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Diels–Alder Reactions with Ethyl 1-Benzofuran-3-carboxylates

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Abstract—Substituted salicylaldehydes reacted with ethyl diazoacetate to give ethyl 1-benzofuran-3-carboxylates containing various substituents in the aromatic ring. The Diels–Alder reaction of these compounds with Danishefsky's diene was regioselective, and it provided an effective method for the construction of the heterocyclic skeleton of hexahydrodibenzo[*b*,*d*]furan-7-one or tetrahydrodibenzo[*b*,*d*]furan-7-one. The adducts were found to undergo rearrangement to substituted 4′-hydroxybiphenyl-2-yl methyl carbonates during column chromatography on silica gel.

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Tricyclic hexa- or tetrahydrodibenzo[*b*,*d*]furan fragment is a structural element of many pharmacologically important substances, e.g., plant alkaloids morphine [1], galanthamine [2], lycoramine [2], and lunarine [3], melanin biosynthesis inhibitor (±)-linderol A isolated from *Lindera umbellata* [4], and a number of selective estrogen receptor β agonists [5].

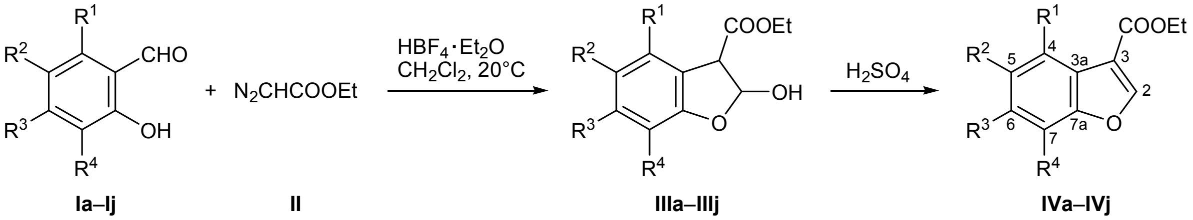
In the past decade, classical procedures for building up hexa(tetra)hydrodibenzo[*b*,*d*]furan skeleton, such as oxidative coupling of phenols [2, 6] and radical cyclization reactions [2], have been successfully supplemented by approaches based on the Birch reaction–Cope rearrangement sequence [7], Claisen rearrangement [8], intramolecular cyclization of functionalized bis-aryl compounds [9], intramolecular oxa-Michael reactions [10], and intramolecular cross-couplings [2, 5, 11].

Development of methods for the selective construction of a hexa- or tetrahydrodibenzo[*b*,*d*]furan skeleton attracts interest not only from the viewpoint of the design of rational schemes for total synthesis of natural compounds; it is also important for the synthesis of their structural analogs [12].

In the present communication we describe synthetic approaches to ethyl 7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate, ethyl 7-oxo-5a,6,7,9a-tetrahydrodibenzo[*b*,*d*]furan-9a-carboxylate, and their derivatives on the basis of the Diels–Alder reaction of substituted ethyl 1-benzofuran-3-carboxylates with Danishefsky's diene (1-methoxy-3-trimethylsilyloxybuta-1,3-diene). Diels–Alder reactions with 3-formyl- and 3-(2-oxoacetyl)-1-benzofurans as dienophiles were reported in [13, 14]; 3-ethoxycarbonyl-substituted derivatives were not brought into cycloaddition reactions.

Ethyl 1-benzofuran-3-carboxylate and its derivatives were synthesized by reaction of substituted salicylaldehydes **Ia**–**Ij** with ethyl diazoacetate (**II**) [15]. Treatment of aldehydes **Ia**–**Ij** in methylene

Scheme 1.



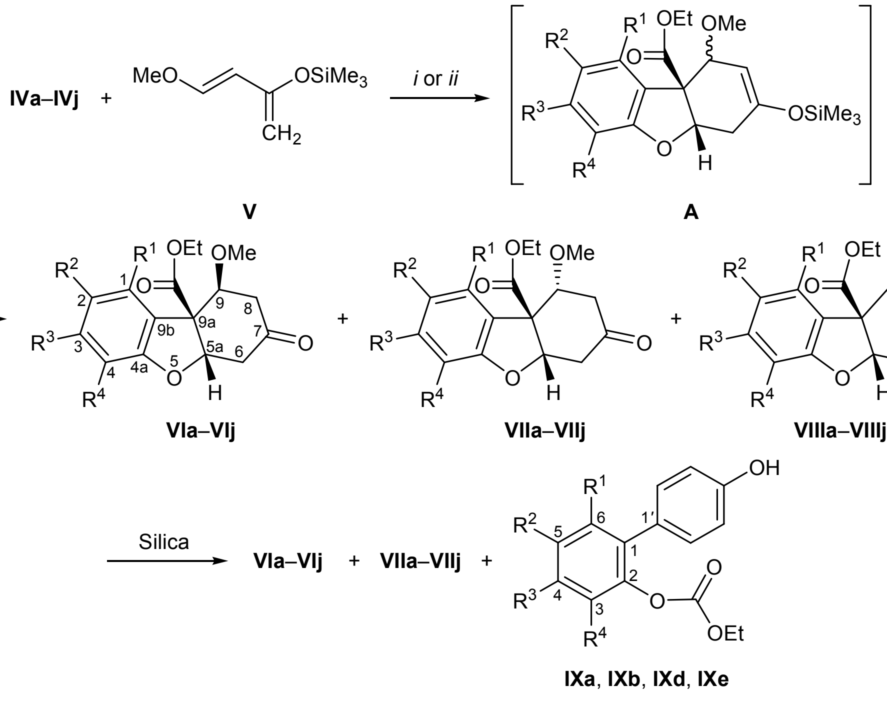
$R^1 = R^2 = R^3 = R^4 = H$ (**a**); $R^1 = R^2 = R^3 = H$, $R^4 = MeO$ (**b**); $R^1 = R^2 = R^4 = H$, $R^3 = MeO$ (**c**); $R^1 = R^3 = R^4 = H$, $R^2 = MeO$ (**d**); $R^1 = MeO$, $R^2 = R^3 = R^4 = H$ (**e**); $R^1 = R^3 = H$, $R^2 = R^4 = t\text{-}Bu$ (**f**); $R^1 = R^3 = R^4 = H$, $R^2 = O_2N$ (**g**); $R^1 = R^2 = R^4 = H$, $R^3 = Et_2N$ (**h**); $R^1 = R^3 = R^4 = H$, $R^2 = Br$ (**i**); $R^1 = R^3 = H$, $R^2 = I$, $R^4 = MeO$ (**j**).

chloride with a catalytic amount of tetrafluoroboric acid in diethyl ether ($Et_2O \cdot HBF_4$, 0.1 equiv) and subsequent reaction with excess diazo ester **II** gave ethyl 2-hydroxy-2,3-dihydro-1-benzofuran-3-carboxylates **IIIa–IIIj** which were subjected to dehydration by the action of concentrated sulfuric acid. As a result, ethyl 1-benzofuran-3-carboxylates **IVa–IVj** were isolated in 40–92% yield (Scheme 1). Intermediate compounds **IIIa–IIIj** were not isolated. We failed to achieve complete conversion of initial compounds **Ia–Ij** when the synthesis of **IVa–IVj** was carried out according to the procedure described in [15]. Therefore, we changed some reaction conditions. Increase of the amount of $Et_2O \cdot HBF_4$ from 10 to 20 mol % did not affect the yield of **IV** to an appreciable extent, whereas increase of the amount of ethyl diazoacetate (**II**) from 1.6 to 3.2 equiv improved the yield of **IV**. Further rise in the amount of **II** had no effect. Reduction of the amount of sulfuric acid by half (down to 0.5 ml per 0.005 mol of the initial aldehyde) led to incomplete dehydration and formation of mixtures of **III** and **IV**. While optimizing the conditions, in one experiment we obtained a mixture of compounds **IIIb** and **IVb**, from which 2,3-dihydro-1-benzofuran **IIIb** was isolated by column chromatography on silica gel.

Compounds **IVa–IVj** turned out to be highly reactive in the Diels–Alder cycloaddition with Danishefsky's diene (**V**) (Scheme 2). The reactions were carried out in toluene in two versions: (*a*) in a sealed ampule at a bath temperature of 165–170°C and (*b*) under microwave irradiation (190°C). The conversion of benzofuran derivatives **IVa–IVj** was 84–100%. The regioselectivity of the reaction did not depend on the thermal activation mode, and in both cases the ratios of stereoisomeric cycloadducts **A** with (9*S*) and (9*R*) configuration were similar (according to the ^1H NMR data). Primary adducts **A** were decomposed by treatment with (*c*) ammonium fluoride in methanol [14], (*d*) *p*-toluenesulfonic acid in methanol [16], (*e*) trifluoroacetic acid in methylene chloride [17], or (*f*) *p*-toluenesulfonic acid in boiling toluene.

Decomposition of adducts **A** with ammonium fluoride, followed by chromatographic separation, afforded stereoisomeric ethyl (9*S*)- and (9*R*)-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylates **VIa–VIj** (7–50%) and **VIIa–VIIj** (15–49%). In this case, no tetrahydrodibenzo[*b*,*d*]furan derivatives **VIII** were isolated; according to the ^1H NMR data, their concentration in the hydrolysis product mixture was 2–8%. Instead, we isolated biphenylyl

Scheme 2.



$R^1 = R^2 = R^3 = R^4 = H$ (**a**); $R^1 = R^2 = R^3 = H$, $R^4 = MeO$ (**b**); $R^1 = R^2 = R^4 = H$, $R^3 = MeO$ (**c**); $R^1 = R^3 = R^4 = H$, $R^2 = MeO$ (**d**); $R^1 = MeO$, $R^2 = R^3 = R^4 = H$ (**e**); $R^1 = R^3 = H$, $R^2 = R^4 = t\text{-Bu}$ (**f**); $R^1 = R^3 = R^4 = H$, $R^2 = O_2N$ (**g**); $R^1 = R^2 = R^4 = H$, $R^3 = Et_2N$ (**h**); $R^1 = R^3 = R^4 = H$, $R^2 = Br$ (**i**); $R^1 = R^3 = H$, $R^2 = I$, $R^4 = MeO$ (**j**); *i*: PhMe, sealed ampule, 165–170°C, 48–52 h; *ii*: PhMe, microwave irradiation, 190°C, 4 h; *iii*: NH_4F–MeOH, –15 to 20°C; *iv*: TsOH–MeOH, 20°C; *v*: CF_3CO_2H–CH_2Cl_2, 20°C; *vi*: TsOH–PhMe, 110°C.

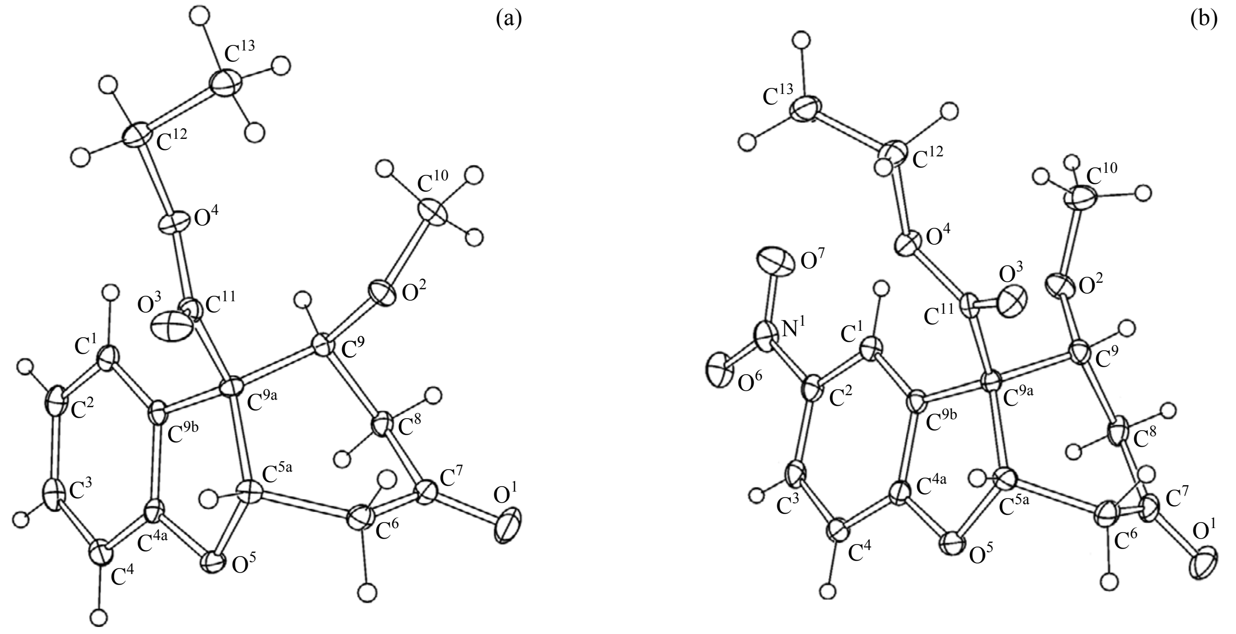


Fig. 1. Structures of the molecules of (a) ethyl (5a*S*,9*S*,9a*S*)-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (**VIa**) and (b) ethyl (5a*S*,9*R*,9a*S*)-9-methoxy-2-nitro-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (**VIIg**) according to the X-ray diffraction data.

carbonates **IXb**, **IXd**, and **IXe** (13–41%) which were likely to be formed during chromatographic separation on silica gel (the ^{1}H NMR spectra of the reaction mixtures contained no signals assignable to compounds like **IX**). Analogous results were obtained when adducts **A** were decomposed with *p*-toluenesulfonic acid in methanol or with trifluoroacetic acid in methylene chloride (methods *d* and *e*) at 20°C. By column chromatography on silica gel we isolated stereoisomeric hexahydrodibenzo[*b*,*d*]furans **VIa**, **VId**, **VIf**, and **VIj** (10–35%) and **VIIa**, **VIIb**, **VIId**, **VIIf**, and **VIIj** (10–40%), as well as biphenylyl carbonates **IXa**, **IXb**, and **IXd** (13–44%).

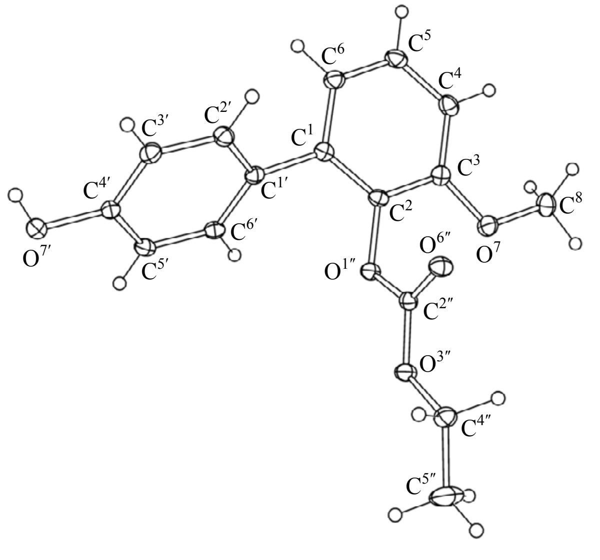


Fig. 2. Structure of the molecule of ethyl 4′-hydroxy-3-methoxybiphenyl-2-yl carbonate (**IXb**) according to the X-ray diffraction data.

Decomposition of adduct **A** with *p*-toluenesulfonic acid in toluene (110°C) gave ethyl (5a*S*,9a*R*)-4-methoxy-7-oxotetrahydrodibenzo[*b*,*d*]furan-9a-carboxylate (**VIIIb**) as the major product, the ratio (**VIb**+**VIIb**)/**VIIIb** being 1:7. It is seen that treatment with TsOH at elevated temperature favors formation of unsaturated tricyclic ketones **VIII**.

The structure of the synthesized compounds was confirmed by their IR, UV, ^{1}H and ^{13}C NMR, and mass spectra. The regioselectivity of the Diels–Alder reaction of substituted ethyl 1-benzofuran-3-carboxylates **IV** with Danishefsky's diene follows from the ^{1}H NMR spectra of compounds **VI**–**VIII**. Tricyclic ketones **VI** and **VII** characteristically displayed in the ^{1}H NMR spectra signals from protons on C^6 and C^8 as doublets of doublets in the region δ 1.93–3.03 ppm (^2J = 17–18, ^3J = 2–12 and 3.5–8 Hz for 8-H and 6-H, respectively). In the spectra of esters **VIII**, distinguishing signals are those from 5a-H, 8-H, and 9-H. The 5a-H signal was a double doublet of doublets at δ 5.42–5.48 ppm (^3J = 4, ^4J= 2, 2 Hz). The 8-H and 9-H protons resonated as doublets of doublets at δ 6.65–6.75 and 6.80–6.90 ppm, respectively (^3J = 10.0–10.4, ^4J = 1–2 Hz). The vicinal coupling constant (10.0–10.4 Hz) unambiguously indicates *Z* configuration of the double $C^8{=}C^9$ bond.

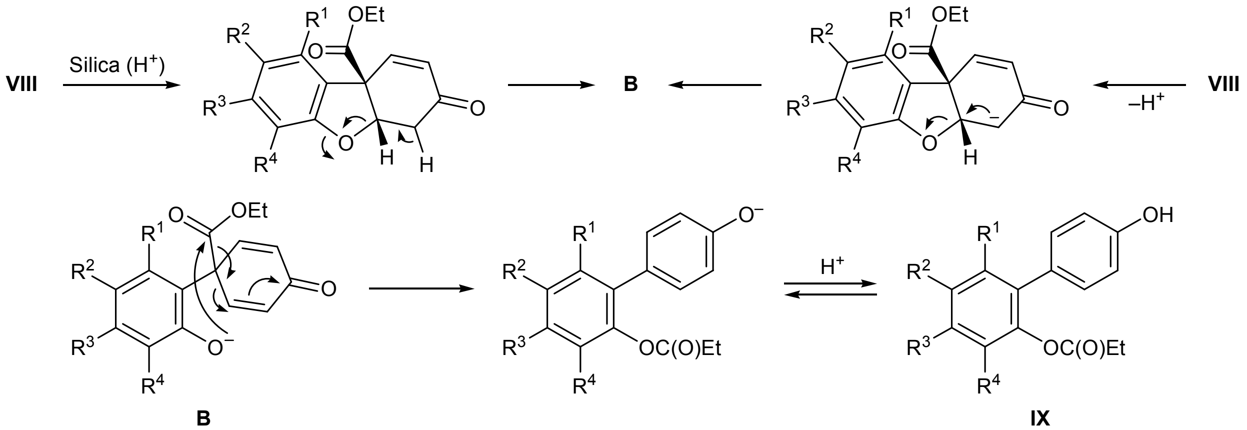
The structure of **VIa**, **VIIg**, and **IXb** was proved by X-ray analysis (Figs. 1, 2). The geometric parameters of two independent molecules of compound **VIIg** almost coincide. The bond lengths in **VIIg** are close to the corresponding bond lengths in **VIa**, the largest difference being observed for the $C^9–C^{9a}$ bonds [1.564(2) and 1.566(2) Å in the two independent molecules of **VIIg** and 1.542(2) Å in **VIa**]. The conformation of the tricyclic fragment of **VIa** is similar to that of *exo-N,N*-diethyl-2-[9-methoxy-7-oxo-6,7,8,9-tetrahydrodibenzo-[*b*,*d*]furan-9a(5a*H*)-yl]-2-oxoacetamide [14], and the conformation of **VIIg**, to that of (4a*S*,9b*S*)-8-hydroxy-1,2,3,4,4a,9b-hexahydrodibenzofuran-3-one [18]. The furan ring has an *envelope* conformation with the C^{5a} atom deviating from the plane formed by the other ring atoms; the folding angles are 12.9 and 14.3° for **VIIg** and 18.9° for **VIa**. The cyclohexane fragment in **VIIg** adopts a *distorted boat* conformation, whereas its conformation in molecule **VIa** is *twist*. There are also differences in the orientation of the ester group. The ester group in **VIa** is eclipsed by the $C^{5a}–C^{9a}$ bond, and the intramolecular contact $C^{5a}–H\cdots O^3$, 2.33Å ($C^{5a}\cdots O^3$ 2.792(2)Å, ∠CHO 107°) is appreciably shortened (the sums of the van der Waals radii of the oxygen and hydrogen and oxygen and carbon atoms are 2.68 and 3.35 Å, respectively [19]), and the $C^{13}H_3$ methyl group is located above the cyclohexane ring. In both independent molecules of **VIIg** the carboxylate group resides above the cyclohexane fragment, and the ethyl group appears in the *trans* position with respect to the $C^{11}–O^4$ bond. Different configurations of C^9 in molecules **VIa** and **VIIg** should also be noted. The nitro group in **VIIg** is planar, and it forms with the benzene ring plane a dihedral angle of –3.9(3) and 15.3(3)° ($O^6N^1C^2C^3$).

The three-dimensional crystalline structure of compound **VIa** is formed due to $C^9–H\cdots\pi(C^1–C^{9b})$ interactions (the distance to the plane and to the center of the phenyl group is 2.84Å) and numerous $C–H\cdots O$ contacts, the shortest of which are $C^3–H\cdots O^5$ and $C^{10}–H\cdots O^3$ (2.44–2.46Å), $C\cdots O$ 3.370(2) and 3.390(2) Å, ∠CHO 158 and 168°, respectively. In the crystalline structure of **VIIg** alternating stacks parallel to the *b* axis are formed via π-stacking interactions of phenyl groups in the two independent molecules with an interplanar angle of 6.2°, an intercentroid distance of 3.834(1) Å, and distances of 3.4353(8) and 3.5672(8) Å from the centroid to the benzene ring plane of the neighboring molecule; the latter alternates with the pair interaction $O\cdots\pi$ with the distances between O^6 and the centroid of the $C^{1'}C^{2'}C^{3'}C^{4'}C^{4a'9b'}$ benzene ring 3.837(2) and 3.771 Å and between $O^{6'}$ and the centroid of the $C^1C^2C^3C^4C^{4a}C^{9b}$ benzene ring 3.863(2) and 3.777 Å. The stacks are linked to form a three-dimensional structure through shortened $C\cdots O$ and $C–H\cdots O$ contacts, the shortest of which are $O^3\cdots C^{7'}$ 2.933(2) and $H^{9'}\cdots O^3$ 2.41Å.

Figure 2 shows the structure of molecule **IXb** in crystal. The aromatic rings $C^1C^2C^3C^4C^5C^6$ and $C^{1'}C^{2'}C^{3'}C^{4'}C^{5'}C^{6'}$ are planar within ±0.0065(9) and ±0.0129(8) Å, respectively, and their planes form a dihedral angle of 51.22(4)°. The $O^{1''}C^{2''}O^{6''}O^{3''}C^{4''}$ fragment is planar within ±0.0157(6) Å, and it is turned through an angle of 80.56(3)° with respect to the $C^1C^2C^3C^4C^5C^6$ benzene ring. The hydroxy group deviates from the benzene ring plane, the torsion angle $C^{3'}C^{4'}O^{7'}H$ being 13°. The methoxy group is oriented almost in one plane with the $C^1C^2C^3C^4C^5C^6$ benzene ring [the torsion angle $C^2C^3O^7C^8$ is 175.9(1)°]. Molecules **IXb** in crystal are linked by intermolecular hydrogen bonds $O^{7'}–H\cdots O^{6''}$ [O–H 0.84, $H\cdots O$ 1.94, $O\cdots O$ 2.767(1) Å, ∠OHO 170°] to form zigzag chains along the *b* axis. In addition, hydrogen bonds $C^{4''}–H\cdots O^{6''}$ [C–H 0.99, $H\cdots O$ 2.40, $C\cdots O$ 3.354(2) Å, ∠CHO 162°] connecting the chains to layers parallel to the (*a*+*c*, *b*) plane were detected.

Thus the Diels–Alder reaction of ethyl substituted 1-benzofuran-3-carboxylates **IVa–IVj** with Danishefsky's diene (**V**) regioselectively yields stereoisomeric ethyl (9*S*)- and (9*R*)-9-methoxy-7-oxohexahydrodibenzo[*b*,*d*]furan-9a-carboxylates **VI** and **VII** or ethyl 7-oxotetrahydrodibenzo[*b*,*d*]furan-9a-carboxylates **VIII**. Biphenylyl carbonates **IXa**, **IXb**, **IXd**, and **IXe** were also isolated as a result of transformation of tricyclic compounds **VIII** during chromatographic separation of the products on silica gel. Presumably, this transformation is initiated by acid or basic centers on the silica surface (Scheme 3); it is likely to involve opening of the furan ring with formation of dienone intermediate **B**. The latter undergoes rearrangement through migration of the ethoxycarbonyl group, which is analogous to the fast step in the retro-Fries rearrangement [20], and it smoothly affords biphenylyl carbonates **IX**. Partial isomerization of cycloaddition products derived from Danishefsky's diene (**V**), e.g., of methyl 6-methyl-4-oxocyclohex-2-ene-1-carboxylate into methyl 6-methyl-4-oxocyclohex-1-enecarboxylate, on silica gel was reported in [21]; an example of

Scheme 3.



furan ring opening in 9a-substituted 5a,9a-dihydrobenzo[*b*,*d*]furans with migration of the substituents was described in [22].

EXPERIMENTAL*

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300 [300.13 (^{1}H) and 75.48 MHz (^{13}C)], AV-400 [400.13 (^{1}H) and 100.61 MHz (^{13}C)], and AV-600 spectrometers [600.30 (^{1}H) and 150.95 MHz (^{13}C)] from solutions in $CDCl_3$. The chemical shifts were measured relative to the residual proton and carbon signals of the solvent ($CHCl_3$, δ 7.24 ppm, $CDCl_3$, δ_C 76.90 ppm). Signals were assigned using one-dimensional ^{1}H and ^{13}C NMR experiments and two-dimensional ^{1}H–^{1}H and ^{13}C–^{1}H shift correlation techniques (COSY, COXH, COLOC, BSMS). The molecular weights and elemental compositions were determined from the high-resolution mass spectra which were obtained on a DFS Thermo Scientific mass spectrometer (electron impact, 70 eV; vaporizer temperature 180–250°C). The IR spectra were measured on a Bruker Vector spectrometer with Fourier transform from samples prepared as KBr pellets (crystalline products) or thin films (liquids). The UV spectra were recorded on a Hewlett Packard HP 8453-Vis spectrophotometer from solutions in chloroform or ethanol. The melting points were determined using a Stuart SMP melting point apparatus. X-Ray analysis of single crystals of compounds **VIa**, **VIIg**, and **IXb** was performed on a Bruker APEX diffractometer (MoK_α irradiation, graphite monochromator, CCD detector, $2\theta_{max}$ = 56.6, 54.2, and 53.5°, respectively).

Silica gel from Acros Organics (0.035–0.070 mm) was used for column chromatography. The solvents (toluene, methylene chloride, methanol, diethyl ether, petroleum ether) were purified by standard methods. Danishefsky’s diene, tetrafluoroboric acid (50%) in diethyl ether, and ethyl diazoacetate were commercial products (from Alfa Aesar).

Microwave-activated syntheses were carried out in CEM Discovery (300 W) and Anton Paar Monowave (850 W) single mode microwave ovens.

Ethyl 1-benzofuran-3-carboxylates IVa–IVj (*general procedure*)**.** Substituted 2-hydroxybenzaldehyde **Ia**–**Ij**, 5 mmol, was dissolved in 10 ml of methylene chloride, 0.08 ml of tetrafluoroboric acid in diethyl ether (0.5 mmol of HBF_4) was added dropwise under stirring, and a solution of 2.0 ml (16 mmol) of ethyl diazoacetate (**II**) in 10 ml of methylene chloride was then added dropwise under stirring. The mixture was stirred until nitrogen no longer evolved and for 20–30 min more and concentrated, and 1.0 ml of concentrated sulfuric acid was added under stirring. After 10 min, the mixture was diluted with 10 ml of methylene chloride and neutralized with solid sodium hydrogen carbonate. The precipitate was filtered off and washed with a 9 : 1 mixture of petroleum ether and diethyl ether. The filtrate was subjected to double column chromatography on silica gel using petroleum ether–diethyl ether (9 : 1 and 19 : 1) as eluent. Removal of the solvent from the eluate gave esters **IVa**–**IVj**.

Ethyl 1-benzofuran-3-carboxylate (IVa). The ^{1}H and ^{13}C NMR spectra of **IVa** coincided with those given in [15]. Mass spectrum, *m*/*z* (I_{rel}, %): 190.1 (49.5) $[M]^+$, 175.0 (2.34), 162.0 (24.0), 145.0 (100), 118.0 (5.06), 89.0 (15.1). Found: *m*/*z* 190.0624 $[M]^+$. $C_{11}H_{10}O_3$. Calculated: *M* 190.0625.

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* Analytical and spectral studies were carried out at the Shared Chemical Service Center of the Siberian Branch of the Russian Academy of Sciences.

Ethyl 7-methoxy-1-benzofuran-3-carboxylate (IVb). mp 41–42°C. The ^{1}H and ^{13}C NMR spectra of **IVb** coincided with those given in [15]. IR spectrum, ν, cm^{-1}: 3149, 3107, 2981, 2843, 1718, 1626, 1592, 1498, 1277, 1153, 1111, 1042. UV spectrum, λ_{max}, nm (log ε): 242 (3.65), 265 (3.60). Mass spectrum, *m*/*z* (I_{rel}, %): 220 (100), 192 (43), 175 (82.5), 160 (16), 148 (33), 119 (3.7). Found: *m*/*z* 220.0729 $[M]^+$. $C_{12}H_{12}O_4$. Calculated: *M* 220.0730.

In one experiment during optimization of the reaction conditions, we isolated compound **IVb** and ethyl 2-hydroxy-2,3-dihydro-1-benzofuran-3-carboxylate (**IIIb**) (from **Ib** and **II**). Yield of **IIIb** 0.40 g (5.6%), transparent oily substance. IR spectrum, ν, cm^{-1}: 3430, 2980, 2938, 2840, 1737, 1620, 1494, 1462, 1283, 1191, 1102. UV spectrum, λ_{max}, nm (log ε): 242 (3.37), 279 (3.44). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.23 t (3H, $CH_2C\mathbf{H}_3$, $J = 7.1$), 3.86 s (3H, OCH_3), 4.10 d (1H, 3-H, $J = 2.9$), 4.18 q (2H, OCH_2, $J = 7.1$), 6.08 s (1H, 2-H, $J = 2.9$), 6.80 d.d (1H, 6-H, $J = 8.0, 0.9$), 6.85 d.d (1H, 5-H, $J = 8.0, 8.0$), 6.96 d.d (1H, 4-H, $J = 8.0, 0.9$). ^{13}C NMR spectrum, δ_C, ppm: 14.03 ($CH_2\mathbf{C}H_3$), 54.69 (OCH_3), 55.95 (C^3), 61.44 (OCH_2), 108.17 (C^2); 112.42, 117.24, 121.47 (C^4, C^5, C^6), 122.23 (C^{3a}), 146.71 (C^{2a}, C^7), 169.52 (C=O).

Ethyl 6-methoxy-1-benzofuran-3-carboxylate (IVc). Yield 0.62 g (56%), mp 54–55°C; published data [23]: mp 55–56°C. IR spectrum, ν, cm^{-1}: 3132, 3086, 2992, 2841, 1709, 1624, 1558, 1501, 1437, 1379, 1273, 1103, 1051. UV spectrum, λ_{max}, nm (log ε): 242 (3.65), 296 (3.63). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.39 t (3H, $CH_2C\mathbf{H}_3$, $J = 7.1$), 3.83 s (3H, OCH_3), 4.37 q (2H, OCH_2, $J = 7.1$), 6.96 d.d (1H, 6-H, $J = 8.6, 2.2$), 7.01 d.d (1H, 7-H, $J = 2.2, 0.5$), 7.88 d.d (1H, 4-H, $J = 8.6, 0.5$), 8.14 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.33 ($CH_2\mathbf{C}H_3$), 55.63 (OCH_3), 60.45 (OCH_2), 95.86 (C^7), 113.19 (C^5), 114.59 (C^3), 117.78 (C^{3a}), 122.05 (C^4), 149.88 (C^2), 156.52 (C^6), 158.48 (C^{7a}), 163.49 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 220.2 (100) $[M]^+$, 205.1 (9.12), 192.1 (44.2), 177.1 (52.4), 175.1 (47.8), 160.1 (3.21), 148.1 (9.54), 119.1 (18.3). Found: *m*/*z* 220.0728 $[M]^+$. $C_{12}H_{12}O_4$. Calculated: *M* 220.0730.

Ethyl 5-methoxy-1-benzofuran-3-carboxylate (IVd). Yield 0.93 g (85%), mp 55.5–56.0°C. IR spectrum, ν, cm^{-1}: 3144, 3098, 2982, 2835, 1720, 1616, 1562, 1481, 1373, 1267, 1204, 1128, 1049. UV spectrum, λ_{max}, nm (log ε): 251 (3.74), 297 (3.60). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.39 t (3H, $CH_2C\mathbf{H}_3$, $J = 7.1$), 3.85 s (3H, OCH_3), 4.38 q (2H, OCH_2, $J = 7.1$), 6.93 d.d (1H, 6-H, $J = 9.0, 2.7$), 7.38 d (1H, 7-H, $J = 9.0$), 7.50 d (1H, 4-H, $J = 2.7$), 8.19 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.30 ($CH_2\mathbf{C}H_3$), 55.76 (OCH_3), 60.40 (OCH_2), 103.63 (C^4), 112.12 and 114.40 (C^6, C^7), 114.52 (C^3), 125.32 (C^{3a}), 150.41 (C^{7a}), 151.40 (C^2), 156.86 (C^5), 163.43 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 220.1 (100) $[M]^+$, 192.1 (28.9), 177.1 (19.4), 175.1 (79.4), 160.1 (7.28), 148.1 (15.9), 119.1 (7.66). Found: *m*/*z* 220.0728 $[M]^+$. $C_{12}H_{12}O_4$. Calculated: *M* 220.0730.

Ethyl 4-methoxy-1-benzofuran-3-carboxylate (IVe). Yield 0.57 g (52%), oily substance. IR spectrum, ν, cm^{-1}: 3145, 3086, 2982, 2840, 1739, 1597, 1558, 1501, 1465, 1374, 1291, 1136, 1082, 1046. UV spectrum, λ_{max}, nm (log ε): 243 (3.90), 265 (3.74). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.37 t (3H, $CH_2C\mathbf{H}_3$, $J = 7.1$), 3.95 s (3H, OCH_3), 4.35 q (2H, OCH_2, $J = 7.1$), 6.75 d.d (1H, 5-H, 7-H, $J = 8.1, 0.7$), 7.13 d.d (1H, 7-H, $J = 8.3, 0.7$), 7.27 d.d (1H, 6-H, $J = 8.3, 8.1$), 8.13 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.27 ($CH_2\mathbf{C}H_3$), 55.88 (OCH_3), 60.58 (OCH_2), 104.71 and 105.13 (C^5, C^7), 113.84 and 115.00 (C^3, C^{3a}), 126.20 (C^6), 150.12 (C^2), 154.40 (C^4), 157.19 (C^{7a}), 162.65 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 220 (100) $[M]^+$, 192 (6.00), 175 (90.0), 160 (21.7), 145 (42.9), 117 (9.29), 105 (9.86), 89 (28.0). Found: *m*/*z* 220.0729 $[M]^+$. $C_{12}H_{12}O_4$. Calculated: *M* 220.0730.

Ethyl 5,7-di-*tert*-butyl-1-benzofuran-3-carboxylate (IVf). Yield 1.4 g (92%), light yellow crystals, mp 80–81°C. IR spectrum, ν, cm^{-1}: 3138, 3097, 2964, 2872, 1712, 1603, 1570, 1483, 1363, 1302, 1227, 1124. UV spectrum, λ_{max}, nm (log ε): 241 (3.55), 267 (3.61). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.38 s (9H, *t*-Bu), 1.40 t (3H, $CH_2C\mathbf{H}_3$, $J = 7.1$), 1.47 s (9H, *t*-Bu), 4.38 q (2H, OCH_2, $J = 7.1$), 7.30 d.d (1H, 6-H, $J = 2.0$), 7.93 d (1H, 4-H, $J = 2.0$), 8.22 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.34 ($CH_2\mathbf{C}H_3$), 29.80 [$C(\mathbf{C}H_3)_3$], 31.80 [$\mathbf{C}(CH_3)_3$], 34.42 (7-C), 34.99 (5-C), 60.29 (OCH_2), 114.30 (C^3), 115.81 and 119.82 (C^4, C^6), 124.75 (C^{3a}), 134.24 (C^7), 147.06 (C^5), 150.12 (C^2), 152.30 (C^{7a}), 163.74 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 302 (15.4) $[M]^+$, 287 (100), 257 (6.75), 203.1 (4.56), 185.1 (3.84), 128.1 (4.57), 115.1 (3.83), 57.0 (21.8). Found: *m*/*z* 302.1869 $[M]^+$. $C_{19}H_{26}O_3$. Calculated: *M* 302.1876.

Ethyl 5-nitro-1-benzofuran-3-carboxylate (IVg). Yield 0.66 g (56%), colorless crystals, mp 129–130°C. IR spectrum, ν, cm^{-1}: 3143, 3095, 2985, 1712, 1595, 1564, 1525, 1448, 1344, 1250, 1169, 1115, 1086, 1039. UV spectrum, λ_{max}, nm (log ε): 239 (4.00), 276 (3.56).

^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.44 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 4.44 q (2H, OCH_2, *J* = 7.1), 7.62 d (1H, 7-H, *J* = 9.1), 8.28 d.d (1H, 6-H, *J* = 9.1, 2.3), 8.95 d (1H, 4-H, *J* = 2.3), 8.37 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.32 ($CH_2\mathbf{C}H_3$), 61.19 (OCH_2), 112.27 (C^7), 115.70 (C^3), 118.82 (C^4), 121.13 (C^6), 125.21 (C^{3a}), 145.12 (C^5), 153.29 (C^2), 157.92 (C^{7a}), 162.14 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 235 (61.3) $[M]^+$, 207 (57.8), 190 (100), 174 (18.7), 143 (43.8), 88 (14.9). Found: *m*/*z* 235.0476. $C_{11}H_9NO_5$. Calculated: *M* 235.0475.

Ethyl 6-(diethylamino)-1-benzofuran-3-carboxylate (IVh). Yield 0.52 g (40%), yellow oily liquid. IR spectrum, ν, cm^{-1}: 3149, 3094, 2974, 2932, 1718, 1632, 1563, 1509, 1450, 1357, 1258, 1217, 1101, 1047. UV spectrum, λ_{max}, nm (logε): 245 (4.20), 336 (3.78). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.17 t [6H, $N(CH_2C\mathbf{H}_3)_2$, *J* = 7.0], 1.39 t (3H, $OCH_2C\mathbf{H}_3$, *J* = 7.2), 3.38 q (4H, NCH_2, *J* = 7.0), 4.36 q (2H, OCH_2, *J* = 7.2), 6.74 d.d (1H, 7-H, *J* = 7.0, 0.6), 6.77 d.d (1H, 5-H, *J* = 8.6, 2.3), 7.78 d.d (1H, 4-H, *J* = 8.6, 0.6), 8.03 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 12.41 [$N(CH_2\mathbf{C}H_3)_2$], 14.35 ($OCH_2\mathbf{C}H_3$), 44.91 (NCH_2), 60.24 (OCH_2), 94.04 (C^7), 110.68 (C^5), 113.61 and 114.59 (C^3, C^{3a}), 121.87 (C^4), 146.92 (C^6), 148.33 (C^2), 157.98 (C^{7a}), 163.91 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 261 (46.3) $[M]^+$, 246 (100), 218 (18.3), 190 (9.92), 172 (3.76). Found: *m*/*z* 261.1358 $[M]^+$. $C_{15}H_{19}NO_3$. Calculated: *M* 261.1360.

Ethyl 5-bromo-1-benzofuran-3-carboxylate (IVi). Yield 0.70 g (52%), mp 80–81°C. IR spectrum, ν, cm^{-1}: 3082, 2982, 1709, 1562, 1441, 1373, 1340, 1279, 1227, 1163, 1122, 1063, 1040. UV spectrum, λ_{max}, nm (logε): 239 (4.00), 276 (3.56). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.41 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 4.39 q (2H, OCH_2, *J* = 7.1), 7.38 d (1H, 7-H, *J* = 8.8), 7.44 d.d (1H, 6-H, *J* = 8.8, 2.0), 8.18 d (1H, 4-H, *J* = 2.0), 8.22 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.36 ($CH_2\mathbf{C}H_3$), 60.78 (OCH_2), 113.12 (C^7), 114.39, 117.51 (C^3, C^5), 124.84 (C^4), 126.54 (C^{3a}), 128.33 (C^6), 151.78 (C^2), 154.30 (C^{7a}), 162.82 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 270 (71.9) $[M + 2]^+$, 269 (9.73) $[M + 1]^+$, 268 (75.3) $[M]^+$, 242 (36.6), 240 (38.2), 225 (99.3), 223 (100), 198 (5.88), 197 (6.14), 196 (5.25), 195 (4.94), 169 (17.0), 167 (17.2), 143 (15.7), 88 (22.4). Found: *m*/*z* 267.9736 $[M]^+$. $C_{11}H_9BrO_3$. Calculated: *M* 267.9730.

Ethyl 5-iodo-7-methoxy-1-benzofuran-3-carboxylate (IVj). Yield 1.00 g (58%), mp 128–129°C. IR spectrum, ν, cm^{-1}: 3020, 2981, 1699, 1620, 1578, 1470, 1431, 1294, 1271, 1196, 1173, 1115, 1039, 933, 820, 769, 739, 623. UV spectrum: λ_{max} 216 nm (logε 4.17). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.39 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 3.97 s (3H, OCH_3), 4.38 q (2H, OCH_2, *J* = 7.1), 7.11 d (1H, 6-H, *J* = 1.5), 7.99 d (1H, 4-H, *J* = 1.5), 8.17 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.32 ($CH_2\mathbf{C}H_3$), 56.31 (OCH_3), 60.78 (OCH_2), 87.95 (C^5), 114.24 (C^3), 116.38 (C^6), 123.09 (C^4), 128.13 (C^{3a}), 144.58 and 145.72 (C^7, C^{7a}), 151.10 (C^2), 162.78 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 346 (100) $[M]^+$, 318 (18.2), 301 (30.4), 274 (26.1), 191 (9.2), 173 (16.7), 147 (6.21), 75 (15.2). Found: *m*/*z* 345.9699 $[M]^+$. $C_{12}H_{11}IO_4$. Calculated: *M* 345.9697.

Diels–Alder reaction of ethyl 1-benzofuran-3-carboxylates IVa–IVj with Danishefsky's diene (V) (*general procedures*). *a.* A glass ampule was filled with argon and charged with a solution of 0.0005 mol of compound **IVa**–**IVj** and 0.33 ml (0.0015 mol) of Danishefsky's diene (**V**) in 4.0 ml of toluene. The ampule was sealed and heated for 48–52 h at 165–170°C on an oil bath. The ampule was cooled and opened, the reaction mixture was transferred into a round-bottom flask, the ampule was washed with methylene chloride (3 × 5 ml), the solvent was removed under reduced pressure, and the residue was subjected to desilylation.

b. A test tube was filled with argon and charged with 0.0005 mol of compound **IVa**–**IVj** and 0.0025 mol (0.55 ml) of diene **V** in 2.5 ml of toluene. The test tube was placed in a microwave oven, and the mixture was heated to 190°C and stirred for 4 h at that temperature. The test tube was then withdrawn from the oven, the reaction mixture was transferred into a round-bottom flask, and the test tube was washed with methylene chloride (2 × 5 ml). If necessary, the solvent was removed under reduced pressure.

c. The residue obtained after evaporation of the solvent was treated with 5 ml of methanol, the solution was cooled to –15°C, and ammonium fluoride in equimolar amount to initial diene **V** was added under stirring. The mixture was stirred for 18 h, gradually allowing it to warm up to room temperature, the solvent was distilled off, and the residue was subjected to column chromatography on silica gel.

d. The residue obtained after evaporation of the solvent was treated with 6 ml of methanol and 10 mg of *p*-toluenesulfonic acid monohydrate, the mixture was stirred for 18 h at 20°C and evaporated, 10 ml of methylene chloride was added to the residue, and 5 ml of a saturated aqueous solution of sodium hydrogen carbonate was then added. The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×4 ml), the extracts were combined with the organic phase, dried over magnesium sulfate, and evaporated, and the residue was subjected to column chromatography on silica gel.

e. The residue obtained after evaporation of the solvent was treated with 6 ml of methylene chloride and 0.03 ml of trifluoroacetic acid, the mixture was stirred for 18 h at 20°C and transferred into a separatory funnel containing 5 ml of a saturated aqueous solution of $NaHCO_3$. The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×4 ml), the extracts were combined with the organic phase, dried over magnesium sulfate, and filtered, the solvent was distilled off, and the residue was subjected to column chromatography on silica gel.

f. The reaction mixture was transferred from the ampule into a round-bottom flask, and the ampule was washed with toluene (3×2 ml) for complete transfer. *p*-Toluenesulfonic acid monohydrate, 38 mg (0.0001 mol), was added to the mixture, and the mixture was heated for 3 h under reflux with stirring. The mixture was treated with 5 ml of a 5% aqueous solution of sodium hydrogen carbonate, the organic phase was separated, the aqueous phase was extracted with methylene chloride (3×3 ml), the extracts were combined with the organic phase and dried over magnesium sulfate, and the solvent was removed under reduced pressure.

By column chromatography we isolated in succession compounds **IVa–IVj** (eluent petroleum ether or hexane–diethyl ether, 95:5 to 90:10), **VIa–VIj** [petroleum ether (or hexane)–diethyl ether, 80:20], **VIIa–VIIj**, and **IXa**, **IXb**, **IXd**, or **IXe** [methylene chloride–petroleum ether (hexane), 70:30 to 100:0].

Ethyl (5a*S*,9*S*,9a*S*)-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIa). Yield 35% (*e*), mp 79–80°C (from petroleum ether). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.00 d.d (1H, 8-H, *J* = 17.8, 1.8), 2.63 d.d (1H, 8-H, *J* = 17.8, 3.7), 2.91 d.d (1H, 6-H, *J* = 17.8, 2.9), 2.94 d.d (1H, 6-H, *J* = 17.8, 3.3), 3.30 s (3H, OCH_3), 4.06 d.d (1H, 9-H, *J* = 3.7, 1.8), 4.32 q (2H, OCH_2, *J* = 7.1), 5.74 d.d (1H, 5a-H, *J* = 3.3, 2.9), 6.75 d.d (1H, 4-H, *J* = 8.1, 1.0), 6.90 d.d.d (1H, 2-H, *J* = 7.6, 7.5, 1.0), 7.21 d.d.d (1H, 3-H, *J* = 8.1, 7.5, 1.3), 7.51 d.d (1H, 1-H, *J* = 7.6, 1.3). ^{13}C NMR spectrum, δ_C, ppm: 14.24 ($CH_2\mathbf{C}H_3$), 37.99 (C^8), 41.31 (C^6), 57.33 (OCH_3), 59.29 (C^{9a}), 61.71 (OCH_2), 81.26 (C^{5a}), 81.66 (C^9), 110.19 (C^4), 121.10 (C^2), 125.23 (C^1), 125.67 (C^{1a}), 130.52 (C^3), 159.03 (C^{4a}), 170.13 (9a-C=O), 206.40 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 290.2 (13.3) $[M]^+$, 217.2 (4.18), 190.1 (100), 162.1 (28.4), 145.1 (36.6), 131.1 (26.8), 100.1 (66.8). Found: *m*/*z* 290.1147 $[M]^+$. $C_{16}H_{18}O_5$. Calculated: *M* 290.1149.

Ethyl (5a*S*,9*S*,9a*S*)-4,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIb). Yield 10% (*c*), 7% (*d*); oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.06 d.d (1H, 8-H, *J* = 17.6, 1.8), 2.64 d.d (1H, 8-H, *J* = 17.6, 3.8), 2.92 d.d (1H, 6-H, *J* = 17.9, 3.5), 2.99 d.d (1H, 6-H, *J* = 17.9, 2.7), 3.29 s (3H, 9-OCH_3), 3.84 s (3H, 4-OCH_3), 4.08d.d (1H, 9-H, *J* = 3.8, 1.8), 4.31 q (2H, OCH_2, *J* = 7.1), 5.80 d.d (1H, 5a-H, *J* = 3.5, 2.7), 6.81 d.d (1H, 3-H, *J* = 8.0, 1.2), 6.87 d.d (1H, 2-H, *J* = 8.0, 7.6), 7.12 d.d (1H, 1-H, *J* = 7.6, 1.2). ^{13}C NMR spectrum, δ_C, ppm: 14.22 ($CH_2\mathbf{C}H_3$), 38.17 (C^8), 41.11 (C^6), 56.00 (4-OCH_3), 57.32 (9-OCH_3), 59.86 (C^{9a}), 61.70 (OCH_2), 82.11 (C^{5a}), 81.48 (C^9) 112.96 (C^3), 117.00 (C^1), 121.76 (C^2), 126.75 (C^{1a}), 144.64 (C^4), 147.68 (C^{4a}), 170.00 (9a-C=O), 206.05 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 320.2 (19.9) $[M]^+$, 247.2 (3.05), 220.2 (100), 192.1 (14.5), 175.1 (14.0), 161.1 (17.1), 100.1 (35.4). Found: *m*/*z* 320.1256 $[M]^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*S*,9a*S*)-3,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIc). Yield 25% (*c*), oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7), 2.03 d.d (1H, 8-H, *J* = 17.8,1.8), 2.63 d.d (1H, 8-H, *J* = 17.8, 3.6), 2.87 d.d (1H, 6-H, *J* = 17.7, 3.0), 2.94 d.d (1H, 6-H, *J* = 17.7, 3.3), 3.29 s (3H, 9-OCH_3), 3.74 s (3H, 3-OCH_3), 4.03 d.d (1H, 9-H, *J* = 3.6, 1.8), 4.31 q (2H, OCH_2, *J* = 7.1), 5.75 d.d (1H, 5a-H, *J* = 3.3, 3.0), 6.32 d (1H, 4-H, *J* = 2.3), 6.45 d.d (1H, 2-H, *J* = 8.6, 2.3), 7.35 d (1H, 1-H, *J* = 8.6). ^{13}C NMR spectrum, δ_C, ppm: 14.26 ($CH_2\mathbf{C}H_3$), 37.97 (C^8), 41.46 (C^6), 55.52 (3-OCH_3), 57.31 (9-OCH_3), 58.76 (C^{9a}), 61.61 (OCH_2), 81.69 and 82.15 (C^{5a}, C^9), 96.00 (C^4), 107.55 (C^2), 117.63 (C^{1a}), 125.42 (C^1), 160.40 (C^3), 162.15 (C^{4a}), 170.38 (9a-C=O), 206.49 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 320.2 (38.7) $[M]^+$, 274.1 (15.9), 247.1 (8.69), 220.1 (100), 192.1 (22.6), 175.1 (10.8), 161.1 (42.5), 100.1 (35.5). Found: *m*/*z* 320.1249 $[M]^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*S*,9a*S*)-2,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VId). Yield 25% (*c*), 7% (*d*); oily substance.

^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.04 d.d (1H, 8-H, *J* = 17.8, 1.8), 2.63 d.d (1H, 8-H, *J* = 17.9, 3.8), 2.87 d.d (1H, 6-H, *J* = 17.7, 3.0), 2.92 d.d (1H, 6-H, *J* = 17.7, 3.3), 3.29 s (3H, 9-OCH_3), 3.75 s (3H, 3-OCH_3), 4.05 d.d (1H, 9-H, *J* = 3.8, 1.8), 4.31 q (2H, OCH_2, *J* = 7.1), 5.71 d.d (1H, 5a-H, *J* = 3.3, 3.0), 6.66 d (1H, 4-H, *J* = 8.7), 6.76 d.d (1H, 2-H, *J* = 8.7, 2.7), 7.08 d (1H, 1-H, *J* = 2.7). ^{13}C NMR spectrum, δ_C, ppm: 14.26 ($CH_2\mathbf{C}H_3$), 38.06 (C^8), 41.32 (C^6), 56.02 (3-OCH_3), 57.33 (9-OCH_3), 59.65 (C^{9a}), 61.70 (OCH_2), 81.45 (C^{5a}), 81.64 (C^9), 110.24 (C^4), 111.10 (C^1), 115.76 (C^3), 126.44 (C^{1a}), 153.16 (C^{4a}), 154.37 (C^2), 169.98 (9a-C=O), 206.36 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 320.2 (33.0) [*M*]$^+$, 247.2 (4.21), 220.2 (100), 192.1 (9.06), 175.1 (9.73), 161.1 (18.3), 100.1 (33.7). Found: *m*/*z* 320.1255 [*M*]$^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*S*,9a*S*)-1,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIe). Yield 7% (*c*), oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.27 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.08 d.d (1H, 8-H, *J* = 18.3, 2.3), 2.60 d.d (1H, 8-H, *J* = 18.3, 3.3), 2.71 d.d (1H, 6-H, *J* = 16.9, 2.0), 3.03 d.d (1H, 6-H, *J* = 16.9, 5.3), 3.36 s (3H, 9-OCH_3), 3.80 s (3H, 3-OCH_3), 4.23 q (2H, OCH_2, *J* = 7.1), 4.77 d.d (1H, 9-H, *J* = 3.3, 2.33), 5.81 d.d (1H, 5a-H, *J* = 5.3, 2.0), 6.38 d.d (1H, 4-H, *J* = 8.2, 0.8), 6.38 d.d (1H, 2-H, *J* = 8.2, 0.8), 7.12 d.d (1H, 3-H, *J* = 8.2, 8.2). ^{13}C NMR spectrum, δ_C, ppm: 14.26 ($CH_2\mathbf{C}H_3$), 38.70 (C^8), 43.54 (C^6), 55.39 (3-OCH_3), 57.59 (9-OCH_3), 59.97 (C^{9a}), 61.43 (OCH_2), 76.69 (C^9), 82.88 (C^{5a}), 103.56 and 103.66 (C^2, C^4), 111.78 (C^{1a}), 131.70 (C^3), 157.49 (C^1), 160.79 (C^{4a}), 170.87 (9a-C=O), 207.27 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 320.2 (30.6) [*M*]$^+$, 274.1 (10.1), 247.2 (4.19), 220.1 (100), 192.1 (1.83), 175.1 (13.2), 161.1 (16.9), 100.1 (14.8). Found: *m*/*z* 320.1253 [*M*]$^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*S*,9a*S*)-2,4-di-*tert*-butyl-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIf). Yield 50% (*c*), 10% (*d*); oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.27 s and 1.28 s (9H each, *t*-Bu), 1.36 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.00 d.d (1H, 8-H, *J* = 17.8, 1.8), 2.61 d.d (1H, 8-H, *J* = 17.8, 3.7 Hz), 2.94 d.d (1H, 6-H, *J* = 17.8, 3.2), 2.94 d.d (1H, 6-H, *J* = 17.8, 2.9), 3.30 s (3H, 9-OCH_3), 4.03 d.d (1H, 9-H, *J* = 3.7, 1.8), 4.31 q (2H, OCH_2, *J* = 7), 5.71 d.d (1H, 5a-H, *J* = 3.2, 2.9), 7.17 d (1H, *J* = 2.1), 7.38 d (1H, *J* = 2.1). ^{13}C NMR spectrum, δ_C, ppm: 14.29 ($CH_2\mathbf{C}H_3$), 29.18 and 31.73 [$C(\mathbf{C}H_3)_3$], 34.32 and 34.62 [$\mathbf{C}(CH_3)_3$], 38.08 (C^8), 41.54 (C^6), 57.27 (9-OCH_3), 59.19 (C^{9a}), 61.43 (OCH_2), 80.72 (C^9), 81.85 (C^{5a}), 119.21 and 124.23 (C^1, C^3), 125.43 (C^{1a}), 132.76 (C^4), 143.75 (C^2), 154.75 (C^{4a}), 170.49 (9a-C=O), 206.97 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 402.3 (23.5) [*M*]$^+$, 387.3 (16.9), 370.3 (6.24), 329.3 (3.14), 315.2 (5.98), 302.2 (40.4), 287.2 (100), 243.2 (10.4), 100.0 (35.3). Found: *m*/*z* 402.2404 [*M*]$^+$. $C_{24}H_{34}O_5$. Calculated: *M* 402.2401.

Ethyl (5a*S*,9*S*,9a*S*)-9-methoxy-2-nitro-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIg). Yield 25% (*c*), mp 145–145.5°C (from hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.39 t (3H, $CH_2\mathbf{C}H_3$, *J* = 7.1), 1.93 d.d (1H, 8-H, *J* = 18.0, 1.9), 2.70 d.d (1H, 8-H, *J* = 18.1, 3.6), 2.95 d.d (1H, 6-H, *J* = 17.8, 3.0), 2.99 d.d (1H, 6-H, *J* = 17.8, 3.4), 3.33 s (3H, 9-OCH_3), 4.11 d.d (1H, 9-H, *J* = 3.6, 1.9), 4.37 q (2H, OCH_2, *J* = 7.1), 5.92 d.d (1H, 5a-H, *J* = 3.4, 3.0), 6.85 d (1H, 4-H, *J* = 8.9), 8.19 d.d (1H, 3-H, *J* = 8.9, 2.5), 8.43 d (1H, 1-H, *J* = 2.5). ^{13}C NMR spectrum, δ_C, ppm: 14.24 ($CH_2\mathbf{C}H_3$), 37.81 (C^8), 40.98 (C^6), 57.53 (9-OCH_3), 58.60 (C^{9a}), 62.44 (OCH_2), 81.35 (C^9), 83.94 (C^{5a}), 110.36 (C^4), 122.11 (C^3), 127.17 (C^{1a}), 127.70 (C^1), 142.41 (C^2), 163.96 (C^{4a}), 168.90 (9a-C=O), 204.77 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 335.2 (1.15) [*M*]$^+$, 262.1 (4.77), 235.1 (63.1), 207.1 (40.8), 190.0 (21.7), 176.1 (16.8), 143.0 (10.6), 130.0 (11.1), 100.0 (100). Found: *m*/*z* 335.0997 [*M*]$^+$. $C_{16}H_{17}NO_7$. Calculated: *M* 335.0999.

Ethyl (5a*S*,9*S*,9a*S*)-3-diethylamino-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIh). Yield 45% (*c*), oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 t [6H, $N(CH_2C\mathbf{H}_3)_2$, *J* = 7.1], 1.34 t (3H, $OCH_2C\mathbf{H}_3$, *J* = 7.1), 2.10 d.d (1H, 8-H, *J* = 17.7, 1.9), 2.61 d.d (1H, 8-H, *J* = 17.7, 3.8), 2.86 d.d (1H, 6-H, *J* = 17.6, 3.0), 2.92 d.d (1H, 6-H, *J* = 17.6, 3.5), 3.28 q [4H, $N(C\mathbf{H}_2CH_3)_2$, *J* = 7.1], 3.28 s (3H, 9-OCH_3), 4.01 d.d (1H, 9-H, *J* = 3.8, 1.9), 4.28 q (2H, OCH_2, *J* = 7.1), 5.69 d.d (1H, 5a-H, *J* = 3.5, 3.0), 6.04 d (1H, 4-H, *J* = 2.3), 6.20 d.d (1H, 2-H, *J* = 8.6, 2.3), 7.25 d (1H, 1-H, *J* = 8.6). ^{13}C NMR spectrum, δ_C, ppm: 12.49 [$N(CH_2\mathbf{C}H_3)_2$], 14.28 ($OCH_2\mathbf{C}H_3$), 38.13 (C^8), 41.58 (C^6), 44.60 [$N(\mathbf{C}H_2CH_3)_2$], 57.25 (9-OCH_3), 58.72 (C^{9a}), 61.34 (OCH_2), 81.56 and 81.79 (C^{5a}, C^9), 92.82 (C^4), 104.66, (C^2) 111.83 (C^{1a}), 125.36 (C^1), 150.20 (C^3), 160.75 (C^{4a}), 170.80 (9a-C=O), 207.15 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 361.3 (45.9) [*M*]$^+$, 346.2 (11.9), 330.2 (1.66), 315.2 (2.35), 288.2 (19.6), 274.2 (61.5), 261.2 (64.9), 246.2 (100), 218.1 (16.4), 202.2 (31.6), 158.1 (8.20). Found: *m*/*z* 361.1882 [*M*]$^+$. $C_{20}H_{27}NO_5$. Calculated: *M* 361.1884.

Ethyl (5a*S*,9*S*,9a*S*)-2-bromo-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIi). Yield 13% (*c*), transparent light brown oily liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.36 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 1.99 d.d (1H, 8-H, *J* = 17.9, 1.8), 2.66 d.d (1H, 8-H, *J* = 17.9, 3.8), 2.88 d.d (1H, 6-H, *J* = 17.8, 3.0), 2.94 d.d (1H, 6-H, *J* = 17.8, 3.4), 3.29 s (3H, 9-OCH_3), 4.03 d.d (1H, 9-H, *J* = 3.8, 1.8), 4.33 q (2H, OCH_2, *J* = 7.1), 5.75 d.d (1H, 5a-H, *J* = 3.4, 3.0), 6.65 d (1H, 4-H, *J* = 8.6), 7.31 d.d (1H, 2-H, *J* = 8.6, 2.2), 7.61 d (1H, 1-H, *J* = 2.2). ^{13}C NMR spectrum, $δ_C$, ppm: 14.24 ($CH_2\mathbf{C}H_3$), 37.95 (C^8), 41.12 (C^6), 57.40 (9-OCH_3), 59.20 (C^{9a}), 62.01 (OCH_2), 81.54 (C^9), 82.04 (C^{5a}), 111.84 (C^4), 112.80 (C^{1a}), 127.94 (C^2), 128.28 (C^3), 133.42 (C^1), 158.18 (C^{4a}), 169.52 (9a-C=O), 205.73 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 370.1 (12.2) $[M + 2]^+$, 369.1 (2.29) $[M + 1]^+$, 368.1 (11.9) $[M]^+$, 297.0 (2.91), 295.0 (2.86), 270.0 (49.8), 268.0 (49.2), 242.0 (11.8), 240.0 (12.8), 225.0 (14.4), 223.0 (13.0), 211.0 (13.3), 209.0 (13.5), 100.0 (100). Found: *m*/*z* 368.0258 $[M]^+$. $C_{16}H_{17}BrO_5$. Calculated: *M* 368.0254.

Ethyl (5a*S*,9*S*,9a*S*)-2-iodo-4,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIj). Yield 32% (*c*), 14% (*d*). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.04 d.d (1H, 8-H, *J* = 17.7, 1.8), 2.66 d.d (1H, 8-H, *J* = 17.7, 3.9), 2.90 d.d (1H, 6-H, *J* = 17.9, 3.4), 2.97 d.d (1H, 6-H, *J* = 17.9, 2.8), 3.28 s (3H, 9-OCH_3), 3.81 s (3H, 4-OCH_3), 4.04 d.d (1H, 9-H, *J* = 3.9, 1.8), 4.32 q (2H, OCH_2, *J* = 7.1), 5.79 d.d (1H, 5a-H, *J* = 3.4, 2.8), 7.06 d (1H, *J* = 1.6), 7.43 d (1H, *J* = 1.6). ^{13}C NMR spectrum, $δ_C$, ppm: 14.20 ($CH_2\mathbf{C}H_3$), 38.08 (C^8), 40.89 (C^6), 56.26 (4-OCH_3), 57.36 (9-OCH_3), 59.51 (C^{9a}), 61.95 (OCH_2), 81.27 (C^9), 82.06 (C^2), 82.54 (C^{5a}), 122.01 (C^3), 126.00 (C^1), 128.70 (C^{1a}), 145.36 (C^4), 147.79 (C^{4a}), 169.42 (9a-C=O), 205.41 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 369.1 (2.29) $[M + 1]^+$, 446.1 (40.5) $[M]^+$, 373.0 (3.01), 346.0 (90.0), 318.0 (8.77), 301.0 (6.76), 287.0 (19.9), 274.0 (14.6), 220.1 (19.7), 100.1 (100). Found: *m*/*z* 446.0218 $[M]^+$. $C_{17}H_{19}IO_6$. Calculated: *M* 446.0221.

Ethyl (5a*S*,9*R*,9a*S*)-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIa). Yield 39% (*e*), transparent oily liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.04 d.d (1H, 8-H, *J* = 17.9, 11.5), 2.58 d.d (1H, 8-H, *J* = 17.9, 3.6), 2.76 d.d (1H, 6-H, *J* = 17.0, 3.7), 2.95 d.d (1H, 6-H, *J* = 17.0, 4.0), 3.34 s (3H, OCH_3), 4.26 d.d (1H, 9-H, *J* = 11.5, 3.6), 4.26 q (2H, OCH_2, *J* = 7.1), 5.20 d.d (1H, 5a-H, *J* = 4.0, 3.7), 6.76 d.d.d (1H, 4-H, *J* = 8.0, 1.0, 0.6), 6.93 d.d.d (1H, 2-H, *J* = 7.6, 7.5, 1.0), 7.21 d.d.d (1H, 3-H, *J* = 8.0, 7.5, 1.5), 7.46 d.d.d (1H, 1-H, *J* = 7.6, 1.5, 0.6). ^{13}C NMR spectrum, $δ_C$, ppm: 14.09 ($CH_2\mathbf{C}H_3$), 40.52 (C^8), 41.98 (C^6), 57.88 (9-OCH_3), 59.59 (C^{9a}), 62.08 (OCH_2), 77.96 (C^9), 82.21 (C^{5a}), 109.50 (C^4), 120.93 (C^2), 123.58 (C^{1a}), 128.75 (C^1), 129.90 (C^3), 159.66 (C^{4a}), 172.74 (9a-C=O), 205.89 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 290.1 (18.1) $[M]^+$, 217.2 (6.24), 190.1 (100), 162.0 (26.7), 145.0 (33.7), 131.0 (26.4), 100.1 (66.8). Found: *m*/*z* 290.1146 $[M]^+$. $C_{16}H_{18}O_5$. Calculated: *M* 290.1149.

Ethyl (5a*S*,9*R*,9a*S*)-4,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIb). Yield 23% (*c*), 32% (*d*); transparent oily liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.27 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.2), 2.12 d.d (1H, 8-H, *J* = 17.7, 11.2), 2.57 d.d (1H, 8-H, *J* = 17.7, 3.4), 2.76 d.d (1H, 6-H, *J* = 17.3, 4.0), 3.03 d.d (1H, 6-H, *J* = 17.3, 4.1), 3.33 s (3H, 9-OCH_3), 3.84 s (3H, 4-OCH_3), 4.26 d.d (1H, 9-H, *J* = 11.2, 3.4), 4.26 q (2H, OCH_2, *J* = 7.2), 5.28 d.d (1H, 5a-H, *J* = 4.1, 4.0), 6.81 d.d (1H, 3-H, *J* = 8.2, 1.3), 6.89 d.d (1H, 2-H, *J* = 8.2, 7.5), 7.07 d.d (1H, 1-H, *J* = 7.5, 1.3). ^{13}C NMR spectrum, $δ_C$, ppm: 14.08 ($CH_2\mathbf{C}H_3$), 40.61 (C^8), 41.88 (C^6), 55.86 (4-OCH_3), 57.94 (9-OCH_3), 60.19 (C^{9a}), 62.12 (OCH_2), 77.93 (C^9), 83.02 (C^{5a}), 112.25 (C^3), 120.35 (C^1), 121.42 (C^2), 124.83 (C^{1a}), 144.19 (C^4), 148.33 (C^{4a}), 172.53 (9a-C=O), 205.68 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 320.2 (14.6) $[M]^+$, 274.2 (2.63), 247.2 (2.15), 220.1 (100), 192.1 (11.1), 175.1 (10.0), 161.1 (13.8), 148.1 (10.1), 100.1 (26.9). Found: *m*/*z* 320.1253 $[M]^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*R*,9a*S*)-3,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIc). Yield 25% (*c*), oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.03 d.d (1H, 8-H, *J* = 17.9, 11.6), 2.58 d.d (1H, 8-H, *J* = 17.9, 3.6), 2.74 d.d (1H, 6-H, *J* = 17.1, 3.6), 2.92 d.d (1H, 6-H, *J* = 17.1, 3.8), 3.34 s (3H, 9-OCH_3), 3.75 s (3H, 3-OCH_3), 4.22 d.d (1H, 9-H, *J* = 11.6, 3.6), 4.25 q 2H, $CO_2CH_2CH_3$, *J* = 7.1), 5.20 d.d (1H, 5a-H, *J* = 3.8, 3.6), 6.32 d (1H, 4-H, *J* = 2.3), 6.49 d.d (1H, 2-H, *J* = 8.5, 2.3), 7.33 d (1H, 1-H, *J* = 8.5). ^{13}C NMR spectrum, $δ_C$, ppm: 14.09 ($CH_2\mathbf{C}H_3$), 40.52 (C^8), 42.05 (C^6), 55.42 (3-OCH_3), 57.83 (9-OCH_3), 59.08 (C^{9a}), 61.99 (OCH_2), 78.02 (C^9), 83.02 (C^{5a}), 95.46 (C^4), 107.34 (C^2), 115.38 (C^{1a}), 128.95 (C^1), 160.96 (C^3), 161.94 (C^{4a}), 173.02 (9a-C=O), 205.94 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 320.2 (12.6) $[M]^+$, 274.2 (4.91), 247.2 (3.79), 220.2 (100), 192.1 (11.9), 175.1 (3.92), 161.2 (19.3), 148.1 (1.54), 100.1 (8.54). Found: *m*/*z* 320.1257 $[M]^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*R*,9a*S*)-2,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIId). Yield 25% (*c*), 10% (*e*); oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.29 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.0), 2.06 d.d (1H, 8-H, *J* = 17.7, 11.7), 2.59 d.d (1H, 8-H, *J* = 17.7, 3.7), 2.74 d.d (1H, 6-H, *J* = 17.1, 3.7), 2.92 d.d (1H, 6-H, *J* = 17.1, 3.7), 3.34 s (3H, 9-OCH$_3$), 3.76 s (3H, 3-OCH$_3$), 4.24 d.d (1H, 9-H, *J* = 11.7, 3.7), 4.26 q (2H, OCH$_2$, *J* = 7.0), 5.18 d.d (1H, 5a-H, *J* = 3.7, 3.7), 6.66 d (1H, 4-H, *J* = 8.7), 6.76 d.d (1H, 2-H, *J* = 8.7, 2.8), 7.03 d (1H, 1-H, *J* = 2.8). ^{13}C NMR spectrum, δ_C, ppm: 14.11 ($CH_2\mathbf{C}H_3$), 40.49 (C^8), 42.04 (C^6), 55.97 (3-OCH$_3$), 57.84 (9-OCH$_3$), 59.95 (C^{9a}), 62.08 (OCH$_2$), 77.97 (C^9), 82.51 (C^{5a}), 109.40 (C^4), 114.52 (C^1), 115.38 (C^3), 124.47 (C^{1a}), 153.95 (C^{4a}), 154.13 (C^2), 172.65 (9a-C=O), 205.87 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 320.2 (21.5) $[M]^+$, 247.2 (2.67), 220.1 (100), 192.1 (10.8), 175.1 (11.8), 161.1 (18.1), 147.1 (1.59), 100.1 (31.2). Found: *m*/*z* 320.1253 $[M]^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*R*,9a*S*)-1,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIe). Yield 15% (*c*), oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.19 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.57 d.d (1H, 8-H, *J* = 18.1, 3.4), 2.62 d.d (1H, 8-H, *J* = 18.1, 6.2), 2.77 d.d (1H, 6-H, *J* = 16.4, 5.1), 2.96 d.d (1H, 6-H, *J* = 16.4, 7.9), 3.26 s (3H, 9-OCH$_3$), 3.80 s (3H, 1-OCH$_3$), 4.19 q (2H, OCH$_2$, *J* = 7.1), 4.55 d.d (1H, 9-H, *J* = 6.2, 3.4), 5.19 d.d (1H, 5a-H, *J* = 7.9, 5.1), 6.46 d.d (1H, 4-H, *J* = 8.2, 0.7), 6.46 d.d (1H, 2-H, *J* = 8.0, 0.7), 7.17 d.d (1H, 3-H, *J* = 8.2, 8.0). ^{13}C NMR spectrum, δ_C, ppm: 14.01 ($CH_2\mathbf{C}H_3$), 41.10 (C^8), 42.75 (C^6), 55.38 (1-OCH$_3$), 58.14 (9-OCH$_3$), 59.66 (C^{9a}), 61.78 (OCH$_2$), 75.96 (C^9), 83.64 (C^{5a}), 103.14 and 103.68 (C^2, C^4), 113.58 (C^{1a}), 130.93 (C^3), 157.36 (C^1), 160.75 (C^{4a}), 172.26 (9a-C=O), 206.62 (C^7). Found: *m*/*z* 320.1256 $[M]^+$. $C_{17}H_{20}O_6$. Calculated: *M* 320.1254.

Ethyl (5a*S*,9*R*,9a*S*)-2,4-di-*tert*-butyl-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIf). Yield 29% (*c*), 10% (*d*); oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 s (9H, *t*-Bu), 1.30 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 1.30 s (9H, *t*-Bu), 2.05 d.d (1H, 8-H, *J* = 17.8, 11.3), 2.55 d.d (1H, 8-H, *J* = 17.7, 3.6), 2.77 d.d (1H, 6-H, *J* = 16.9, 3.6), 2.96 d.d (1H, 6-H, *J* = 16.9, 4.0), 3.31 s (3H, OCH$_3$), 4.23 d.d (1H, 9-H, *J* = 11.3, 3.6), 4.26 q (2H, OCH$_2$, *J* = 7.1), 5.19 d.d (1H, 5a-H, *J* = 3.6, 4.0), 7.17 d (1H, *J* = 2.2), 7.32 d (1H, *J* = 2.2). ^{13}C NMR spectrum, δ_C, ppm: 14.11 ($CH_2\mathbf{C}H_3$), 29.23 and 31.72 [$C(\mathbf{C}H_3)_3$], 34.15 and 34.48 [$\mathbf{C}(CH_3)_3$], 40.71 (C^8), 42.09 (C^6), 57.82 (9-OCH$_3$), 59.39 (C^{9a}), 61.85 (OCH$_2$), 78.09 (C^9), 81.63 (C^{5a}), 123.23 and 123.50 (C^1, C^3), 123.30 (C^{1a}), 131.66 (C^4), 143.04 (C^2), 155.38 (C^{4a}), 173.13 (9a-C=O), 206.41 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 402.3 (52.1) $[M]^+$, 387.3 (26.6), 370.3 (1.50), 329.3 (3.04), 315.3 (2.75), 302.2 (56.4), 287.2 (100), 243.2 (10.9), 100.1 (45.1). Found: *m*/*z* 402.2397 $[M]^+$. $C_{24}H_{34}O_5$. Calculated: *M* 402.2401.

Ethyl (5a*S*,9*R*,9a*S*)-9-methoxy-2-nitro-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIg). Yield 32% (*c*), mp 113–113.5°C (from hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 1.98 d.d (1H, 8-H, *J* = 18.2, 11.4), 2.65 d.d (1H, 8-H, *J* = 18.1, 3.8), 2.81 d.d (1H, 6-H, *J* = 17.1, 4.0), 2.99 d.d (1H, 6-H, *J* = 17.1, 3.9), 3.36 s (3H, OCH$_3$), 4.29 d.d (1H, 9-H, *J* = 11.4, 3.8), 4.30 q (2H, OCH$_2$, *J* = 7.1), 5.36 d.d (1H, 5a-H, *J* = 4.0, 3.9), 6.82 d (1H, 4-H, *J* = 9.0), 8.18 d.d (1H, 3-H, *J* = 9.0, 2.6), 8.36 d (1H, 1-H, *J* = 2.6). ^{13}C NMR spectrum, δ_C, ppm: 14.06 ($CH_2\mathbf{C}H_3$), 40.22 (C^8), 41.79 (C^6), 57.89 (9-OCH$_3$), 59.00 (C^{9a}), 62.73 (OCH$_2$), 77.52 (C^9), 84.32 (C^{5a}), 109.60 (C^4), 125.24 (C^{1a}), 125.57 (C^3), 127.02 (C^1), 142.46 (C^2), 164.45 (C^{4a}), 171.45 (9a-C=O), 204.42 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 335.2 (0.78) $[M]^+$, 262.1 (4.27), 235.1 (77.4), 207.1 (52.4), 190.0 (31.0), 176.1 (18.7), 143.0 (14.3), 130.0 (13.4), 100.0 (100). Found: *m*/*z* 335.1000 $[M]^+$. $C_{16}H_{17}NO_7$. Calculated: *M* 335.0999.

Ethyl (5a*S*,9*R*,9a*S*)-3-diethylamino-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIh). Yield 42% (*c*), oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 t [6H, $N(CH_2C\mathbf{H}_3)_2$, *J* = 7.1], 1.29 t (3H, $OCH_2C\mathbf{H}_3$, *J* = 7.2), 2.09 d.d (1H, 8-H, *J* = 17.8, 11.8), 2.57 d.d (1H, 8-H, *J* = 17.8, 3.6), 2.72 d.d (1H, 6-H, *J* = 17.1, 3.6), 2.91 d.d (1H, 6-H, *J* = 17.0, 3.7), 3.28 q [4H, $N(C\mathbf{H}_2CH_3)_2$, *J* = 7.1], 3.35 s (3H, 9-OCH$_3$), 4.18 d.d (1H, 9-H, *J* = 11.8, 3.6), 4.24 q (2H, OCH$_2$, *J* = 7.2), 5.14 d.d (1H, 5a-H, *J* = 3.7, 3.6), 6.05 d (1H, 4-H, *J* = 2.3), 6.25 d.d (1H, 2-H, *J* = 8.6, 2.3), 7.23 d (1H, 1-H, *J* = 8.6). ^{13}C NMR spectrum, δ_C, ppm: 12.55 [$N(CH_2\mathbf{C}H_3)_2$], 14.15 ($OCH_2\mathbf{C}H_3$), 40.66 (C^8), 42.98 (C^6), 44.50 [$N(\mathbf{C}H_2CH_3)_2$], 57.85 (9-OCH$_3$), 59.04 (C^{9a}), 61.80 (OCH$_2$), 78.34 (C^9), 82.56 (C^{5a}), 92.20 (C^4), 104.89 (C^2), 109.32 (C^{1a}), 128.85 (C^1), 149.85 (C^3), 161.40 (C^{4a}), 173.61 (9a-C=O), 206.62 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 361.3 (84.6) $[M]^+$, 346.2

(20.1), 330.2 (0.73), 315.2 (3.76), 288.2 (36.7), 274.2 (95.6), 261.2 (85.1), 246.1 (100), 218.1 (8.76), 202.1 (54.5), 158.1 (11.4). Found: *m*/*z* 361.1882 $[M]^+$. $C_{20}H_{27}NO_5$. Calculated: *M* 361.1884.

Ethyl (5a*S*,9*R*,9a*S*)-2-bromo-9-methoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIi). Yield 23% (*c*), oily substance. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.29 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.01 d.d (1H, 8-H, *J* = 17.9, *J* = 11.6), 2.61 d.d (1H, 8-H, *J* = 18.0, 3.7), 2.75 d.d (1H, 6-H, *J* = 17.1, 3.8), 2.93 d.d (1H, 6-H, *J* = 17.1, 3.8), 3.34 s (3H, 9-OCH_3), 4.23 d.d (1H, 9-H, *J* = 11.6, 3.4), 4.28 q (2H, OCH_2, *J* = 7.1), 5.20 d.d (1H, 5a-H, *J* = 3.8, 3.8), 6.64 d (1H, 4-H, *J* = 8.5), 7.31 d.d (1H, 3-H, *J* = 8.5, 2.2), 7.56 d (1H, 1-H, *J* = 2.2). ^{13}C NMR spectrum, δ_C, ppm: 14.09 ($CH_2\mathbf{C}H_3$), 40.37 (C^8), 41.92 (C^6), 57.85 (9-OCH_3), 59.62 (C^{9a}), 62.35 (OCH_2), 77.75 (C^9), 82.85 (C^{5a}), 111.04 (C^4), 112.82 (C^{1a}), 125.88 (C^2), 131.72 (C^3), 132.79 (C^1), 158.83 (C^{4a}), 172.17 (9a-C=O), 205.33 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 370.1 (8.76) $[M + 2]^+$, 369.1 (1.60) $[M + 1]^+$, 368.1 (8.61) $[M]^+$, 297.1 (1.90), 295.1 (1.99), 270.0 (50.0), 268.0 (52.4), 242.0 (14.5), 240.0 (15.2), 225.0 (17.4), 223.0 (16.0), 211.0 (13.9), 209.0 (13.4), 189.1 (2.19), 100.1 (100). Found: *m*/*z* 368.0258 $[M]^+$. $C_{16}H_{17}BrO_5$. Calculated: *M* 368.0254.

Ethyl (5a*S*,9*R*,9a*S*)-2-iodo-4,9-dimethoxy-7-oxo-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIj). Yield 49% (*c*), 40% (*d*); oily substance. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.28 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.10 d.d (1H, 8-H, *J* = 17.9, 11.2), 2.59 d.d (1H, 8-H, *J* = 17.8, 3.5), 2.75 d.d (1H, 6-H, *J* = 17.1, 4.0), 3.00 d.d (1H, 6-H, *J* = 17.2, 4.0), 3.33 s (3H, 9-OCH_3), 3.81 s (3H, 4-OCH_3), 4.21 d.d (1H, 9-H, *J* = 11.2, 3.5), 4.26 q (2H, OCH_2, *J* = 7.1), 5.26 d.d (1H, 5a-H, *J* = 4.0, 4.0), 7.06 d (1H, 3-H, *J* = 1.6), 7.43 d (1H, 1-H, *J* = 1.6). ^{13}C NMR spectrum, δ_C, ppm: 14.08 ($CH_2\mathbf{C}H_3$), 40.47 (C^8), 41.86 (C^6), 56.17 (4-OCH_3), 57.92 (9-OCH_3), 60.07 (C^{9a}), 62.36 (OCH_2), 77.77 (C^9), 82.09 (C^2), 83.34 (C^{5a}), 121.45 (C^3), 126.84 (C^{1a}), 129.29 (C^1), 144.91 (C^4), 148.55 (C^{4a}), 171.99 (9a-C=O), 205.13 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 446.1 (31.0) $[M]^+$, 346.0 (100), 318.0 (9.98), 301.0 (8.00), 287.0 (24.0), 274.0 (11.5), 220.1 (2.77), 100.1 (77.2). Found: *m*/*z* 446.0223 $[M]^+$. $C_{17}H_{19}IO_6$. Calculated: *M* 446.0221.

Ethyl (5a*S*,9a*R*)-4-methoxy-7-oxo-5a,6,7,9a-tetrahydrodibenzo[*b*,*d*]furan-9a-carboxylate (VIIIb). Yield 56% (*f*), oily substance. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.35 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 2.91 d.d (1H, 6-H, *J* = 17.8, 4.1), 3.17 d.d.d (1H, 6-H, *J* = 17.8, 2.6, 1.0), 3.85 s (3H, 4-OCH_3), 4.33 q (2H, OCH_2, *J* = 7.1), 5.48 d.d.d (1H, 5a-H, *J* = 4.1, 2.6, 1.9), 6.70 d.d (1H, 9-H, *J* = 10.1, 1.9), 6.83 d.d (1H, 3-H, *J* = 10.2, 1.9), 6.85 d.d (1H, 8-H, *J* = 10.2, 1.0), 6.93 d.d (1H, 2-H, *J* = 7.9, 7.6), 7.08 d.d (1H, 1-H, *J* = 7.6, 1.0). ^{13}C NMR spectrum, δ_C, ppm: 14.16 ($CH_2\mathbf{C}H_3$), 37.86 (C^6), 56.08 (4-OCH_3), 62.53 (C^{9a}), 62.73 (OCH_2), 82.77 (C^{5a}), 112.98 (C^3), 115.22 (C^2), 122.55 (C^1), 129.72 (C^8), 133.76 (C^{1a}), 142.54 (C^9), 145.04 (C^4), 147.14 (C^{4a}), 165.29 (9a-C=O), 196.71 (C^7).

Ethyl 4′-hydroxybiphenyl-2-yl carbonate (IXa). Yield 13% (*e*). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.18 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 4.11 q (2H, OCH_2, *J* = 7.1), 5.11 br.s (1H, OH), 6.84 m (2H, 3′-H, 5′-H), 7.18 d.d (1H, *J* = 7.0, 2.1), 7.29 d.d (1H, *J* = 7.0, *J* = 2.1), 7.31 d.d (1H, *J* = 7.0, 2.0), 7.32 m (2H, 2′-H, 6′-H), 7.36 d.d (1H, *J* = 7.0, 2.0). ^{13}C NMR spectrum, δ_C, ppm: 14.07 ($CH_2\mathbf{C}H_3$), 64.71 (OCH_2), 115.28 ($C^{3'}$, $C^{5'}$), 122.29, 126.56, 128.17, 129.67, 130.26 ($C^{2'}$, $C^{6'}$), 130.82, 134.31, 148.10, 153.26, 155.13. Mass spectrum, *m*/*z* (I_{rel}, %): 258.1 (40.9) $[M]^+$, 214.1 (16.8), 199.1 (12.6), 186.1 (100), 171.1 (3.72), 157.1 (35.3), 139.1 (10.4), 128.1 (22.5). Found: *m*/*z* 258.0889 $[M]^+$. $C_{16}H_{16}O_5$. Calculated: *M* 258.0887.

Ethyl 4′-hydroxy-3-methoxybiphenyl-2-yl carbonate (IXb). Yield 25% (*c*), 44% (*d*); mp 136.5–137°C (from CH_2Cl_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.26 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 3.88 s (3H, OCH_3), 4.20 q (2H, OCH_2, *J* = 7.1), 5.06 br.s (1H, OH), 6.84 m (2H, 3′-H, 5′-H), 6.94 d.d (1H, 4-H, *J* = 8.3, 1.0), 6.96 d.d (1H, 6-H, *J* = 7.8, 1.0), 7.24 d.d (1H, 5-H, *J* = 8.3, 7.8), 7.33 m (2H, 2′-H, 6′-H). ^{13}C NMR spectrum, δ_C, ppm: 14.09 ($CH_2\mathbf{C}H_3$), 56.13 (OCH_3), 64.83 (OCH_2), 111.00, 115.21 ($C^{3'}$, $C^{5'}$), 122.24, 126.58, 129.38, 130.27 ($C^{2'}$, $C^{6'}$), 135.49, 137.32, 151.66, 153.10, 155.22. Mass spectrum, *m*/*z* (I_{rel}, %): 288.2 (16.1) $[M]^+$, 244.2 (23.9), 229.1 (7.77), 216.1 (100), 200.1 (24.8), 184.1 (23.2), 173.1 (17.4), 155.1 (7.28), 144.1 (12.6), 115.1 (12.4). Found: *m*/*z* 288.0994 $[M]^+$. $C_{16}H_{16}O_5$. Calculated: *M* 288.0992.

Ethyl 4′-hydroxy-5-methoxybiphenyl-2-yl carbonate (IXd). Yield 16% (*d*), oily substance. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.17 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1), 3.80 s (3H, OCH_3), 4.10 q (2H, OCH_2, *J* = 7.1), 5.95 br.s (1H, OH), 6.80 m (2H, 3′-H, 5′-H), 6.82 d.d (1H, 4-H, *J* = 8.8, 3.0), 6.88 d (1H, 6-H, *J* = 3.0), 7.08 d (1H, 3-H, *J* = 8.8), 7.29 m (2H, 2′-H, 6′-H). ^{13}C NMR spectrum, δ_C, ppm: 14.03 ($CH_2\mathbf{C}H_3$), 55.61 (OCH_3), 64.70 (OCH_2), 113.16, 115.28 ($C^{3'}$, $C^{5'}$), 115.69, 122.98, 129.25, 130.08 ($C^{2'}$, $C^{6'}$), 135.21, 141.74, 153.75, 155.58, 157.55.

Ethyl 4′-hydroxy-6-methoxybiphenyl-2-yl carbonate (IXe). Yield 41% (*c*), oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 t (3H, $CH_2\mathbf{CH}_3$, *J* = 7.1), 3.74 s (3H, OCH_3), 4.07 q (2H, OCH_2, *J* = 7.1), 5.58 br.s (1H, OH), 6.81 m (2H, 3′-H, 5′-H), 6.82 d.d (1H, 5-H, *J* = 8.2, 1.0), 6.96 d.d (1H, 3-H, *J* = 8.3, 1.0), 7.17 m (2H, 2′-H, 6′-H), 7.29 d.d (1H, 4-H, *J* = 8.3, 8.2). ^{13}C NMR spectrum, δ_C, ppm: 14.08 ($CH_2\mathbf{CH}_3$), 56.04 (OCH_3), 64.76 (OCH_2), 109.09, 114.38, 114.95 ($C^{3'}$, $C^{5'}$), 123.98, 125.49, 128.40, 131.54 ($C^{2'}$, $C^{6'}$), 149.29, 153.33, 155.03, 157.83. Mass spectrum, *m*/*z* (I_{rel}, %): 288.2 (84.9) $[M]^+$, 244.2 (21.1), 229.2 (14.7), 216.2 (100), 200.1 (34.9), 184.1 (28.4), 173.1 (11.1), 155.1 (10.9), 144.1 (11.3), 115.1 (14.1). Found: *m*/*z* 288.0989 $[M]^+$. $C_{16}H_{16}O_5$. Calculated: *M* 288.0992.

X-Ray diffraction data for compounds VIa, VIIg, and IXb. Single crystals of **VIa** were grown from a solution in petroleum ether. Intensities of 3252 independent reflections were measured from a 0.50×0.32×0.03-mm single crystal; $C_{16}H_{18}O_5$; rhombic crystal system, space group $Pca2_1$; unit cell parameters: $a = 10.3050(6)$, $b = 14.0742(7)$, $c = 9.6976(4)$ Å; $V = 1406.5(1)$ Å^3; $Z = 4$; $d_{calc} = 1.371$ g/cm^3; $\mu = 0.102$ mm^{-1}.

The X-ray diffraction data for compound **VIIg** were acquired from a 0.58×0.32×0.06-mm single crystal grown from a solution of hexane; intensities of 6759 independent reflections were measured; $C_{16}H_{17}NO_7$; rhombic crystal system, space group $Pca2_1$; unit cell parameters: $a = 26.1891(7)$, $b = 7.2924(2)$, $c = 16.1801(5)$ Å; $V = 3090.1(1)$ Å^3; $Z = 8$; $d_{calc} = 1.441$ g/cm^3; $\mu = 0.114$ mm^{-1}.

Intensities of 2994 independent reflections were measured from a 0.56×0.18×0.11-mm single crystal of **IXb** (from methylene chloride); $C_{16}H_{16}O_5$; monoclinic crystal system, space group $P2_1/n$; unit cell parameters: $a = 9.480(1)$, $b = 12.483(2)$, $c = 12.120(2)$ Å; $\beta = 99.094(6)°$; $V = 1416.3(3)$ Å^3; $Z = 4$; $d_{calc} = 1.352$ g/cm^3; $\mu = 0.101$ mm^{-1}.

For all samples, a correction for absorption was introduced using SADABS program (transmission 0.9499–0.9970, 0.9366–0.9932, and 0.8871–0.9703, respectively). The structures were solved by the direct method using SHELXS-97 and were refined in anisotropic (isotropic for hydrogen atoms) approximation using SHELXL-97. The positions of hydrogen atoms were calculated on the basis of geometry considerations and were refined in isotropic approximation according to the riding model. The coordinates of atoms and bond lengths and angles in structures **VIa**, **VIIg**, and **IXb** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 860246, 860247, and 824884, respectively).

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