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Synthetic Transformations of Methylenelactones of Eudesmanic Type. Behavior of Isoalantolactone under the Conitions of Heck Reaction

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Abstract—By Heck reaction of isoalantolactone with aryl bromides or aryl iodides (3a*R*,4a*S*, 8a*R*,9a*R*,*E*)-3-arylmethylidene-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-ones and (4a*S*,8a*R*,9a*S*)-3-arylmethyl-8a-methyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octahydronaphtho[2,3-*b*]furan-2(4*H*)-ones, products of the double bond shift, were synthesized. The yields of the arylation products depend on the nature of the catalytic system and on the structure of the aryl halide. The structures of (3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(3,4-dimethoxybenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-one and (4a*S*,8a*R*,9a*S*)-3-(2-methylsulfanylbenzyl)-8a-methyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octahydronaphtho[2,3-*b*]furan-2(4*H*)-one were proved by XRD analysis.

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Compounds containing in their structure an α-methylidene-γ-lactone moiety, in particular, sesquiterpene lactones, attract attention due to their versatile physiological activity, including anticancer action [1]. It was established in the course of the study of structure–activity interrelation in the series of sesquiterpene lactones that the high cytotoxicity correlated with the presence of an exocyclic double bond in the lactone ring [2]. An available lactone of eudesmanic type is isoalantolactone (**I**), a characteristic metabolite of various species of elecampane *Inula sp*. [3]; the protocols of its complete synthesis are described both for the racemic [4] and the optically active form [5].

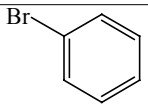
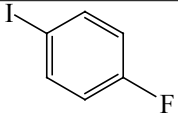
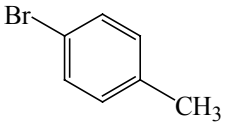
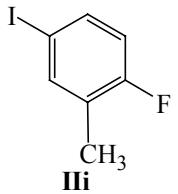
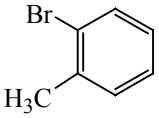
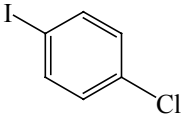
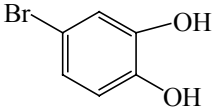
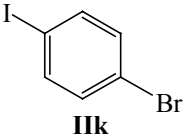
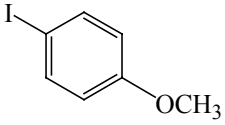
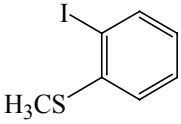
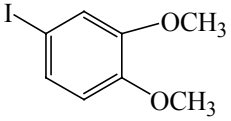
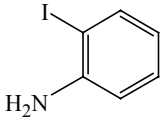
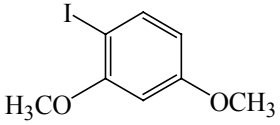
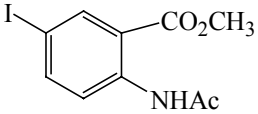
In a recent publication [6] we described the first application of Heck reaction to the structural modification of sesquiterpene methylenelactones. Here we report on the C^{13}-arylation of isoalantolactone (**I**).

Reaction of compound **I** with aryl bromides **IIa–IId** or aryl iodides **IIe–IIn** catalyzed by the system palladium acetate–phosphine ligand proceeds in DMF in the presesnce of triethylamine. The main reaction products are (3a*R*,4a*S*, 8a*R*,9a*R*,*E*)-3-arylmethylidene-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-ones **IIIa–IIIn** and (4a*S*,8a*R*,9a*S*)-3-arylmethyl-8a-methyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octahydronaphtho[2,3-*b*] furan- 2(4*H*)-ones **IVb, IVd, IVe–IVl** (Scheme 1, Table 1). Compounds **IIIa–IIIn**, **IVe, IVf, IVh, IVj, IVk, IVl** were isolated in the individual state by column chromatography on silica gel. The ratio of compounds **III** and the products **IV** of the double bond shift will be further shown to depend on such factors as the type and the structure of the aryl halide, the structure of the phosphine ligand and the palladium component of the catalyst.

Table 1 compiled the results of experiments on the reaction of isoalantolactone with the aryl halides under the action of the system $Pd(OAc)_2$–(*o*-Tol)$_3$P. The first pemittable conclusion consist in the statement of the increase in the yield of isomeric lactones **IV** at the use of aryl iodides **IIe–IIl**. The bringing into the reaction of bromo(iodo)arenes **IId, IIm, IIn** made it possible to obtain only the corresponding lactones **IIId, IIIm, IIIn**. The minimum yield of isomeric lactones **IVa–IVd** was obtained in the runs with aryl bromides **IIa–IId**.

In Table 2 by an example of the reaction of isoalantolactone (**I**) with 3,4-dimethoxyiodobenzene (**IIf**) the

Table 1. Effect of halide structure on the ratio of reaction products[a]

Initial halide	Reaction products (yield, %)	Initial halide	Reaction products (yield, %)
 **IIa**	**IIIa** (52), **IVa** (0)	 **IIh**	**IIIh** (50), **IVh** (18)
 **IIb**	**IIIb** (75), **IVb** (6)	 **IIi**	**IIIi** (57), **IVi** (21)
 **IIc**	**IIIc** (75), **IVc** (3)	 **IIj**	**IIIj** (60), **IVj** (25)
 **IId**	**IIId** (55), **IVd** (0)	 **IIk**	**IIIk** (55), **IVk** (20)
 **IIe**	**IIIe** (85), **IVe** (9)	 **III**	**IIIl** (79), **IVl** (17)
 **IIf**	**IIIf** (81), **IVf** (13)	 **IIm**	**IIIm** (62), **IVm** (0)
 **IIg**	**IIIg** (80), **IVg** (10)	 **IIn**	**IIIn** (54), **IVn** (0)

[a] Reaction conditions: 4 mol% $Pd(OAc)_2$, 16 mol% $(o\text{-Tol})_3P$, 1.4 equiv Et_3N, 120°C, 8–10 h, DMF. Conversion in all runs 80–100%.

effect of the phosphine structure and the temperature is shown on the substrate conversion and the relative yields of lactones **IIIf** and **IVf**. As seen, the highest yield of arylation product **IIIf** was obtained at the use of tris(*o*-tolylphosphine) as the ligand. The going over to trialkylphosphines and tri(2-furyl)phosphine favored the increase in the yield of the isomeric lactone **IVf**. Besides it turned out that the formation of the product of the double bond shift is favored by a higher reaction temperature (Table 2, runs nos. *1*, *6*, *7*).

Interesting results were obtained are the use of the catalytic system $Pd(dba)_2$–Ph_3P (120°C). At isoalantolactone (**I**) conversion 80% the ratio if eudesmanolides **IIIf** and **IVf** was 2 : 1.

The reaction of isoalantolactone (**I**) with aryl iodides **IIf, IIk** proceeded also in the absence of a phosphine ligand under the action of the system $Pd(OAc)_2$–Et_3N–CH_3CN resulting in an enhanced yield of compounds **IVf** and **IVk** [40 (**IIIf**), 27 (**IVf**), 70 (**IIIk**), 20% (**IVk**)]. Noteworthy that aryl bromides **IIa–IId** did not react with lactone **I** both in the absence of phosphine ligand and at the replacement of $(o\text{-Tol})_3P$ by Ph_3P, $(2\text{-Fu})_3P$, or by

Table 2. Effect of the ligand nature and the reaction conditions on the yield and reaction products ratio in reaction of isoalantolactone (**I**) with 3,4-dimethoxyiodobenzene (**IIf**) in DMF in the presence of 1.4 equiv of Et_3N

Run no.	Ligand (16 mol%)	*T*, °C	Time, h	Conversion, % of lactone (**I**)	Yield, %	
					IIIf	**IVf**
1	(*o*-Tol)$_3$P	120	8	95	81	13
2	Ph_3P	120	8	80	50	15
3	(*t*-Bu)$_3$P	100	16	100	55	25
4	(*p*-Bu)$_3$P	120	8	90	55	20
5	(2-Fu)$_3$P	120	8	80	40	25
6	(*o*-Tol)$_3$P	90	8	75	85	8
7	(*o*-Tol)$_3$P	140	8	92	70	20

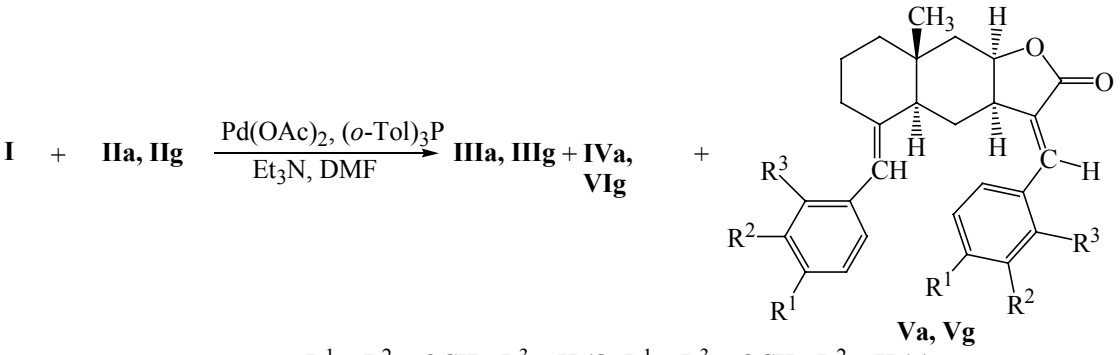
alkylphosphines.

Hence the optimum catalytic system for the arylation of isoalantolactone (**I**) is $Pd(OAc)_2$–(*o*-Tol)$_3$P.

The formation of some minor components that we have detected is worth mentioning. For instance, in reactions of isoalantolactone (**I**) with aryl iodides **IIf** and **IIg** the products were additionally isolated of the lactone arylation at the C^4–C^{15} bond, compounds **Vf** and **Vg** (Scheme 2). Similar bisadducts were also detected jn reactions of compound **I** with aryl bromides **IIa–IId** (according to ^{1}H NMR spectra of the reaction mixtures). The increase in the excess of the aryl halide to 20% did not result in the notable growth of the yields of the products of lactone diarylation; in these conditions increased the content of the dimerization products of the initial aryl halides (according to the data of GC-MS analysis of the reaction mixtures). Arylidene-susbstituted derivatives of isoalantolactone **IIIa–IIIn** possess the (*E*)-configuration of the double bond. In the reaction of isoalantolactone (**I**) with 4-iodo-1-fluorobenzene (**IIh**) alongside the main reaction products **IIIh, IVh** (*Z*)-isomer 13-arylideneisoalantolactone **VI** was isolated (yield 2%).

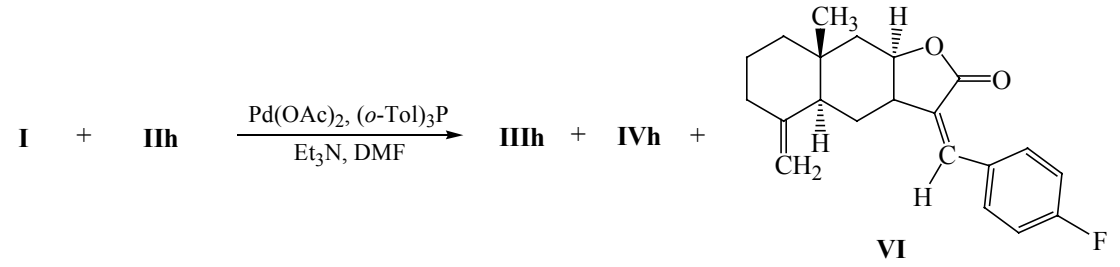
Proceeding to discuss the causes and the ways of the formation of isomeric lactones **III** and **IV** we wish to draw attention to the change in the configuration at the atom C^8 in compounds **IV**. Using the main principles of the palladium catalysis [7] it is possible to assume the scheme of C^8-epimerization proceeding through the intermediate σ-π complexes **A**–**C** (Scheme 3). Apparently the driving force of the epimerization is the energy gain

Scheme 2.



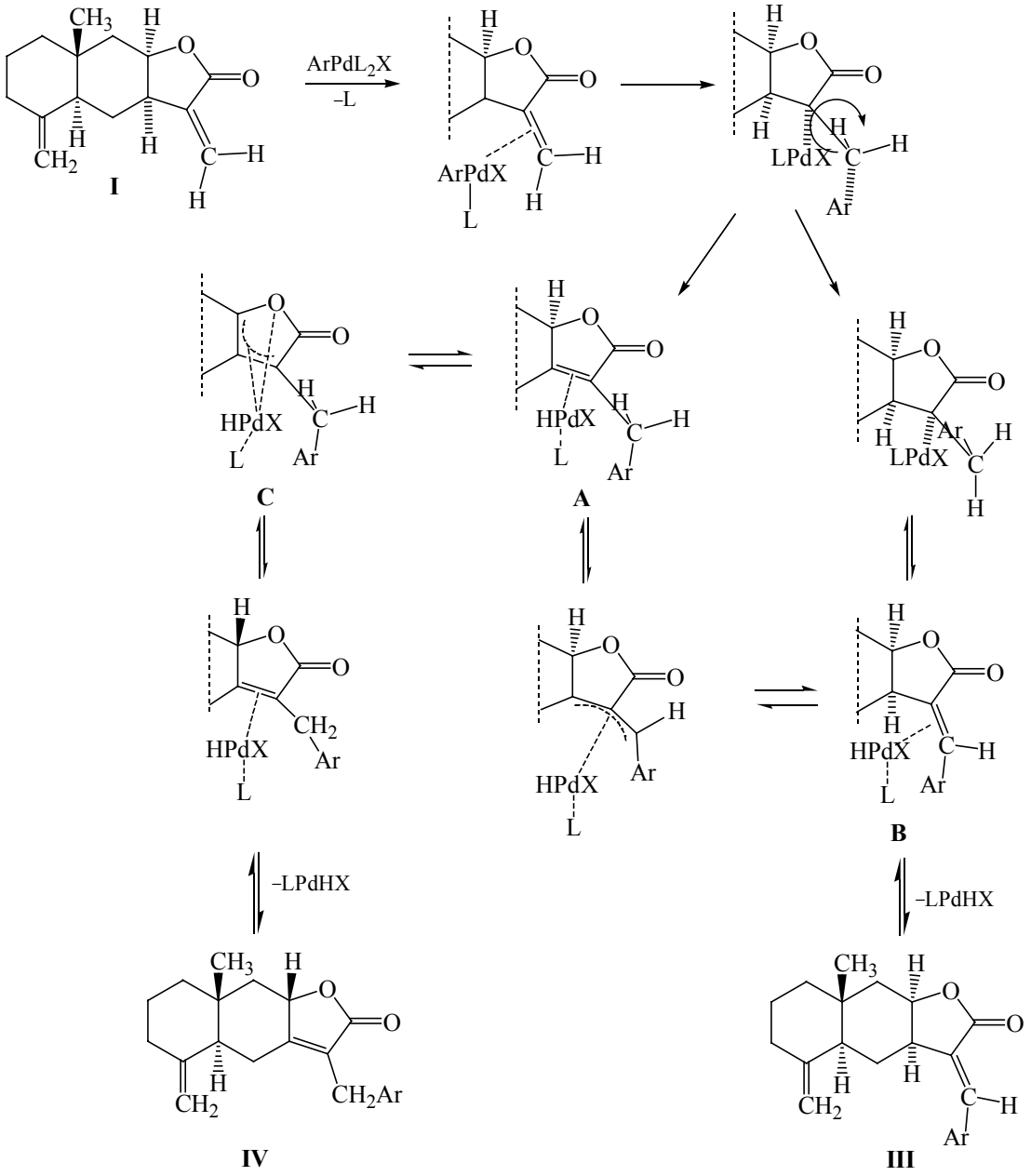
Va, Vg

$R^1 = R^2 = OCH_3$, $R^3 = H$ (**f**); $R^1 = R^3 = OCH_3$, $R^2 = H$ (**g**).



VI

Scheme 3.



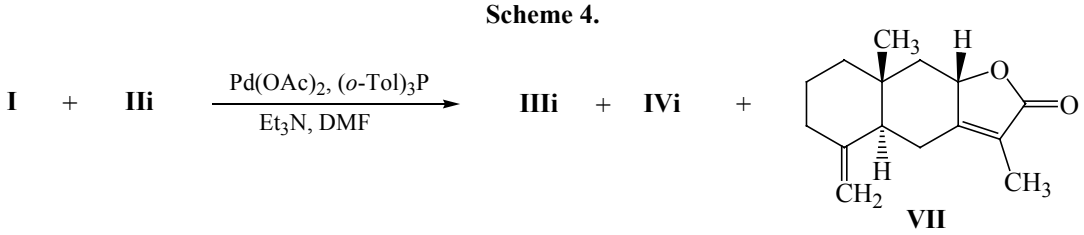
in this process resulting from a relief of the steric strains. It was shown using the molecular mechanics method MM-2 that the **C** ring of the C^{8}-epimer should be in the *boat* conformation whereas in compounds **IV** this ring existed in more energy feasible *chair* conformation ($\Delta E \approx$ 5 kcal mol^{-1}).

The assumed scheme of lactones epimerization is confirmed by the isolation of (4a*S*,8a*R*,9a*S*)-3,8a-dimethyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octahydronaphtho[2,3-*b*]furan-2(4*H*)-one (**VII**) (yield 4%) in the condensation of lactone **I** with iodoarene **IIi**. The ^{1}H NMR spectrum and the sign of the angle of the optical rotation of lactone **VII** coincide with the data for the metabolite of the plant *Aster umbellatus*, asterolide [8].

The attention should be drawn to the formation in small yields of abnormal products of lactone **I** reaction with aryl halides **IId, IIf, IIm**.

We observed a rare instance of the transfer of an aryl substituent of the phosphine ligand on palladium with the subsequent involvement of this substituent in the

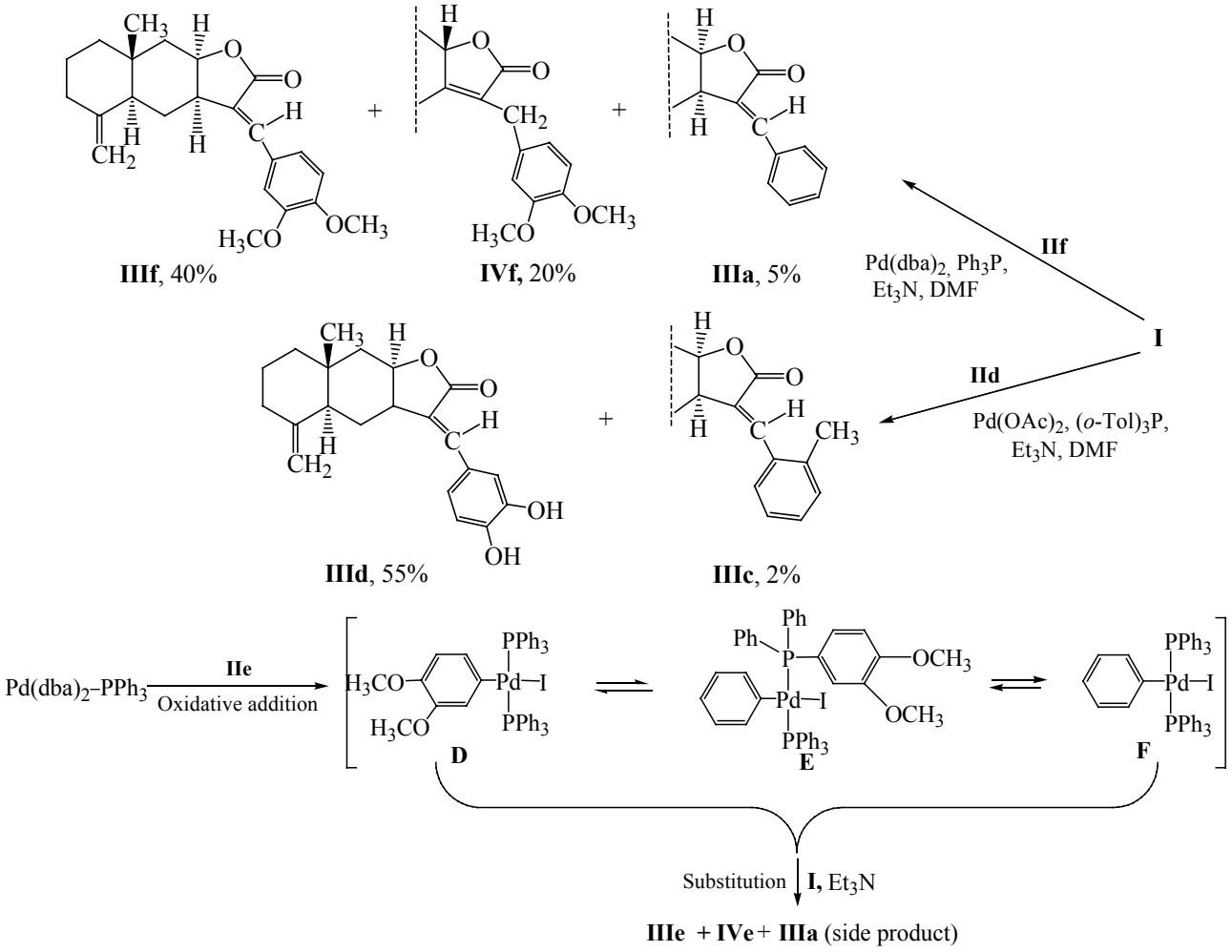
Scheme 4.



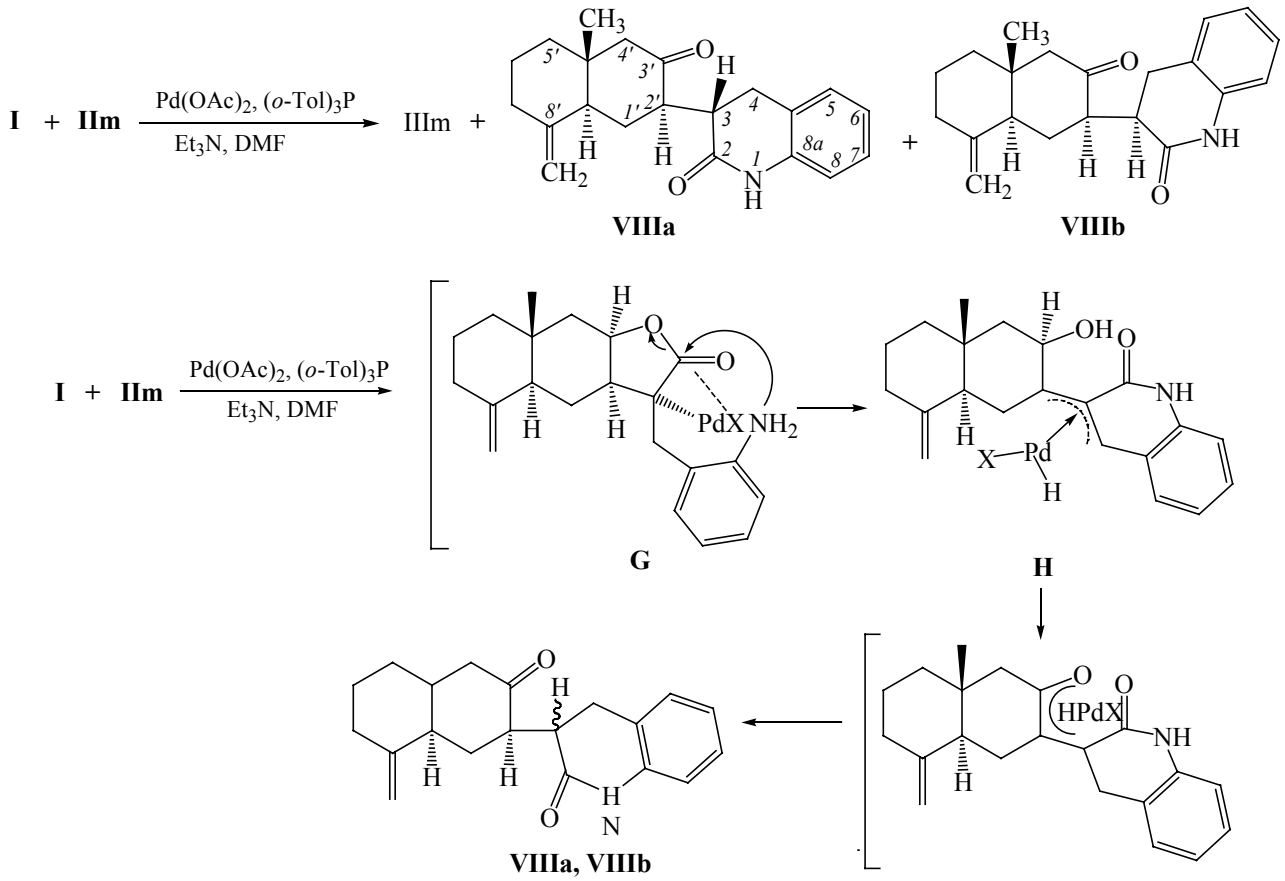
formation of the reaction product [9]. For example, in the reaction of isoalantolactone (**I**) with 4-iodoveratrol (**IIf**) [Pd(dba)$_2$–Ph_3P–Et_3N–DMF] alongside the expected products **IIIf** and **IVf** lactone **IIIa** was isolated in 5% yield, completely identical to the compound, obtained in the reaction of isoalantolactone with bromobenzene (Scheme 5). Analogous situation was observed in the reaction of isoalantolactone (**I**) with 3,4-dihydroxybromobenzene (**IId**) [Pd(OAc)$_2$–(*o*-Tol)$_3$P–Et_3N–DMF] where as a side product compound **IIIc** was isolated (yield 2%). In Scheme 5 the possible isomeric transformations of arylpalladium intermediate **D** involving the aryl-aryl exchange between the Pd(II) center and the coordinated phosphine ligand. The subsequent reaction of aryl-palladium complexes **E**, **F** with the methylidene group of lactone **I** results in the formation of side products. Thus the possibility of the existence of arylpalladium intermediates **E**, **F** (which is determined by their stability) governs the formation of side products **IIIa, IIIc**.

In the reaction of isoalantolactone (**I**) with 2-iodoaniline (**IIm**) alongside reaction product **IIIm** we isolated diastereomers 3-(*S*)- and 3-(*R*)-3-(3-oxodecahydronaph-

Scheme 5.



Scheme 6.



thalen-2-yl)-substituted 3,4-dihydroquinolin- 2(1*H*)-ones (**VIIIa, VIIIb**) (yield 2 and 4% respectively) (Scheme 6). Diastereomers **VIIIa, VIIIb** were separated by chromatography on silica gel. The formation of compounds **VIII** is apparently favored by the stabilization of the transition complex **G** through the coordination of the carbonyl group with the covalently bound palladium and the spatially approached amino group. Further follow the transformations of complex **G** including the formation of quinolone ring **H** and subsequent reduction with the participation of palladium compounds.

The structure of lactones **IIIa–IIIn, IVb, IVc, IVe–IVl** was established based on the spectral data and elemental analysis. The (*E*)-configuration of the double bond C^{11}–C^{13} in arylidenelactones **IIIa–IIIn** follows from the presence in the ^{13}C NMR spectrum registered in the monoresonance mode the coupling carbon-proton *cis*-constant of an olefin proton and the carbonyl carbon atom of the lactone (^3J 6.9–7.5 Hz); the respective trans-constant ^3J in (*Z*)-isomer **VI** amounts to 13.2 Hz. The signal of H^{13} proton in the ^1H NMR spectrum of (*E*)-isomers **IIIa–IIIn** is located in the region 7.23–7.48 ppm; for (*Z*)-isomer **VI**, at 6.82 ppm. Characteristic feature of ^1H NMR spectra of compounds **IIIa–IIIn** is the downfield shift of the signal of H^7 proton (δ 3.31–3.48 ppm) compared with the corresponding proton in the spectrum of isoalantolactone (**I**) or of (*Z*)-isomer **VI** (δ 2.93 ppm).

The formation of compounds **IVb, IVcc, IVe–IVl** is confirmed by the presence in the ^1H NMR spectra of the proton signals of the methylidene group at the atom C^{13} [e.g., for compound **IVk** δ 3.50 and 3.56 ppm (d, *J* 15.0 Hz)] and by the significantly increased difference between the chemical shifts of protons H^9 (Δδ ~1.2 ppm). The axial-axial coupling constant of the upfield H^9 proton [δ 1.12 ppm (**IVk**)] with proton H^8 is *J* 11.8 Hz.

The distinguishing features of the ^1H NMR spectra of the diarylation products **Vf, Vg** are the proton signals of the second aryl substituent, the one-proton signal of H^{15} in the region 5.90–5.93 ppm, and also the downfield shift of the proton signals of the methyl group and the proton H^3. The configuration of the center C^{15} is confirmed by the data of the ^1H–^1H NOESY experiment. The presence

of NOE-effect between the protons H^{15} and H^{6} of compound **Vg** confirms the (*E*)-configuration of the double bond C^{4}–C^{15} of arylidenelactones **Vf, Vg**.

Compounds **III–V** have characteristic UV spectra permitting assignments of the structures. For instance, the spectrum of compound **IIIb** contains absorption bands with the maxima at 202, 224, 228 (sh), and 294 nm of similar intensity (log ε 4.12, 4.08, 4.04, and 4.32 respectively); in the spectra of the diarylation products **V** the absorption maxima are shifted to the longwave region [e.g., for compound **Vg**: λ_{max} (log ε) 204 (4.45), 248 (4.20), 296 (4.04), 327 (4.09) nm]. In the UV spectra of compounds **IV** the absorption considerably changes in the region 250–300 nm; the absorption maxima of the aromatic ring are shifted, and their intensity significantly decreases [e.g., in the spectrum of lactone **IVh** absorption maxima are observed at λ 266 and 273 nm (log ε 3.16 and 3.12 respectively)].

The structure of stereoisomers 3-(3-oxodecahydronaphthalen-2-yl)-3,4-dihydroquinolin-2(1*H*)-ones (**VIIIa, VIIIb**) follows from the data of ^{1}H and ^{13}C NMR spectra. The downfield shift of the proton H^{3} in the ^{1}H NMR spectrum of compound **VIIIa** and the value of the coupling constant between the protons H$^{3,2'}$ confirms the (3*S*,2'*R*)-configuration of substituents ($J_{2',3}$ 10.2 Hz). The pseudoequatorial orientation of the proton H^{3} also follows from the downfield shift of this proton (δ 3.22 ppm) and small values of the coupling constants with protons H$^{4\alpha}$ and H$^{4\beta}$. The cisoid position of protons H$^{8a',2'}$ follows from the existence of a NOE-effect between them. Small values of the coupling constants between protons H$^{2',3}$ and the upfield shift of the proton H^{3} in the ^{1}H NMR spectrum of compound **VIIIb** (δ 2.90 ppm compared to 3.22 ppm for **VIIIa**) indicates the (3*R*,2'*R*)-configuration of the substituents.

The structure of isomeric lactones **III** and **IV** was proved by the XRD analysis of compounds **IIIf** and **IVl**. The spatial arrangement of the molecule of compound **IIIf** according to XRD data is shown in Fig. 1. The analysis of the geometry and the intermolecular interactions was performed using PLATON program [10]. The bond lengths and bond angles in the molecule **IIIf** are close to the average values [11]. The *trans*-joined six-membered rings of the decahydronaphthalene fragment have a *chair* form. In the A ring the atoms C^{1}, C^{2}, C^{4}, C^{5} are in the same plane (mean-square deviation 0.003 Å), atoms C^{3} and C^{10} deviate from this plane in different directions by 0.637(4) and 0.688(3) Å respectively. In

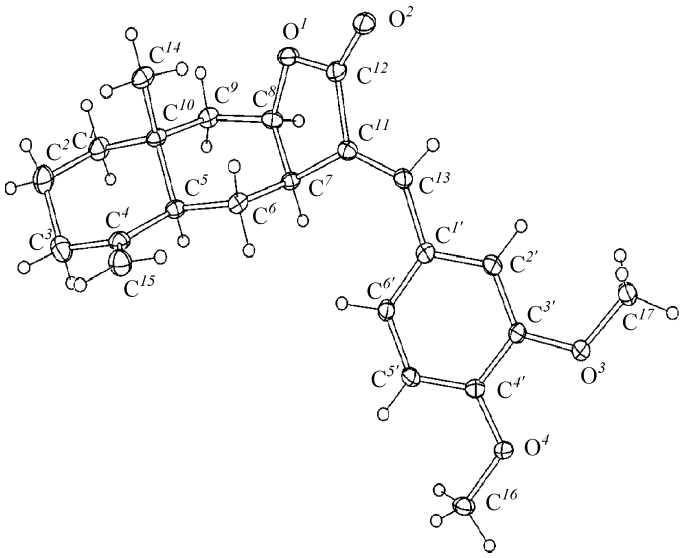


Fig. 1. Spatial arrangement of the molecule of compound **IIIf** by XRD data.

the C ring atoms C^{6}, C^{7}, C^{9}, C^{10} are in the same plane (mean-square deviation 0.003 Å), atoms C^{5} and C^{8} deviate from this plane in different directions by 0.710(3) and 0.452(3) Å respectively. The lactone ring is strongly twisted along the C^{7}–C^{8} bond, torsion angle O^{1}C^{8}C^{7}C^{11} –32.9(2)°. The lactone fragment has the usual geometry: bonds O^{1}–C^{12} 1.355(3), O^{2}–C^{12} 1.202(3) Å, torsion angle C^{8}O^{1}C^{12}O^{2} 172.4(2)°. All nonhydrogen atoms of the aromatic substituent are in the same plane [mean-square deviation 0.028 Å, maximum deviation from the plane 0.044(2) Å of the atom C$^{5'}$]. In the Cambridge Structural Database [12] among 15 structures of versatile linear methylidenelactones of eudesmanic type we did not find compounds containing an aromatic substituent in the position C^{13} of the eudesmanic skeleton. The structure of the molecule of lactone **IVl** is shown in Fig. 2. The bond lengths in molecule **IVl** are common. Same as in lactone **IIIf** the six-membered rings are in the chair conformation. However the lactone ring in molecule **IVl** is flat with the mean-square deviation of atoms 0.008 Å. The same conformation of the rings was found in an analogous compound, (±)-3,8a-dimethyl-5-methylidene-9a-hydroxy-4,4a,5,6,7,8,8a,9-octahydronaphtho[2,3-*b*]furan-2-one [(±)-hydroxyatractilolide] [13]. 2-(Methylsulfanyl)sulfanylbenzyl fragment of molecule **IVl** is brought out of the lactone ring plane, the angle between these planes is 81.2(1)°.

In the crystal molecules **IIIf** form a 3D-network by weak hydrogen bonds C^{7}H···O^{2}, C^{17}–H···O^{2} (parameters are given in Table 3). The crystal structure of compound

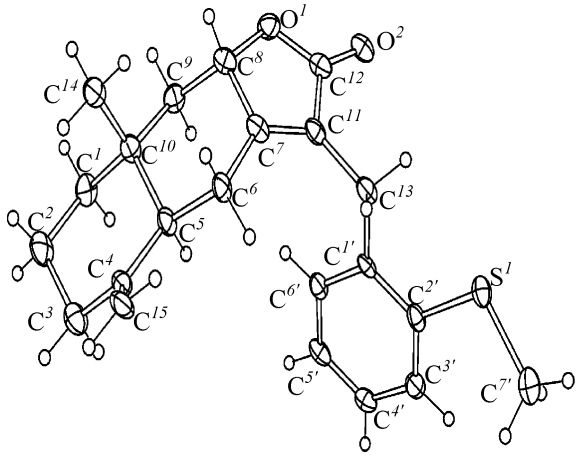


Fig. 2. Spatial arrangement of the molecule of compound **IVl** by XRD data

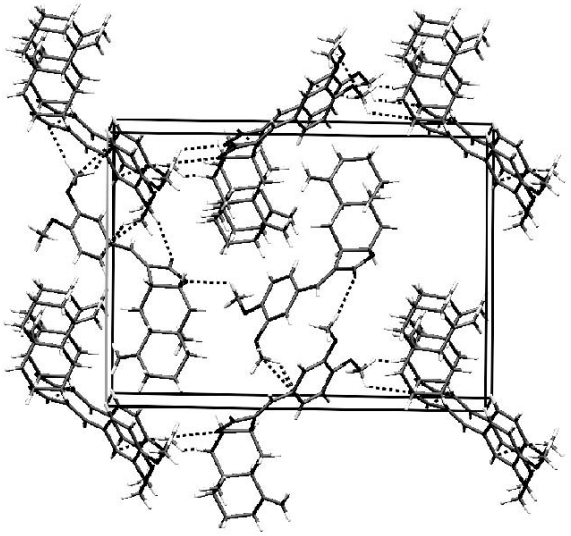


Fig. 3. Fragment of packing of compound **IIIf** molecules in the crystal.

IIIf is additionally stabilized by the intermolecular interaction C–H···π [14], the distance C^{17}–H···the center of the π-system of the benzene ring is 2.67 Å. The packing of molecules of compound **IIIf** in the crystal is shown in Fig. 3. In the crystal of compound **IVl** the 3D-network also formed by weak hydrogen bonds C–H···O (parameters are given in Table 3) and by intermolecular interactions C–H···π (the distance C^{1}–H···the center of the benzene ring 2.76, $C^{7'}$–H···centroid 2.95 Å).

Hence a method is developed of the chemical modification of the structure of the available sesquiterpene α-methylidene-γ-lactone isoalantolactone by means of palladium-catalyzed reaction with versatile aryl halides. For the first time the derivatives of α-methylidene-γ-lactones containing aromatic substituents in the position C^{13} were synthesized.

EXPERIMENTAL

NMR spectra were registered on spectrometers Bruker AV-300 [operating frequencies 300.13 (^{1}H) and 75.47 MHz (^{13}C)], AV-400 [operating frequencies 400.13 (^{1}H) and 100.78 MHz (^{13}C)], DRX-500 [operating frequencies 500.13 (^{1}H) and 125.76 MHz (^{13}C)], and AV-600 [operating frequencies 600.30 (^{1}H) and 150.96 MHz (^{13}C)].[1] The assignment of signals in the NMR spectra was performed with the use of various types of proton-proton and carbon-proton correlation spectra (COSY, COXH, COLOC, NOESY). The multiplicity of signals in the ^{13}C NMR spectra was established by recording the spectra in the *J*-modulation mode.

For recording mass spectra, evaluation of molecular mass and elemental composition mass spectrometer of high resolution DFS Thermo Scientific was applied (energy of ionizing electrons 70 eV, vaporizer temperature 230–280°C). IR spectra were recorded on a spectrophotometer Vector-22 from pellets with KBr. UV absorption spectra were taken on a spectrophotometer HP 8453 UV-Vis in ethanol. The specific rotation $[\alpha]_D^{20}$ was measured with a polarimeter PolAAr3005. XRD experiment on compounds **IIIf** and **IVl** was performed on a diffractometer Bruker Kappa Apex II with two-coordinate CCD detector using ω-φ scanning.

The reaction products were isolated by column chromatography on silica gel (Acros, 0.035–0.070 mm) and when required, with the use of preparative TLC on an non-fixed silica gel layer containing 1% of luminophor Q-35, on plates of dimensions 20×20 cm with the sorbent layer 1 mm thick (eluents benzene–ethyl acetate, chloroform–ethanol).

Table 3. Parameters of hydrogen bonds in the crystals of compounds **IIIf** and **IVl**

Compd.	Bond	C–H, Å	H···O, Å	C···O, Å	Angle CH···O, deg
IIIf	C^{7}–H···O^{2}	0.98	2.53	3.287(2)	132
	C^{17}–H···O^{2}	0.98	2.55	3.394(3)	144
IVl	$C^{7'}$–H···O^{2}	0.98	2.53	3.361(6)	143
	C^{15}–H···O^{2}	0.95	2.55	3.488(5)	171

In experiments freshly distilled solvents and reagents of "pure" grade were used.

$Pd(OAc)_2$ was synthesized as described in [15], $Pd(dba)_2$, as described in [16], and they were used without recrystallization. Lactone **I** was isolated by extraction from vegetal matter with subsequent separation through morpholine adducts by procedure [17]. 3,4-Dihydroxybromobenzene (**IId**) was obtained by method [18], 2,4-dimethoxyiodobenzene (**IIg**), by method [19], 4-iodochlorobenzene (**IIj**) and 4-iodobromobenzene (**IIk**), by method [20], methyl 2-(acetylamino)-5-iodobenzoate (**IIn**), by procedure [21]. Spectral data of compounds **IIIe, IIIf, IIIl, IVe, IVf, IVl** were published in [6].

Heck reaction. General procedure. A two-neck glass ampule was filled with argon. In an argon flow the ampule was charged in succession with 2.15 mmol (500 mg) of isoalantolactone (**I**), 2.36 mmol of aromatic halide, 0.086 mmol (4 mol%) of palladium acetate, 0.34 mmol (16 mol%) of tris(*o*-tolyl)-phosphine, 7 ml of DMF, 3.61 mmol of triethylamine, and molecular sieves (3 Å). The ampule was sealed under a slight excessive pressure of argon, the reaction mixture was heated for 8–10 h at 120°C. The condensation in the presence of the other catalytic systems or without phosphine ligand was carried out similarly (Table 2). On completion of the reaction the ampule was cooled, opened, and its content was poured into a Petri dish. The solid residue was dissolved in a minimal amount of chloroform and was subjected to chromatography on silica gel (eluent chloroform–ethanol, 100 : 0 → 10 : 1). In succession tris(*o*-tolyl)-phosphine, initial lactone, a mixture of the lactone and the reaction product, and a mixture of two reaction products were eluted (eluent chloroform). Individual compounds **III** and **IV** were obtained by repeated chromatography and recrystallization from an appropriate solvent. In some cases the purification of analytic samples was performed by preparative TLC.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-Benzylidene-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-one (IIIa). Yield 52%, mp 202–204°C (ethyl acetate), $[\alpha]_{589}$ +539° (*c* 1.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3090, 1743, 1650, 1450, 1224, 1198, 1171, 1000, 936, 900, 891, 689. UV spectrum, λ_{max}, nm (lgε): 201 (4.18), 220 (4.06), 228 (3.80), 285 (4.29). ^{1}H NMR spectrum($CDCl_3$), δ, ppm: 0.87 s (3H, $C^{14}H_3$), 1.27 m (1H, H^1), 1.42 d.d.d (1H, H^6, *J* 13.5, 12.6, 12.3 Hz), 1.50–1.63 m (4H, $H^{1,2,2,9}$), 1.96–2.07 m (3H, $H^{3,5,6}$), 2.24 d (1H, H^9, *J* 15.5 Hz), 2.34 d (1H, H^3, *J* 14.0 Hz), 3.43 d.d.d (1H, H^7, *J* 12.0, 6.0, 5.1 Hz), 4.42 br.s (1H, H^{15}), 4.49 d.d (1H, H^8, *J* 4.4, 3.2 Hz), 4.76 br.s (1H, H^{15}), 7.37–7.43 m (4H, $H^{2',4',6',13}$), 7.51 d (2H, $H^{3',5'}$, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.49 q (C^{14}), 22.52 t (C^2), 24.43 t (C^6), 34.27 C (C^{10}), 36.64 t (C^3), 39.33 d (C^7), 41.10 t (C^9), 41.96 t (C^1), 46.12 d (C^5), 76.77 d (C^8), 106.49 t (C^{15}), 128.83 d ($C^{3',5'}$), 129.43 d ($C^{2',4',6'}$), 132.30 s (C^{11}), 133.98 s ($C^{1'}$), 134.75 d (C^{13}), 148.86 s (C^4), 172.20 s (C^{12}). Mass spectrum, *m/z* (I_{rel}, %): 310 (3), 309 (10), 308 (48), 172 (100), 129 (21), 128 (23), 115 (51), 91 (42), 79 (21), 41 (20). Found $[M]^+$ 308.1767. $C_{21}H_{24}O_2$. Calculated *M* 308.1771.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(4-Methylbenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]-furan-2(3*H*)-one (IIIb). Yield 75%, mp 220–222°C (ethyl acetate), $[\alpha]_D^{20}$ +516° (*c* 1.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3092, 1735, 1650, 1605, 1512, 1439, 1379, 1288, 1261, 1228, 1212, 1170, 1073, 1034, 1001, 945, 932, 889, 814, 532, 481. UV spectrum, λ_{max}, nm (log ε): 202 (4.12), 224 (4.08), 228 (4.04), 294 (4.32). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s (3H, $C^{14}H_3$), 1.26 m (1H, H^1), 1.39 d.d.d (1H, H^6, *J* 13.7, 12.3, 12.3 Hz), 1.48–1.65 m (4H, $H^{1,2,2,9}$), 1.92 d (1H, H^5, *J* 12.9 Hz), 1.95 m (2H, $H^{3,6}$), 2.25 d.d (1H, H^9, *J* 15.5, 1.8 Hz), 2.33 m (1H, H^3), 2.37 s (3H, C^7H_3), 3.41 d.d.d (1H, H^7, *J* 12.0, 6.0, 5.1 Hz), 4.41 d (1H, H^{15}, *J* 1.5 Hz), 4.48 d.d.d (1H, H^8, *J* 4.6, 4.5, 1.5 Hz), 4.76 d (1H, H^{15}, *J* 1.5 Hz), 7.21 d (2H, $H^{3',5'}$, *J* 8.2 Hz), 7.40 s (1H, H^{13}), 7.42 d (2H, $H^{2',6'}$, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 17.52 q (C^{14}), 21.24 q ($C^{7'}$), 22.57 t (C^2), 24.40 t (C^6), 34.32 s (C^{10}), 36.69 t (C^3), 39.37 d (C^7), 41.20 t (C^9), 42.03 t (C^1), 46.18 d (C^5), 76.74 d (C^8), 106.50 t (C^{15}), 129.52 d ($C^{2',3',5',6'}$), 131.18 s and 131.26 s ($C^{1',11}$), 134.84 d (C^{13}), 140.06 s ($C^{4'}$), 148.94 s (C^4), 172.41 s (C^{12}). Found, %: C 81.48; H 7.95. $C_{22}H_{26}O_2$. Calculated, %: C 81.95; H 8.13.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(2-Methylbenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]-furan-2(3*H*)-one (IIIc). Yield 85%, mp 125–126°C (ethyl acetate), $[\alpha]_D^{20}$ +327° (*c* 2.1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 2927, 1743, 1645, 1440, 1224, 1211, 1173, 1033, 1001, 894, 762, 717. UV spectrum, λ_{max}, nm (log ε): 202 (4.19), 223 (4.00), 284 (4.12). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s (3H, $C^{14}H_3$), 1.26 d.d.d (1H, H^1, *J* 12.2, 11.2, 4.7 Hz), 1.38–1.48 m (2H, $H^{1,6}$), 1.51–1.61 m (3H, $H^{2,2,9}$), 1.83–1.89 m (2H, $H^{5,6}$), 1.99 d.d.d (1H, H^3, *J* 12.5, 11.9, 6.0 Hz), 2.22 d.d (1H, H^9, *J* 15.6, 1.7 Hz), 2.33 d.m (1H, H^3, *J* 12.6 Hz), 2.38 s (3H, CH_3 at $C^{2'}$), 3.27 d.d.d (1H, H^7, *J* 11.8, 5.2, 4.9 Hz), 4.41 d.d (1H, H^{15}, *J* 3.0, 1.5 Hz), 4.48 d.d.d (1H, H^8, *J* 6.5, 4.6, 1.8 Hz), 4.75 d.d (1H, H^{15}, *J* 3.0, 1.5 Hz), 7.20–7.25 m (3H, $H^{3',4',5'}$), 7.43 d.d (1H, $H^{6'}$, *J* 7.6, 2.0 Hz), 7.64 d (1H,

H*13*, *J* 1.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.31 q (C*14*), 19.66 q (CH_3 прand C*2′*), 22.30 t (C*2*), 25.15 t (C*6*), 34.04 s (C*10*), 36.42 t (C*3*), 38.82 d (C*7*), 40.98 t (C*9*), 41.77 t (C*1*), 46.00 d (C*5*), 76.76 d (C*8*), 106.23 t (C*15*), 125.80 d (C*5′*), 127.05 d (C*4′*), 129.03 d (C*3′*), 130.35 d (C*6′*), 132.70 d (C*13*), 132.98 s (C*1′*), 133.20 s (C*11*), 137.71 s (C*2′*), 148.71 s (C*4*), 171.80 s (C*12*). Found, %: C 81.59; H 7.88. $C_{22}H_{26}O_2$. Calculated, %: C 81.95; H 8.13.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(3,4-Dihydroxybenzylid-ene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-one (IIId). Yield 55%, mp 171–173°C (chloroform), $[\alpha]_D^{20}$ +511° (*c* 0.7, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3090, 1718, 1645, 1604, 1517, 1443, 1374, 1337, 1293, 1259, 1219, 1166, 1113, 1089, 1033, 1000, 968, 889, 811. UV spectrum, λ_{max}, nm (lgε): 201 (4.15), 221 (3.99), 238 (3.89), 334 (4.17). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 0.82 s (3H, C*14*H$_3$), 1.17–1.36 m (2H, H*1,6*), 1.51–1.62 m (4H, H*1,2,2,9*), 1.96 d (1H, H*5*, *J* 12.5 Hz), 1.95–2.15 m (3H, H*3,6,9*), 2.32 d.m (1H, H*3*, *J* 12.5 Hz), 3.48 d.d.d (1H, H*7*, *J* 11.5, 5.6, 5.6 Hz), 4.41 d (1H, H*15*, *J* 1.2 Hz), 4.44 d.d.d (1H, H*8*, *J* 4.8, 4.5, 1.3 Hz), 4.74 d (1H, H*15*, *J* 1.3 Hz), 4.91 br.s (2H, OH, $J_{1/2W}$ 8.0 Hz), 6.83 d (1H, H*5′*, *J* 8.3 Hz), 6.98 d.d (1H, H*6′*, *J* 8.3, 2.0 Hz), 7.12 d (1H, H*2′*, *J* 2.0 Hz), 7.23 d (1H, H*13*, *J* 1.0 Hz). ^{13}C NMR spectrum, δ, ppm: 18.16 q (C*14*), 23.94 t (C*2*), 25.72 t (C*6*), 35.43 s (C*10*), 37.93 t (C*3*), 40.49 d (C*7*), 42.23 t (C*9*), 43.20 t (C*1*), 47.09 d (C*5*), 79.00 d (C*8*), 106.48 t (C*15*), 116.77 d (C*2′*), 117.18 d (C*5′*), 124.96 d (C*6′*), 127.27 s (C*1′*), 129.94 s (C*11*), 136.96 d (C*13*), 146.83 s (C*3′*), 149.17 s (C*4′*), 150.68 s (C*4*), 175.34 s (C*12*). Found, %: C 73.79; H 7.12. $C_{21}H_{24}O_4$. Calculated, %: C 74.09; H 7.11.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(2,4-Dimethoxybenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-one (IIIg). Yield 80%, mp 150–152°C (ether), $[\alpha]_D^{20}$ +534° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3090, 1738, 1646, 1606, 1575, 1501, 1462, 1441, 1420, 1302, 1279, 1253, 1214, 1167, 1120, 1032, 1000, 939, 892. UV spectrum, λ_{max}, nm (lgε): 201 (4.42), 221 (3.87), 241 (3.92), 296 (3.98), 335 (4.20). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 s (3H, C*14*H$_3$), 1.25 d.d.d (1H, H*1*, *J* 12.3, 12.3, 3.4 Hz), 1.39 d.d.d (1H, H*6*, *J* 13.6, 12.5, 12.2 Hz), 1.48–1.61 m (4H, H*1,2,2,9*), 1.89 d (1H, H*5*, *J* 12.5 Hz), 1.93–2.04 m (2H, H*3,6*), 2.21 d (1H, H*9*, *J* 15.3 Hz), 2.32 d.m (1H, H*3*, *J* 14.0 Hz), 3.31 d.d.d (1H, H*7*, *J* 11.6, 5.8, 5.5 Hz), 3.82 s (2×3H, OCH_3), 4.41 br.s (1H, H*15*), 4.44 d.d.d (1H, H*8*, *J* 4.4, 3.5, 1.3 Hz), 4.74 br.s (1H, H*15*), 6.44 d (1H, H*3′*, *J* 2.4 Hz), 6.50 d.d (1H, H*5′*, *J* 8.6, 2.4 Hz), 7.46 d (1H, H*6′*, *J* 8.6), 7.82 br.s (1H, H*13*). ^{13}C NMR spectrum, δ, ppm: 17.62 q (C*14*), 22.70 t (C*2*), 24.97 t (C*6*), 34.48 C (C*10*), 36.82 t (C*3*), 39.49 d (C*7*), 41.39 t (C*9*), 42.15 t (C*1*), 46.40 d (C*5*), 55.30 q (OCH_3), 55.50 q (OCH_3), 76.74 d (C*8*), 98.23 d (C*3′*), 105.21 d (C*5′*), 106.52 t (C*15*), 116.19 s (C*1′*), 129.19 d, 129.47 d (C*6′,13*), 130.22 s (C*11*), 149.22 s (C*4*), 159.88 s (C*2′*), 162.37 s (C*4′*), 172.92 s (C*12*). Mass spectrum, *m/z* (I_{rel}, %): 368 $[M]^+$ (100), 323 (11), 245 (16), 232 (15), 175 (15), 151 (15), 115 (51), 91 (42), 79 (21), 41 (20). Found $[M]^+$ 368.1977. $C_{23}H_{28}O_4$. Calculated *M* 368.1982.

(4a*S*,8a*R*,9a*S*)-3-(2,4-Dimethoxybenzyl)-8a-methyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octadecahydronaphtho[2,3-*b*]furan-2(4*H*)-one (IVg). Yield 10% (from ^{1}H NMR spectrum of reaction mixture). By chromatography compound **IVg** was isolated in 80% purity (impurity compound **III g**). Characteristic signals of compound **IVg** in ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 s (3H, C*14*H$_3$), 1.10 d.d (1H, H*9*, *J* 10.8, 10.8 Hz), 1.26 d.d.d (1H, H*1*, *J* 13.4, 13.4, 4.8 Hz), 1.49–1.65 m (3H, H*2,2,9*), 1.76 d.d.d.d (1H, H*5*, *J* 12.5, 3.3. 1.7 Hz), 1.93 m (1H, H*3*, *J* 12.8, 12.8, 5.8 Hz), 2.28 m (2H, H*6,9*), 2.35 d.d.d.d (1H, H*3*, *J* 13.4, 3.8, 2.2, 1.8 Hz), 2.97 d.d (1H, H*6*, *J* 13.8, 3.8 Hz), 3.46 d (1H, H*13*, *J* 13.5 Hz), 3.53 d (1H, H*13*, *J* 13.5 Hz), 3.75 s (3H, OCH_3), 3.78 s (3H, OCH_3), 4.59 br.s (1H, H*15*), 4.78 d.d (1H, H*8*, *J* 11.5, 6.3 Hz), 4.86 br.s (1H, H*15*), 6.42 d.d (1H, H*6′*, *J* 8.5, 2.0 Hz), 7.25 d (1H, H*5′*, *J* 8.5 Hz), 7.26 d (1H, H*2′*, *J* 2.0 Hz). ^{13}C NMR spectrum, δ, ppm: 16.41 q (C*14*), 22.23 t (C*2*), 23.21 t (C*13*), 25.58 t (C*6*), 36.21 t (C*3*), 36.83 s (C*10*), 40.74 t (C*1*), 47.57 t (C*9*), 50.06 d (C*5*), 54.81 q and 55.22 q (2×OCH_3), 77.68 d (C*8*), 98.19 d (C*3′*), 103.75 d (C*5′*), 106.75 t (C*15*), 118.60 s (C*1′*), 130.93 d (C*6′*), 148.54 s (C*4*), 159.57 s (C*2′*), 163.12 s (C*4′*), 174.19 s (C*12*). Found, %: C 74.90; H 7.92. $C_{23}H_{28}O_4$. Calculated, %: C 74.97; H 7.66.

(3*E*,3a*R*,4a*R*,5*E*,8a*R*,9a*R*)-3,5-bis(2,4-dimethoxybenzylidene)-8a-methyldecahydronaphtho[2,3-*b*]-furan-2(3*H*)-one (Vg). Yield 4%. Oily substance, $[\alpha]_D^{20}$ +534° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3090, 1747, 1646, 1607, 1576, 1503, 1296, 1210, 1160, 1120, 1032, 992, 939, 900, 833, 758, 636. UV spectrum, λ_{max}, nm (log ε) (ethanol): 201 (4.66), 245 (4.18), 289 (4.04), 336 (4.16). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 s (3H, C*14*H$_3$), 1.22 m (1H, H*1*), 1.51–1.61 m (5H, H*1,2,2,6,9*), 1.76 m (1H, H*3*), 2.04–2.10 m (2H, H*5,6*), 2.28 d.d (1H, H*9*, *J* 15.4, 1.5 Hz), 2.80 br.d (1H, H*3*, *J* 12.7 Hz), 3.34 d.d.d (1H, H*7*, *J* 12.0, 6.1, 4.7 Hz), 3.74 s (3H, OCH_3), 3.78 s (3H, OCH_3), 3.82 s (3H, OCH_3), 3.83 s (3H, OCH_3), 4.46 d.d.d (1H, H*8*,

J 4.4, 4.4, 1.2 Hz), 5.90 br.s (1H, H^{15}), 6.41–6.43 m (2H, H$^{3'',5''}$), 6.45 d (1H, H$^{3'}$, *J* 2.3 Hz), 6.52 d.d (1H, H$^{5'}$, *J* 8.6, 2.3 Hz), 6.98 d (1H, H$^{6''}$, *J* 9.0 Hz), 7.51 d (1H, H$^{6'}$, *J* 8.6 Hz), 7.84 s (1H, H^{13}). ^{13}C NMR spectrum, δ, ppm: 17.92 q (C^{14}), 22.64 t (C^{2}), 25.11 t (C^{6}), 30.89 t (C^{3}), 35.26 s (C^{10}), 39.81 d (C^{7}), 41.70 t (C^{9}), 42.65 t (C^{1}), 47.48 d (C^{5}), 55.24 q (OCH_3), 55.32 q (OCH_3), 55.36 q (OCH_3), 55.50 q (OCH_3), 76.76 d (C^{8}), 98.29 d (C$^{3',3''}$), 103.71 d (C$^{5''}$), 105.26 d (C$^{5'}$), 116.36 s (C$^{1'}$), 117.02 d (C^{15}), 119.84 s (C$^{1''}$), 129.12 d (C^{13}), 129.51 s (C^{11}), 129.62 d (C$^{6'}$), 130.53 d (C$^{6''}$), 141.48 s (C^{4}), 158.03 s (C$^{4''}$), 159.48 s (C$^{2''}$), 159.90 s (C$^{4'}$), 162.35 s (C$^{2'}$), 173.02 s (C^{12}). Found, %: C 73.54; H 7.06. $C_{31}H_{36}O_6$. Calculated, %: C 73.79; H 7.19.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-8a-Methyl-5-methylidene-3-(4-fluorobenzylidene)decahydronaphtho[2,3-*b*]furan-2(3*H*)-one (IIIh). Yield 5%, conversion of lactone **I** 70%, mp 208–209°C, $[\alpha]_D^{20}$ +454° (*c* 1.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3090, 1743, 1656, 1599, 1510, 1239, 1223, 1171, 1159, 999, 890, 833. UV spectrum, λ_{max}, nm (log ε): 201 (4.25), 220 (4.02), 226 (3.94), 284 (4.26), 292 (4.22). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 s (3H, C^{14}H$_3$), 1.25 m (1H, H^{1}), 1.39 d.d.d (1H, H^{6}, *J* 13.9, 12.6, 12.2 Hz), 1.48–1.61 m (4H, H^{1,2,2,9}), 1.90–2.06 m (3H, H^{3,5,6}), 2.23 d.d (1H, H^{9}, *J* 15.5, 1.7 Hz), 2.32 d.m (1H, H^{3}, *J* 13.4 Hz), 3.39 d.d.d (1H, H^{7}, *J* 12.0, 6.0, 5.4 Hz), 4.39 d (1H, H^{15}, *J* 1.2 Hz), 4.48 d.d.d (1H, H^{8}, *J* 4.7, 3.5, 1.3 Hz), 4.75 d (1H, H^{15}, *J* 1.2 Hz), 7.08 d.d.d.d (2H, H$^{3',5'}$, *J* 8.8, 8.5, 2.8, 1.9 Hz), 7.36 br.s (1H, H^{13}), 7.49 d.d.d (2H, H$^{2',6'}$, *J* 8.8, 8.3, 2.7, 1.9 Hz). ^{13}C NMR spectrum, δ, ppm: 17.56 q (C^{14}), 22.59 t (C^{2}), 24.47 t (C^{6}), 34.38 s (C^{10}), 36.72 t (C^{3}), 39.29 d (C^{7}), 41.20 t (C^{9}), 42.06 t (C^{1}), 46.22 d (C^{5}), 76.82 d (C^{8}), 106.61 t (C^{15}), 116.07 d (C$^{3',5'}$), 130.34 s (C$^{1'}$), 131.41 d (C$^{2',6'}$), 131.94 s (C^{11}), 133.59 d (C^{13}), 148.92 s (C^{4}), 163.16 d (C$^{4'}$, $J_{C\text{-}F}$ 251.6 Hz), 172.15 s (C^{12}). Found, %: C 76.87; H 7.09; F 5.87. $C_{21}H_{23}O_2F$. Calculated, %: C 77.27; H 7.10; F 5.82.

(4a*S*,8a*R*,9a*S*)-8a-Methyl-5-methylidene-3-(4-fluorobenzyl)-4a,5,6,7,8,8a,9,9a-octahydronaphtho-[2,3-*b*]furan-2(4*H*)-one (IVh). Yield 18%, mp 135–137°C (ethyl acetate), $[\alpha]_D^{20}$ +134° (*c* 0.4, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3090, 1748, 1682, 1642, 1600, 1508, 1442, 1383, 1339, 1219, 1158, 1125, 1096, 1059, 1044, 1014, 896, 857, 843, 798, 744, 627, 614, 527, 492. UV spectrum, λ_{max}, nm (lgε): 202 (4.26), 210 (4.24), 221 (4.21), 266 (3.16), 273 (3.12). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 s (3H, C^{14}H$_3$), 1.14 d.d (1H, H^{9}, *J* 12.1, 11.8 Hz), 1.29 d.d.d (1H, H^{1}, *J* 13.4, 13.4, 4.8 Hz), 1.55–1.65 m (3H, H^{1,2,2}), 1.81 d.m (1H, H^{5}, *J* 13.0 Hz), 1.94 d.d.d (1H, H^{3}, *J* 12.9, 12.6, 6.2 Hz), 2.27–2.39 m (3H, H^{3,6,9}), 2.73 d.d (1H, H^{6}, *J* 14.0, 3.8 Hz), 3.51 d (1H, H^{13}, *J* 14.8 Hz), 3.58 d (1H, H^{13}, *J* 14.8 Hz), 4.56 d (1H, H^{15}, *J* 1.0 Hz), 4.84–4.89 m (1H, H^{8}), 4.86 d (1H, H^{15}, *J* 1.0 Hz), 6.96 d.d.d.d (2H, H$^{3',5'}$, *J* 8.9, 8.7, 2.3, 2.0 Hz), 7.20 d.d.d.d (2H, H$^{2',6'}$, *J* 8.9, 8.7, 3.0, 2.4 Hz). ^{13}C NMR spectrum, δ, ppm: 16.33 q (C^{14}), 22.16 t (C^{2}), 25.70 t (C^{6}), 28.39 t (C^{13}), 36.12 t (C^{3}), 36.82 s (C^{10}), 40.63 t (C^{1}), 47.45 t (C^{9}), 49.93 d (C^{5}), 77.91 d (C^{8}), 106.90 t (C^{15}), 115.29 d (C$^{3',5'}$, *J* 21.4 Hz), 123.42 s (C^{11}), 129.75 d (C$^{2',6'}$), 133.91 s (C$^{1'}$), 148.13 s (C^{4}), 161.47 d (C$^{4'}$, $J_{C\text{-}F}$ 244.7 Hz), 163.70 C (C^{7}), 173.85 s (C^{12}). Found, %: C 77.08; H 7.25. $C_{21}H_{23}O_2F$. Calculated, %: C 77.27; H 7.10.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(3-Methyl-4-fluorobenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]-furan-2(3*H*)-one (IIIi). Yield 57%, mp 188–191°C, $[\alpha]_D^{20}$ +427° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3089, 1744, 1657, 1501, 1298, 1246, 1230, 1206, 1173, 1120, 998, 932, 889, 816. UV spectrum, λ_{max}, nm (log ε): 200 (4.28), 210 (4.10), 224 (4.13), 287 (4.31). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 s (3H, C^{14}H$_3$), 1.25 d.d.d (1H, H^{1}, *J* 12.1, 11.9, 5.0 Hz), 1.39 d.d.d (1H, H^{6}, *J* 13.6, 13.4, 11.4 Hz), 1.51–1.59 m (4H, H^{1,2,2,9}), 1.90–2.03 m (3H, H^{3,5,6}), 2.23 d.d (1H, H^{9}, *J* 15.7, 1.0 Hz), 2.27 s (3H, CH_3), 2.32 br.d (1H, H^{3}, *J* 12.0 Hz), 3.40 d.d.d (1H, H^{7}, *J* 11.9, 6.1, 5.8 Hz), 4.39 br.s (1H, H^{15}), 4.47 d.d.d (1H, H^{8}, *J* 4.5, 3.2, 1.0 Hz), 4.74 br.s (1H, H^{15}), 7.01 d.d (1H, H$^{5'}$, *J* 8.9, 8.8 Hz), 7.30–7.35 m (3H, H$^{2',6',13}$). ^{13}C NMR spectrum, δ, ppm: 14.55 q (CH_3), 17.56 q (C^{14}), 22.64 t (C^{2}), 24.54 t (C^{6}), 34.40 s (C^{10}), 36.77 t (C^{3}), 39.26 d (C^{7}), 41.25 t (C^{9}), 42.10 t (C^{1}), 46.24 d (C^{5}), 76.82 d (C^{8}), 106.61 t (C^{15}), 115.80 d (C$^{5'}$, *J* 21.2), 125.80 s (C$^{3'}$), 128.42 d (C$^{6'}$), 130.10 s (C$^{1'}$), 131.68 s (C^{11}), 133.32 d (C$^{2'}$), 133.94 d (C^{13}), 148.98 s (C^{4}), 163.08 d (C$^{4'}$, *J* 248.6 Hz), 172.15 s (C^{12}). Mass spectrum, *m/z* (I_{rel}, %): 342 (3), 341 (20), 340 (76), 312 (5), 296 (5), 268 (5), 205 (18), 204 (100), 176 (20), 147 (29), 146 (18), 123 (17), 121 (15), 57 (20), 41 (17). Found $[M]^+$ 340.1840. $C_{22}H_{25}O_2F$. Calculated *M* 340.1833.

(4a*S*,8a*R*,9a*S*)-3-(3-Methyl-4-fluorobenzyl)-8a-methyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octahydronaphtho[2,3-*b*]furan-2(3*H*)-one (IVi). Oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (characteristic signals from the mixture containing 80% of compound **IVi**): 0.84 s (3H, C^{14}H$_3$), 1.11 d.d (1H, H^{9}, *J* 11.8, 11.8 Hz), 1.28 d.d.d (1H, H^{1}, *J* 13.4, 13.2, 4.8 Hz), 1.52–1.62 m

(3H, H^{1,2,2}), 1.79 d.m (1H, H^{5}, *J* 12.4 Hz), 1.94 d.d.d (1H, H^{3}, *J* 13.94, 13.2, 5.6 Hz), 2.19 br.s (1H, C$^{3'}$CH$_3$), 2.26–2.37 m (3H, H^{3,6,9}), 2.73 d.d (1H, H^{6}, *J* 14.0, 3.8 Hz), 3.46 d (1H, H^{13}, *J* 14.8 Hz), 3.53 d (1H, H^{13}, *J* 14.8 Hz), 4.54 d (1H, H^{15}, *J* 1.1 Hz), 4.81–4.85 m (1H, H^{8}), 4.84 d (1H, H^{15}, *J* 1.1 Hz), 6.86 d.d (1H, H$^{5'}$, *J* 9.1, 8.6 Hz), 6.96 m (1H, H$^{6'}$), 7.02 d.m (1H, H$^{2'}$, *J* 7.0 Hz). ^{13}C NMR spectrum, δ, ppm: 16.34 q (C^{14}), 22.18 t (C^{2}), 25.69 t (C^{6}), 28.34 t (C^{13}), 36.13 t (C^{3}), 36.81 s (C^{10}), 40.65 t (C^{1}), 47.49 t (C^{9}), 49.94 d (C^{5}), 77.86 d (C^{8}), 106.89 t (C^{15}), 114.85 d (C$^{5'}$, *J* 22.0 Hz), 123.50 s (C^{11}), 124.72 s (C$^{3'}$), 126.87 d (C$^{6'}$), 131.34 d (C$^{2'}$), 133.59 s (C$^{1'}$), 148.14 s (C^{4}), 159.98 d (C$^{4'}$, J_{C-F} 243.5), 163.63 s (C^{7}), 173.90 s(C^{12}).

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-8a-Methyl-5-methylidene-3-(4-chlorobenzylidene)decahydronaphtho[2,3-*b*]-furan-2(3H)-one (IIIj). Yield 60%, mp 207–209°C (from ethanol–ethyl acetate, 10:1), $[\alpha]_{589}$ +357° (*c* 0.7, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3088, 1744, 1651, 1492, 1304, 1259, 1225, 1199, 1168, 1092, 1033, 1012, 999, 892, 829. UV spectrum, λ_{max}, nm (lgε): 201 (4.23), 222 (4.11), 229 (4.04), 289 (4.37), 296 (4.35). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s (3H, C^{14}H$_3$), 1.26 d.d.d (1H, H^{1}, *J* 12.8, 12.6, 4.7 Hz), 1.40 d.d.d (1H, H^{6}, *J* 13.6, 13.2, 12.6 Hz), 1.51–1.62 m (4H, H^{1,2,2,9}), 1.91–1.97 m (2H, H^{5,6}), 2.02 d.d.d (1H, H^{3}, *J* 12.9, 12.8, 5.6 Hz), 2.25 d.d (1H, H^{9}, *J* 15.5, 1.3 Hz), 2.34 br.d (1H, H^{3}, *J* 13.5 Hz), 3.39 d.d.d (1H, H^{7}, *J* 11.9, 6.0, 5.0 Hz), 4.40 d (1H, H^{15}, *J* 0.9 Hz), 4.49 d.d.d (1H, H^{8}, *J* 4.7, 4.7, 1.8 Hz), 4.76 d (1H, H^{15}, *J* 0.9 Hz), 7.36 br.s (1H, H^{13}), 7.37 d.d.d (2H, H$^{2',6'}$, *J* 8.6, 2.3, 2.1 Hz), 7.44 d.d.d (2H, H$^{3',5'}$, *J* 8.6, 1.9, 1.3 Hz). ^{13}C NMR spectrum, δ, ppm: 17.27 q (C^{14}), 22.28 t (C^{2}), 24.15 t (C^{6}), 34.08 s (C^{10}), 36.43 t (C^{3}), 39.11 d (C^{7}), 40.89 t (C^{9}), 41.77 t (C^{1}), 45.94 d (C^{5}), 76.53 d (C^{8}), 106.36 t (C^{15}), 128.91 d (C$^{3',5'}$), 130.38 d (C$^{2',6'}$), 132.29 s (C^{11}), 132.62 s (C$^{1'}$), 133.21 d (C^{13}), 135.32 s (C$^{4'}$),148.57 s (C^{4}), 171.74 C (C^{12}). Found, %: C 73.25; H 6.87; Cl 9.82. $C_{21}H_{23}O_2Cl$. Calculated, %: C 73.57; H 6.76; Cl 10.34.

(4a*S*,8a*R*,9a*S*)-8a-Methyl-5-methylidene-3-(4-chlorobenzyl)-4a,5,6,7,8,8a,9,9a-octahydronaphtho-[2,3-*b*]furan-2(4*H*)-one (IVj). Yield 20%, mp 126–128°C (chloroform), $[\alpha]_D^{20}$ +165° (*c* 0.7, $CHCl_3$). IR spectrum, ν, cm^{-1}: 2979, 2934, 2841, 1745, 1680, 1645, 1490, 1440, 1170, 1090, 1060, 1049, 1014, 889, 803. UV spectrum, λ_{max}, nm (lgε): 201 (4.31), 222 (4.22), 288 (3.57), 311 (3.32). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s (3H, C^{14}H$_3$), 1.12 d.d (1H, H^{9}, *J* 12.1, 11.8 Hz), 1.29 d.d.d (1H, H^{1}, *J* 13.4, 13.4, 5.1 Hz), 1.53–1.66 m (3H, H^{1,2,2}), 1.79 d.m (1H, H^{5}, *J* 12.9 Hz), 1.95 d.d.d (1H, H^{3}, *J* 12.6, 12.1, 4.8 Hz), 2.27–2.38 m (3H, H^{3,6,9}), 2.73 d.d (1H, H^{6}, *J* 14.0, 3.8 Hz), 3.51 d (1H, H^{13}, *J* 15.0 Hz), 3.58 d (1H, H^{13}, *J* 15.0 Hz), 4.54 d (1H, H^{15}, *J* 1.1 Hz), 4.82–4.87 m (1H, H^{8}), 4.85 d (1H, H^{15}, *J* 1.1 Hz), 7.15 d.d.d (2H, H$^{2',6'}$, *J* 8.6, 2.4, 2.1 Hz), 7.22 d.d.d (2H, H$^{3',5'}$, *J* 8.6, 2.4, 2.1 Hz). ^{13}C NMR spectrum, δ, ppm: 16.34 q (C^{14}), 22.15 t (C^{2}), 25.74 t (C^{6}), 28.53 t (C^{13}), 36.11 t (C^{3}), 36.83 s (C^{10}), 40.60 t (C^{1}), 47.43 t (C^{9}), 49.93 d (C^{5}), 77.94 d (C^{8}), 106.95 t (C^{15}), 123.11 s (C^{11}), 128.62 d (C$^{2',6'}$), 129.66 d (C$^{3',5'}$), 132.18 C (C$^{4'}$), 136.72 s (C$^{1'}$), 148.10 s (C^{4}), 163.95 s (C^{7}), 173.80 s (C^{12}). Found, %: C 73.32; H 6.63; Cl 10.62. $C_{21}H_{23}O_2Cl$. Calculated, %: C 73.57; H 6.76; Cl 10.34.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(4-Bromobenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-one (IIIk). Yield 55%, mp 196–198°C (ethyl acetate), $[\alpha]_D^{20}$ +388° (*c* 0.93, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3092, 1744, 1649, 1487, 1259, 1223, 1171, 1072, 1000, 894, 829, 818. UV spectrum, λ_{max}, nm (log ε): 200 (4.29), 223 (4.02), 290 (4.32), 298 (4.31). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s (3H, C^{14}H$_3$), 1.25 m (1H, H^{1}), 1.39 d.d.d (1H, H^{6}, *J* 13.7, 13.5, 13.3 Hz), 1.50–1.62 m (4H, H^{1,2,2,9}), 1.91–2.07 m (3H, H^{3,5,6}), 2.25 d.d (1H, H^{9}, *J* 15.5, 1.5 Hz), 2.34 br.d (1H, H^{3}, *J* 14.2 Hz), 3.38 d.d.d (1H, H^{7}, *J* 12.0, 5.9, 5.1), 4.40 d (1H, H^{15}, *J* 1.2 Hz), 4.49 d.d.d (1H, H^{8}, *J* 4.7, 4.6, 1.5 Hz), 4.76 d (1H, H^{15}, *J* 1.2 Hz), 7.35 br.s (1H, H^{13}), 7.37 br.d (2H, H$^{2',6'}$, *J* 8.8 Hz), 7.53 br.d (2H, H$^{3',5'}$, *J* 8.8 Hz). ^{13}C NMR spectrum, δ, ppm: 17.58 q (C^{14}), 22.61 t (C^{2}), 24.45 t (C^{6}), 34.38 s (C^{10}), 36.74 t (C^{3}), 39.43 d (C^{7}), 41.21 t (C^{9}), 42.08 t (C^{1}), 46.25 d (C^{5}), 76.84 d (C^{8}), 106.66 t (C^{15}), 123.96 d (C$^{4'}$), 130.88 d (C$^{2',6'}$), 132.19 d (C$^{3',5'}$), 133.05 s (C$^{1'}$), 133.18 s (C^{11}), 133.55 d (C^{13}), 148.86 s (C^{4}), 171.99 s (C^{12}). Found, %: C 64.48; H 5.64; Br 19.78. $C_{21}H_{23}O_2Br$. Calculated, %: C 65.12; H 5.99; Br 20.63.

(4a*S*,8a*R*,9a*S*)-3-(4-Bromobenzyl)-8a-methyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octahydronaphtho-[2,3-*b*]furan-2(4*H*)-one (IVk). Yield 20%. Oily substance, $[\alpha]_D^{20}$ +63° (*C* 0.12, $CHCl_3$). UV spectrum, λ_{max}, nm (log ε): 204 (4.25), 223 (4.23), 277 (3.10). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 s (3H, C^{14}H$_3$), 1.12 d.d (1H, H^{9}, *J* 11.9, 11.7 Hz), 1.30 d.d.d (1H, H^{1}, *J* 13.2, 13.2, 4.9 Hz), 1.55–1.64 m (3H, H^{1,2,2}), 1.79 d.m (1H, H^{5}, *J* 13.0 Hz), 1.95 d.d.d (1H, H^{3}, *J* 12.8, 12.6, 5.7 Hz), 2.28–2.33 m (2H, H^{6,9}), 2.35 d.m (1H, H^{3}, *J* 13.2 Hz), 2.73 d.d (1H, H^{6}, *J* 13.8, 5.7 Hz), 3.50 d (1H, H^{13}, *J* 15.0 Hz), 3.56 d (1H, H^{13}, *J* 15.0 Hz), 4.54 d

(1H, H^{15}, *J* 0.8 Hz), 4.83–4.86 m (1H, H^{8}), 4.85 d (1H, H^{15}, *J* 0.8 Hz), 7.09 d.d.d (2H, H$^{2',6'}$, *J* 8.4, 2.6, 1.9 Hz), 7.38 d.d.d (2H, H$^{3',5'}$, *J* 8.4, 2.6, 1.9 Hz). ^{13}C NMR spectrum, δ, ppm: 16.35 q (C^{14}), 22.19 t (C^{2}), 25.77 t (C^{6}), 28.64 t (C^{13}), 36.15 t (C^{3}), 36.85 s (C^{10}), 40.67 t (C^{1}), 47.51 t (C^{9}), 49.99 d (C^{5}), 77.93 d (C^{8}), 106.93 t (C^{15}), 120.27 s (C^{11}), 123.09 s (C$^{4'}$), 130.07 d (C$^{2',6'}$), 131.60 d (C$^{3',5'}$), 137.29 s (C$^{1'}$), 148.13 s (C^{4}), 163.90 s (C^{7}), 173.73 s (C^{12}). Found, %: C 64.69; H 5.72; Br 20.12. $C_{21}H_{23}BrO_2$. Calculated, %: C 65.12; H 5.99; Br 20.63.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(2-Aminobenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]-furan-2(3*H*)-one (IIIm). Conversion of lactone 85%. Yield 62%, mp 155–157°C (ethyl acetate), $[\alpha]_D^{20}$ +417° (*c* 1.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3463, 3383, 3090, 1726, 1662, 1603, 1564, 1490, 1457, 1414, 1250, 1220, 1204, 1175, 1159, 1089, 1033, 1001, 900, 858, 764, 746. UV spectrum, λ_{max}, nm (lgε): 202 (4.29), 236 (4.03), 287 (3.88), 329 (3.41), 370 (3.63). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 s (3H, C^{14}H$_3$), 1.25 m (1H, H^{1}), 1.39 d.d.d (1H, H^{6}, *J* 13.0, 12.8, 11.8 Hz), 1.48–1.59 m (4H, H^{1,2,2,9}), 1.85–1.89 m (2H, H^{5,6}), 1.99 d.d.d (1H, H^{3}, *J* 12.8, 11.6, 5.8 Hz), 2.20 d (1H, H^{9}, *J* 15.5 Hz), 2.33 br.d (1H, H^{3}, *J* 13.3 Hz), 3.31 d.d.d (1H, H^{7}, *J* 11.6, 6.0, 5.3 Hz), 4.05 br.s (2H, NH_2), 4.41 br.s (1H, H^{15}), 4.48 d.d (1H, H^{8}, *J* 4.2, 4.1 Hz), 4.75 br.s (1H, H^{15}, *J* 1.5 Hz), 6.70 d (1H, H$^{3'}$, *J* 8.0 Hz), 6.73 d.d (1H, H$^{5'}$, *J* 7.8, 7.5 Hz), 7.14 d.d (1H, H$^{4'}$, *J* 8.0, 7.8 Hz), 7.31 d (1H, H$^{6'}$, *J* 7.5 Hz), 7.48 C (1H, H^{13}). ^{13}C NMR spectrum, δ, ppm: 17.66 q (C^{14}), 22.67 t (C^{2}), 25.56 t (C^{6}), 34.36 s (C^{3}), 36.77 t (C^{10}), 39.24 d (C^{7}), 41.31 t (C^{9}), 42.09 t (C^{1}), 46.29 d (C^{5}), 77.16 d (C^{8}), 106.60 t (C^{15}), 116.36 d (C$^{3'}$), 118.39 d (C$^{5'}$), 119.30 s (C$^{1'}$), 128.18 d (C$^{6'}$), 129.96 d (C$^{4'}$), 130.75 d (C^{13}), 132.95 s (C^{11}), 145.91 s (C$^{2'}$), 149.03 s (C^{4}), 172.39 s (C^{12}). Found, %: C 78.21; H 7.67; N 4.59. $C_{21}H_{25}NO_2$. Calculated, %: C 77.98; H 7.79; N 4.33.

(3a*R*,4a*S*,8a*R*,9a*R*,*E*)-3-(3'-Acetamido-4'-methoxycarbonylbenzylidene)-8a-methyl-5-methylidenedecahydronaphtho[2,3-*b*]furan-2(3*H*)-one (IIIn). Yield 54%, mp 201–203°C, $[\alpha]_D^{20}$ +293° (*c* 1.3, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3465, 3090, 1739, 1655, 1601, 1572, 1513, 1442, 1302, 1264, 1224, 1166, 1073, 1032, 999, 890, 840, 810, 539, 527. UV spectrum, λ_{max}, nm (log ε): 198 (4.24), 231 (4.22), 245 (4.25), 309 (4.42). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s (3H, C^{14}H$_3$), 1.26 d.d.d (1H, H^{1}, *J* 12.5, 12.5, 4.9 Hz), 1.39 d.d.d (1H, H^{6}, *J* 13.9, 12.5, 12.2 Hz), 1.51–1.63 m (4H, H^{1,2,2,9}), 1.91 d (1H, H^{5}, *J* 12.5 Hz), 1.95 d.d.d (1H, H^{6}, *J* 14.2, 6.6, 2.4 Hz), 2.02 d.d.d (1H, H^{3}, *J* 12.7, 11.7, 5.6 Hz), 2.23 s (3H, $COCH_3$), 2.25 m (1H, H^{9}), 2.34 d.d.d (1H, H^{3}, *J* 13.4, 1.8, 1.5 Hz), 3.40 d.d.d (1H, H^{7}, *J* 11.7, 6.0, 5.9 Hz), 3.92 s (3H, OCH_3), 4.39 d (1H, H^{15}, *J* 1.2 Hz), 4.49 d.d.d (1H, H^{8}, *J* 4.6, 4.5, 1.5 Hz), 4.75 d (1H, H^{15}, *J* 1.2 Hz), 7.36 s (1H, H^{13}), 7.71 d.d (1H, H$^{6'}$, *J* 8.8, 2.2 Hz), 8.16 d (1H, H$^{2'}$, *J* 2.2 Hz), 8.76 d (1H, H$^{5'}$, *J* 8.8 Hz), 11.10 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.56 q (C^{14}), 22.64 t (C^{2}), 24.68 t (C^{6}), 25.42 q ($\underline{C}H_3CO$), 34.42 s (C^{10}), 36.79 t (C^{3}), 39.47 d (C^{7}), 41.31 t (C^{9}), 42.15 t (C^{1}), 46.30 d (C^{5}), 52.57 q (OCH_3), 76.86 d (C^{8}), 106.61 t (C^{15}), 114.95 s (C$^{4'}$), 120.65 d (C$^{5'}$), 128.38 s (C$^{3'}$), 132.25 s (C^{11}), 133.11 d (C$^{2'}$), 133.33 d (C^{13}), 134.26 d (C$^{6'}$), 142.32 s (C$^{1'}$), 148.82 C (C^{4}), 168.04 s ($\underline{C}OOCH_3$), 169.07 s ($\underline{C}OCH_3$), 172.09 s (C^{12}). Mass spectrum, *m/z* (I_{rel}, %): 424 (22), 423 $[M]^+$ (83), 391 (26), 382 (26), 381 (100), 258 (21), 255 (62), 245 (21), 188 (19), 156 (22), 123 (23), 79 (23), 44 (46), 43 (36). Found, %: C 70.33; H 6.34; N 3.11. $C_{25}H_{29}NO_5$. Calculated, %: C 70.90; H 6.90; N 3.31. *M* 423.2040.

(3a*R*,4a*R*,8a*R*,9a*R*,3*E*,5*E*)-3,5-bis(3,4-dimethoxybenzylidene)-8a-methyldecahydronaphtho[2,3-*b*]-furan-2(3*H*)-one (Vf). Yield 6%. Oily substance, $[\alpha]_D^{20}$ +534° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3092, 1749, 1649, 1599, 1583, 1515, 1463, 1418, 1377, 1333, 1253, 1248, 1185, 1161, 1144, 1101,1084, 1026, 995, 954, 900, 872, 809, 757, 667, 630. UV spectrum, λ_{max}, nm (log ε) (ethanol): 204 (4.45), 248 (4.20), 296 (4.04), 327 (4.09). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.93 s (3H, C^{14}H$_3$), 1.33 d.d.d (1H, H^{1}, *J* 13.8, 13.0, 4.9 Hz), 1.51 d.d.d (1H, H^{6}, *J* 13.7, 12.7, 12.2 Hz), 1.56–1.65 m (4H, H^{1,2,2,9}), 1.78 d.d.d (1H, H^{3}, *J* 13.2, 12.7, 4.4 Hz), 2.06 br.d (1H, H^{6}, *J* 12.7 Hz), 2.10 d.d.d (1H, H^{5}, *J* 14.2, 6.8, 2.0 Hz), 2.28 d.d (1H, H^{9}, *J* 15.5, 1.8 Hz), 3.0 br.d (1H, H^{3}, *J* 14.2 Hz), 3.45 d.d.d (1H, H^{7}, *J* 11.7, 5.9, 5.4 Hz), 3.82 s (3H, OCH_3), 3.83 s (3H, OCH_3), 3.88 s (3H, OCH_3), 3.89 s (3H, OCH_3), 4.50 d.d.d (1H, H^{8}, *J* 4.8, 4.5, 1.7 Hz), 5.93 br.s (1H, H^{15}), 6.65 d (1H, H$^{2''}$, *J* 2.0 Hz), 6.70 d.d (1H, H$^{6''}$, *J* 8.2, 2.0 Hz), 6.78 d (1H, H$^{5''}$, *J* 8.2 Hz), 6.91 d (1H, H$^{5'}$, *J* 8.4 Hz), 7.03 C (1H, H$^{2'}$, *J* 2.0 Hz), 7.19 d.d (1H, H$^{6'}$, *J* 8.4, 2.0 Hz), 7.38 s (1H, H^{13}). ^{13}C NMR spectrum, δ, ppm: 17.85 q (C^{14}), 22.57 t (C^{2}), 24.75 t (C^{6}), 30.52 t (C^{3}), 35.26 s (C^{10}), 39.65 d (C^{7}), 41.59 t (C^{9}), 42.46 t (C^{1}), 47.24 d (C^{5}), 55.94 q (4×OCH_3), 76.56 d (C^{8}), 110.89 d (C$^{5''}$), 111.41 d (C$^{5'}$), 112.29 d (C$^{2''}$), 113.17 d (C$^{2'}$), 121.00 d (C$^{6''}$), 121.27 d (C^{15}), 122.82 d (C$^{6'}$), 127.11 s (C$^{1'}$), 130.14 C (C^{11}),

130.95 s (C$^{1''}$), 134.91 d (C^{13}), 141.58 s (C^{4}), 147.33 s (C$^{3''}$), 148.45 s (C$^{4''}$), 149.08 s (C$^{3'}$), 150.54 s (C$^{4'}$), 172.46 s (C^{12}). Found, %: C 73.45; H 6.96. $C_{31}H_{36}O_6$. Calculated, %: C 73.79; H 7.19.

(3a*R*,4a*S*,8a*R*,9a*R*,*Z*)-8a-Methyl-5-methylidene-3-(4-fluorobenzylidene)decahydronaphtho[2,3-*b*]furan-2(3*H*)-one (VI). Yield 4%, mp 99–115°C, $[\alpha]_D^{20}$ +55° (*c* 1.4, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3085, 1739, 1646, 1599, 1508, 1375, 1230, 1160, 1124, 1103, 1089, 1036, 1000, 961, 938, 895, 882, 838, 780, 555, 528. UV spectrum, λ_{max}, nm (lgε): 202 (4.19), 221 (3.94), 292 (4.01). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 s (3H, C^{14}H$_3$), 1.24 d.d.d (1H, H^{1}, *J* 13.2, 12.9, 5.0 Hz), 1.49 m (1H, H^{6}), 1.53–1.56 m (4H, H^{1,2,2,9}), 1.76 d.d.d (1H, H^{6}, *J* 14.5, 7.0, 2.6 Hz), 1.85 d.d (1H, H^{5}, *J* 12.6, 1.5 Hz), 2.00 d.d.d (1H, H^{3}, *J* 12.6, 12.6, 5.8 Hz), 2.17 d.d (1H, H^{9}, *J* 15.5, 1.5 Hz), 2.33 d.d.d (1H, H^{3}, *J* 12.9, 2.0, 1.5 Hz), 2.93 d.d.d (1H, H^{7}, *J* 11.7, 5.6, 5.3 Hz), 4.46 d (1H, H^{15}, *J* 1.5 Hz), 4.58 d.d.d (1H, H^{8}, *J* 4.7, 4.7, 1.5 Hz), 4.77 d (1H, H^{15}, *J* 1.5 Hz), 6.82 s (1H, H^{13}), 7.03 d.d.d.d (2H, H$^{3',5'}$, *J* 8.8, 8.5, 2.9, 2.0 Hz), 7.91 d.d.d.d (2H, H$^{2',6'}$, *J* 8.8, 8.6, 2.9, 2.3 Hz). ^{13}C NMR spectrum, δ, ppm: 17.71 q (C^{14}), 22.59 t (C^{2}), 27.88 t (C^{6}), 34.28 C (C^{10}), 36.73 t (C^{3}), 41.35 t (C^{9}), 42.15 t (C^{1}), 44.38 d (C^{7}), 46.20 d (C^{5}), 76.32 d (C^{8}), 106.54 t (C^{15}), 115.15 d (C$^{3',5'}$, *J* 22.2 Hz), 129.80 s (C$^{1'}$), 131.97 s (C^{11}), 132.83 d (C$^{2',6'}$, *J* 8.5 Hz), 136.56 d (C^{13}), 148.98 s (C^{4}), 163.17 d (C$^{4'}$, *J* 251.1 Hz), 168.93 s (C^{12}). Mass spectrum, *m/z* (I_{rel}, %): 328 (2), 327 (15), 326 [*M*]$^+$ (61), 305 (13), 284 (12), 214 (44), 213 (37), 191 (15), 190 (100), 185 (25) 183 (26), 170 (18), 165 (20), 133 (30), 123 (18), 109 (19), 91 (16). Found [*M*]$^+$ 326.1675. $C_{21}H_{23}O_2F$. Calculated *M* 326.1677.

(4a*S*,8a*R*,9a*S*)-3,8a-Dimethyl-5-methylidene-4a,5,6,7,8,8a,9,9a-octahydronaphtho[2,3-*b*]furan-2(4*H*)-one (VII). Yield 4%, mp 150–152°C (ethyl ether), $[\alpha]_D^{20}$ +238° (*c* 1.1, $CHCl_3$). UV spectrum, λ_{max}, nm (log ε): 192 (3.80), 199 (4.00), 220 (4.18). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 s (3H, C^{14}H$_3$), 1.12 d.d (1H, H^{9}, *J* 11.8, 11.7 Hz), 1.30 d.d.d (1H, H^{1}, *J* 13.3, 13.0, 4.3 Hz), 1.55–1.64 m (3H, H^{1,2,2}), 1.80 s (3H, H^{13}), 1.81–1.86 m (1H, H^{5}), 1.96 d.d.d (1H, H^{3}, *J* 13.0, 12.3, 6.5 Hz), 2.26–2.33 m (2H, H^{6,9}), 2.36 d.d.d.d (1H, H^{3}, *J* 13.0, 3.8, 2.0, 1.8 Hz), 2.72 d.d (1H, H^{6}, *J* 13.8, 3.8 Hz), 4.59 d (1H, H^{15}, *J* 1.5 Hz), 4.82 d.d (1H, H^{8}, *J* 11.5, 6.3 Hz), 4.86 d (1H, H^{15}, *J* 1.5 Hz). ^{13}C NMR spectrum, δ, ppm: 8.14 q (C^{13}),16.33 q (C^{14}), 22.22 t (C^{2}), 25.60 t (C^{6}), 36.16 t (C^{3}), 36.89 s (C^{10}), 40.74 t (C^{1}), 47.41 t (C^{9}), 49.83 d (C^{5}), 77.90 d (C^{8}), 106.81 t (C^{15}), 120.06 C (C^{11}), 148.37 s (C^{4}), 162.41 s (C^{7}), 174.70 s (C^{12}).

(*S*)-3-[(2*R*,4a*R*,8a*S*)-4a-Methyl-8-methylene-3-oxodecahydronaphthalen-2-yl]-3,4-dihydroquinolin-2(1*H*)-one (VIIIa). Yield 2%, $[\alpha]_D^{20}$ +7° (*c* 0.6, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3435, 3208, 3079, 2931, 1702, 1680, 1595, 1492, 1439, 1392, 1290, 1253, 1237, 1221, 888, 751. UV spectrum, λ_{max}, nm (log ε): 205 (4.45), 252 (3.99). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.74 s (3H, CH_3), 1.48–1.53 m (3H, H$^{5',5',6'}$), 1.57–1.68 m (1H, H$^{6'}$), 1.77 d.d. (1H, H$^{1'}$, *J* 12.3, 12.0 Hz), 1.98–2.08 m (2H, H$^{1',7'}$), 2.24 d (1H, H$^{4'}$, *J* 13.6 Hz), 2.32–2.37 m (2H, H$^{4',7'}$), 2.44 br.d (1H, H$^{8a'}$, *J* 8.5 Hz), 2.91 m (2H, H^{4}), 3.22 d.d.d (1H, H^{3}, *J* 10.2, 2.7, 2.0 Hz), 3.34 m (1H, H$^{2'}$, $J_{2',3}$ 10.2 Hz), 4.43 br.s, 4.78 br.s (2H, CH_2), 6.71 d (1H, H^{8}, *J* 8.5 Hz), 6.96 d.d (1H, H^{6}, *J* 8.2, 8.4 Hz), 7.14 d.d (1H, H^{7}, *J* 8.5, 8.4 Hz), 7.15 d (1H, H^{5}, *J* 8.2 Hz), 8.04 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.28 q (CH_3), 22.88 t (C$^{6'}$), 27.27 t (C$^{1',4}$), 36.45 t (C$^{7'}$), 38.27 d (C^{3}), 40.46 s (C$^{4'a}$), 41.28 t (C$^{5'}$), 48.13 d (C$^{8a'}$), 48.61 d (C$^{2'}$), 55.82 t (C$^{4'}$), 107.08 t (CH_2=), 114.73 d (C^{8}), 122.96 d (C^{6}), 124.13 C (C^{4a}), 127.27 d and 127.95 d (C^{5,7}), 136.55 s (C^{8a}), 148.34 s (C$^{8'}$), 172.37 s (C^{2}), 209.78 s (C$^{3'}$). Mass spectrum, *m/z* (I_{rel}, %): 325 (3), 324 (4), 323 [*M*]$^+$ (3), 319 (5), 308 (7), 306 (7), 305 (13), 288 (5), 266 (8), 232 (10), 184 (100), 167 (66), 146 (25), 100 (40), 93 (28). Found [*M*]$^+$ 323.1877. $C_{21}H_{25}NO_2$. Calculated *M* 323.1880.

(*R*)-3-[(2*R*,4a*R*,8a*S*)-4a-Methyl-8-methylidene-3-oxodecahydronaphthalen-2-yl]-3,4-dihydro-quinolin-2(1*H*)-one (VIIIb). Yield 4%, $[\alpha]_D^{20}$ +13° (*c* 0.3, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3436, 3206, 3078, 2928, 1701, 1679, 1649, 1596, 1493, 1439, 1393, 1294, 1274, 1256, 891, 752. UV spectrum, λ_{max}, nm (lgε): 203 (4.55), 251 (4.03). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.75 s (3H, CH_3), 1.46–1.51 m (3H, H$^{5',5',6'}$), 1.56 m (1H, H$^{6'}$), 1.88–2.06 m (3H, H$^{1',1',7'}$), 1.98–2.21 m (1H, H$^{4'}$), 2.30 m (1H, H$^{4'}$), 2.35 m (1H, H$^{7'}$), 2.48 m (1H, H$^{8a'}$), 2.85 m (1H, H^{4}), 2.90 m (1H, H^{3}, *J* 3.0, 1.8, 1.6 Hz), 3.04 m (1H, H$^{2'}$, *J* 3.0, 2.7, 2.5, 1.8 Hz), 3.17 m (2H, H^{4}), 4.52 br.s, 4.80 br.s (2H, CH_2=), 6.71 d (1H, H^{8}, *J* 8.6 Hz), 6.94 d.d (1H, H^{6}, *J* 8.2, 8.3 Hz), 7.10 d (1H, H^{5}, *J* 8.2 Hz), 7.14 d.d (1H, H^{7}, *J* 8.3, 8.6 Hz), 8.20 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 16.83 q (CH_3), 22.55 t (C$^{6'}$), 27.57 t (C^{4}), 28.45 (C$^{1'}$), 36.16 t (C$^{7'}$), 39.66 d (C^{3}), 40.01 s (C$^{4'a}$), 40.94 t (C$^{5'}$), 47.95 d (C$^{8a'}$), 47.95 d (C$^{2'}$), 55.58 t (C$^{4'}$), 106.89 t (CH_2=), 114.73 d (C^{8}), 122.49 d (C^{6}), 122.93 s (C^{4a}), 127.00 d (C^{7}), 127.80 d (C^{5}), 136.46 s (C^{8a}), 148.06 s (C$^{8'}$), 171.48 s (C^{2}), 208.45 s (C$^{3'}$). Mass spectrum, *m/z* (I_{rel}, %): 323 [*M*]$^+$ (2), 305 (2), 172 (1), 159 (1), 147 (11),

146 (100), 145 (2), 130 (3), 117 (3), 106 (3), 91 (4). Found $[M]^+$ 323.1869. $C_{21}H_{25}NO_2$. Calculated M 323.1880.

XRD investigation of compound IIIf. For the experiment a colorless needle crystal was selected of dimensions 0.06×0.20×0.90 mm. The analysis of geometry and intermolecular interactions was performed with the use of PLATON program [10]. Crystals rhombic: a 6.2067(4), b 15.298(1), c 21.059(2) Å, V 1999.5(2) Å^3, space group $P2_12_12_1$, Z 4, d_{calc} 1.221 g/cm^3. At –100°C in the range up to 2θ 55° the intensity of 8736 reflections were measured, among them 4517 independent (R_{int} 0.047). The correction for extinction was done using SADABS program [22] that used multiple measurements of the same reflections at different orientations of the crystal (transmission 0.62–0.75). The structure was solved by the direct method and refined in the anisotropic approximation of the thermal oscillations of the nonhydrogen atoms applying SHELXL software [23]. The hydrogen atoms positions were geometrically calculated and refined in the rider model (the parameters of hydrogen atoms were calculated in every refinement cycle from the coordinates of the corresponding C atoms). The final refinement of the structure was performed for all F^2 till wR_2 0.1345, S 1.04, 245 parameters were refined (R 0.0510 for 3740 $F > 4\sigma$). CIF file containing complete information on the investigated structure is deposited to the Cambridge Crystallographic Database Center under the number CCDC 729045, and the data are available by the address: www.ccdc.cam.ac.uk/data_request/cif.

XRD investigation of compound IVl. For the experiment a colorless needle crystal was selected of dimensions 0.05×0.20×0.24 mm. Crystals monoclinic: a 7.597(3), b 11.664(5), c 10.728(5) Å, β 97.082(16)°, V 943.4(7) Å^3, space group $P2_1$, Z 2, d_{calc} 1.248 g/cm^3. At –123°C in the range up to 2θ 52° the intensity of 6134 reflections were measured, among them 3061 independent (R_{int} 0.0627). The correction for extinction was done using SADABS program (transmission 0.67–0.97). The structure was solved by the direct method and refined in the anisotropic approximation of the thermal oscillations of the nonhydrogen atoms applying SHELXL software [23]. The hydrogen atoms positions were refined in the *rider* model. The final refinement of the structure was performed for all F^2 till wR_2 0.1382, S 1.018, 229 parameters were refined (R 0.0542 для 2270 $F > 4\sigma$). CIF file containing complete information on the investigated structure is deposited under the number CCDC 755906.

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REFERENCES

1. Zhang, S., Wong, Y.K., Ong, C.N., and Shen, H.M., *Curr. Med. Chem. Anticancer Agents*, 2005, vol. 5, p. 239; Zhao, Y.-M., Zhang, M.L., Shi, Q.-W., and Kiyota, H., *Chem. & Biodiversity*, 2006, vol. 3, p. 371; Wu, Q.-X., Shi, Y.-P., and Jia, Z-J., *Nat. Prod. Rep.,* 2006, vol. 23, p. 699.
2. Lee, K.-H., Huang, E.-S., Piantadosi, C., Pagano, J.S., and Geissman, T.A., *Cancer Res*., 1971, vol. 31, p. 1649.
3. Milman, I.A., *Khim. Polim. Soedin*., 1990, p. 307; Fischer, N.H., Olivier, E.J., and Fischer, H.D., *Fortschr. Chem. Org. Natursch*., 1980, vol. 38, p. 47.
4. Minato, H. and Horibe, I., *J. Chem. Soc. C*, 1967, p. 1575; Miller, R.B. and Nash, R.D., *Tetrahedron*, 1974, vol. 30, p. 2961; Cooper, J.L. and Harding, K.E., *Tetrahedron Lett*., 1977, vol. 38, p. 3321; Wender, P.A. and Letendre, L.J., *J. Org. Chem*., 1980, vol. 45, p. 367.
5. Blay, G., Cardona, L., Garcia, B., Pedro, J.R., and Serrano, A., *Tetrahedron*, 1992, vol. 48, p. 5265.
6. Belovodskii, A.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Dokl. Akad. Nauk*, 2009, vol. 426, p. 762.
7. Heck, R.F., *Palladium Reagents in Organic Synthesis*, New York: Academic Press, 1985, p. 2764; Larhed, M. and Hallberg, A., *Hand-book of Organopalladium Chemistry for Organic Synthesis*, New York: Wiley, 2002, p. 1133; Beletskaya, I.P. and Cheprakov, A.V., *Chem. Rev*., 2000, vol. 100, p. 3009.
8. Bohlmann, F., Dutta, L.N., Knauf, W., Robinson, H., and King, R.M., *Phytochem*., 1980, vol. 19, p. 433.
9. Kikukawa, K., Yamane, T., Ohbe, Y., Takagi, and M., Matsudo, T., *Bull. Chem. Soc. Jpn.,* 1979, vol. 52, p. 1187; Herrmann, W.A., BroYamer, C., Öfele, K., Beller, M., and Fischer, H., *J. Mol. Catal. A: Chem.,* 1995, vol. 103, p. 133.
10. Spek, A.L., PLATON. A, *Multipurpose Crystallographic Tool* (Version, 10M). Utrecht, Univ., The Netherlands, 2003; Spek, A.L., *J. Appl. Cryst.,* 2003, vol. 36, p. 7.
11. Allen, F.H., Kenard, O., Watson, D.G., Bramer, L., Orpen, A.G., and Taylor, R., *J. Chem. Soc*., *Perkin Trans. 2*, 1987, p. 1.
12. Bruno, I.J., Cole, J.C., Edgington, P.R., Kessler, M., Macrae, C.F., McCabe, P., Pearson, J., and Taylor, R., *Acta Cryst*., 2002, vol. 58, p. 389.
13. Bagal, S.K., Adlington, R.M., Baldwin, J.E., and Marquez, R., *J. Org. Chem*., 2004, vol. 69, p. 9100.

14. Emmanuel, A. Meyer, Roland, K. Castellano, and. Diederich, F., *Angew. Chem., Int. Ed*., 2003, vol. 42, p. 1210.
15. Shul'pin, G.B., *Organicheskie reaktsii kataliziruemye kompleksami metallov* (Organic Reaction Catalyzed by Metal Complexes), Moscow: Nauka, 1988, p. 275.
16. Ukai, T., Kawazura, H., Ishii, Y., Bonnet, J.I., and Ibers, J.A., *J. Organometal Chem.,* 1974, vol. 65, p. 253.
17. Srivastava, S.C., Mehra, M.M., Trivedi, G.K., and Bhattacharyy, S.C., *Ind. J. Chem*., 1971, vol. 9, p. 512.
18. Caldwell, S.T., Petersson, H.M., Farrugia, L.J., Mullen, W., Crozier, A., and Hartley, R.C., *Tetrahedron,* 2006, vol. 62, p. 7257.
19. Pavlinac, J., Zupan, M., and Stavber, S., *J. Org. Chem*., 2006, vol. 71, p. 1027.
20. Chaikovskii, V.K. and Novikov, A.N., *Zh. Prikl. Khim.,* 1984, vol. 57, p. 134.
21. Sadchii, S.A., Shul'ts, E.E., Polukhina, E.V., Shakirov, M.M., and Tolstikov, G.A., *Izv. Akad. Nauk, Ser. Khim.,* 2006, p. 1038.
22. Sheldrick, G.M., *SADABS. Version, 2.01*, Madison: Bruker AXS Inc., 2004.
23. Sheldrick, G.M., *SHELX-97, Release, 97-2*, Univ. Göttingen, Germany, 1998.