scheme is indirectly confirmed by the study of the rearrangement of the above-mentioned dimethylamino derivative **1** in D_2SO_4 (Scheme 6). In both cases, **1** and **3**, the most basic nitrogen function is initially protonated. However, in compound **1** the dimethylamino group at the C(3) atom rather than the oxime group at the C(4) atom is more basic. The change in the position of the charged group in the six-membered ring leads to a change in the pathway of cleavage of the cyclopropane fragment resulting in the formation of compound **23** of the *p*-menthane series, which undergoes a 1,2-hydride shift to give dication **24**. Dication **24** is the final product of the transformation of dimethylamino oxime **1** in sulfuric acid, and compound **2** is formed in the step of neutralization. The equilibrium **24** ⇌ **27** ⇌ **26** accounts for the pres-

Scheme 6



ence of deuterium in the methyl groups of the isopropyl fragment and the formation of compound **25** as the final product, the equilibrium **24** ⇌ **28** ⇌ **27** being insignificant for the process as a whole.

To summarize, the rearrangement of α-(*N*-acylamino)-substituted oximes of the carane series in the presence of sulfuric acid affords 2-oxa-4-azabicyclo[3.3.1]non-3-en-6-ones, which are functionalized *m*-menthane derivatives.

Experimental

All solvents were distilled immediately before use. Thin-layer chromatography (TLC) was carried out on Silufol plates with a fixed layer of SiO_2; spots were visualized by spraying the plates with ethanolic solutions of vanilline (2 g of vanilline + 5 mL of concentrated H_2SO_4 in 150 mL of EtOH) or iron chloride (10% $FeCl_3 \cdot 6H_2O$ solution in EtOH) followed by heating. Preparative column chromatography was carried out with the use of KSK silica gel (particle size 0.140—0.315 mm) activated at 140 °C for 6—7 h. The IR spectra were measured on a Bruker Vector-22 instrument in $CHCl_3$ (*c* 1%) or KBr (*c* 0.25%). The mass spectra were obtained on a Finnigan MAT 8200 spectrometer (50—100 °C, EI, 70 eV). The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 and 125.75 MHz, respectively) for solutions in $CDCl_3$ (70—100 mg mL^{-1}) at 25—27 °C. The signal of the solvent (δ_C = 76.900 and δ_H = 7.240; the residual protons) was used as the internal standard. The assignment of the signals was made using ^{13}C NMR spectra with *J* modulation (proton-noise-decoupled spectra, opposite phases for the signals of the atoms with the odd and even numbers of the attached protons, tuning to the constant J = 135 Hz) and based on the data from the following 2D spectra: (1) homonuclear $^1H—^1H$ correlation, (2) heteronuclear $^{13}C—^1H$ correlation at the direct spin-spin coupling constants (J = 135 Hz), and (3) heteronuclear $^{13}C—^1H$ correlation at the long-range spin-spin coupling constants (J = 10 Hz). The optical rotation angles were measured on a Polamat A polarimeter for solutions in $CHCl_3$. The melting points were determined on a Kofler hot-stage apparatus.

(+)-3-Carene nitrosochloride was prepared according to a known procedure.[3]

(1*S*,3*S*,6*R*)-3-Aminocaran-4-one (*E*)-oxime (4). A 30% aqueous NH_3 solution (10 mL) was added to a suspension of carene nitrosochloride[3] (3 g, 14.7 mmol) in MeOH (100 mL). The reaction mixture was stirred at room temperature until nitrosochloride was completely dissolved. The methanol was distilled off *in vacuo*, the residue was dissolved in Bu^{t}OMe, and the solution was extracted with 1 *M* HCl (2×20 mL). The acidic aqueous solution was treated with NH_3 (25% aqueous solution) until pH 10—11 was reached and then extracted with Bu^{t}OMe (2×15 mL). The organic extract was dried over Na_2SO_4, the solvent was evaporated at ~10 Torr, the residue was dried at ~1 Torr, and amino oxime **4** was obtained in a yield of 1.55 g (58%).

Synthesis of *N*-acyl derivatives 3a—h (general procedure). An equimolar amount of Et_3N was added to a solution of amino oxime **4** (0.240—0.610 g, 1.32—3.35 mmol) in Bu^{t}OMe (15 mL). Then a solution of an equimolar amount of carboxylic acid chloride in Bu^{t}OMe (2 mL) was added dropwise with stirring. The reaction mixture was stirred at room temperature for 30 min, H_2O (15 mL) was added, the organic layer was separated, and the aqueous layer was extracted with Bu^{t}OMe (2×10 mL). The organic extract was successively washed with 1 *M* HCl (5 mL), a 0.5 *M* aqueous Na_2CO_3 solution (10 mL), and a saturated aqueous NaCl solution (10 mL) and dried over Na_2SO_4. The solvent was dried *in vacuo* using a water-jet pump, and the residue was dried *in vacuo* using an oil pump. The product was purified by column chromatography on silica gel.

(1*S*,3*S*,6*R*)-3-(Acetamido)caran-4-one (*E*)-oxime (3a). The yield was 71%. Colorless crystals with m.p. 150—153 °C (Bu^{t}OMe); $[\alpha]^{20}_{578}$ +155 (*c* 0.57, $CHCl_3$). MS, *m/z* (I_{rel} (%)): 224.15149 (M^+, 6%, calculated for $C_{12}H_{20}N_2O_2$ 224.16149), 207 (25), 165 (23), 150 (41), 149 (22), 148 (100), 132 (11), 125 (10), 123 (24), 122 (12), 108 (14), 107 (190), 106 (23), 105 (12), 100 (20), 91 (10), 81 (14), 79 (14), 67 (13), 57 (23), 43 (68), 42 (34), 41 (29), 39 (10), 28 (20). IR (KBr), ν/cm^{-1}: 3384, 3281, 1656. ^1H NMR ($CDCl_3$), δ: 8.82 (s, 1 H, N=O—H); 5.99 (s, 1 H, N—H); 2.91 (dd, 1 H, H(5β), J = 18.0 and 2.0 Hz); 2.52 (dd, 1 H, H(2α), J = 15.5 and 9.0 Hz); 2.32 (dd, 1 H, H(5α), J = 18.0 and 9.0 Hz); 1.95 (s, 3 H, CO—CH$_3$); 1.42 (s, 3 H, H(9)); 1.26 (dd, 1 H, H(2β), J = 15.5 Hz, J = 6.0 Hz); 0.99 (s, 3 H, H(10),); 0.89 (ddd, 1 H, H(6), J = 9.0 Hz, J = 9.0 Hz, J = 2.0 Hz); 0.81 (s, 3 H, H(8)); 0.71 (ddd, 1 H, H(1), J = 9.0 Hz, J = 9.0 Hz, J = 6.0 Hz).

(1*S*,3*S*,6*R*)-3-(Propionylamido)caran-4-one (*E*)-oxime (3b). Colorless glassy substance. The yield was 85%, $[\alpha]^{20}_{578}$ +152 (*c* 0.34, $CHCl_3$). High-resolution MS, found: *m/z* 238.16843 $[M]^+$. $C_{13}H_{22}N_2O_2$. Calculated: M = 238.16812. MS, *m/z* (I_{rel} (%)): 238 (6), 221 (23), 150 (28), 148 (100), 132 (8), 130 (10), 123 (14), 106 (13), 100 (16), 57 (37), 42 (18), 42 (15), 41 (19), 29 (31). IR (KBr), ν/cm^{-1}: 3428, 1652. ^1H NMR ($CDCl_3$), δ: 8.20 (s, 1 H, N=O—H); 6.96 (s, 1 H, N—H); 2.94 (d, 1 H, H(5β), J = 17.9 Hz); 2.55 (dd, 1 H, H(2α), J = 15.2 Hz, J = 9.2 Hz); 2.28 (m, 1 H, H(5α)); 1.43 (s, 3 H, H(9)); 1.30 (dd, 1 H, H(2β), J = 15.2 Hz, J = 5.1 Hz); 0.98 (s, 3 H, H(10)); 0.91 (ddd, 1 H, H(6), J = 9.5 Hz, J = 9.5 Hz, J = 1.9 Hz); 0.79 (s, 3 H, H(8)); 0.86 (ddd, 1 H, H(1), J = 9.8 Hz, J = 9.5 Hz, J = 5.1 Hz); signals for the propionic acid residue: 2.27 (m, 2 H, CO—CH$_2$); 1.10 (t, 3 H, CH$_3$, J = 7.6 Hz). ^{13}C NMR (C_6D_6), δ: 174.94 (C(4)); 54.68 (C(3)); 34.28 (C(2)); 27.82 (C(10)); 22.22 (C(7)); 22.60 (C(9)); 20.56 (C(6)); 18.38 (C(5)); 16.91 (C(1)); 14.30 (C(8)); signals for the propionic acid residue: 163.88 (C=O); 29.71 (CH$_2$); 9.94 (CH$_3$)

(1*S*,3*S*,6*R*)-3-(Heptanoylamido)caran-4-one (*E*)-oxime (3c). Colorless glassy substance. The yield was 490 mg (94%); $[\alpha]^{20}_{578}$ +113 (*c* 0.62, $CHCl_3$). High-resolution MS, found: *m/z* 294.2307 $[M]^+$. $C_{17}H_{30}N_2O_2$. Calculated: M = 294.2310. MS, *m/z* (I_{rel} (%)): 294 (4), 277 (10), 165 (20), 150 (24), 148 (100), 122 (13), 100 (17), 57 (10), 43 (53), 42 (15), 41 (23). IR (KBr), ν/cm^{-1}: 3303, 1647. ^1H NMR ($CDCl_3$), δ: 8.85 (s, 1 H, N=O—H); 5.88 (s, 1 H, N—H); 2.86 (dd, 1 H, H(5β), J = 18.4 Hz, J = 1.5 Hz); 2.74 (dd, 1 H, H(2α), J = 15.1 Hz, J = 9.6 Hz); 2.30 (dd, 1 H, H(5α), J = 18.4 Hz, J = 8.8 Hz); 1.41 (s, 3 H, H(9)); 1.16 (dd, 1 H, H(2β), J = 15.2 Hz, J = 5.7 Hz); 1.00 (s, 3 H, H(10)); 0.84 (ddd, 1 H, H(6), J = 9.2 Hz, J = 8.8 Hz, J = 5.7 Hz); 0.83 (s, 3 H, H(8)); 0.70 (ddd, 1 H, H(1), J = 9.2 Hz, J = 9.2 Hz, J = 5.7 Hz); signals for the heptanoic acid residue: 1.57 (tt, 2 H, CO—CH$_2$, J = 7.1 Hz, J = 7.1 Hz); 1.24 (m, 32 H, (CH$_2$)$_{17}$); 0.84 (t, 3 H, CH$_3$, J = 1.0 Hz). ^{13}C NMR

(C_6D_6), δ: 173.26 (C(4)); 54.25 (C(3)); 33.12 (C(2)); 28.26 (C(10)); 22.65 (C(7)); 22.60 (C(9)); 20.33 (C(6)); 18.98 (C(5)); 17.48 (C(1)); 14.60 (C(8)); signals for the heptanoic acid residue: 161.26 (C=O); 37.23 (C(1)); 31.66 (C(4)); 28.98 (C(3)); 26.10 (C(2)); 18.05 (C(5)); 14.18 (C(6)).

(1*S*,3*S*,6*R*)-3-(Nonadecanoylamido)caran-4-one (*E*)-oxime (3d). Colorless glassy substance. The yield was 85%; $[\alpha]^{20}_{578}$ +100 (*c* 0.70, $CHCl_3$). High-resolution MS, found: *m/z* 462.41853 $[M]^+$. $C_{29}H_{54}N_2O_2$. Calculated: M = 462.41853. MS, *m/z* (I_{rel} (%)): 462 (5), 447 (12), 165 (4), 150 (20), 148 (100), 132 (10), 130 (12), 123 (15), 106 (3), 100 (15), 57 (12), 43 (55), 42 (11), 41 (26), 29 (9). IR (KBr), ν/cm^{-1}: 3303, 1647. ^{1}H NMR ($CDCl_3$), δ: 8.85 (s, 1 H, N=O—H); 5.88 (s, 1 H, N—H); 2.86 (dd, 1 H, H(5β), *J* = 18.6 Hz, *J* = 1.5 Hz); 2.65 (dd, 1 H, H(2α), *J* = 15.1 Hz, *J* = 9.6 Hz); 2.30 (dd, 1 H, H(5α), *J* = 18.4 Hz, *J* = 8.8 Hz); 1.41 (s, 3 H, H(9)); 1.28 (m, 1 H, H(2β)); 1.01 (s, 3 H, H(10)); 0.84 (ddd, 1 H, H(6); *J* = 9.2 Hz, *J* = 8.8 Hz, *J* = 1.5 Hz); 0.83 (s, 3 H, H(8)); 0.70 (ddd, 1 H, H(1), *J* = 9.2 Hz, *J* = 9.2 Hz, *J* = 5.7 Hz); signals for the nonadecanoic acid residue: 1.58 (tt, 2 H, CO—CH_2, *J* = 7.3 Hz, *J* = 7.3 Hz); 1.24 (m, 32 H, $(CH_2)_{16}$); 0.87 (t, 3 H, CH_3, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 172.62 (C(4)); 54.66 (C(3)); 33.52 (C(2)); 28.29 (C(10)); 22.66 (C(7)); 22.60 (C(9)); 20.49 (C(6)); 17.87 (C(5)); 17.38 (C(1)); 14.60 (C(8)); signals for the nonadecanoic acid residue: 161.16 (C=O); 31.96 (C(1)); 29.74 (9 S, CH_2); 29.69 (CH_2); 29.66 (CH_2); 29.48 (CH_2); 29.39 (CH_2); 29.34 (CH_2); 25.96 (CH_2); 19.15 (CH_2); 14.17 (C(18)).

(1*S*,3*S*,6*R*)-3-(2-Chloroacetamido)caran-4-one (*E*)-oxime (3e). Colorless glassy substance. The yield was 94%; $[\alpha]^{20}_{578}$ +125 (*c* 0.64, $CHCl_3$). High-resolution MS, found: *m/z* 258.11089 $[M]^+$. $C_{12}H_{19}N_2O_2Cl$. Calculated: M = 258.1135. MS, *m/z* (I_{rel} (%)): 258 (3), 250 (18), 165 (27), 150 (43), 148 (100), 133 (13), 132 (12), 123 (27), 106 (23), 105 (21), 94 (10), 79 (16), 42 (31), 41 (26). ^{1}H NMR ($CDCl_3$), δ: 8.53 (s, 1 H, N=O—H); 6.74 (s, 1 H, N—H); 2.95 (dd, 1 H, H(5β), *J* = 18.2 Hz, *J* = 1.3 Hz); 2.55 (dd, 1 H, H(2α), *J* = 15.0 Hz, *J* = 9.5 Hz); 2.27 (dd, 1 H, H(5α), *J* = 18.2 Hz, *J* = 8.6 Hz); 1.46 (s, 3 H, H(9)); 1.35 (dd, 1 H, H(2β), *J* = 15.1 Hz, *J* = 5.6 Hz); 1.03 (s, 3 H, H(10)); 0.92 (ddd, 1 H, H(6), *J* = 8.6 Hz, *J* = 8.6 Hz, *J* = 1.3 Hz); 0.84 (s, 3 H, H(8)); 0.74 (ddd, 1 H, H(1), *J* = 9.5 Hz, *J* = 8.6 Hz, *J* = 5.6 Hz); signals for the monochloroacetic acid residue: 3.97 and 3.94 (both d, 1 H each, *J* = 14.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 164.84 (C(4)); 160.21 (C=O); 55.01 (C(3)); 34.05 (C(2)); 26.16 (C(10)); 22.01 (C(9)); 20.32 (C(6)); 19.40 (C(7)); 17.76 (C(5)); 16.76 (C(1)); 14.52 (C(8)); signals for the monochloroacetic acid residue: 42.77 (CO—CH_2Cl).

(1*S*,3*S*,6*R*)-3-(Adamantane-1-carboxamido)caran-4-one (*E*)-oxime (3f). Colorless crystals with m.p. 222—225 °C (Bu^{t}OMe), The yield was 90%; $[\alpha]^{20}_{578}$ +105 (*c* 0.77, $CHCl_3$). High-resolution MS, found: *m/z* 344.24618 $[M]^+$. $C_{20}H_{26}N_2O_2$. Calculated: M = 344.26149. MS, *m/z* (I_{rel} (%)): 327 (13), 180 (24), 165 (15), 149 (15), 148 (16), 147(100), 135 (77), 106 (11), 93 (17), 78 (23), 67 (11), 55 (9), 41 (11). IR (KBr), ν/cm^{-1}: 3461, 3341, 1644. ^{1}H NMR ($CDCl_3$), δ: 8.83 (s, 1 H, N=O—H); 5.60 (s, 1 H, N—H); 2.87 (dd, 1 H, H(5β), *J* = 18.0 Hz, *J* = 1.5 Hz); 2.74 (dd, 1 H, H(2α), *J* = 15.0 Hz, *J* = 10.0 Hz); 2.38 (dd, 1 H, H(5α), *J* = 18.0 Hz, *J* = 9.0 Hz); 1.39 (s, 3 H, H(9)); 1.29 (dd, 1 H, H(2β), *J* = 15.0 Hz, *J* = 5.0 Hz); 1.00 (s, 3 H, H(10)); 0.92 (ddd, 1 H, H(6), *J* = 9.0 Hz, *J* = 5.0 Hz, *J* = 1.5 Hz); 0.83 (s, 3 H, H(8)); 0.66 (ddd, 1 H, H(1), *J* = 9.0 Hz, *J* = 9.0 Hz, *J* = 4.0 Hz); signals for the adamantane-1-carboxylic acid residue: 2.00 (s, 3 H, H(3)); 1.90 (m, 6 H, H(2)); 1.69 (m, 6 H, H(4)). ^{13}C NMR ($CDCl_3$), δ: 177.14 (C=O); 161.61 (C(4)); 54.03 (C(3)); 34.16 (C(2)); 27.97 (C(10)); 22.20 (C(9)); 20.59 (C(6)); 19.30 (C(7)); 17.68 (C(5)); 16.75 (C(11)); 14.18 (C(8)); signals for the adamantyl fragment: 40.89 (C(2′)); 39.21 (C(4′)); 36.38 (C(1′)); 28.04 (C(3′)).

(1*S*,3*S*,6*R*)-3-(Benzamido)caran-4-one (*E*)-oxime (3g). Colorless crystals with m.p. 124—127 °C (Bu^{t}OMe), The yield was 78%; $[\alpha]^{20}_{578}$ +146 (*c* 0.65, $CHCl_3$). High-resolution MS, found: *m/z* 286.16812 $[M]^+$. $C_{17}H_{22}N_2O_2$. Calculated: M = 286.16812. MS, *m/z* (I_{rel} (%)): 286 (12), 269 (19), 165 (14), 150 (21), 149 (13), 148 (93), 122 (15), 106 (15), 105 (100), 77 (47), 41 (7). IR (KBr), ν/cm^{-1}: 3323, 3242, 1637. UV, λ_{max}/nm (logε): 202 (5.26), 236 (5.01). ^{1}H NMR ($CDCl_3$), δ: 8.93 (s, 1 H, N=O—H); 6.36 (s, 1 H, N—H); 2.95 (d, 1 H, H(5β), *J* = 19.5 Hz); 2.65 (dd, 1 H, H(2α), *J* = 15.0 Hz, *J* = 10.0 Hz); 2.38 (dd, 1 H, H(5α), *J* = 19.0 Hz, *J* = 9.0 Hz); 1.57 (s, 3 H, H(9)); 1.26 (dd, 1 H, H(2β), *J* = 15.0 Hz, *J* = 6.0 Hz); 1.00 (s, 3 H, H(10)); 0.92 (dd, 1 H, H(6), *J* = 9.0 Hz, *J* = 7.0 Hz); 0.85 (s, 3 H, H(8)); 0.71 (ddd, 1 H, H(1), *J* = 10.0 Hz, *J* = 9.0, *J* = 6.0 Hz); signals for the benzoic acid residue: 7.38 (t, 2 H, H_{meta}); 7.45 (t, 1 H, H_{para}); 7.70 (d, 2 H, H_{ortho}). ^{13}C NMR (C_6D_6), δ: 166.60 (C(4)); 161.35 (C=O); 54.99 (C(3)); 33.98 (C(2)); 27.90 (C(10)); 22.24 (C(9)); 20.30 (C(6)); 19.35 (C(7)); 17.75 (C(5)); 16.78 (C(1)); 14.23(C(8)); signals for the benzoic acid residue: 135.09 (CO—C); 131.23 (C_{para}); 128.41 (2 C, C_{meta}); 126.71 (2 C, C_{ortho}).

(1*S*,3*S*,6*R*)-3-(2-Thenoylamido)caran-4-one (*E*)-oxime (3h). Colorless crystals with m.p. 173—175 °C (Bu^{t}OMe), The yield was 65%; $[\alpha]^{20}_{578}$ +184 (*c* 0.58, $CHCl_3$). High-resolution MS, found *m/z* 292.1262 $[M]^+$. $C_{14}H_{20}N_2O_2S$. Calculated: M = 292.16149. MS, *m/z* (I_{rel} (%)): 193 (4), 165 (8), 150 (12), 148 (48), 111 (100), 83 (7), 39 (12). IR (KBr), ν/cm^{-1}: 3323, 3242, 1637. UV, λ_{max}/nm (logε): 201 (4.94). ^{1}H NMR ($CDCl_3$), δ: 8.77 (s, 1 H, N=O—H); 6.27 (s, 1 H, N—H); 2.93 (dd, 1 H, H(5β), *J* = 17.5 Hz, *J* = 1.5 Hz); 2.74 (dd, 1 H, H(2α), *J* = 16.0 Hz, *J* = 10.0 Hz); 2.38 (dd, 1 H, H(5α), *J* = 17.5 Hz, *J* = 9.0 Hz); 1.52 (s, 3 H, H(9)); 1.26 (dd, 1 H, H(2β), *J* = 16.0 Hz, *J* = 4.0 Hz); 1.02 (s, 3 H, H(10)); 0.92 (ddd, 1 H, H(6), *J* = 9.0 Hz, *J* = 9.0 Hz, *J* = 1.5 Hz); 0.86 (s, 3 H, H(8)); 0.71 (ddd, 1 H, H(1), *J* = 10.0 Hz, *J* = 9.0 Hz, *J* = 4.0 Hz); signals for the thiophene-1-carboxylic acid residue: 7.35 (dd, 1 H, H(1), *J* = 5.0 Hz, *J* = 4.0 Hz); 7.42 (dd, 1 H, H(2), *J* = 5.0 Hz, *J* = 1.0 Hz); 7.52 (dd, 1 H, H(3), *J* = 4.0 Hz, *J* = 1.0 Hz).

(1*S*,3*S*,6*R*)-3-(3-Phenylureido)caran-4-one (*E*)-oxime (3i). An equimolar amount of phenyl isocyanate (238 mg, 0.217 mL, 2 mmol) was added to a solution of imidazole (136 mg, 2 mmol) in CH_2Cl_2 (3 mL) at room temperature. The resulting mixture was kept for 15 min and added dropwise with stirring to a solution of amino oxime **4** (364 mg, 2 mmol) in Bu^{t}OMe (15 mL). Then the reaction mixture was stirred for 30 min after which H_2O (15 mL) was added. The organic phase was separated and successively washed with water (2×30 mL), 1 *M* HCl (5 mL), a 0.5 *M* aqueous Na_2CO_3 solution (10 mL), and a saturated aqueous NaCl solution (10 mL) and dried over Na_2SO_4. The solvent was removed at ~10 Torr, the residue was dried at ~1 Torr, and the product was obtained as colorless crystals (90% yield), m.p. 98—101°C (CH_3CN), $[\alpha]^{20}_{578}$ + 149 (*c* 0.46, $CHCl_3$). High-resolution MS, found: *m/z* 301/17883 $[M]^+$. $C_{17}H_{23}N_3O_2$. Calculated: M = 301.15903. MS, *m/z* (I_{rel} (%)): 301 (8), 200 (8), 165 (13), 150 (11), 148 (41), 133 (11), 124 (13), 118 (35),

106 (12), 94 (13), 93 (100), 77 (34), 66 (23), 41 (23). IR, ν/cm^{-1} (KBr): 3373, 1657; ν/cm^{-1} ($CHCl_3$, 2%): 3650, 3584. ^{1}H NMR ($CDCl_3$), δ: 8.60 (s, 1 H, N=O—H); 7.46 (br.s, 1 H, N—H); 5.47 (br.s, 1 H, N—H); 2.85 (dd, 1 H, H(5β), J = 18.6 Hz, J = 1.7 Hz); 2.38 (dd, 1 H, H(2α), J = 15.4 Hz, J = 9.4 Hz); 2.30 (dd, 1 H, H(5α), J = 18.6 Hz, J = 8.8 Hz); 1.44 (s, 3 H, H(9)); 1.31 (dd, 1 H, H(2β), J = 15.4 Hz, J = 5.8 Hz); 0.94 (s, 3 H, H(10)); 0.79 (ddd, 1 H, H(6), J = 9.1 Hz, J = 8.8 Hz, J = 1.7 Hz); 0.78 (s, 3 H, H(8)); 0.70 (ddd, 1 H, H(1), J = 9.4 Hz, J = 8.8 Hz, J = 5.8 Hz); signals for the phenylurea residue: 6.97 (m, 1 H, CH_{para}); 7.22 (m, 2 H, CH_{meta}); 7.35 (m, 2 H, CH_{ortho}). ^{13}C NMR ($CDCl_3$), δ: 162.56 (C(4)); 53.53 (C(3)); 34.84 (C(2)); 27.84 (C(10)); 23.31 (C(9)); 19.97 (C(6)); 19.00 (C(7)); 17.87 (C(5)); 16.68 (C(1)); 14.27 (C(8)); signals for the phenylurea residue: 155.50 (C=O); 139.00 (C—NH); 128.85 (CH_{meta}); 122.87 (CH_{para}); 119.69 (CH_{ortho}).

Isomerization of *N*-acyl derivatives 3a—i (general procedure). Concentrated H_2SO_4 (2.5 mL) was added dropwise with vigorous stirring to a solution of compound **3** (0.110—0.312 g) in $CHCl_3$ (15 mL). The reaction mixture was stirred at room temperature for 2 h. After the complete transformation of the starting compound (TLC data), an aqueous concentrated ammonia solution was added to the reaction mixture until pH 10—11 was reached, the organic layer was separated, and the aqueous layer was extracted with Bu^{t}OMe (2×10 mL). The combined organic extracts were successively washed with a 0.5 *M* aqueous Na_2CO_3 solution (10 mL) and a saturated aqueous NaCl solution (10 mL) and dried over Na_2SO_4. The solvent was evaporated, and the residue was dried at ~1 Torr. Crude product **6** thus prepared was purified by column chromatography on silica gel followed by crystallization from CH_3CN.

The rearrangement with the use of D_2SO_4 (99.8% D) was carried out according to the same procedure.

(1*S*,5*S*)-1-Isopropyl-3,5-dimethyl-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one (*E*)-oxime (6a). The yield was 71%. Colorless crystals, m.p. 216—220 °C (CH_3CN); $[\alpha]^{20}_{578}$ +429 (*c* 0.83, $CHCl_3$). The spectral parameters and results of X-ray diffraction study have been published earlier.[2]

(1*S*,5*S*)-3-Ethyl-1-isopropyl-5-methyl-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one (*E*)-oxime (6b). The yield was 70%. Colorless crystals, m.p. 79—81 °C (CH_3CN); $[\alpha]^{20}_{578}$ +125 (*c* 0.72, $CHCl_3$). High-resolution MS, found: *m/z* 238.16819 $[M]^+$. $C_{13}H_{22}N_2O_2$. Calculated: M = 238.16812. MS, *m/z* (I_{rel} (%)): 238 (27), 221 (14), 165 (100), 150 (22), 148 (22), 135 (10), 123 (19), 74 (16), 57 (54), 41 (21), 29 (28). IR (KBr), ν/cm^{-1}: 3443, 1648, 960. ^{1}H NMR ($CDCl_3$), δ: 9.50 (br.s, 1 H, N=O—H); 3.26 (ddd, 1 H, H(7β), J = 15.5 Hz, J = 6.0 Hz, J = 1.5 Hz); 1.93 (dddd, 1 H, H(8α), J = 13.3 Hz, J = 6.5 Hz, J = 3.0 Hz, J = 1.5 Hz); 1.78 (ddd, 1 H, H(7α), J = 15.5 Hz, J = 13.3 Hz, J = 6.5 Hz); 1.74 (qq, 1 H, H(10), J = 6.9 Hz, J = 6.9 Hz); 1.73 (d, 1 H, H(9β), J = 13.1 Hz); 1.58 (ddd, 1 H, H(8β), J = 13.4 Hz, J = 13.4 Hz, J = 6.0 Hz); 1.48 (dd, 1 H, H(9α), J = 13.1 Hz, J = 3.1 Hz); 1.35 (s, 3 H, H(13)); 0.92 (d, 3 H, H(11), J = 6.9 Hz); 0.91 (d, 3 H, H(12), J = 6.9 Hz); signals for the ethyl group at the C(3) atom: 2.25 (q, 1 H, CH_2, J = 7.5 Hz); 1.13 (t, 1 H, CH_3, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 164.07 (C(6)); 159.37 (C(3)); 79.13 (C(1)); 54.27 (C(5)); 37.98 (C(9)); 36.57 (C(10)); 33.36 (C(8)); 25.01 (C(13)); 16.96 (C(7)); 16.73 (C(12)); 16.59 (C(11)); signals for the ethyl group at the C(3) atom: 28.70 (1 C, CH_2); 11.18 (1 C, CH_3).

(1*S*,5*S*)-3-Chloromethyl-1-isopropyl-5-methyl-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one *E*-oxime (6e). The yield was 69%. Colorless crystals with m.p. 157—160 °C (CH_3CN); $[\alpha]^{20}_{578}$ +209 (*c* 0.18, $CHCl_3$). ^{1}H NMR (DMSO-d_6), δ: 9.00 (s, 1 H, N=O—H); 3.29 (ddd, 1 H, H(7β), J = 15.8 Hz, J = 6.2 Hz, J = 1.1 Hz); 2.03 (dddd, 1 H, H(8α), J = 13.7 Hz, J = 6.3 Hz, J = 2.9 Hz, J = 1.5 Hz); 1.83 (ddd, 1 H, H(7α), J = 15.8 Hz, J = 13.4 Hz, J = 6.3 Hz); 1.82 (qq, 1 H, H(10), J = 6.8 Hz, J = 6.8 Hz); 1.78 (d, 1 H, H(9β), J = 13.4 Hz); 1.64 (ddd, 1 H, H(8β), J = 13.5 Hz, J = 13.5 Hz, J = 6.2 Hz); 1.55 (dd, 1 H, H(9α), J = 13.4 Hz, J = 3.1 Hz); 1.37 (s, 3 H, H(13)); 0.99 (d, 3 H, H(11), J = 6.8 Hz); 0.95 (d, 3 H, H(12), J = 6.8 Hz); signals for the chloromethyl group: 4.03 and 3.97 (both d, 1 H each, J = 11.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 158.88 (C(6)); 158.31 (C(3)); 80.73 (C(1)); 55.08 (C(5)); 43.34 (—CH_2Cl); 37.60 (C(9)); 36.49 (C(10)); 33.32 (C(8)); 24.69 (C(13)); 16.98 (C(7)); 16.84 (C(12)); 16.75 (C(11)).

(1*S*,5*S*)-3-Adamant-1-yl-1-isopropyl-5-methyl-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one (*E*)-oxime (6f). The yield was 65%. Colorless crystals with m.p. 230—233 °C (CH_3CN); $[\alpha]^{20}_{578}$ +136 (*c* 0.62, $CHCl_3$). High-resolution MS, found: *m/z* 344.24618 $[M]^+$. $C_{20}H_{26}N_2O_2$. Calculated: M = 344.2261. MS, *m/z* (I_{rel} (%)): 344 (10), 180 (42), 179 (22), 166 (31), 165 (42), 162 (18), 148 (18), 136 (13), 135 (100), 134 (11), 107 (13), 93 (27), 91 (12), 79 (27), 77 (11), 67 (15), 55(14), 43(14), 41(22), 28 (12). IR (KBr), ν/cm^{-1}: 3244, 1635, 943. ^{1}H NMR ($CDCl_3$), δ: 9.00 (s, 1 H, N=O—H); 3.21 (ddd, 1 H, H(7β), J = 15.3 Hz, J = 9.3 Hz, J = 1.2 Hz); 1.92 (m, 1 H, H(8α)); 1.82 (m, 1 H, H(7α)); 1.86 (qq, 1 H, H(10), J = 7.7 Hz, J = 7.7 Hz); 1.84 (d, 1 H, H(9β), J = 13.0 Hz); 1.61 (ddd, 1 H, H(8β), J = 13.5 Hz, J = 13.5 Hz, J = 5.9 Hz); 1.58 (dd, 1 H, H(9α), J = 12.9 Hz, J = 5.9 Hz); 1.31 (s, 3 H, H(14)); 0.93 (d, 3 H, H(11), J = 7.7 Hz); 0.92 (d, 3 H, H(12), J = 7.7 Hz); signals for the adamantyl fragment: 1.98 (m, 3 H, H(3)); 1.84 (s, 6 H, H(2)); 1.69 (m, 6 H, H(4)). ^{13}C NMR (C_6D_6), δ: 166.60 (C(6)); 160.26 (C(3)); 77.93 (C(1)); 54.08 (C(5)); 38.07 (C(9)); 36.78 (C(10)); 33.76 (C(8)); 25.47 (C(14)); 17.02 (C(7)); 16.88 (C(12)); 16.82 (C(11)); signals for the adamantyl fragment: 28.36 (3 C, C(3′)); 36.95, (3 C, C(2′)); 39.78 (3 C, C(4′)); 39.36 (C(1′)).

(1*S*,5*S*)-1-Isopropyl-5-methyl-3-phenyl-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one (*E*)-oxime (6g). The yield was 83%. Colorless crystals with m.p. 177—180 °C (CH_3CN); $[\alpha]^{20}_{578}$ +193 (*c* 0.38, $CHCl_3$). High-resolution MS, found: *m/z* 286.16879 $[M]^+$. $C_{17}H_{22}N_2O_2$. Calculated: M = 286.16812. MS, *m/z* (I_{rel} (%)): 286 (4), 279 (10), 167 (40), 165 (17), 149 (100), 122 (12), 113 (13), 105 (74), 77 (34), 71 (27), 57 (37), 42 (15), 55 (15), 43 (26). IR (KBr), ν/cm^{-1}: 3392, 1624, 954. UV, λ_{max}/nm (logε): 203 (5.20), 236 (5.01). ^{1}H NMR ($CDCl_3$), δ: 10.76 (s, 1 H, N=O—H); 3.16 (m, 1 H, H(7β)); 2.00 (m, 1 H, H(8α)); 1.95 (d, 1 H, H(9β), J = 13.3 Hz); 1.89 (qq, 1 H, H(10), J = 6.8 Hz, J = 6.8 Hz); 1.65 (ddd, 1 H, H(8β), J = 13.4 Hz, J = 13.4 Hz, J = 5.5 Hz); 1.60 (m, 1 H, H(7α)); 1.58 (m, 1 H, H(9α)); 1.39 (s, 3 H, H(14)); 1.00 (d, 3 H, H(11), J = 6.8 Hz); 0.97 (d, 3 H, H(12), J = 6.8 Hz); signals for the phenyl group: 7.41 (t, 2 H, H$_{meta}$); 7.47 (t, 1 H, H$_{para}$); 7.87 (d, 2 H, H$_{ortho}$). ^{13}C NMR ($CDCl_3$), δ: 157.29 (C(6)); 155.89 (C(3)); 79.74 (C(1)); 54.73 (C(5)); 37.64 (C(9)); 36.21 (C(10)); 32.41 (C(8)); 25.61 (C(14)); 16.91 (C); 16.77 (C); 16.59 (C(11)); signals for the phenyl group: 133.42 (C$_{ipso}$); 130.65 (C$_{para}$); 128.56 (2 C, C$_{meta}$); 126.821 (2 C, C$_{ortho}$).

(1*S*,5*S*)-1-Isopropyl-5-methyl-3-(2-thienyl)-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one (*E*)-oxime (6h). The yield was 78%. Colorless crystals with m.p. 164 °C (with decomp., CH_3CN); $[\alpha]^{20}_{578}$ +92 (*c* 0.087, $CHCl_3$). High-resolution MS, found: *m/z* 292.12420 $[M]^+$. $C_{15}H_{20}N_2O_2S$. Calculated: M = 292.12420. MS, *m/z* (I_{rel} (%)): 292 (8), 165 (30), 150 (14), 149 (11), 148 (12), 128 (12), 111 (100), 57 (8), 41 (12), 39 (11), 28 (56). IR (KBr), ν/cm^{-1}: 3363, 3088, 1631, 954. UV, λ_{max}/nm (log ε): 200 (4.90), 253 (4.85), 267 (4.82). ^{1}H NMR (DMSO-d_6), δ: 10.43 (s, 1 H, N=O—H); 3.23 (ddd, 1 H, H(7β), *J* = 14.3 Hz, *J* = 6.1 Hz, *J* = 2.0 Hz); 2.02 (ddd, 1 H, H(8α), *J* = 12.9 Hz, *J* = 5.6 Hz, *J* = 2.0 Hz); 1.82 (ddd, 1 H, H(7α), *J* = 14.3 Hz, *J* = 14.3 Hz, *J* = 5.6 Hz); 1.86 (qq, 1 H, H(10), *J* = 6.8 Hz, *J* = 6.8 Hz); 1.84 (d, 1 H, H(9β), *J* = 13.0 Hz); 1.61 (ddd, 1 H, H(8β), *J* = 12.9 Hz, *J* = 14.3 Hz, *J* = 5.6 Hz); 1.58 (dd, 1 H, H(9α), *J* = 13.0 Hz, *J* = 2.8 Hz); 1.39 (s, 3 H, H(13)); 1.00 (d, 3 H, H(11), *J* = 6.8 Hz); 0.97 (d, 3 H, H(12), *J* = 6.8 Hz); signals for the thienyl residue: 6.97 (dd, 1 H, H(2′), *J* = 5.1 Hz, *J* = 3.7 Hz); 7.34 (dd, 1 H, H(3′), *J* = 5.1 Hz, *J* = 1.2 Hz); 7.43 (dd, 1 H, H(4′), *J* = 3.7 Hz, *J* = 1.2 Hz). ^{13}C NMR (DMSO-d_6), δ: 157.29 (C(6)); 152.71 (C(3)); 79.70 (C(1)); 54.50 (C(5)); 37.86 (C(9)); 36.12 (C(10)); 32.34 (C(8)); 25.86 (C(14)); 16.49 (C(7)); 16.39 (C(12)); 16.16 (C(11)); signals for the thienyl residue: 156.09 (C(1′)); 127.93, 127.22 (2C, C(2′), C(3′)); 126.53 (C(4′)).

(1*S*,5*S*)-1-Isopropyl-5-methyl-3-phenylamino-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one (*E*)-oxime (6i). The yield was 58%. Colorless crystals with m.p. 167—170 °C (CH_3CN); $[\alpha]^{20}_{578}$ +125 (*c* 0.087, $CHCl_3$). High-resolution MS, found: *m/z* 301.17883 $[M]^+$. $C_{17}H_{23}N_3O_2$. Calculated: M = 301.17902. MS, *m/z* (I_{rel} (%)): 301 (40), 284 (15), 165 (100), 150 (22), 148 (24), 137 (47), 123 (18), 107 (14), 93 (52), 77 (20), 57 (23), 55 (18), 43 (26), 41 (26). IR (KBr), ν/cm^{-1}: 3427, 1631, 954. ^{1}H NMR (DMSO-d_6 : $CDCl_3$ = 1 : 4), δ: 10.40 (br.s, 1 H, N=O—H); 3.21 (ddd, 1 H, H(7β), *J* = 15.3 Hz, *J* = 6.2 Hz, *J* = 1.1 Hz); 1.93 (dddd, 1 H, H(8α), *J* = 13.0 Hz, *J* = 6.0 Hz, *J* = 2.3 Hz, *J* = 0.9 Hz); 1.82 (ddd, 1 H, H(7α), *J* = 14.3 Hz, *J* = 14.3 Hz, *J* = 5.6 Hz); 1.80 (qq, 1 H, H(10), *J* = 6.7 Hz, *J* = 6.7 Hz); 1.78 (d, 1 H, H(9β), *J* = 13.0 Hz); 1.59 (ddd, 1 H, H(8β), *J* = 12.9 Hz, *J* = 14.3 Hz, *J* = 5.6 Hz); 1.58 (dd, 1 H, H(9α), *J* = 13.0 Hz, *J* = 2.8 Hz); 1.34 (s, 3 H, H(14)); 0.94 (d, 3 H, H(11), *J* = 6.7 Hz); 0.92 (d, 3 H, H(12), *J* = 6.7 Hz); signals for the aniline residue: 6.79 (dt, 2 H, H_o, *J* = 6.0 Hz, *J* = 1.0 Hz); 7.10 (m, 1 H, H_{para}); 7.48 (d, 2 H, H_{meta}, *J* = 6.0 Hz). ^{13}C NMR (DMSO-d_6 : $CDCl_3$), δ: 158.76 (C(6)); 150.04 (C(3)); 80.30 (C(1)); 53.32 (C(5)); 38.13 (C(9)); 36.12 (C(10)); 32.13 (C(8)); 25.63 (C(14)); 16.51 (C(7)); 16.42 (C(12)); 16.20 (C(11)); signals for the aniline residue: 146.88 (NH—C); 127.80 (2 H, CH_{meta}), 120.09 (1 C, CH_{para}), 118,11 (2 C, CH_{ortho}).

(1*S*,5*S*)-1-[$^2H_7$]-Isopropyl-3,5-dimethyl-2-oxa-4-azabicyclo[3.3.1]non-3-en-6-one (*E*)-oxime (6a-d_7). The yield was 70%. Colorless crystals with m.p. of 215—217 °C (CH_3CN). ^{1}H NMR (DMSO-d_6), δ: 10.57 (s, 1 H, N=O—H); 3.10 (ddd, 1 H, H(7β), *J* = 15.5 Hz, *J* = 6.2 Hz, *J* = 0.8 Hz); 1.98 (s, 6 H, N(CH$_3$)$_2$); 1.94 (ddd, 1 H, H(8α), *J* = 13.4 Hz, *J* = 3.2 Hz, *J* = 0.8 Hz); 1.82 (ddd, 1 H, H(7α), *J* = 15.5 Hz, *J* = 13.1 Hz, *J* = 6.6 Hz); 1.75 (qq, 1 H, H(10), *J* = 6.8 Hz); 1.74 (d, 1 H, H(9β), *J* = 13.2 Hz); 1.59 (ddd, 1 H, H(8β), *J* = 13.4 Hz, *J* = 13.1 Hz, *J* = 6.6 Hz); 1.51 (dd, 1 H, H(9α), *J* = 13.2 Hz, *J* = 3.2 Hz); 1.39 (s, 3 H, H(14)); 0.91 (d, 11 CH_3, *J* = 6.8 Hz); 0.89 (d, 0.6 H, 3 H, H(12), *J* = 6.8 Hz). ^{13}C NMR (DMSO-d_6), δ: 158.14 (C(3)); 158.03 (C(6)); 79.80 (C(1)); 53.98 (C(5)); 38.25 (C(9)); 32.54 (C(8)); 25.27 (C(14)); 20.86 (C(13)); 16.68 (C(7)).

(1*S*)-1-Dimethylamino-[7-$^2H_1$,8-$^2H_3$,9-$^2H_3$]-*p*-menth-3-en-2-one (*E*)-oxime (25). ^{1}H NMR ($CDCl_3$), δ: 8.60 (s, 1 H, =NOH); 6.51 (s, 1 H, H(3)); 2.37 (m, 1 H, H_a(6)); 2.20 (m, 2 H, H(5)); 2.20 (s, 6 H, (2 CH_3—N)); 1.58 (m, 1 H, H_b(6)); 1.10 (s, 3 H, H(10)). ^{13}C NMR ($CDCl_3$), δ: 157.08 (C(2)); 156.15 (C(4)); 108.36 (C(3)); 58.10 (C(1)); 38.49 (N(CH$_3$)$_2$); 34.71 (C(7)); 32.60 (C(6)); 24.22 (C(5)); 20.30 and 20.35 (C(8) and C(9)); 14.94 (C(10)).

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