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Povarov Reaction of Glyoxylate Imines Derived from 12-Aminodehydroabietic Acid

A. V. Tarantin[a], V. A. Glushkov[a], K. Yu. Suponitskii[b], A. A. Kudryashov[c], O. A. Maiorova[a], and A. G. Tolstikov[a]

[a] *Institute of Technical Chemistry, Ural Division, Russian Academy of Sciences, ul. Akademika Koroleva 3, Perm, 614013 Russia*
e-mail: glusha55@gmail.com

[b] *Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

[c] *Perm State University, ul. Bukireva 15, Perm, 614990 Russia*

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Abstract—Glyoxylate and arylglyoxal imines based on 12-aminodehydroabietic acid undergo hetero-Diels–Alder (Povarov) reaction with ethyl vinyl ether, cyclopentadiene, and indene to give, respectively, methyl (8a*R*,9*R*,12a*S*)-3-aroyl-5-isopropyl-9,12a-dimethyl-7,8,8a,9,10,11,12,12a-octahydronaphtho[1,2-*f*]quinoline-9-carboxylates, methyl (7*R*,10a*S*,10d*R*,13a*S*)-1-aroyl-3-isopropyl-7,10a-dimethyl-2,5,6,6a,7,8,9,10,10a,10d,13,13a-dodecahydro-1*H*-naphtho[1,2-*f*]cyclopenta[*c*]quinoline-7-carboxylates, and methyl (6a*S*,11b*S*,11e*S*,15*R*,15a*R*)-6-aroyl-4-isopropyl-11e,15-dimethyl-2,5,6,6a,7,11b,11e,12,13,14,15,15a-1*H*-dodecahydroindeno[2,1-*c*]-naphtho[1,2-*f*]quinoline-15-carboxylates.

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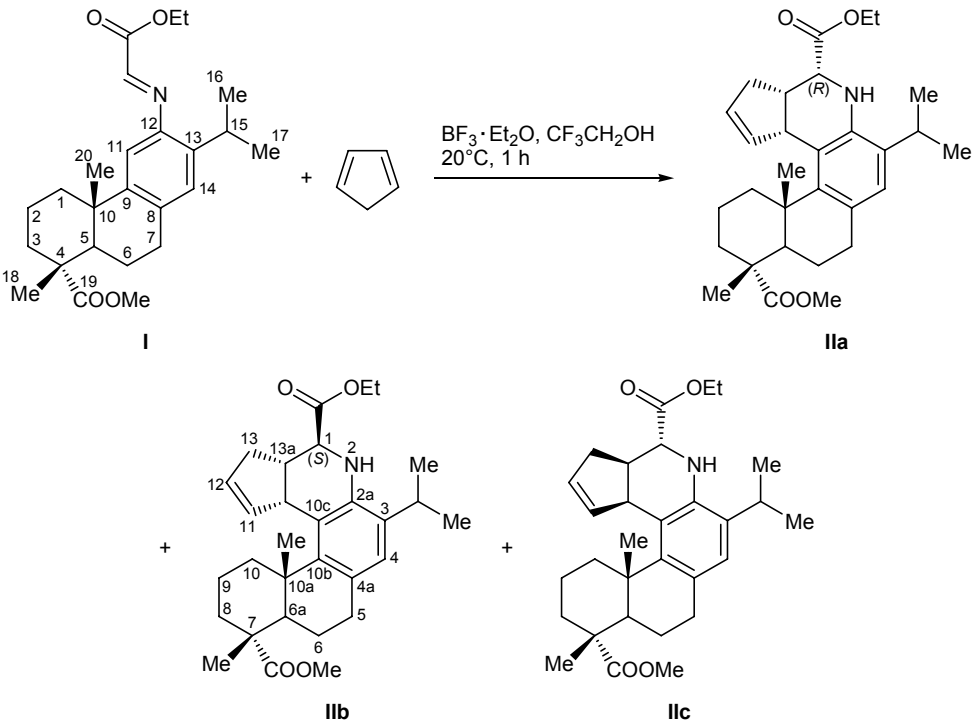
Chemical modification of known natural matrices may be regarded as an approach to design of novel biologically active substances. We anticipated that introduction of a heterocyclic fragment into a chiral diterpene molecule could give rise to compounds possessing unusual physical and chemical properties (for example, liquid crystals and reagents for asymmetric synthesis), as well as to biologically active compounds with new kinds of activity.

In terms of the concept implying synthesis of new useful organic compounds from renewable natural resources [1, 2] we synthesized substituted naphtho-[1,2-*f*]quinolines incorporating abietane fragments. For this purpose we used the Povarov reaction [3–5]. Following this approach we previously synthesized naphtho[1,2-*f*]quinolines having a diterpene fragment and an aryl group on C^2 in the quinoline ring [6]. In the present work we selected as starting compounds more reactive Schiff bases derived from ethyl glyoxylate and arylglyoxals, taking into account that such imines are known to readily react with dienophiles according to Povarov [7–10]. As dienophiles we used ethyl vinyl ether, cyclopentadiene, and indene.

The reaction conditions were optimized using as model process the reaction of cyclopentadiene with Schiff base **I** (abietic acid numbering) which was reported in preliminary communication [11] (Scheme 1). The reaction smoothly occurred in 2,2,2-trifluoroethanol at room temperature in the presence of boron trifluoride–ether complex as Lewis acid catalyst.

We also tried to use other solvents, such as acetonitrile, methylene chloride, and 1,1,1,3,3,3-hexafluoropropan-2-ol. In the first series of experiments we examined solvent effect on the conversion of imine **I** and yields of the adducts. The reaction was carried out with 3 equiv of cyclopentadiene and 15 mol % of $BF_3 \cdot Et_2O$ as catalyst. The optimal reaction temperature was 20°C. The reaction at –20°C was slow, whereas elevated temperature (above 20°C) favored tarring due to oligomerization of cyclopentadiene. After 1 h, the reaction was terminated by adding a saturated aqueous solution of sodium hydrogen carbonate. The conversion of **I** and yields of adducts **IIa**–**IIc** were determined by gas chromatography–mass spectrometry, and the structure of diastereoisomers **IIa**–**IIc** (purified by column chromatography) was determined by ^1H and

Scheme 1.



^{13}C NMR spectroscopy using double resonance techniques; in addition, data of [6] for structurally related compounds derived from aromatic aldehydes were taken into account. The structure of (1*R*)-isomer **IIa** (*cis*) was proved by X-ray diffraction data (Fig. 1). Presumably, *cis* isomer **IIa** separated as single crystals due to conglomeration.

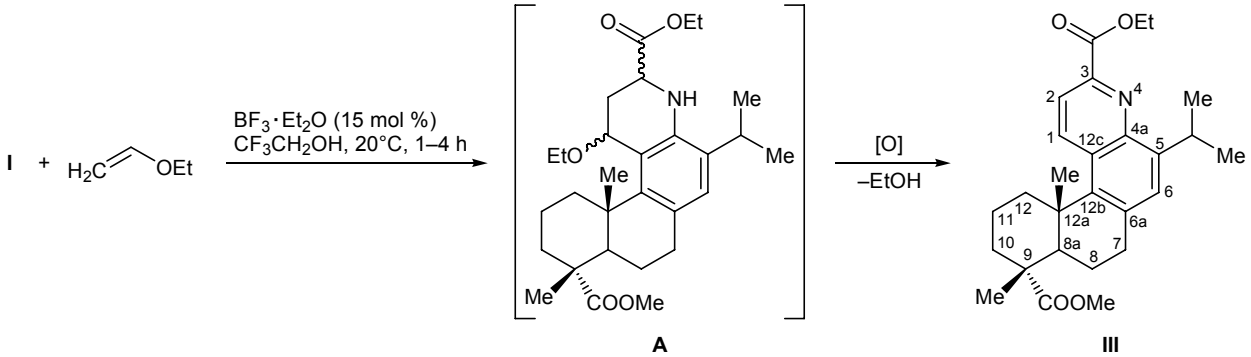
The data in Table 1 show that the conversion reaches 100% only in 1,1,1,3,3,3-hexafluoropropan-2-ol. Thus the optimal solvents for the reaction under study are 2,2,2-trifluoroethanol (yield of diastereoisomers **IIa**/**IIb** 82%) and 1,1,1,3,3,3-hexafluoropropan-2-ol (yield of diastereoisomers **IIa**–**IIc** 80%). Acetonitrile is less appropriate: the overall yield of adducts **IIa**–**IIc** is 78%. In acetonitrile, as well as in 1,1,1,3,3,3-hexafluoropropan-2-ol, a small amount of diastereoisomer **IIc** (1–2%) with *exo*-fused cyclopentene ring is formed together with enantiomers **IIa**/**IIb**. The best results were obtained in fluorinated alcohols, in keeping with the data of [12, 13]. Taking into account relatively high cost of 1,1,1,3,3,3-hexafluoropropan-2-ol, 2,2,2-trifluoroethanol was used as solvent in our subsequent experiment.

Table 1. Povarov reaction of Schiff base **I** with cyclopentadiene in different solvents

Solvent	Conversion of Schiff base **I**, %	Yield, %		
		IIa	**IIb**	**IIc**
Acetonitrile	93	46	30	2
Methylene chloride	89	32	23	–
2,2,2-Trifluoroethanol	90	46	36	–
1,1,1,3,3,3-Hexafluoropropan-2-ol	100	40	39	1

It is known that, apart from boron trifluoride–ether complex, indium(III) chloride [14] and dysprosium and ytterbium trifluoromethanesulfonates [15, 16] are highly effective catalysts in the Povarov reaction. Therefore, we tested the above catalysts in the above model reaction. Insofar as dysprosium(III) and ytterbium(III) trifluoromethanesulfonates are fairly poorly soluble in 2,2,2-trifluoroethanol, we used acetonitrile as solvent in this series of experiments. The procedure was analogous to that described above. The amount of the catalyst was 20 mol %, and the results are collected in Table 2. It is seen that the best catalysts for the Povarov reaction with substrate **I** are indium(III) chloride (conversion 100%, yield of **IIa**/**IIb** 96%), ytterbium(III) trifluoromethanesulfonate (conversion 99%, yield of **IIa**/**IIb** 94%), and boron trifluoride–diethyl ether complex (conversion 90%, yield of **IIa**/**IIb** 84%). The conversion of **I** in the presence of dysprosium(III) trifluoromethanesulfonate was lower (61%), while the use of trifluoromethanesulfonic acid

Scheme 2.



reduced the conversion to 9%. Thus indium(III) chloride and ytterbium(III) trifluoromethanesulfonate ensured the best results, but we also tried $BF_3 \cdot Et_2O$ as catalyst with a view to compare our new results with the data obtained by us previously [6, 11].

Under the optimized conditions (2,2,2-trifluoroethanol as solvent; $BF_3 \cdot Et_2O$, 15 mol %) we performed the reaction of Schiff base **I** with ethyl vinyl ether. During the isolation procedure, intermediate **A** loses ethanol molecule, and subsequent oxidation with at-

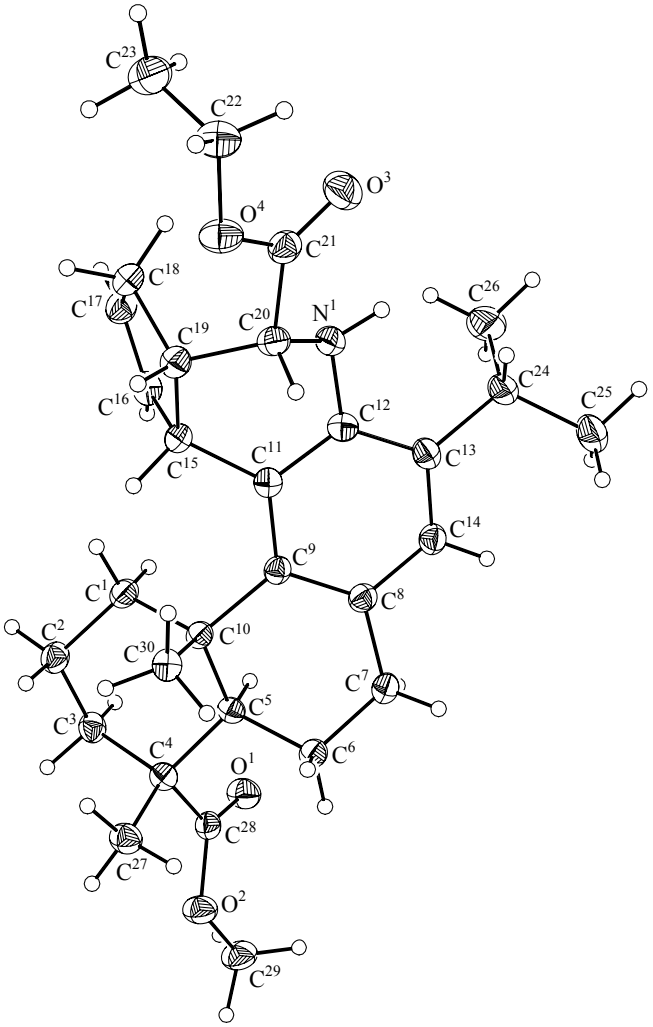


Fig. 1. Structure of the molecule of compound **IIa** according to the X-ray diffraction data.

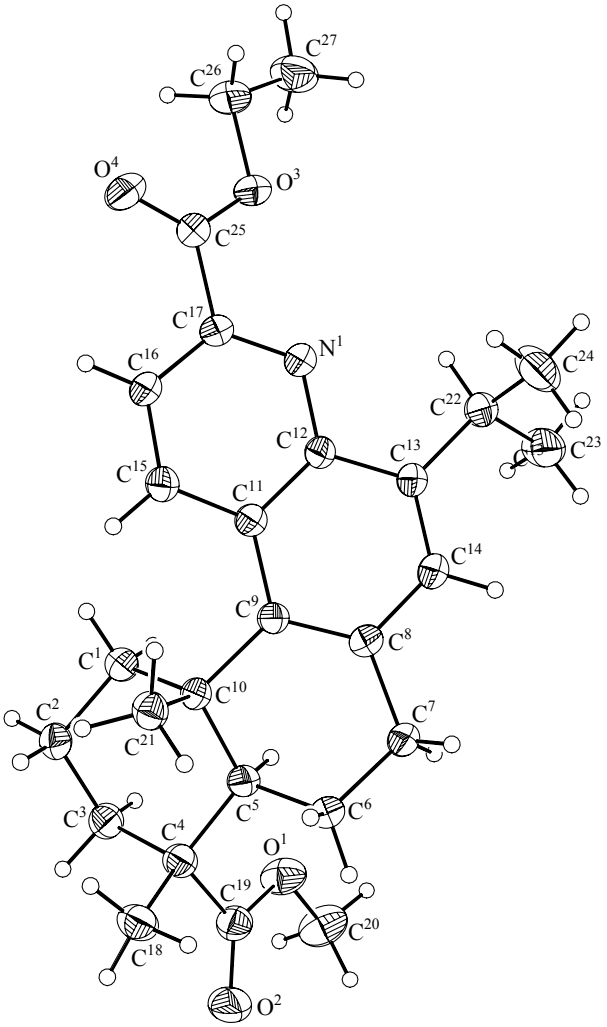


Fig. 2. Structure of the molecule of compound **III** according to the X-ray diffraction data.

Table 2. Povarov reaction of Schiff base **I** with cyclopentadiene in the presence of different catalysts

Catalyst	Conversion of Schiff base **I**, %	Yield, %	
		IIa	**IIb**
$BF_3 \cdot OEt_2$	90	54	30
$InCl_3$	100	53	43
$Yb(CF_3SO_3)_3 \cdot H_2O$	99	50	44
$Dy(CF_3SO_3)_3$	61	26	21
CF_3SO_3H	9	9	0

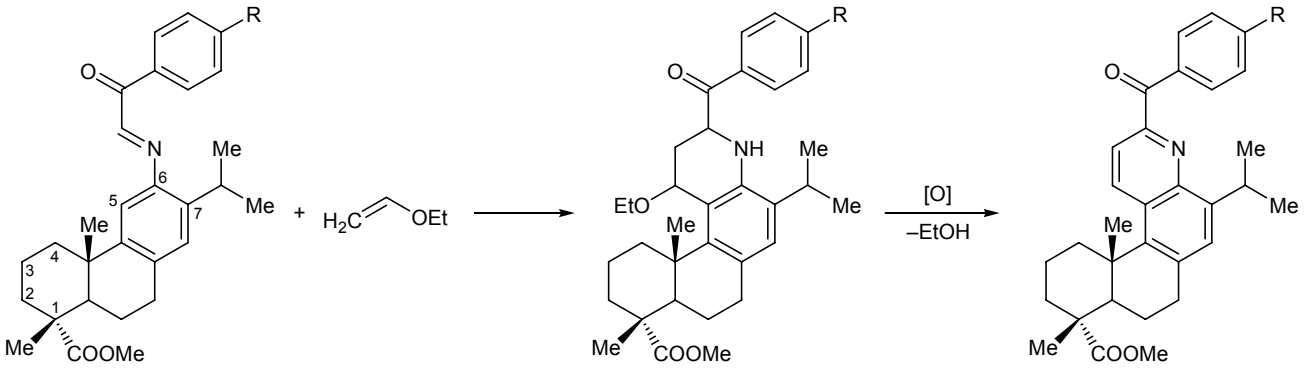
mospheric oxygen yields adduct **III**, as was described previously for analogous reactions [3] (Scheme 2). The ^{1}H NMR spectrum of compound **III** contained signals from protons on C^1 and C^2 as doublets at δ 8.66 and 7.94 ppm, respectively, with a coupling constant ^3J of 9 Hz, which indicates aromatization of the heteroring. The structure of **III** was confirmed by the X-ray diffraction data (Fig. 2).

Unlike **IIa**, compound **III** in crystal is represented by two molecules with similar conformations in the symmetry-independent part of unit cell. Figure 2 shows the structure of one independent molecule. Both compounds **IIa** and **III** are characterized by almost similar structures of the A, B, and C rings: the cyclohexane fragment A has a *chair* conformation, the aromatic ring C is planar, and the cyclohexene ring B adopts *half-chair* conformation (distorted in molecule **III**). The structure of the rings A–C is analogous to the structure of the corresponding fragments in structurally related Schiff base which was studied previously [6]. The D ring in molecule **III** is obviously planar, whereas the D ring in **IIa** has a conformation intermediate between *twist* and *boat*. The cyclopentene fragment E in compound **IIa** is almost planar and is oriented *trans* relative to the methyl substituent on C^{30} (for atom numbering, see Figs. 1 and 2); *cis* orientation of the cyclopentene fragment should give rise to strong steric repulsion. The shortest distance between the 15a-H and 30-H atoms is 2.12 Å, i.e. it is slightly smaller than the sum of the corresponding van der Waals radii (2.2 Å) [17]. In addition, compound **IIa** displayed a very short contact (1.85 Å) between 15a-H and 1-H_B. These H···H contacts are likely to affect conformation of the D ring. The crystal packing of both compounds is determined by common van der Waals interactions.

In order to extend the series of new compounds, by reaction of 12-aminodehydroabietic acid methyl ester with arylglyoxals we obtained Schiff bases **IVa**–**IVd** and examined their cyclocondensation with ethyl vinyl ether, cyclopentadiene, and indene according to Povarov. Schiff bases **IVa**–**IVd** reacted with ethyl vinyl ether as shown in Scheme 3. As in the reaction of compound **I** with ethyl vinyl ether, elimination of ethanol molecule from intermediate **B** and subsequent oxidation yields methyl (9*R*,12a*S*)-3-aroyl-5-isopropyl-9,12a-dimethyl-7,8,8a,9,10,11,12,12a-octahydronaphtho[1,2-*f*]quinoline-9-carboxylates **Va**–**Vd** (for atom numbering, see structure **III** in Scheme 2). The structure of compounds **Va**–**Vd** was confirmed by the ^{1}H NMR and mass spectra.

Schiff bases **IVa**–**IVd** also showed high reactivity in the reactions with cyclopentadiene and indene. In the reaction with cyclopentadiene we isolated methyl 1-aroyl-3-isopropyl-7,10a-dimethyl-2,5,6,6a,7,8,9,10,-10a,10d,13,13a-dodecahydro-1*H*-naphtho[1,2-*f*]cyclopenta[*c*]quinoline-7-carboxylates **VIa**–**VId** (for atom numbering, see Scheme 1) as mixtures of two diastereoisomers with respect to C^1 (Scheme 4). The (1*R*)-to-(1*S*) (or *cis*/*trans*) isomer ratio in different

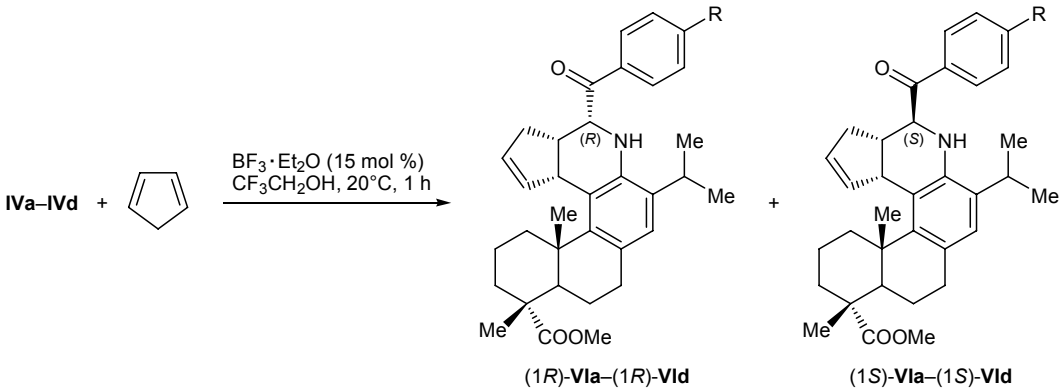
Scheme 3.



IVa–IVd **B** **Va–Vd**

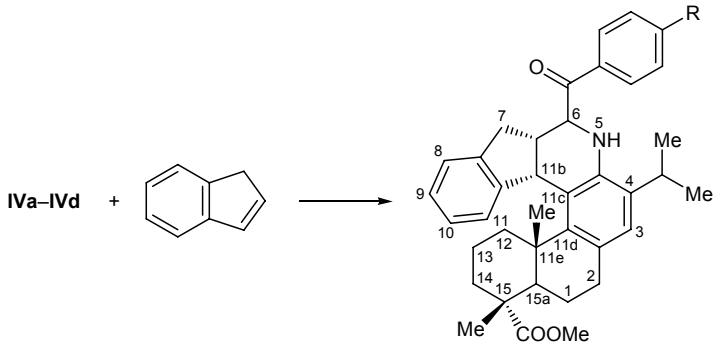
R = H (**a**), Me (**b**), MeO (**c**), Cl (**d**).

Scheme 4.



(1*R*)-**VIa**–(1*R*)-**VId** (1*S*)-**VIa**–(1*S*)-**VId**

Scheme 5.



VIIa–**VIId**

experiments ranged from 1:1 to ~2:1 (5:6 for **VIb**). The diastereoisomers were distinguished by the coupling constant $J_{1,13a}$ for the 1-H proton which resonated as a doublet. The $J_{1,13a}$ value was 4.5–4.8 Hz for the (1*R*)-isomer and 5.1–5.4 Hz for the (1*S*)-isomer of **VIb** and **VIc** (cf. [6]). Furthermore, the 11-H and 12-H signals of the (1*S*)-isomers of **VIa**–**VId** appeared in a weaker field. The 1-H protons in both diastereoisomers of **VIa** and **VId** had similar chemical shifts (δ 4.22–4.27 ppm), and they resonated as broadened doublets (J = 4.8–5.4 Hz); the stereoisomers were distinguished by the 11-H and 12-H signals.

Likewise, the reaction of compounds **IVa**–**IVd** with indene afforded in each case (according to the ^{1}H NMR data) a mixture of two diastereoisomeric (with respect to C^6) methyl (6a*S*,11b*S*,11e*S*,15*R*,15a*R*)-6-aroyl-4-isopropyl-11e,15-dimethyl-2,5,6,6a,7,11b,11e,12,13,14,15,15a-dodecahydro-1*H*-indeno[2,1-*c*]naphtho[1,2-*f*]quinoline-15-carboxylates **VIIa**–**VIId**, the (6*R*)/(6*S*) ratio ranging from 1:1 to 3:2 (Scheme 5; steric configuration at C^6 is not shown). Different stereoisomers were distinguished by the $J_{6,6a}$ value for the doublet signal of 6-H, which was larger for the (6*S*)-isomer; for example, $J_{6,6a}$ = 6.6 and 7.5 Hz for the (1*R*)- and (1*S*)-isomers of **VIIa**, respectively. The (6*S*)-isomers of **VIIa**–**VIId** were also characterized by downfield shift of the 11b-H signal in the ^{1}H NMR spectrum: δ 6.24 ppm (d, J = 6.9 Hz) for (6*S*)-**VIIa** and δ 5.19 ppm (d, J = 8.1 Hz). This may be due to magnetic anisotropy of the aroyl group. As a rule, signals from the NH protons in compounds **VI** and **VII** are not observed in their ^{1}H NMR spectra recorded in $CDCl_3$ as a result of proton exchange, but their IR spectra contain broadened absorption bands in the region 3390–3420 cm^{-1}, which belong to NH stretching vibrations.

Compounds **VIIa**–**VIId** may be regarded as partly hydrogenated azanorhelicenes, and the described reaction provides a convenient synthetic approach to these unusual compounds. In the recent years, helicenes and helicene-like structures have found increasing applications as photoactive materials and organic semiconductors [18–20].

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer from samples dispersed in mineral oil. The ^{1}H and ^{13}C NMR spectra were measured from

Table 3. Crystallographic data for compounds **IIa** and **III** and parameters of X-ray diffraction experiments

Parameter	**IIa**	**III**
Formula	$C_{30}H_{41}NO_4$	$C_{27}H_{35}NO_4$
Molecular weight	479.64	437.56
Color	Light yellow	Light yellow
Shape of crystals	Prisms	Plates
Crystal habit, mm	0.25×0.15×0.15	0.25×0.25×0.05
Crystal system	Rhombic	Trigonal
Space group	$P2_12_12_1$	$P3_1$
a, Å	9.3224(12)	10.4074(3)
b, Å	11.1600(14)	10.4074(3)
c, Å	24.833(3)	38.341(2)
V, Å^3	2583.5(6)	3596.5(2)
Z	4	6
d_{calc}, g/cm^3	1.233	1.212
Absorption coefficient μ, mm^{-1}	0.081	0.080
F(000)	1040	1416
Scan range θ, deg	1.64–30.06	2.26–30.00
Total number of reflections	29908	41759
Number of independent reflections	4204	6961
R_{int}	0.0796	0.0346
Number of refined parameters	322	589
Number of reflections with $I > 2\sigma(I)$	3183	6224
Completeness of reflection array, %	98.9	99.3
Goodness of fit	1.018	1.023
Divergence factor $R_1(F)$[a] [reflections with $I > 2\sigma(I)$]	0.0487	0.0522
Divergence factor $wR_2(F^2)$[b] (all reflections)	0.1251	0.1220
Residual electronic density, min/max, e/Å^3	0.312/–0.236	0.490/–0.323

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$.
[b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.

solutions in $CDCl_3$ on a Varian Mercury Plus 300 instrument operating at 300 and 75 MHz, respectively. The chemical shifts were determined relative to hexamethyldisiloxane as internal reference (^{1}H) or deuterated solvent (^{13}C). The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol plates using hexane–ethyl acetate (9:1) as eluent; the chromatograms were developed by treatment with a solution of phosphomolybdic acid in ethanol, followed by heating to 100–150°C. The mass spectra (electron impact, 70 eV) were obtained on an Agilent Technologies 5975B Network mass spectrometer coupled with an Agilent Technologies 6890N gas chromatograph; HP-5MS capillary column, 30000×0.25 mm; injector temperature 240°C; oven temperature programming at a rate of 20–40 deg/min; carrier gas helium. Column chromatography was performed on Silicagel 60 (0.035–0.070 mm, Merck) using hexane–ethyl acetate (19:1) as eluent. Ethyl vinyl ether, indene, ethyl glyoxylate (a 40% solution in toluene), 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoropropan-2-ol were commercial products (Lancaster, Alfa Aesar).

Single crystals of compounds **IIa** and **III**, suitable for X-ray analysis, were obtained by slow evaporation of solutions of these compounds in hexane–ethyl acetate (2:1, by volume). Experimental sets of reflection intensities were acquired on a Smart 1000 CCD diffractometer (λMoK_α = 0.71073 Å, graphite monochromator, ω-scanning) at 120 K. The initial intensity arrays were processed using SAINT Plus [21] and SADABS programs [22]. The structures were solved

by the direct method and were refined by F^2_{hkl} by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed into positions calculated on the basis of geometry considerations (except for the hydrogen atom on the nitrogen in **IIa**, which was localized by difference synthesis of electron density and then normalized by a distance of 0.90 Å). The positions of all hydrogen atoms were refined in terms of the riding model [U_{iso}(H) = nU_{eq}(C,N), where n = 1.5 for methyl carbon atoms and n = 1.2 for the other carbon and nitrogen atoms]. The structures were solved and refined using SHELXTL software package [23]. The principal crystallographic data and parameters of X-ray diffraction experiments are collected in Table 3.

Optimization of the Povarov reaction conditions. *a*. *Solvent*. Compound **I**, 25.0 mg (0.056 mmol), was dissolved in 3 ml of a solvent, 1.1 μl (0.0084 mmol, 15 mol %) of $BF_3 \cdot Et_2O$ was added using a microsyringe, the mixture was stirred for 10 min, and 14 μl (3 equiv) of cyclopentadiene was added. The mixture was stirred for 1 h at room temperature, the reaction was terminated by adding a saturated aqueous solution of $NaHCO_3$ to pH 7, the mixture was extracted with 20 ml of ethyl acetate, the extract was dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was analyzed by gas chromatography–mass spectrometry.

b. Catalyst. Compound **I**, 25.0 mg (0.056 mmol), was dissolved in 3 ml of acetonitrile, 0.0084 mmol (15 mol %) of catalyst was added, the mixture was stirred for 10 min, and 14 μl (3 equiv) of cyclopentadiene was added. The mixture was stirred for 1 h at room temperature, the reaction was terminated, and the mixture was treated and analyzed, as described above.

Compounds **I**–**III** were reported previously [11].

Schiff bases IVa–IVd (*general procedure*). A solution of 1 mmol of arylglyoxal in 30 ml of toluene was added to 0.328 g (1 mmol) of 12-aminodehydroabietic acid methyl ester in the presence of 100 mg of 4-Å molecular sieves or 2–3 g of anhydrous $MgSO_4$. The mixture was stirred for 6–12 h at room temperature. When the reaction was complete (TLC), the mixture was filtered, the filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography.

Methyl (1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-6-[(*E*)-2-oxo-2-phenylethylideneamino]-1,2,3,4,-4a,9,10,10a-octahydrophenanthrene-1-carboxylate (IVa). Yield 76%, yellow crystals, mp 134–136°C (from hexane–ethyl acetate). ^{1}H NMR spectrum, δ, ppm: 1.19 d (3H, Me, J = 6.9 Hz), 1.22 s (3H, Me), 1.27 s (3H, Me, J = 6.9 Hz), 1.35 d (3H, Me, J = 6.9 Hz), 1.39–1.90 m (7H, 4-H$_{ax}$, 2-H, 3-H), 2.23 m (1H, 10a-H), 2.31 m (1H, 4-H$_{eq}$), 2.92 m (2H, 9-H), 3.42 m (1H, 7-CH), 3.66 s (3H, OMe), 6.89 s (1H, 5-H), 6.98 s (1H, 8-H), 7.48 m (2H, *m*-H), 7.60 m (1H, *p*-H), 8.21 s (1H, CH=N), 8.33 m (2H, *o*-H). ^{13}C NMR spectrum, δ_C, ppm: 16.51 (Me), 18.47 (C^3), 21.59 (C^{10}), 23.04 (Me), 23.39 (Me), 25.10 (Me), 27.96 (7-CH), 29.83 (C^9), 36.61 (C^2), 37.23 (C^{4a}), 38.05 (C^4), 44.74 (C^1), 47.61 (C^{10a}), 51.93 (OMe), 112.69 (C^5), 126.48 (C^8), 128.24 (C^m), 130.71 (C^o), 133.31 (C^p), 135.44 (C^i), 136.05 (C^{8a}), 141.15 (C^7), 145.15 (C^{4b}), 148.03 (C^6), 155.55 (CH=N), 178.92 (OC=O), 190.97 (C=O). Found, %: C 78.04; H 7.88; N 3.07. $C_{29}H_{35}NO_3$. Calculated, %: C 78.17; H 7.92; N 3.14.

Methyl (1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-6-[(*E*)-2-(4-methylphenyl)-2-oxoethylideneamino]-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (IVb). Yield 77%, yellowish oily substance. ^{1}H NMR spectrum, δ, ppm: 1.19 d (3H, Me, J = 6.6 Hz), 1.22 s (3H, Me), 1.23 s (3H, Me, J = 6.9 Hz), 1.27 d (3H, Me, J = 6.9 Hz), 1.46–1.87 m (7H, 4-H$_{ax}$, 2-H, 3-H), 2.22 d.d (1H, 10a-H, J = 12.3, 2.1 Hz), 2.30 m (1H, 4-H$_{eq}$), 2.43 s (3H, *p*-Me), 2.90 m (2H, 9-H), 3.42 m (1H, 7-CH), 3.66 s (3H, OMe), 6.88 s (1H, 5-H), 6.98 s (1H, 8-H), 7.30 d (2H, *m*-H, J = 8.1 Hz), 8.19 s (1H, CH=N), 8.26 d (2H, *o*-H, J = 8.1 Hz). Found, %: C 78.28; H 8.15; N 3.12. $C_{30}H_{37}NO_3$. Calculated, %: C 78.40; H 8.11; N 3.05.

Methyl (1*R*,4a*S*,10a*R*)-7-isopropyl-6-[(*E*)-2-(4-methoxyphenyl)-2-oxoethylideneamino]-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (IVc). Yield 69%, yellow crystals, mp 53–57°C (from hexane–ethyl acetate). ^{1}H NMR spectrum, δ, ppm: 1.20 d (3H, Me, J = 6.9 Hz), 1.22 s (3H, Me), 1.23 s (3H, Me, J = 6.9 Hz), 1.26 d (3H, Me, J = 6.9 Hz), 1.41–1.87 m (7H, 4-H$_{ax}$, 2-H, 3-H), 2.22 m (1H, 10a-H, J = 12.3, 2.1 Hz), 2.30 m (1H, 4-H$_{eq}$), 2.90 m (2H, 9-H), 3.43 m (1H, 7-CH), 3.66 s (3H, OMe), 3.88 s (1H, OMe), 6.87 s (1H, 5-H), 6.97 d (2H, *m*-H, J = 8.7 Hz), 6.98 s (1H, 8-H), 8.18 s (1H, CH=N), 8.40 d (2H, *o*-H, J = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.48 (Me), 18.46 (C^3), 21.59 (C^{10}), 23.02 (Me), 23.36 (Me), 25.05 (Me), 27.97 (7-CH), 29.80 (C^9), 36.61 (C^2), 37.22 (C^{4a}), 38,04 (C^4), 44.76 (C^1), 47.59 (C^{10a}), 51.87 (OMe), 55.45 (C$_6$H$_4$O**Me**), 112.76 (C^5), 113.61 (C^m), 126.38 (C^8), 128.34 (C^o), 133.12 (C^{8a}), 135.66 (C^i), 140.84 (C^7), 145.42 (C^{4b}), 148.01 (C^6), 156.26 (CH=N), 163.95 (C^p), 178.90

(OC=O), 189.08 (C=O). Found, %: C 75.97; H 7.79; N 3.27. $C_{30}H_{37}NO_4$. Calculated, %: C 75.79; H 7.79; N 2.95.

Methyl (1*R*,4a*S*,10a*R*)-6-[(*E*)-2-(4-chlorophenyl)-2-oxoethylideneamino]-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (IVd). Yield 55%, yellowish oily substance. ^{1}H NMR spectrum, δ, ppm: 1.19 d (3H, Me, *J* = 6.9 Hz), 1.22 s (3H, Me), 1.23 s (3H, Me, *J* = 6.9 Hz), 1.27 d (3H, Me, *J* = 6.9 Hz), 1.41–1.87 m (7H, 4-H$_{ax}$, 2-H, 3-H), 2.22 d.d (1H, 10a-H, *J* = 12.3, 2.1 Hz), 2.30 m (1H, 4-H$_{eq}$), 2.91 m (2H, 9-H), 3.40 m (1H, 7-CH), 3.66 s (3H, OMe), 6.90 s (1H, 5-H), 6.99 s (1H, 8-H), 7.46 d (2H, *m*-H, *J* = 8.4 Hz), 8.19 s (1H, CH=N), 8.32 d (2H, *o*-H, *J* = 8.4 Hz). Mass spectrum: *m*/*z* 479 $[M]^+$. Found, %: C 72.44; H 7.21; N 2.97. $C_{29}H_{34}ClNO_4$. Calculated, %: C 72.56; H 7.14; N 2.92.

Condensation of Schiff bases IVa–IVd with activated olefins (*general procedure*). Schiff base **IVa–IVd**, 0.27 mmol, was dissolved in 10 ml of 2,2,2-trifluoroethanol, 0.005 ml (15 mol %) of $BF_3 \cdot Et_2O$ was added, the mixture was stirred for 10 min, and 0.81 mmol of activated olefin (ethyl vinyl ether, freshly distilled cyclopentadiene, or indene) was added. The mixture was stirred for ~1 h at room temperature (TLC), the solvent was distilled off under reduced pressure, the residue was treated with a solution of $NaHCO_3$, 10 ml of ethyl acetate was added, and the organic phase was separated and dried over $MgSO_4$. The solvent was distilled off, and the residue was analyzed by GC–MS and subjected to column chromatography. Solid products were additionally purified by recrystallization from hexane–ethyl acetate.

Methyl (8a*R*,9*R*,12a*S*)-3-benzoyl-5-isopropyl-9,12a-dimethyl-7,8,8a,9,10,11,12,12a-octahydronaphtho[1,2-*f*]quinoline-9-carboxylate (Va). Yield 20%, mp 121–122°C. IR spectrum, ν, cm^{-1}: 1720 (C=O, ester), 1660 (C=O), 1600 (C=C), 1318, 1310, 1280, 1250, 1170, 1145, 1002, 954, 884. ^{1}H NMR spectrum, δ, ppm: 1.28 d (6H, Me, *J* = 6.9 Hz), 1.36 s (3H, Me), 1.40–1.94 m (7H, 8-H, 10-H, 11-H, 12-H$_{ax}$), 1.70 s (3H, Me), 2.24 m (1H, 12-H$_{eq}$), 2.93 m (2H, 7-H), 3.15 m (1H, 8a-H), 3.70 s (3H, OMe), 4.12 m (1H, 5-CH), 7.26 s (1H, 6-H), 7.48 m (2H, *m*-H), 7.59 m (1H, *p*-H), 8.06 d (1H, 2-H, *J* = 9.0 Hz), 8.29 m (2H, *o*-H), 8.80 d (1H, 1-H, *J* = 9.0 Hz). Found, %: C 79.27; H 7.45; N 2.84. $C_{31}H_{35}NO_3$. Calculated, %: C 79.28; H 7.51; N 2.98.

Methyl (8a*R*,9*R*,12a*S*)-5-isopropyl-9,12a-dimethyl-3-(4-methylbenzoyl)-7,8,8a,9,10,11,12,12a-octahydronaphtho[1,2-*f*]quinoline-9-carboxylate (Vb). Yield 25%, yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.25 d (6H, Me, *J* = 6.6 Hz), 1.34 s (3H, Me), 1.50–1.92 m (7H, 8-H, 10-H, 11-H, 12-H$_{ax}$), 1.67 s (3H, Me), 2.23 m (1H, 12-H$_{eq}$), 2.39 s (3H, *p*-CH_3), 2.90 m (2H, 7-H), 3.11 m (1H, 8a-H), 3.68 s (3H, OMe), 4.14 m (1H, 5-CH), 7.17 s (1H, 6-H), 7.25 d (2H, *m*-H, *J* = 8.4 Hz), 7.82 d (2H, *o*-H, *J* = 8.4 Hz), 8.01 d (1H, 2-H, *J* = 9.0 Hz), 8.77 d (1H, 1-H, *J* = 9.0 Hz). Mass spectrum: *m*/*z* 483 $[M]^+$. Found, %: C 79.38; H 7.65; N 2.83. $C_{32}H_{37}NO_3$. Calculated, %: C 79.47; H 7.71; N 2.90,

Methyl (8a*R*,9*R*,12a*S*)-5-isopropyl-3-(4-methoxybenzoyl)-9,12a-dimethyl-7,8,8a,9,10,11,12,12a-octahydronaphtho[1,2-*f*]quinoline-9-carboxylate (Vc). Yield 26%, yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.14 d (6H, Me, *J* = 6.9 Hz), 1.28 s (3H, Me), 1.40–1.95 m (7H, 8-H, 10-H, 11-H, 12-H$_{ax}$), 1.60 s (3H, Me), 2.20 m (1H, 12-H$_{eq}$), 2.88 m (2H, 7-H), 3.10 m (1H, 8a-H), 3.68 s (3H, OMe), 3.89 s (3H, OMe), 4.07 m (1H, 5-CH), 6.90 d (2H, *m*-H, *J* = 8.7 Hz), 7.09 s (1H, 6-H), 7.88 m (2H, *o*-H, *J* = 8.7 Hz), 8.04 d (1H, 2-H, *J* = 9.1 Hz), 8.78 d (1H, 1-H, *J* = 8.7 Hz). Mass spectrum: *m*/*z* 499 $[M]^+$. Found, %: C 79.75; H 7.32; N 2.77. $C_{32}H_{37}NO_4$. Calculated, %: C 79.92; H 7.46; N 2.80.

Methyl (8a*R*,9*R*,12a*S*)-3-(4-chlorobenzoyl)-5-isopropyl-9,12a-dimethyl-7,8,8a,9,10,11,12,12a-octahydronaphtho[1,2-*f*]quinoline-9-carboxylate (Vd). Yield 37%, yellow crystals, mp 119–120°C. ^{1}H NMR spectrum, δ, ppm: 1.29 d (6H, Me, *J* = 6.9 Hz), 1.36 s (3H, Me), 1.43–1.95 m (7H, 8-H, 10-H, 11-H, 12-H$_{ax}$), 1.69 s (3H, Me), 2.23 m (1H, 12-H$_{eq}$), 2.93 m (2H, 7-H), 3.15 m (1H, 8a-H), 3.70 s (3H, OMe), 4.10 m (1H, 5-CH), 7.27 s (1H, 6-H), 7.46 m (2H, *m*-H, *J* = 9.0 Hz), 8.06 d (1H, 2-H, *J* = 9.3 Hz), 8.29 d (2H, *o*-H, *J* = 9.0 Hz), 8.80 d (1H, 1-H, *J* = 9.3 Hz). Mass spectrum: *m*/*z* 503 $[M]^+$. Found, %: C 73.85; H 6.77; N 2.74. $C_{31}H_{34}ClNO_3$. Calculated, %: C 73.87; H 6.80; N 2.78.

Methyl (7*R*,10a*S*,10d*R*,13a*S*)-1-benzoyl-3-isopropyl-7,10a-dimethyl-2,5,6,6a,7,8,9,10,10a,10d,13,13a-dodecahydro-1*H*-naphtho[1,2-*f*]cyclopenta[*c*]quinoline-7-carboxylate (VIa). Yield 38%, yellow oily substance. ^{1}H NMR spectrum, δ, ppm: (1*R*)-isomer: 1.17 d (3H, Me, *J* = 6.6 Hz), 1.20 d (3H, Me, *J* = 6.6 Hz), 1.29 s (3H, Me), 1.53 s (3H, Me), 1.55–1.82 m (7H, 6-H, 8-H, 9-H, 10-H$_{ax}$), 2.25 m (2H, 13-H), 2.32 m (1H, 10-H$_{eq}$), 2.68 m (2H, 5-H), 2.92 m (2H, 6a-H, 3-CH), 3.46 m (1H, 13a-H), 3.68 s (3H, OMe), 4.27 d (1H, 1-H, *J* = 4.8 Hz), 4.40 br.s (1H, NH), 4.85 m (1H, 10d-H), 5.32 m (1H, 11-H), 5.74 m (1H, 12-H), 6.74 s

(1H, 4-H), 7.46 m (2H, *m*-H), 7.56 m (1H, *p*-H), 7.87 m (2H, *o*-H); (1*S*)-isomer: 0.98 d (3H, Me, *J* = 6.9 Hz), 1.08 d (3H, Me, *J* = 6.9 Hz), 1.25 s (3H, Me), 1.44 s (3H, Me), 1.55–1.82 m (7H, 6-H, 8-H, 9-H, 10-H_{ax}), 2.25 m (2H, 13-H), 2.32 m (1H, 10-H_{eq}), 2.68 m (2H, 5-H), 2.92 m (2H, 6a-H, 3-CH), 3.46 m (1H, 13a-H), 3.68 s (3H, OMe), 4.27 d (1H, 1-H, *J* = 4.8 Hz), 4.40 br.s (1H, NH), 4.85 m (1H, 10d-H), 5.60 m (1H, 11-H), 5.94 m (1H, 12-H), 6.90 s (1H, 4-H), 7.46 m (2H, *m*-H), 7.76 m (1H, *p*-H), 8.05 m (2H, *o*-H). Mass spectrum: *m*/*z* 509 $[M - 2]^+$. Found (for isomer mixture), %: C 79.67; H 7.96; N 2.65. $C_{34}H_{41}NO_3$. Calculated, %: C 79.81; H 8.08; N 2.74.

Methyl (7*R*,10a*S*,10d*R*,13a*S*)-3-isopropyl-7,10a-dimethyl-1-(4-methylbenzoyl)-2,5,6,6a,7,8,9,10,-10a,10d,13,13a-dodecahydro-1*H*-naphtho[1,2-*f*]-cyclopenta[*c*]quinoline-7-carboxylate (VIb). Yield 78% (mixture of diastereoisomers). IR spectrum, ν, cm^{-1}: 3400 (NH), 1730 (C=O, ester), 1686 (C=O), 1686 w, 1606 (C=C), 1584, 1520, 1212, 1160, 1080, 1040, 936. ^{1}H NMR spectrum, δ, ppm: (1*R*)-isomer: 1.15 d (3H, Me, *J* = 6.9 Hz), 1.21 d (3H, Me, *J* = 6.9 Hz), 1.31 s (3H, Me), 1.47 s (3H, Me), 1.55–1.85 m (7H, 6-H, 8-H, 9-H, 10-H_{ax}), 2.12–2.35 m (3H, 13-H, 10-H_{eq}), 2.42 s (3H, C_6H_4**Me**), 2.67–2.99 m (4H, 5-H, 6a-H, 3-CH), 3.50 m (1H, 13a-H), 3.67 s (3H, OMe), 4.33 d (1H, 1-H, *J* = 4.8 Hz), 4.86 m (1H, 10d-H), 5.05 m (1H, 11-H), 5.61 m (1H, 12-H), 6.69 s (1H, 4-H), 7.28 d (2H, *m*-H, *J* = 8.1 Hz), 7.83 d (2H, *o*-H, *J* = 8.1 Hz); (1*S*)-isomer: 1.16 d (3H, Me, *J* = 6.6 Hz), 1.20 d (3H, Me, *J* = 6.6 Hz), 1.29 s (3H, Me), 1.53 s (3H, Me), 1.55–1.85 m (7H, 6-H, 8-H, 9-H, 10-H_{ax}), 2.12–2.35 m (3H, 13-H, 10-H_{eq}), 2.40 s (3H, C_6H_4**Me**), 2.67–2.99 m (4H, 5-H, 6a-H, 3-CH), 3.50 m (1H, 13a-H), 3.68 s (3H, OMe), 4.24 d (1H, 1-H, *J* = 5.1 Hz), 4.86 m (1H, 10d-H), 5.34 m (1H, 11-H), 5.74 m (1H, 12-H), 6.74 s (1H, 4-H), 7.26 d (2H, *m*-H, *J* = 8.4 Hz), 7.78 d (2H, *o*-H, *J* = 8.4 Hz). Mass spectrum: *m*/*z* 523 $[M]^+$. Found, %: C 79.69; H 8.05; N 2.70. $C_{35}H_{43}NO_3$. Calculated, %: C 79.96; H 8.24; N 2.66.

Methyl (7*R*,10a*S*,10d*R*,13a*S*)-3-isopropyl-1-(4-methoxybenzoyl)-7,10a-dimethyl-2,5,6,6a,7,8,9,10,-10a,10d,13,13a-dodecahydro-1*H*-naphtho[1,2-*f*]-cyclopenta[*c*]quinoline-7-carboxylate (VIc). Yield 96% (mixture of diastereoisomers). ^{1}H NMR spectrum, δ, ppm: (1*R*)-isomer: 1.15 d (3H, Me, *J* = 6.9 Hz), 1.21 d (3H, Me, *J* = 6.9 Hz), 1.31 s (3H, Me), 1.53 s (3H, Me), 1.24–1.82 m (7H, 6-H, 8-H, 9-H, 10-H_{ax}), 2.16–2.35 m (3H, 13-H, 10-H_{eq}), 2.73 m (2H, 5-H), 2.90 m (3H, 6a-H, 3-CH), 3.44 m (1H, 13a-H), 3.67 s (3H, OMe), 3.87 s (3H, OMe), 4.30 d (1H, 1-H, *J* = 4.5 Hz), 4.88 m (1H, 10d-H), 5.05 m (1H, 11-H), 5.62 m (1H, 12-H), 6.68 s (1H, 4-H), 6.93 d (2H, *m*-H, *J* = 8.7 Hz), 7.88 m (2H, *o*-H, *J* = 8.7 Hz); (1*S*)-isomer: 1.16 d (3H, Me, *J* = 6.9 Hz), 1.20 d (3H, Me, *J* = 6.9 Hz), 1.25 s (3H, Me), 1.47 s (3H, Me), 1.24–1.82 m (7H, 6-H, 8-H, 9-H, 10-H_{ax}), 2.16–2.35 m (3H, 13-H, 10-H_{eq}), 2.73 m (2H, 5-H), 2.90 m (3H, 6a-H, 3-CH), 3.50 m (1H, 13a-H), 3.68 s (3H, OMe), 3.86 s (3H, OMe), 4.22 d (1H, 1-H, *J* = 5.1 Hz), 4.88 m (1H, 10d-H), 5.33 m (1H, 11-H), 5.76 m (1H, 12-H), 6.74 s (1H, 4-H), 6.96 d (2H, *m*-H, *J* = 8.7 Hz), 7.93 m (2H, *o*-H, *J* = 8.7 Hz). Found, %: C 77.56; H 7.93; N 2.64. $C_{35}H_{43}NO_4$. Calculated, %: C 77.60; H 8.00; N 2.59.

Methyl (7*R*,10a*S*,10d*R*,13a*S*)-1-(4-chlorobenzoyl)-3-isopropyl-7,10a-dimethyl-2,5,6,6a,7,8,9,10,-10a,10d,13,13a-dodecahydro-1*H*-naphtho[1,2-*f*]-cyclopenta[*c*]quinoline-7-carboxylate (VId). Yield 76% (mixture of diastereoisomers). IR spectrum, ν, cm^{-1}: 3420 (NH), 1738 (C=O, ester), 1696 (C=O), 1678 w, 1608 (C=C), 1246, 1180, 1154. ^{1}H NMR spectrum, δ, ppm: (1*R*)-isomer: 0.98 d (3H, Me, *J* = 7.2 Hz), 1.09 d (3H, Me, *J* = 7.2 Hz), 1.31 s (3H, Me), 1.44 s (3H, Me), 1.58–1.79 m (7H, 6-H, 8-H, 9-H, 10-H_{ax}), 2.13 m (2H, 13-H), 2.29 m (1H, 10-H_{eq}), 2.57 m (2H, 5-H), 2.82 m (1H, 6a-H), 2.98 m (1H, 13a-H), 3.49 m (1H, 3-CH), 3.69 s (3H, OMe), 4.22 d (1H, 1-H, *J* = 5.4 Hz), 4.62 m (1H, 10d-H), 5.35 m (1H, 11-H), 5.85 m (1H, 12-H), 6.89 s (1H, 4-H), 7.41 d (2H, *m*-H, *J* = 8.4 Hz), 8.01 d (2H, *o*-H, *J* = 8.4 Hz); (1*S*)-isomer: 0.98 d (3H, Me, *J* = 6.9 Hz), 1.13 d (3H, Me, *J* = 6.9 Hz), 1.28 s (3H, Me), 1.44 s (3H, Me), 1.58–1.79 m (7H, 6-H, 8-H, 9-H, 10-H_{ax}), 2.13 m (2H, 13-H), 2.29 m (1H, 10-H_{eq}), 2.57 m (2H, 5-H), 2.82 m (1H, 6a-H), 2.98 m (1H, 13a-H), 3.49 m (1H, 3-CH), 3.67 s (3H, OMe), 4.22 d (1H, 1-H, *J* = 5.4 Hz), 4.41 m (1H, 10d-H), 5.58 m (1H, 11-H), 5.93 m (1H, 12-H), 6.91 s (1H, 4-H), 7.41 d (2H, *m*-H, *J* = 8.4 Hz), 8.01 d (2H, *o*-H, *J* = 8.4 Hz). Mass spectrum: *m*/*z* 543 $[M]^+$. Found, %: C 74.68; H 7.35; N 2.62. $C_{34}H_{40}ClNO_3$. Calculated, %: C 74.77; H 7.38; N 2.56.

Methyl (6a*S*,11b*S*,11e*S*,15*R*,15a*S*)-6-benzoyl-4-isopropyl-11e,15-dimethyl-2,5,6,6a,7,11b,11e,12,-13,14,15,15a-dodecahydro-1*H*-indeno[2,1-*c*]naphtho[1,2-*f*]quinoline-15-carboxylate (VIIa). Yield 88% (mixture of diastereoisomers), mp 175–176°C. IR spectrum, ν, cm^{-1}: 3392 (NH), 1724 (C=O, ester), 1692 (C=O), 1600 (C=C). ^{1}H NMR spectrum, δ, ppm: (6*R*)-isomer: 0.99 d (3H, Me, *J* = 6.6 Hz), 1.10 d (3H, Me, *J* = 6.6 Hz), 1.33 s (3H, Me), 1.55 s (3H, Me), 1.64–1.90 m (7H, 1-H, 13-H, 14-H, 12-H_{ax}), 2.26 d (1H, 15a-H, *J* = 11.1 Hz), 2.42 m (1H, 12-H_{eq}), 2.60–

3.06 m (5H, 7-H, 6a-H, 2-H), 3.36 m (1H, 4-CH), 3.69 s (3H, OMe), 4.44 d (1H, 6-H, J = 6.6 Hz), 5.19 d (1H, 11b-H, J = 8.1 Hz), 6.73 s (1H, 3-H), 6.88–7.05 m (4H, H_{arom}), 7.41–7.62 m (4H, H_{arom}), 7.96 m (1H, H_{arom}); (6*S*)-isomer: 1.00 d (3H, Me, J = 7.2 Hz), 1.05 d (3H, Me, J = 7.2 Hz), 1.31 s (3H, Me), 1.58 s (3H, Me), 1.64–1.90 m (7H, 1-H, 13-H, 14-H, 12-H_{ax}), 2.26 d (1H, 15a-H, J = 11.1 Hz), 2.42 m (1H, 12-H_{eq}), 2.60–3.06 m (5H, 7-H, 6a-H, 2-H), 3.36 m (1H, 4-CH), 3.71 s (3H, OMe), 4.32 d (1H, 6-H, J = 7.5 Hz), 6.24 d (1H, 11b-H, J = 6.9 Hz), 6.82 s (1H, 3-H), 6.88–7.05 m (4H, H_{arom}), 7.41–7.62 m (4H, H_{arom}), 7.96 m (1H, H_{arom}). Mass spectrum: m/z 559 $[M-2]^+$. Found, %: C 81.04; H 7.61; N 2.35. $C_{38}H_{43}NO_3$. Calculated, %: C 81.25; H 7.72; N 2.49.

Methyl (6a*S*,11b*S*,11e*S*,15*R*,15a*R*)-4-isopropyl-11e,15-dimethyl-6-(4-methylbenzoyl)-2,5,6,6a,7,-11b,11e,12,13,14,15,15a-dodecahydro-1*H*-indeno-[2,1-*c*]naphtho[1,2-*f*]quinoline-15-carboxylate (VIIb). Yield 84%, mp 178–180°C. ^{1}H NMR spectrum, δ, ppm: (6*R*)-isomer: 0.97 d (3H, Me, J = 6.6 Hz), 1.09 d (3H, Me, J = 6.6 Hz), 1.32 s (3H, Me), 1.49 s (3H, Me), 1.64–1.90 m (7H, 1-H, 13-H, 14-H, 12-H_{ax}), 2.26 d (1H, 15a-H, J = 11.1 Hz), 2.44 m (4H, *p*-Me, 12-H_{eq}), 2.60–3.06 m (5H, 7-H, 6a-H, 2-H), 3.38 m (1H, 4-CH), 3.68 s (3H, OMe), 4.41 d (1H, 6-H, J = 6.0 Hz), 5.18 d (1H, 11b-H, J = 7.8 Hz), 6.72 s (1H, 3-H), 6.84–7.09 m (4H, H_{arom}), 7.26–7.34 m (3H, H_{arom}), 7.86 m (1H, H_{arom}); (6*S*)-isomer: 0.95 d (3H, Me, J = 6.9 Hz), 1.03 d (3H, Me, J = 6.9 Hz), 1.29 s (3H, Me), 1.55 s (3H, Me), 1.64–1.90 m (7H, 1-H, 13-H, 14-H, 12-H_{ax}), 2.26 d (1H, 15a-H, J = 11.1 Hz), 2.42 m (4H, 11b-H, *p*-Me), 2.60–3.06 m (5H, 7-H, 6a-H, 2-H), 3.36 m (1H, 4-CH), 3.71 s (3H, OMe), 4.29 d (1H, 6-H, J = 7.2 Hz), 6.23 d (1H, 11b-H, J = 7.2 Hz), 6.81 s (1H, 3-H), 6.84–7.09 m (4H, H_{arom}), 7.26–7.34 m (3H, H_{arom}), 7.86 m (1H, H_{arom}). Mass spectrum: m/z 573 $[M-2]^+$. Found, %: C 80.84; H 7.79; N 2.23. $C_{39}H_{45}NO_3$. Calculated, %: C 81.35; H 7.88; N 2.43.

Methyl (6a*S*,11b*S*,11e*S*,15*R*,15a*R*)-4-isopropyl-6-(4-methoxybenzoyl)-11e,15-dimethyl-2,5,6,6a,7,11b,-11e,12,13,14,15,15a-dodecahydro-1*H*-indeno[2,1-*c*]-naphtho[1,2-*f*]quinoline-15-carboxylate (VIIc). Yield 86%, yellow crystals, mp 227–230°C. IR spectrum, ν, cm^{-1}: 3420 (NH), 1736 (C=O, ester), 1686 (C=O), 1610 (C=C), 1590 w, 1520, 1260, 1178, 1142. ^{1}H NMR spectrum, δ, ppm: (6*R*)-isomer: 1.01 d (3H, Me, J = 6.6 Hz), 1.07 d (3H, Me, J = 6.6 Hz), 1.31 s (3H, Me), 1.44 s (3H, Me), 1.58–1.90 m (7H, 1-H, 13-H, 14-H, 12-H_{ax}), 2.22 d (1H, 15a-H, J = 11.1 Hz), 2.34 m (1H, 12-H_{eq}), 2.62–3.02 m (5H, 7-H, 6a-H, 2-H), 3.35 m (1H, 4-CH), 3.68 s (3H, OMe), 3.87 s (3H, OMe), 4.34 d (1H, 6-H, J = 6.0 Hz), 5.18 d (1H, 11b-H, J = 7.8 Hz), 6.78 s (1H, 3-H), 6.84–7.32 m (5H, H_{arom}), 7.84 m (3H, H_{arom}). Found, %: C 78.98; H 7.70; N 2.19. $C_{39}H_{45}NO_4$. Calculated, %: C 79.15; H 7.766; N 2.37.

Methyl (6a*S*,11b*S*,11e*S*,15R,15a*R*)-6-(4-chlorobenzoyl)-4-isopropyl-11e,15-dimethyl-2,5,6,6a,7,-11b,11e,12,13,14,15,15a-dodecahydro-1*H*-indeno-[2,1-*c*]naphtho[1,2-*f*]quinoline-12-carboxylate (VIId). Yield 86%, yellow oily substance. IR spectrum, ν, cm^{-1}: 3430 (NH), 1730 (C=O, ester), 1690 (C=O), 1604 (C=C), 1258, 1180, 1142, 1100. ^{1}H NMR spectrum, δ, ppm: (6*R*)-isomer: 1.04 d (3H, Me, J = 6.9 Hz), 1.09 d (3H, Me, J = 6.9 Hz), 1.31 s (3H, Me), 1.58 s (3H, Me), 1.65–1.90 m (7H, 1-H, 13-H, 14-H, 12-H_{ax}), 2.24 d (1H, 15a-H, J = 11.4 Hz), 2.44 m (1H, 12-H_{eq}), 2.58–3.08 m (5H, 7-H, 6a-H, 2-H), 3.59 m (1H, 4-CH), 3.71 s (3H, OMe), 4.39 d (1H, 6-H, J = 6.3 Hz), 5.19 d (1H, 11b-H, J = 7.2 Hz), 6.73 s (1H, 3-H), 6.86–7.09 m (4H, H_{arom}), 7.46 d (2H, *m*-H, J = 9.0 Hz), 7.89 d (2H, *o*-H, J = 9.0 Hz); (6*S*)-isomer: 0.98 d (3H, Me, J = 6.6 Hz), 1.09 d (3H, Me, J = 6.6 Hz), 1.33 s (3H, Me), 1.55 s (3H, Me), 1.65–1.90 m (7H, 1-H, 13-H, 14-H, 12-H_{ax}), 2.24 d (1H, 15a-H, J = 11.4 Hz), 2.44 m (1H, 12-H_{eq}), 2.58–3.08 m (5H, 7-H, 6a-H, 2-H), 3.59 m (1H, 4-CH), 3.69 s (3H, OMe), 4.27 d (1H, 6-H, J = 7.5 Hz), 6.23 d (1H, 11b-H, J = 7.5 Hz), 6.82 s (1H, 3-H), 6.86–7.09 m (4H, H_{arom}), 7.46 d (2H, *m*-H, J = 9.0 Hz), 7.89 d (2H, *o*-H, J = 9.0 Hz). Mass spectrum: m/z 593 $[M]^+$. Found, %: C 76.77; H 6.77; N 2.24. $C_{38}H_{42}ClNO_3$. Calculated, %: C 76.55; H 7.10; N 2.35.

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