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Derivatives of L-Pimaric Acid in the Synthesis of Chiral Organophosphorus Ligands from Decahydrophenanthrene Series*

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Abstract—Starting with maleopimaric and fumaropimaric acids were prepared chiral organophosphorus ligands from decahydrophenanthrene series. Cationic complexes of Rh(I) prepared therefrom were tested for catalysts of asymmetric hydrogenation of unsaturated precursors of *N*-acethylphenylalanine and its derivatives.

An important part of the fundamental research in asymmetric catalysis is the study of hydrogenation of unsaturated compounds in the presence of transition metal complexes with chiral organophosphorus ligands [1–3]. To this end were prepared numerous phosphines, aminophosphines, and phosphinites proceeding from tartaric acids esters, biogenic amino-acids, carbohydrates, terpenes etc. [4–11]. At the same time no data were published on application of higher terpenes in the synthesis of the organo-elemental ligands. Pursuing the studies on the stereo-selective metal-complex catalysis we turned our attention to tricyclic diterpene acids contained in the galipot of coniferous trees [12–14]. In particular, we took an interest in the L-pimaric acid and its adducts with maleic anhydride and fumaric acid [15–20]. The high optical purity and specific structural features of these compounds are attractive for an attempt to transform them into organoelemental ligands of novel structural types.

Here we report on the synthesis of chiral bis-phosphines of decahydrophenanthrene series with the use of enantiospecific transformations of maleo-pimaric and fumaropimaric acids. Starting with maleopimaric acid (**I**) whose structure was proved by X-ray diffraction analysis [17] we prepared a known triol **II** [15]. The necessary differentiation of its three hydroxy groups was performed in three stages. First we obtained benzylideneoxy derivative **III** that had in the ^{1}H NMR spectrum a characteristic singlet at 5.21 ppm from the methine proton of the benzylidene group. For protection of the hydroxymethyl group attached to C^8 atom compound **III** was treated with benzyl chloride in the presence of tetrabutyl-ammonium hydrogen sulfate and 50% aqueous NaOH in dichloromethane. This reaction gave benzyl ether **IV** in 86% yield. The attempt to relieve the benzylidene protection in compound **IV** with the use of 5% HCl solution in methanol resulted in a mixture of compounds that was subjected to chromatography to afford the target diol **V** (40%) and pentacyclic diterpene with a furan ring **VI** (50%). A fair yield of diol **V** (80%) was obtained only when the hydrolysis of ether **IV** was carried out by a reagent (PyH^+) (TsO^-) in methanol. In the former reaction the furan ring in compound **VI** arises in the strongly acidic medium through an intramolecular cyclization in diol **V** due to protonation of the ethylidene fragment in keeping with the Markownikoff rule followed by reaction between the intermediate carbocation with the nearest hydroxymethyl group.The structure of compounds **V** and **VI** was established from their NMR spectra**.

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** The carbon atoms in all compounds synthesized are numbered so as is convenient for assignment of the signals in the ^{1}H and ^{13}C NMR spectra. The numbering not always is consistent with the IUPAC rules.

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For instance, in the ^{13}C NMR spectrum of diol **V** the significant signals from atoms C^{16} and C^{17} appear at 65.51 and 61.07 ppm respectively. The comparative analysis of the spectra ^1H NMR and two-dimensional COSY H–H (45°) of compound **VI** revealed that a doublet of doublets at 3.48 ppm belonged to the proton H^{16a} that is coupled with the proton H^{16b} whose signal appeared as a doublet at 3.95 ppm. The proton H^{16a} has also a cross-peak with H^2 proton possessing a signal as doublet of triplets at 2.36 ppm ($J_{16a,2}$ 3.7, $J_{2,1} = J_{2,3}$ 9.5 Hz). To the methylene protons at the C^{17} atom that have distinct cross-peaks with each other belong a triplet at 3.67 ppm ($J_{gem} = J_{17a,1}$ 10.3 Hz) and a doublet of doublets at 3.84 ppm ($J_{17b,1}$ 3.8 Hz).

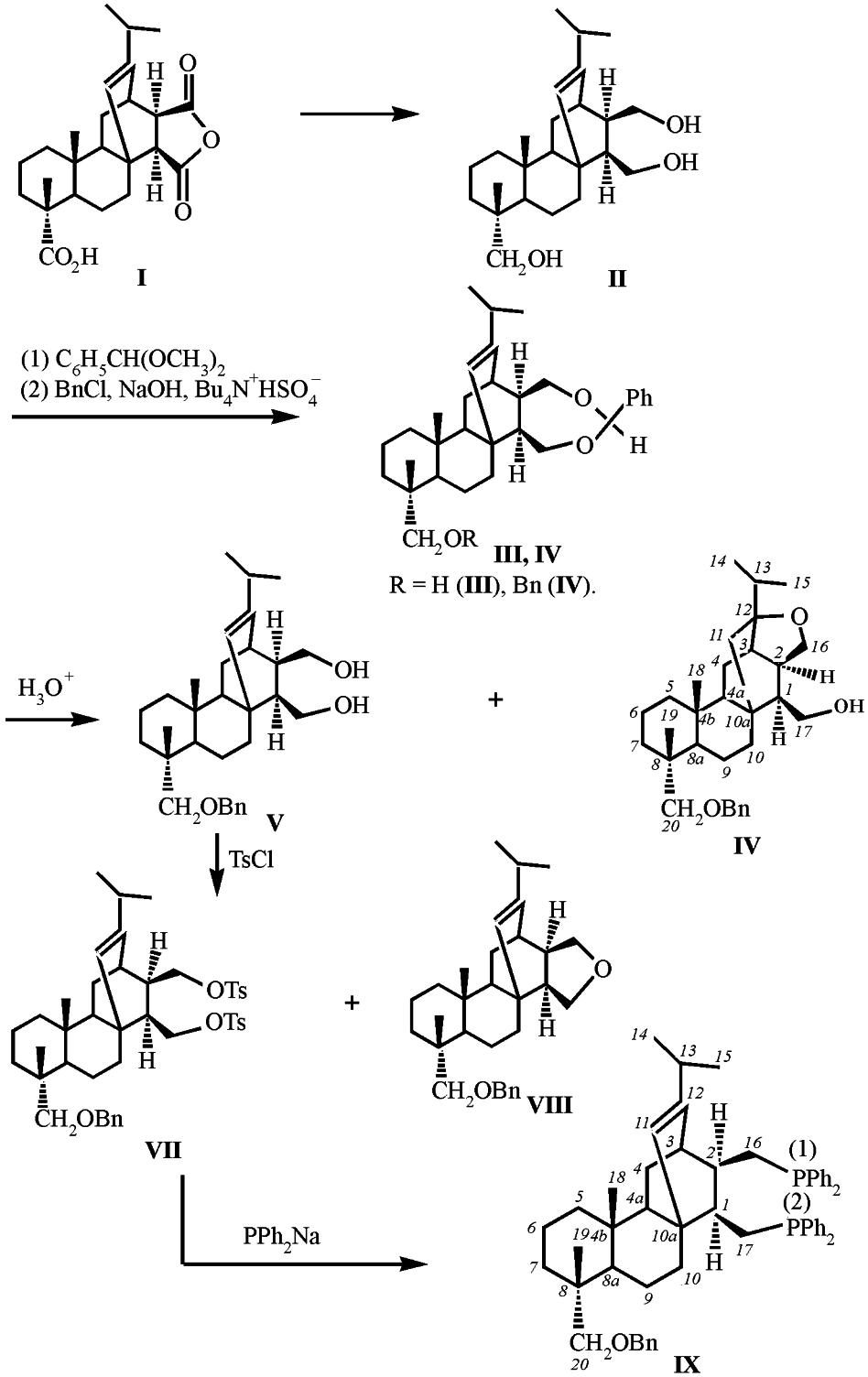
After treating diol **V** with tosyl chloride in pyridine at –20°C we isolated from the reaction mixture key ditosylate **VII** (75%) and furan derivative (**VIII**) as a side product (20%). Note that in reaction carried out at room temperature the yield of compound **VIII** amounted to 80%. The structure of compounds **VII** and **VIII** was confirmed by ^1H and ^{13}C NMR spectra. The furan fragment of molecule **VIII** is revealed in the proton spectrum by four equivalent triplets (δ 3.07–3.86 ppm) from diastereotopic protons $2H^{16}$ and $2H^{17}$ having geminal and vicinal coupling constants equal to 8.5 Hz.

Chiral bisphosphine ligand **IX** was synthesized in 31% yield by treating ditosylate **VII** with sodium diphenylphosphide prepared *in situ* in dioxane [11]. In the ^1H NMR spectrum of bisphosphine **IX** the signals of methylene protons attached to atoms C^{16} and C^{17} appear in the δ 1.90–2.35 ppm range. The multiplets at δ 7.0–7.52 ppm correspond to 25 protons of the five aromatic rings. In the ^{13}C NMR spectrum the doublet at 41.50 ppm ($J_{16,P(1)} = J_{17,P(2)}$ 9 Hz) corresponds to coinciding signals of C^{16} and C^{17} atoms. A quartet at 48.09 ppm ($J_{1,P(1)}$ 12, $J_{1,P(2)}$ 8 Hz) belongs to C^1 atom, and a quartet at 39.26 ppm ($J_{2,P(1)}$ 6, $J_{2,P(2)}$ 14 Hz) originates from C^2 atom. The doublet at 37.71 ppm ($J_{3,P(1)}$ 12 Hz) belongs to C^3, and the doublet at 30.57 ppm ($J_{10,P(2)}$ 14 Hz) is a signal of C^{10a} atom. In the ^{31}P NMR spectrum of bisphosphine **IX** appear two signals in the regions –10.61 and –16.26 ppm. These values are characteristic of P(III) atoms [21]. For compound **IX** we obtained reliable and reproducible values of mp 132–134°C and $[\alpha]_D^{20}$ –55.4° (*c* 1.0, $CHCl_3$). In this connection we should inform that in the previous publication [12] we have reported dissimilar values of mp 102–104°C and $[\alpha]_D^{20}$ –20.3° (*c* 0.7, $CHCl_3$). When the experiments were repeated for quite a number of times we disclosed that the previous data concerned a mixture of bisphosphine **IX** and its oxidized form (up to 15%) [^{31}P NMR spectrum, δ_P, ppm, *J*, Hz: 28.17, 30.05, $P(O)R_3$]. The partial oxidation of the labile ligand with air oxygen readily occurs during the preparation of the samples for measurements, e.g., at the use of insufficiently degassed solvents, or at prolonged measurements.

The synthesis of ligand **XIII**, a diastereomer of bisphosphine **IX** characterized by a formal C_2-symmetry of chiral centers C^1 and C^2, was performed starting with adduct **X** prepared by heating to 180°C diethyl fumarate with benzyl ether of L-pimaric alcohol. The latter was used together with benzyl ethers of related structures that were obtained by treating with benzyl bromide of reduced with $LiAlH_4$ rosin acids mixture which were isolated directly from pine galipot [22]. The structure of compound **X** isolated as individual substance by chromatography was established mainly from the high resolution NMR spectra (500 mHz). In the ^1H NMR spectrum of adduct **X** the doublet at 2.75 ppm belongs to the proton H^1 coupled with the H^2 atom with a coupling constant equal to 5.9 Hz. This value is in agreement with a vicinal coupling constant calculated along Karplus formula for a dihedral angle 131°C; the value is consistent with trans-arrangement of H^1 and H^2 atoms. The signal in the shape of doublet of doublets at 2.55 ppm corresponds to H^2 atom possessing a vicinal constant $J_{2,3}$ 2.7 Hz and a long-range constant $^wJ_{2,4\beta}$ 1.9 Hz [23]. Note that for the similar *ABX*-protons of 1β,2α-isomer of trimethyl fumaropimarate are given the values $J_{1,2}$ 6.0, $J_{2,3}$ 3.0 Hz, and for trimethyl maleopimarate with 1β,2β-configuration of the substituents at C^1 and C^2 atoms these values are $J_{1,2}$ 11.1, $J_{2,3}$ 1.7 Hz [17]. The comparison of our spectral data with those published revealed that the synthesized adduct **X** has 1β,2α-configuration of the ethoxycarbonyl groups at C^1 and C^2 atoms.

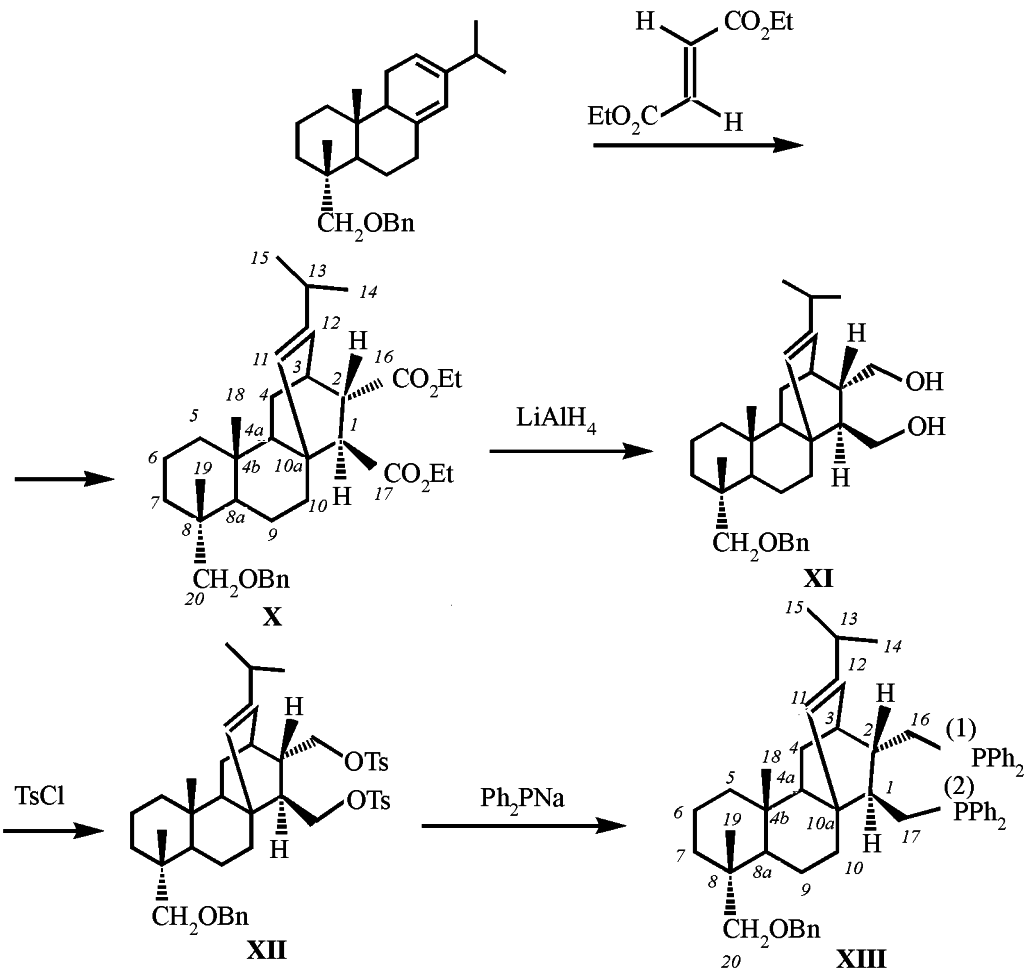
Compound **X** was reduced by $LiAlH_4$ into diol **XI** with quantitative yield. Reaction of diol **XI** with TsCl in pyridine afforded the corresponding tosylate **XII** in 71% yield. The treatment of the latter with sodium diphenylphosphide in dioxane completed the synthesis of chiral bisphosphine **XIII**. Its structure and composition were confirmed by spectral data and elemental analysis. For instance, in the ^{31}P NMR spectrum of the compound are present two characteristic signals at –17.59 and –21.79 ppm belonging to two P(III) atoms in the two diphenylphosphanylmethyl fragments of the molecule.

Scheme 1.



Optically active bisphosphine **XIX** was synthesized from diethyl fumaropimarate **XIV** possessing 1β,2α-configuration of substituents at the C^1 and C^2 centers (according to ^1H NMR data} [17]. The reaction of compound **XIV** with PCl_3 afforded acyl chloride **XV** that without additional purification was converted into amide **XVI** by morpholine action in quantitative yield. The latter was reduced by $LiAlH_4$ in ether to

Scheme 2.



furnish aminodiol **XVII** in 93% yield. In its ^{13}C NMR spectrum appear the following signals: at 69.62 ppm from C^{20} atom of morpholinomethylene fragment, and at 66.63 and 63.95 ppm from C^{16} and C^{17} of hydroxymethylene groups. Tosylation of aminodiol **XVII** resulted in crystalline ditosylate **XVIII** whose structure was proved by X-ray diffraction analysis and NMR spectra. The target ligand **XIX** was prepared in 32% yield by the method used to obtain bisphosphines **IX** and **XIII**. In the ^1H NMR spectrum of compound **XIX** the protons linked to atoms C^{16} and C^{17} undergo upfield shift to the region 2.08–2.41 ppm due to the influence of phosphorus(III) atoms; the latter appear in the ^{31}P NMR spectrum as two characteristic signals at –18.91 and –21.96 ppm.

Reactions of bisphosphines **IX, XIII, XIX** with di-μ-chlorobis(1,5-cyclooctadiene)dirhodium and $NaBF_4$ in dichloromethane furnished complexes **XX–XXII** that were characterized by elemental analyses and ^{31}P NMR spectra. The proton spectra of the complexes contain a set of signals with unclear multiplicity with the chemical shifts close to the proton shifts values in the ^1H NMR spectra of free ligands. We tested the new Rh(I) complexes as catalysts of asymmetric hydrogenation of the unsaturated precursors of N-acetylphenylalanine and its derivatives. At hydrogenation of (*Z*)-*N*-acetylaminocinnamic acid (**XXIII**) in the presence of complex **XX** in ethanol at molar ratio [substrate]/[catalyst] 100 : 1 and hydrogen pressure 1.5 at we obtained in 100% yield optically active *N*-acetylphenylalanine (**XXV**) {optical purity 37%; $[\alpha]_D^{20}$ 17.0° (*c* 1, ethanol), cf. [24]: 46.5° (*c* 1, ethanol)}. The hydrogenation under similar conditions of 3-(3,4-dimethoxyphenyl)-2-acetylamino-2-propenoic acid (**XXIV**) with complex **XX** as catalyst gave with 91% conversion dimethoxyphenylpropanoic acid (**XXVI**) ($[\alpha]_D^{20}$ 15.5°), that was hydrolyzed into *S*-enantiomerically enriched 3-(3,4-dihydroxyphenyl-1)-2-aminopropanoic acid (L-DOPA) (**XXVII**) {optical purity 27% $[\alpha]_D^{20}$ –3.2° (*c* 5, 1 N HCl), cf. [25]: $[\alpha]_D^{20}$ –11.7° (*c* 5.3, 1 N HCl)}. The hydrogenation of aminoacids **XXIII, XXIV** catalyzed

Scheme 3.

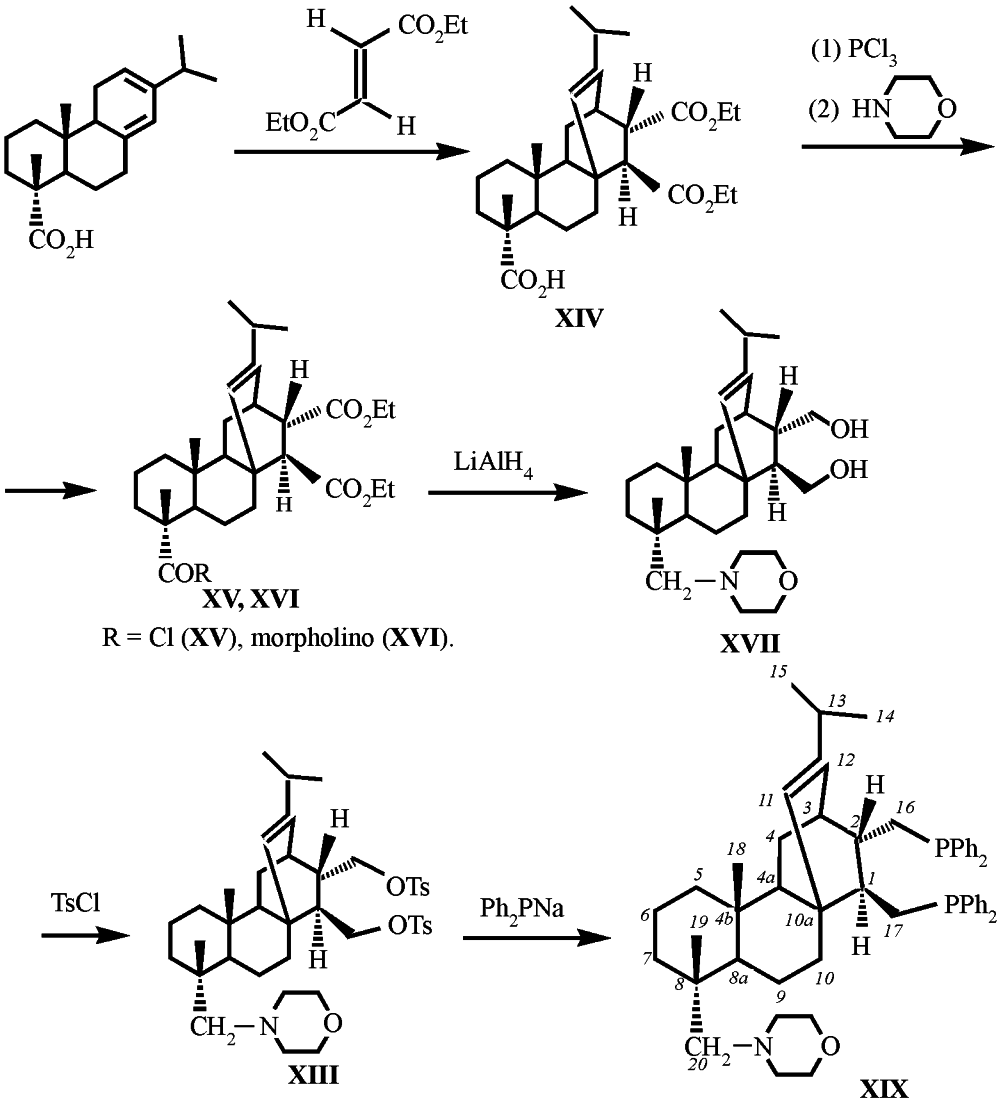


Table 1. Principal parameters and hydrogenation results of unsaturated precursors of *N*-acetylphenylalanine and its derivatives [substrate]/[catalyst] 100 : 1; p_{H_2} 1.5 at, hydrogenation temperature 25°C, process time 3–5 min

Substrate	Catalyst	Conversion, %	Hydrogenation product	Optical purity, %
XXIII	**XX**	100	**XXV**	37 (*S*)
XXIII	**XXI**	100	**XXV**	0
XXIII	**XXII**	100	**XXV**	0
XXIV	**XX**	91	**XXVI**	27 (*S*)
XXIV	**XXI**	100	**XXVI**	0
XXIV	**XXII**	100	**XXVI**	0

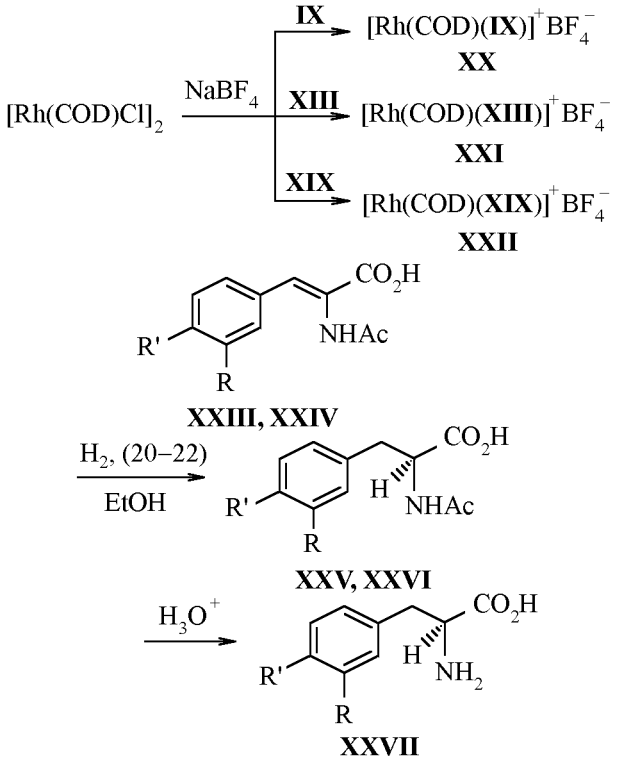
with complexes **XXI, XXII** at molar ratio [substrate]/[catalyst] 100 : 1 and hydrogen pressure 1.5 at is very fast (3–5 min) and afforded in 100% conversion racemic acids **XXV, XXVI** (Table 1).

Thus we for the first time demonstrated the promising aspects of application of the natural diterpene acids as initial compounds for the synthesis of chiral organoelemental ligands for metal complexes suitable as catalysts in homogeneous asymmetric hydrogenation.

EXPERIMENTAL

NMR spectra of compounds **I, II, X, XIV** were registered on spectrometer Bruker DRX 500 in $CDCl_3$ (operating frequencies 500.13 MHz for ^1H,

Scheme 4.



R = R' = H (**XXIII, XXV**), OMe (**XXIV, XXVI**), OH (**XXVII**).

125.77 MHz for ^{13}C spectra). The spectra of the other compounds were recorded on Bruker AC-200 instrument in $CDCl_3$ at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 for ^{31}P spectra. Chemical shifts were measured from chloroform signals used as internal reference (δ_H 7.24 ppm, δ_C 77.10 ppm). The ^{31}P NMR spectra were recorded with heteronuclear decoupling relative to external reference (H_3PO_4). IR spectra were registered on spectrophotometer Specord M-80 from samples as thin films. The optical rotation was measured on polarimeter JASCO model DIP-360. The column chromatography was performed on silica gel l100/160μ. The reactions were monitored by TLC on plates with fixed layer of silica gel (F_{254}, Merck). All operations with ligands **IX, XIV, XIX** and complexes **XX–XXII** were carried out in a flow of dry argon. The solvents were dried and degassed before use. The solvents were degassed in a vacuum by repeated freeze–thaw procedure. The maleopimaric acid used in the study had the following characteristics: $[\alpha]_D^{20}$ −28° (*c* 1.2, $CHCl_3$), cf. [15]: $[\alpha]_D^{20}$ −28.1° (*c* 3.4, $CHCl_3$).

X-ray diffraction study of a single crystal of methyl maleopimarate (**I**) was performed with the use of diffractometer Syntex $P2_1$ (Cu*K*α-irradiation, graphite monochromator). Crystals of compound **I** rhombic, *a* 7.933(2), *b* 11.995(2), *c* 23.361(5) Å, *V* 2222.9(8) $Å^3$, space group $P2_12_12_1$, *Z* 4, $C_{25}H_{34}O_5$, μ 0.682 mm^{-1}, d_{calc} 1.239 $g\,cm^{-3}$. Intensities of 2430 independent reflections with $2\theta < 140°$ were measured, scanning to $\theta/2\theta$. A correction for crystal faces was introduced (transmission 0.61–0.85). The structure was solved by the direct method using SHELX-86 program. The final refinement of parameters was carried out by least-squares procedure in the full-matrix anisotropic approximation (the positions of hydrogen atoms were calculated from geometrical considerations and were not included into refinement) along SHELXL-93 program till wR_2 0.1085, *S* 1.039 for all F^2 (*R* 0.0397 for 2141 $F_0 > 4\sigma$, 272 parameters). Parameter *x* of the absolute structure is equal to −0.05(34). Atom coordinates and equivalent thermal factors of nonhydrogen atoms are presented in Table 2. The structure of the molecule and the absolute configuration of dione **I** are shown in Fig. 1. The structure of the carbocyclic skeleton is as usual, the bond lengths in the skeleton are close to the average values [26]. The orientation of the isopropyl group [torsion angle $C^{15}C^{16}C^{17}C^{19}$ 16.0(4)°] is the same as in the molecule of 4,14b-dimethyl-7,8-dioxo-6a,13-(15-isopropyl)etheno-4-carboxy-1,2,3,4,4a,5,6,6a,6b,7,8,12b,13,14,14a,14b-hexadecahydropicene [27]. Oxolan ring is planar within ±0.025(2) Å. The atoms O^{23} and O^{24} deviate from this plane to different sides by 0.087(4) and −0.021(5) Å respectively. The bond lengths in the oxolan-2,5-dione fragment are consistent within the error of measurement with the average values [C–O 1.387(9), C=O 1.189(6), OC–C 1.502(10) Å] indicated in the Cambridge Structural Databank [28] for 30 structures with σ(C–C) 0.005 Å.

5,9-Dimethyl-16-isopropyl-5,13β,14β-trihydroxymethyltetracyclo[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (II) [15]. $[\alpha]_D^{24}$ 8.1° (*c* 1.5, C_2H_5OH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.68 s (3H, $C^{18}H_3$), 0.79 s (3H, $C^{19}H_3$), 0.89 m (1H, H^5), 1.08 d (3H, $C^{14}H_3$, 6.8), 1.09 d (3H, $C^{15}H_3$, 6.8), 1.20 m (1H, H^4), 1.28 m (2H, H^7, H^{8a}), 1.4 m (6H, H^{4a}, H^5, H^6, H^7, H^9, H^{10}), 1.58 m (2H, H^6, H^9), 1.69 d.d.d (1H, H^4, 12.6, 9.8, 2.8), 1.82 d.t (1H, H^1, $J_{1,2} = J_{1,17B}$ 10, $J_{1,17A}$ 3), 2.08 m (1H, H^{10}), 2.19 m (1H, H^2), 2.27 d.sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.52 m (1H, H^3), 3.08 d (1H, H^{20}, 11.3), 3.29 t (1H, H^{17}, $J_{17A,1} = J_{17A,17B}$ 10), 3.38 d (1H, H^{20}), 3.39 m (1H, H^{16}), 3.70 m (1H, H^{16}), 3.71 d.d (1H, H^{17}), 5.42 s (1H,

Table 2. Coordinates ($\times 10^4$) and equivalent thermal factors (Å^2, $\times 10^3$) of nonhydrogen atoms of methyl maleopimarate (**I**)

Atom	*x/a*	y/b	z/c	U_{eq}
C^{1}	5459(3)	3922(2)	3416(1)	51(1)
C^{2}	5243(4)	2811(3)	3724(1)	60(1)
C^{3}	6901(4)	2173(2)	3734(1)	57(1)
C^{4}	8359(3)	2826(2)	4018(1)	44(1)
C^{5}	8476(3)	4012(2)	3745(1)	38(1)
C^{6}	9869(3)	4732(2)	3994(1)	42(1)
C^{7}	10276(3)	5694(2)	3591(1)	42(1)
C^{8}	8728(3)	6397(2)	3437(1)	36(1)
C^{9}	7176(3)	5654(2)	3274(1)	37(1)
C^{10}	6798(3)	4674(2)	3698(1)	41(1)
C^{11}	5643(3)	6411(2)	3151(1)	47(1)
C^{12}	6150(3)	7649(2)	3194(1)	44(1)
C^{13}	7545(3)	7835(2)	2747(1)	45(1)
C^{14}	9063(3)	7098(2)	2884(1)	43(1)
C^{15}	8224(3)	7227(2)	3892(1)	39(1)
C^{16}	6915(3)	7870(2)	3777(1)	41(1)
C^{17}	6138(4)	8747(2)	4161(1)	55(1)
C^{18}	4440(4)	8331(3)	4382(2)	81(1)
C^{19}	7248(5)	9094(3)	4654(1)	78(1)
C^{20}	6114(4)	5102(2)	4276(1)	52(1)
C^{21}	8187(4)	2821(3)	4675(1)	58(1)
C^{22}	9936(4)	2193(2)	3842(1)	47(1)
C^{23}	8200(4)	9005(2)	2772(1)	53(1)
C^{24}	10506(4)	7906(3)	2937(1)	56(1)
C^{25}	11535(4)	562(3)	4000(2)	73(1)
O^{22}	10864(3)	2417(2)	3455(1)	67(1)
O^{23},	9926(3)	8992(2)	2864(1)	62(1)
$O^{23'}$	7476(3)	9866(2)	2728(1)	79(1)
O^{24}	11953(3)	7761(2)	3025(1)	90(1)
O^{25}	10177(3)	1281(2)	4166(1)	67(1)

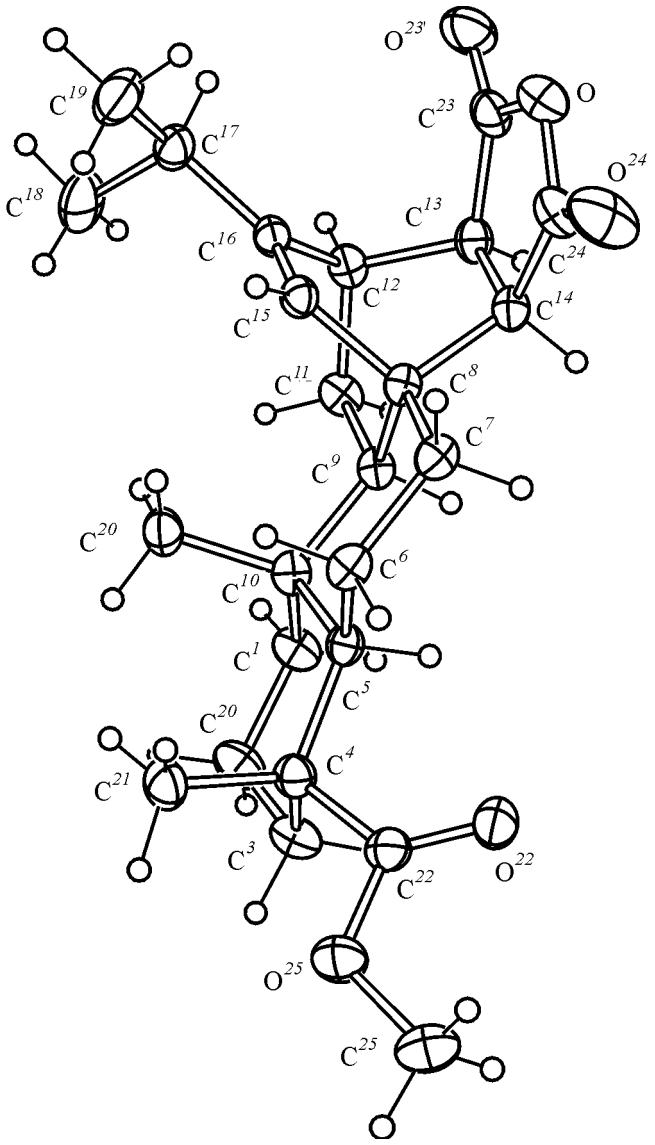


Fig. 1. Crystalline structure of compound **I** according to X-ray diffraction analysis.

H^{11}). ^{13}C NMR spectrum, δ_C, ppm: 16.7 (C^{18}), 18.3 (C^{19}), 18.4 (C^{6}), 20.5 (C^{9}), 20.9 (C^{15}), 21.7 (C^{14}), 31.3 (C^{4}), 34.4 (C^{13}), 36.4 (C^{7}), 37.4 (C^{10}), 38.2 (C^{8}), 38.5 (C^{3}), 39.1 (C^{4b}), 40.1 (C^{5}), 41.1 (C^{10a}), 46.5 (C^{2}), 48.9 (C^{8a}), 55.5 (C^{1}), 56.6 (C^{4a}), 61.2 (C^{17}), 65.2 (C^{16}), 72.1 (C^{20}), 126.2 (C^{11}), 148.8 (C^{12}).

13α,19α-5-Hydroxymethyl-5,9-dimethyl-21-isopropyl-16-phenyl-15,17-dioxapentacyclo-[10.7.2.$0^{1,10}$.$0^{4,9}$.$0^{13,19}$]heneicos-20-ene (III). To a solution of 1.4 g (3.7 mmol) of triol **II** in 40 ml of dichloromethane was added 0.85 g (5.6 mmol) of benzaldehyde dimethylacetal and 0.05 g (0.29 mmol of *p*-toluenesulfonic acid. The reaction mixture was stirred at room temperature for 1 h, washed with %5 solution of $NaHCO_3$ (2 × 50 ml), with water (2 × 50 ml), the organic layer was separated, dried on $MgSO_4$, evaporated, and the residue was crystallized from ethyl acetate. We obtained 1.2 g (70%) of compound **III**, mp 168–170°C, $[\alpha]_D^{20}$ 11.8° (*c* 2.0, $CHCl_3$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.60 s (3H, $C^{18}H_3$), 0.75 s (3H, $C^{19}H_3$), 0.85 m (1H, H^{5}), 1.04 d (3H, $C^{14}H_3$, 6.8), 1.07 d (3H, $C^{15}H_3$, 6.8), 1.10–1.60 m (11H, H^{4}, H^{4a}, H^{5}, $C^{6}H_2$, $C^{7}H_2$, H^{8a}, $C^{9}H_2$, H^{10}), 1.64 d.d.d (1H, H^{4}, 12.6, 9.8, 2.8), 1.94 d.d (1H, H^{10}, 8.8, 2.5), 2.11 d.d.d (1H, H^{1}, $J_{1,2}$ 8.3, $J_{1,17A}$ 12.3, $J_{1,17B}$ 4), 2.23 d.sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.23 m (1H, H^{3}), 2.46 d (1H, H^{2}, $J_{2,3}$ 2.5), 3.11 d (1H, H^{20}, 10.9), 3.49 d (1H, H^{20}), 3.29 t (2H, H^{16}, H^{17}, $J_{17A,1}$ = $J_{17A,17B}$ = $J_{16A,2}$ = $J_{16A,16B}$

12.3), 3.98 d.d (1H, H^{17}, $J_{17B,1}$ 4), 4.23 d.d (1H, H^{16}, $J_{16B,2}$ 4), 5.21 s (1H, C<u>H</u>Ph), 5.42 s (1H, H^{11}), 7.26–7.45 m (5H, C_6H_5). ^{13}C NMR spectrum (δ_C, ppm): 16.13 (C^{18}), 17.33 (C^6), 17.78 (C^{19}), 19.34 (C^9), 20.49 (C^{15}), 21.21 (C^{14}), 29.67 (C^4), 33.34 (C^{13}), 35.30 (C^7), 35.97 (C^{10}), 36.92 (C^3), 37.28 (C^8), 38.04 (C^{4b}), 38.68 (C^5), 39.80 (C^{10a}), 45.22 (C^2), 48.13 (C^{8a}), 53.19 (C^1), 55.23 (C^{4a}), 71.87 (C^{17}), 72.28 (C^{16}), 74.70 (C^{20}), 107.40 (<u>C</u>HPh), 124.79 (C^{11}), 126.00, 128.25, 128.46, 139.19 (C_6H_5), 147.55 (C^{12}).

13α,19α-5-Benzyloxymethyl-5,9-dimethyl-21-isopropyl-16-phenyl-15,17-dioxapentacyclo-[10.7.2.$0^{1,10}$.$0^{4,9}$.$0^{13,19}$]heneicos-20-ene (IV). To a solution of 4.6 g (10 mmol) of compound **III** in 5 ml of dichloromethane was added 5 ml of 50% solution of NaOH, 0.17 g (0.5 mmol) of tetrabutylammonium hydrogen sulfate, and 7 ml (61 mmol) of benzyl chloride. The reaction mixture was vigorously stirred at 45–50°C for 5 h, then washed with water till pH 7, the organic layer was separated, dried on $MgSO_4$, evaporated, and the residue was subjected to chromatography (SiO_2, eluent hexane–ethyl acetate, 7:3). We obtained 4.8 g (86%) of compound **IV**, $[\alpha]_D^{20}$ –77.9° (*c* 1.8, $CHCl_3$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.58 s (3H, $C^{18}H_3$), 0.74 s (3H, $C^{19}H_3$), 0.86 m (1H, H^5), 1.03 d (3H, $C^{14}H_3$, 6.8), 1.07 d (3H, $C^{15}H_3$, 6.8), 1.15 m (1H, H^4), 1.27–1.42 m (8H, H^{4a}, H^5, H^6, C^7H_2, H^{8a}, H^9, H^{10}), 1.54 m (2H, H^6, H^9), 1.64 m (1H, H^4), 1.91 m (1H, H^{10}), 2.12 d.d.d (1H, H^1, $J_{1,2}$ 8.3, $J_{1,17A}$ 12.3, $J_{1,17B}$ 4), 2.22 d.sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.29 m (1H, H^3), 2.46 d.d.d.d (1H, H^2, $J_{2,3}$ 2.5), 2.90 d (1H, H^{20}, 8.9), 3.19 d (1H, H^{20}), 3.48 t (2H, H^{16}, H^{17}, $J_{17A,1}$ = $J_{17A,17B}$ = $J_{16A,2}$ = $J_{16A,16B}$ 12.3), 3.98 d.d (1H, H^{16}, $J_{16B,2}$ 4), 4.25 d.d (1H, H^{17}, $J_{17B,1}$ 4), 4.45 d (1H, C<u>H</u>$_2$Ph), 4.54 d (1H, C<u>H</u>$_2$Ph, 12.5), 5.21 s (C<u>H</u>Ph), 5.41 s (1H, H^{11}), 7.25–7.46 m (10H, $2C_6H_5$). ^{13}C NMR spectrum (δ_C, ppm): 16.15 (C^{18}), 17.43 (C^6), 18.26 (C^{19}), 19.37 (C^9), 20.52 (C^{15}), 21.24 (C^{14}), 29.70 (C^4), 33.36 (C^{13}), 36.08 (C^7, C^{10}), 36.93 (C^3), 37.01 (C^8), 38.05 (C^{4b}), 38.63 (C^5), 39.82 (C^{10a}), 45.24 (C^2), 48.19 (C^{8a}), 53.24 (C^1), 55.13 (C^{4a}), 71.89 (C^{17}), 73.15 (C^{16}), 74.74 (C^{20}), 79.59 (<u>C</u>H$_2$Ph), 107.42 (<u>C</u>HPh), 124.91 (C^{11}), 126.00, 127.47, 128.26, 128.34, 128.46, 139.09, 139.56 ($2C_6H_5$), 147.46 (C^{12}).

5-Benzyloxymethyl-13β,14β-dihydroxymethyl-5,9-dimethyl-16-isopropyltetracyclo[10.2.2.$0^{1,0}$.$0^{4,9}$]-hexadec-15-ene (V). To a solution of 0.55 g (1 mmol) of compound **IV** in 10 ml of methanol was added 0.03 g (0.1 mmol) of pyridinium *p*-toluenesulfonate, and the mixture was stirred at 40°C for 3 h. Then the reaction mixture was evaporated, and the residue was subjected to chromatography (SiO_2, eluent hexane–ethyl acetate, 1:1). We obtained 0.38 g (80%) of compound **V**, $[\alpha]_D^{20}$ 5.0° (*c* 1.3, $CHCl_3$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.55 s (3H, $C^{18}H_3$), 0.73 s (3H, $C^{19}H_3$), 0.85 m (1H, H^5), 0.97 d (3H, $C^{14}H_3$, 6.8), 0.98 d (3H, $C^{15}H_3$, 6.8), 1.07 m (1H, H^4), 1.19–1.52 m (10H, H^{4a}, H^5, C^6H_2, C^7H_2, H^{8a}, C^9H_2, H^{10}), 1.62 d.d.d (1H, H^4, 12.6, 9.8, 2.8), 1.83 d.t (1H, H^1, $J_{1,2}$ = = $J_{1,17B}$ 10.5, $J_{1,17A}$ 2.2), 1.94 d.d (1H, H^{10}, 9, 2), 2.14–2.20 m (2H, H^2, H^{13}), 2.31 m (1H, H^3), 2.91 d (1H, H^{20}, 8.9), 3.18 d (1H, H^{20}), 3.43 t (1H, H^{17}, $J_{17A,1}$ = $J_{17A,17B}$ 10.5), 3.45–3.57 m (2H, $C^{16}H_2$), 3.75 d.d (1H, H^{17}), 4.45 d (1H, C<u>H</u>$_2$Ph, 12.5), 4.54 d (1H, C<u>H</u>$_2$Ph), 5.31 s (1H, H^{11}), 7.26–7.39 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 16.00 (C^{18}), 17.37 (C^6), 18.19 (C^{19}), 19.51 (C^9), 20.48 (C^{15}), 21.16 (C^{14}), 30.28 (C^4), 33.16 (C^{13}), 36.01 (C^7), 36.30 (C^{10}), 36.95 (C^8), 37.96 (C^{4b}), 38.17 (C^3), 38.63 (C^5), 39.91 (C^{10a}), 45.59 (C^2), 48.16 (C^{8a}), 53.96 (C^1), 54.91 (C^{4a}), 61.07 (C^{17}), 65.51 (C^{16}), 73.12 (C^{20}), 79.65 (<u>C</u>H$_2$Ph), 124.86 (C^{11}), 127.39, 128.31, 138.99 (C_6H_5), 147.61 (C^{12}).

16α,17α-5-Benzyloxymethyl-17-hydroxymethyl-5,9-dimethyl-13-isopropyl-14-oxapentacyclo [11.4.1.$0^{1,10}$.$0^{4,9}$.$0^{12,17}$]octadecane (VI). To a solution of 0.26 g (0.47 mmol) of compound **IV** in 5 ml of methanol at 0°C was added 0.5 ml of 5% solution of HCl in methanol, and the mixture was stirred at 20°C for 1 h, evaporated, the residue was dissolved in 5 ml of ethyl acetate, washed with saturated solution of $NaHCO_3$ (2 × 5 ml), with water (5 ml), dried on Na_2SO_4, evaporated, the residue was subjected to chromatography (SiO_2, eluent hexane–ethyl acetate, 1:1). We obtained 0.09 g (40%) of diol **V** and 0.11 g (50%) of compound **VI**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.74 s (3H, $C^{18}H_3$), 0.85 m (1H, H^5), 0.91 s (3H, $C^{19}H_3$), 0.92 d (3H, $C^{14}H_3$, 6.8), 0.97 d (3H, $C^{15}H_3$, 6.8), 1.10–1.67 m (13H, H^4, H^{4a}, H^5, C^6H_2, C^7H_2, H^{8a}, C^9H_2, H^{10}, $C^{11}H_2$, H^{13}), 1.76 m (2H, H^1, H^4), 1.89 d.d (1H, H^{10}, 11, 1.8), 2.07 m(1H, H^3), 2.36 d.t (1H, H^2, $J_{2,1}$ = $J_{2,3}$ 9.5, $J_{2,16A}$ 3.7, $J_{2,16B}$ 0), 2.89 d (1H, H^{20}, 8.9), 3.20 d (1H, H^{20}), 3.48 d.d (1H, H^{16}, $J_{16A,16B}$ 8.4), 3.67 t (1H, H^{17}, $J_{17A,1}$ = $J_{17A,17B}$ 10.3), 3.84 d.d (1H, H^{17}, $J_{17B,1}$ 3.8), 3.95 d (1H, H^{16}), 4.45 d (1H, C<u>H</u>$_2$Ph, 12.5), 4.54 d (1H, C<u>H</u>$_2$Ph), 7.27–7.39 m (5H, C_6H_5). ^{13}C NMR spectrum (δ_C, ppm): 15.79 (C^{18}), 16.59

(C^{19}), 16.88 (C^{15}), 17.48 (C^{6}), 18.09 (C^{14}), 18.82 (C^{9}), 32.63 (C^{13}), 32.97 (C^{4}), 35.94 (C^{7}), 36.98 (C^{10}), 37.41 (C^{8}), 37.99 (C^{4b}), 38.06 (C^{3}), 39.17 (C^{5}), 39.52 (C^{2}), 41.46 (C^{10a}), 48.96 (C^{8a}), 51.86 (C^{1}), 54.77 (C^{4a}), 60.87 (C^{17}), 67.88 (C^{16}), 73.14 (C^{20}), 79.41 ($\underline{C}H_2Ph$), 84.41 (C^{12}), 127.47, 128.33, 139.03 (C_6H_5).

5-Benzyloxymethyl-5,9-dimethyl-13β,14β-ditosyloxymethyl-16-isopropyltetracyclo[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (VII) and 5-benzyloxymethyl-5,9-dimethyl-19-isopropyl-15-oxapentacyclo[10.5.2.0^{1,10}.0^{4,9}.0^{13,17}]nonadec-18-ene (VIII). To a solution of 0.27 g (0.8 mmol) of diol **V** in 2 ml of pyridine at –20°C in a flow of argon was added by portions 0.22 g (1.2 mmol) of tosyl chloride, and stirring at –20°C continued for 24 h. Then was added 10 ml of ice water and 2 ml of ether, the separated viscous oily substance was ground with a glass stick till crystals formed. The crystals were filtered off, washed with ice water, with cold ether, and dried in a high vacuum at 20°C, We obtained 0.34 g (75%) of ditosylate **VII**. From the water-ether filtrate the organic products were extracted into ethyl acetate (2× 10 ml), the combined extracts were dried on Na_2SO_4, evaporated, the residue was subjected to chromatography (SiO_2, eluent hexane–ethyl acetate, 7 : 3). We obtained 0.11 g (20%) of compound **VIII**. The reaction at room temperature in 3 h afforded 15% of compound **VII** and 80% of compound **VIII**.

Compound (VII). mp 60–62°C, $[\alpha]_D^{20}$ +14.3° (*c* 4.7, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.45 s (3H, $C^{18}H_3$), 0.70 s (3H, $C^{19}H_3$), 0.80 m (1H, H^5), 0.82 d (3H, $C^{14}H_3$, 6.8), 0.85 d (3H, $C^{15}H_3$, 6.8), 1.00–1.55 m (12H, C^4H_2, H^{4a}, H^5, C^6H_2, C^7H_2, H^{8a}, C^9H_2, H^{10}), 1.79 m (3H, H^1, H^2, H^{10}), 2.13 m (1H, H^{13}), 2.45 s (3H, $CH_3C_6H_4$), 2.46 s (3H, $CH_3C_6H_4$), 2.58 m (1H, H^3), 2.86 d (1H, H^{20}, 8.9), 3.16 d (1H, H^{20}), 3.43 t (1H, H^{17}, $J_{17A,1}$ = $J_{17A,17B}$ 9.5), 3.58 t (1H, H^{16}, $J_{16A,2}$ = $J_{16A,16B}$ 8), 4.04 d.d (1H, H^{16}, $J_{16B,2}$ 2.5), 4.12 d.d (1H, H^{17}, $J_{17B,1}$ 4.4), 4.43 d (1H, CH_2Ph, 12.5), 4.52 d (1H, CH_2Ph), 5.28 s (1H, H^{11}), 7.30–7.78 m (13H, C_6H_5, $2C_6H_4$). ^{13}C NMR spectrum, δ_C, ppm: 15.92 (C^{18}), 17.25 (C^6), 18.15 (C^{19}), 19.08 (C^9), 19.77 (C^{15}), 20.92 (C^{14}), 21.74 ($2CH_3C_6H_4$), 28.54 (C^4), 32.94 (C^{13}), 35.11 (C^3), 35.27 (C^7), 35.87 (C^{10}), 36.88 (C^8), 37.96 (C^{4b}), 38.37 (C^5), 39.75 (C^{10a}), 41.08 (C^2), 47.91 (C^{8a}), 49.27 (C^1), 55.06 (C^{4a}), 68.34 (C^{17}), 70.87 (C^{16}), 73.06 (C^{20}), 79.32 (CH_2Ph), 125.11 (C^{11}), 127.44, 127.85, 128.05, 128.29, 129.90, 129.96, 132.62, 132.73, 138.94, 144.81, 144.96 ($CH_2\underline{C}_6H_5$, $2CH_3\underline{C}_6H_4$), 147.00 (C^{12}).

Compound (VIII). $[\alpha]_D^{20}$ +10.2° (*c* 2.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.59 s 3H, $C^{18}H_3$), 0.74 s (3H, $C^{19}H_3$), 0.85 m (1H, H^5), 1.01 d (3H, $C^{14}H_3$, 6.8), 1.04 d (3H, $C^{15}H_3$, 6.8), 1.11 m (1H, H^4), 1.24–1.42 m (8H, H^{4a}, H^5, H^6, C^7H_2, H^{8a}, H^9, H^{10}), 1.47–1.65 m (3H, H^4, H^6, H^9), 1.78 d.d (1H, H^{10}, 8.8, 2.5), 2.05 d.t (1H, H^1, $J_{1,2}$ 8.2, $J_{1,17B}$ = $J_{1,17A}$ 8.5), 2.15 d. sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.38 d.d.t (2H, H^3, H^2, $J_{2,3}$ 2.6, $J_{2,16B}$ = $J_{2,16A}$ 8.5), 2.86 d (1H, H^{20}, 8.9), 3.07 t (1H, H^{17}, $J_{17A,17B}$ 8.5), 3.19 d (1H, H^{20}), 3.21 t (1H, H^{16}, 8.5), 3.76 t (1H, H^{16}), 3.86 t (1H, H^{17}), 4.44 d (1H, CH_2Ph, 12.5), 4.53 d (1H, CH_2Ph), 5.37 s (1H, H^{11}), 7.25–7.39 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 15.30 (C^{18}), 16.17 (C^6), 17.42 (C^{19}), 18.17 (C^9), 18.97 (C^{15}), 20.14 (C^{14}), 28.66 (C^4), 33.61 (C^{13}), 36.01 (C^7), 36.11 (C^{10}), 37.04 (C^3), 37.04 (C^8), 37.73 (C^{4b}), 38.78 (C^5), 39.39 (C^{10a}), 45.70 (C^2), 48.54 (C^{8a}), 54.90 (C^1), 54.90 (C^{4a}), 70.75 (C^{17}), 72.45 (C^{16}), 73.09 (C^{20}), 79.61 (CH_2Ph), 125.22 (C^{11}), 127.33, 128.23, 139.03 (C_6H_5), 147.26 (C^{12}).

5-Benzyloxymethyl-13β,14β-bis(diphenylphosphanylmethyl)-5,9-dimethyl-16-isopropyltetracyclo[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (IX). A mixture of 9 ml of dioxane, 0.69 g (30 mmol) of sodium metal, and 1.29 g (5.8 mmol) of diphenylchlorophosphine were refluxed at vigorous stirring in an argon flow for 5 h. The orange dispersion obtained was cooled to room temperature, and 2 g (2.6 mmol) of ditosylate **VIII** was added thereto. The reaction mixture was stirred for 2 h, and a dispersion of 30 g of Al_2O_3 in 70 ml of anhydrous benzene was added. The mixture was filtered, the filtrate was evaporated, the viscous residue containing ligand **IX** was ground in anhydrous ethanol till crystals formation. The solvent was decanted, and the precipitate was recrystallized from methanol. We obtained 0.65 g (31%) of compound **IX**, mp 132–134°C, R_f 0.70 (benzene–ethyl acetate, 9 : 1), $[\alpha]_D^{20}$ –55.4° (*c* 1.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.58 s (3H, $C^{18}H_3$), 0.73 s (3H, $C^{19}H_3$), 0.86–2.32 m (21H, H^1, H^2, H^3, C^4H_2, H^{4a}, C^5H_2, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$, $C^{16}H_2$, $C^{17}H_2$), 1.11 d (3H, $C^{14}H_3$, 6.8), 1.12 d (3H, $C^{15}H_3$, 6.8), 2.49 d.sept. (1H, H^{13}, $J_{13,1}$ 1.3), 2.87 d (1H, H^{20}, 8.9), 3.18 d (1H, H^{20}), 4.44 d (1H, CH_2Ph, 12.5), 4.52 d (1H, CH_2Ph), 5.46 s (1H, H^{11}), 7.25–7.50 m (25H, $4C_6H_5$). ^{13}C NMR spectrum, δ_C, ppm

(*J*, Hz): 15.95 s (C^{18}), 17.24 s (C^{6}), 18.05 s (C^{19}), 19.36 s (C^{9}), 20.32 s (C^{15}), 21.31 s (C^{14}), 29.66 s (C^{4}), 30.57 d (C^{10a}, $J_{10A,P(2)}$ 14), 33.49 s (C^{13}), 35.81 s (C^{7}), 36.35 s (C^{10}), 36.81 s (C^{8}), 37.71 d (C^{3}, $J_{3,P(1)}$ 12), 37.85 s (C^{4b}), 38.31 s (C^{5}), 39.26 q (C^{2}, $J_{2,P(1)}$ 6, $J_{2,P(2)}$ 14), 41.50 d (C^{16}, C^{17}, $J_{16,P(1)} = J_{17,P(2)}$ 9), 47.85 s (C^{8a}), 48.09 q (C^{1}, $J_{1,P(2)}$ 8, $J_{1,P(1)}$ 12), 55.06 s (C^{4a}), 72.90 s (C^{20}), 79.29 s (CH_2Ph), 124.83 s (C^{11}), 127.14, 128.11, 139.00 3 s ($CH_2C_6H_5$), 127.83, 128.73 2d [$8C_{ortho}$, $4(PC_6H_5)$, $J_{C,P}$ 9], 128.24, 128.38 2d [$4C_{para}$, $4(PC_6H_5)$, $J_{C,P}$ 7], 132.15, 133.70, 133.78, 133.82 4d [$8C_{meta}$, $4(PC_6H_5)$, $J_{C,P}$ 19), 137.40, 138.22, 140.25, 140.51 4d [$4C_{opso}$, $4(PC_6H_5)$, $J_{C,P}$ 14], 148.04 s (C^{12}). ^{31}P NMR spectrum, δ_P, ppm: –10.61, –16.26. Found, %: C 82.18; H 7.92. $C_{45}H_{64}OP_2$. Calculated, %: C 82.26; H 8.03.

5-Benzyloxymethyl-5,9-dimethyl-13β,14β-diethoxycarbonyl-16-isopropyltetracyclo-[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (X). A mixture of resin alcohols (20 g), 10 g of sodium hydride, and 18 g of benzyl bromide in 200 ml of THF were stirred for 5 days. Then 30 ml of methanol was added, the mixture was evaporated, the residue was dissolved in 300 ml of ether, washed with 10% solution of HCl (2 × 100 ml) and with water (2 × 50 ml). The organic layer was dried with Na_2SO_4, evaporated, and the residue was subjected to chromatography (SiO_2, hexane–ethyl acetate, 7 : 3). We obtained 22 g of a mixture of benzyl ethers of resin alcohols. 7 g of this mixture and 7 g of diethyl fumarate was heated for 4 h to 180°c, the excess diethyl fumarate was distilled off in a vacuum, and the residue was subjected to chromatography (SiO_2, hexane). We obtained 3.2 g (31%) of compound **X**, oily substance, $[\alpha]_D^{29}$ 27.0° (*c* 1.0, $CHCl_3$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.57 s (3H, $C^{18}H_3$), 0.72 s (3H, $C^{19}H_3$), 0.83 m (1H, H^5), 1.06 d (6H, $C^{14}H_3$, $C^{15}H_3$, 6.8), 1.25 m (6H, $2(OCH_2CH_3)$), 1.29–1.79 m (13H, C^4H_2, H^{4a}, H^5, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$), 2.39 d.sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.55 d.d.d (1H, H^2, $J_{2,1}$ 5.9, $J_{2,3}$ 2.7, $J_{2,4\beta}$ 2.7), 2.75 d (1H, H^1, $J_{1,2}$ 5.9), 2.85 q.d (1H, H^3, $J_{3,2}$ 2.7, $J_{3,4\alpha} = J_{3,4\beta}$ 2.8, $J_{3,11}$ 1.5), 2.89 d (1H, H^{20}, 9), 3.17 d (1H, H^{20}), 4.04 q (2H, OCH_2CH_3, 7), 4.13 q (2H, OCH_2CH_3), 4.42 d (1H, CH_2Ph, 9), 4.52 d (1H, CH_2Ph), 5.36 s (1H, H^{11}), 7.24–7.33 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 14.14 (C^{18}), 16.07 (C^{19}), 17.26 (C^6), 17.96, 19.25 (C^{14}, C^{15}), 19.11 (C^9), 20.54 (C^4), 32.64 (C^{13}), 34.79 (C^{10}), 35.92 (C^3), 36.06 (C^7), 37.01 (C^{4b}), 38.07 (C^5), 38.28 (C^{10a}), 41.05 (C^8), 48.72 (C^2, C^{8a}), 54.59 (C^1, C^{4a}), 59.79, 60.34 ($2CH_2CH_3$), 73.16 (C^{20}), 79.93 (CH_2Ph), 124.69 (C^{11}), 127.13, 127.25, 128.07, 139.04 (C_6H_5), 147.85 (C^{12}), 173.51, 173.98 (2CO).

5-Benzyloxymethyl-13β,14β-dihydroxymethyl-5,9-dimethyl-16-isopropyltetracyclo-[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (XI). To a suspension of 0.4 g (10.5 mmol) of $LiAlH_4$ in 20 ml of ether was added dropwise at 20°C a solution of 3.1 g (5.6 mmol) of compound **X** in 20 ml of ether, The reaction mixture was boiled for 4 h, 50 ml of ethyl acetate was added, then 50 ml of 1 N HCl. The organic layer was separated, washed with water, dried with Na_2SO_4, evaporated, and the residue was subjected to chromatography (SiO_2, chloroform). We obtained 2.5 g (95%) of compound **XI**, oily substance, $[\alpha]_D^{29}$ –2.2° (*c* 1.0, $CHCl_3$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.57 s (3H, $C^{18}H_3$), 0.72 s (3H, $C^{19}H_3$), 0.86 m (1H, H^5), 0.97 d (6H, $C^{14}H_3$, $C^{15}H_3$, 6.8), 1.10–1.90 m (14H, H^2, C^4H_2, H^{4a}, H^5, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$), 2.00 m (1H, H^1), 2.29 d.sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.39 m (1H, H^3), 2.90 m (1H, H^{16}), 2.93 d (1H, H^{20}, 9), 3.15 d (1H, H^{20}), 3.59 t (1H, H^{17}, $J_{17A,1} = J_{17A,17B}$ 10), 3.60 m (2H, H^{16}, H^{17}), 4.41 d (1H, CH_2Ph, 12.5), 4.52 d (1H, CH_2Ph), 5.28 s (1H, H^{11}), 7.31–7.28 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 15.96 (C^{18}), 17.35 (C^6), 18.06 (C^{19}), 19.34 (C^9), 20.62 (C^{14}, C^{15}), 23.36 (C^4), 32.63 (C^{13}), 35.60 (C^3), 35.65 (C^{10}), 36.14 (C^7), 37.05 (C^{4b}), 37.96 (C^5), 38.74 (C^{10a}), 40.03 (C^8), 44.90 (C^2), 48.49 (C^{8a}), 55.53 (C^1), 55.82 (C^{4a}), 64.35 (C^{17}), 66.98 (C^{16}), 73.24 (C^{20}), 79.98 (CH_2Ph), 124.41 (C^{11}), 127.21, 127.30, 128.14, 139.10 (C_6H_5), 150.07 (C^{12}).

5-Benzyloxymethyl-13β,14β-ditosyloxymethyl-5,9-dimethyl-16-isopropyltetracyclo-[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (XII). To a mixture of 3.26 g (7 mmol) of diol **XI** and 20 ml of pyridine cooled to –20°C was added by portions in an argon flow 4 g (21 mmol) of tosyl chloride, and the stirring at this temperature continued for 16 h. The reaction mixtures was poured into 100 ml of water cooled to 5°C, the separated oily substance was extracted with ether (3 × 60 ml). The combined extracts were dried on Na_2SO_4, evaporated, and the residue was subjected to chromatography (SiO_2, hexane–ethyl acetate, 7 : 3). We obtained 4 g (74%) of oily compound **XII**, $[\alpha]_D^{29}$ 11.8° (*c* 1.0, $CHCl_3$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.50 s (3H, $C^{18}H_3$), 0.67 s (3H, $C^{19}H_3$), 0.73 m (1H, H^5), 0.82 d

(3H, $C^{14}H_3$, 6.8), 0.84 d (3H, $C^{15}H_3$, 6.8), 1.05–1.75 m (16H, H^1, H^2, H^3, C^4H_2, H^{4a}, H^5, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$), 2.13 d.sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.40 s (3H, $CH_3C_6H_4$), 2.41 s (3H, $CH_3C_6H_4$), 2.83 d (1H, H^{20}, 9), 3.13 d (1H, H^{20}), 3.28 t (1H, H^{16}, $J_{16A,2}$ = = $J_{16A,16B}$ 10), 3.73 t (1H, H^{17}, $J_{17A,1}$ = $J_{17A,17B}$ 10), 4.02 m (2H, H^{16}, H^{17}), 4.39 d (1H, CH_2Ph, 12.5), 4.50 d (1H, CH_2Ph), 5.16 s (1H, H^{11}), 7.24–7.82 m (13H, C_6H_5, $2C_6H_4$). ^{13}C NMR spectrum, δ_C, ppm: 15.71 (C^{18}), 17.21 (C^6), 17.99 (C^{19}), 18.96 (C^9), 20.36, 20.48 (C^{14}, C^{15}), 21.36 ($2CH_3C_6H_4$), 21.82 (C^4), 32.44 (C^{13}), 33.18 (C^3), 35.09 (C^{10}), 35.95 (C^7), 36.90 (C^{4b}), 37.64 (C^5), 38.51 (C^{10a}), 39.75 (C^8), 41.14 (C^2), 48.23 (C^{8a}), 49.85 (C^1), 54.95 (C^{4a}), 71.60 (C^{17}), 72.65 (C^{16}), 73.17 (C^{20}), 79.67 (CH_2Ph), 123.97 (C^{11}), 127.24, 127.32, 127.61, 127.72, 128.13, 129.68, 129.75, 133.20, 133.38, 138.94, 144.54 (C_6H_5, $2C_6H_4$), 149.96 (C^{12}). Found, %: C 69.81; H 7.48. $C_{45}H_{58}O_7S_2$. Calculated, %: C 69.73; H 7.54.

5-Benzyloxymethyl-13β,14β-bis(diphenylphosphanylmethyl)-5,9-dimethyl-16-isopropyltetracyclo[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (XIII). A mixture of 9 ml of dioxane, 0.69 g (30 mmol) of sodium metal, and 1.29 g (5.8 mmol) of diphenylchlorophosphine were refluxed at vigorous stirring in an argon flow for 5 h. The orange dispersion obtained was cooled to room temperature, and 2 g (2.6 mmol) of ditosylate **XII** was added thereto in one portion. The reaction mixture was stirred for 2 h, and a dispersion of 30 g of Al_2O_3 in 70 ml of anhydrous benzene was added. The mixture was filtered, the filtrate was evaporated, the residue was subjected to chromatography (SiO_2, benzene–ethyl acetate, 9:1). We obtained 0.72 g (35%) of compound **XIII**, R_f 0.70, $[\alpha]_D^{20}$ 1.8° (*c* 1.0, $CHCl_3$). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.58 s (3H, $C^{18}H_3$), 0.73 s (3H, $C^{19}H_3$), 0.87 d (6H, $C^{14}H_3$, $C^{15}H_3$, 6.8), 0.95–2.82 m (22H, H^1, H^2, H^3, C^4H_2, H^{4a}, C^5H_2, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$, H^{13}, $C^{16}H_2$, $C^{17}H_2$), 2.89 d (1H, H^{20}, 8.9), 3.19 d (1H, H^{20}), 4.42 d (1H, CH_2Ph, 12.5), 4.48 d (1H, CH_2Ph), 5.29 s (1H, H^{11}), 7.21–7.91 m (25H, $5C_6H_5$). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 15.75 s (C^{18}), 17.25 s (C^6), 17.94 (C^{19}), 19.26 s (C^9), 20.30, 20.87 2s (C^{14}, (C^{15}), 22.66 s (C^4), 32.19 s (C^{13}), 32.77 d (C^{10a}, $J_{10a,P(2)}$ 14), 35.91 s (C^{10}), 36.00 s (C^7), 36.90 s (C^{4b}), 37.12 s (C^3, $J_{3,P(1)}$ 13), 37.82 s (C^5), 38.59 s (C^8), 42.81 q (C^2, $J_{2,P(1)}$ 6, $J_{2,P(2)}$ 14), 41.67 d (C^{16}, C^{17}, $J_{16,P(1)}$ = $J_{17,P(2)}$ 9), 48.39 s (C^{8a}), 54.43 q (C^1, $J_{1,P(2)}$ 8, $J_{1,P(1)}$ 10), 55.21 s (C^{4a}), 72.98 s (C^{20}), 79.73 s (CH_2Ph), 127.01 s (C^{11}), 127.11, 127.99, 128.30, 138.90 4 s ($CH_2C_6H_5$), 127.62, 128.87 2 d ($8C_{ortho}$, $4PC_6H_5$, $J_{C,P}$ 17), 128.24, 128.58 2d ($4C_{para}$, $4PC_6H_5$, $J_{C,P}$ 7), 131.83, 133.58, 133.84, 134.08 4d ($8C_{meta}$, $4PC_6H_5$, $J_{C,P}$ 19), 136.94, 137.57, 140.16, 140.45 4d ($4C_{ipso}$, $4PC_6H_5$, $J_{C,P}$ 14), 148.50 s (C^{12}). ^{31}P NMR spectrum, δ, ppm: –17.59, –21.79. Found, %: C 82.35; H 8.11. $C_{45}H_{64}OP_2$. Calculated, %: C 82.26; H 8.03.

5,9-Dimethyl-13β,14β-diethoxycarbonyl-16-isopropyl-5-carboxytetracyclo[10.2.2.0^{1,10}.0^{4,9}]-hexadec-15-ene (XIV). A mixture of 23.5 g of pine galipot and 14.9 g of diethyl fumarate was heated to 180°C for 2 h, the excess diethyl fumarate was distilled off in a vacuum, and the residue was subjected to chromatography (SiO_2, hexane–ethyl acetate, 7:3), R_f 0.42. We obtained 9.5 g (25%) of oily compound **XIV**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.55 s (3H, $C^{18}H_3$), 1.04 d (6H, $C^{14}H_3$, $C^{15}H_3$, 6.8), 1.10 s (3H, $C^{19}H_3$), 1.20 m (6H, $2OCH_2CH_3$), 1.32–1.95 m (14H, C^4H_2, H^{4a}, C^5H_2, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$), 2.48 d. sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.53 d.d.d (1H, H^2, $J_{2,1}$ 5.9, $J_{2,3}$ 2.7, $J_{2,4\beta}$ 2.7), 2.72 d (1H, H^1, $J_{1,2}$ 5.9), 2.82 q.d (1H, H^3, $J_{3,2}$ 2.7, $J_{3,4\alpha}$= $J_{3,4\beta}$ =2.8, $J_{3,11}$ 1.5), 4.01 q (2H, OCH_2CH_3, 7), 4.12 q (2H, OCH_2CH_3), 5.35 s (1H, H^{11}). ^{13}C NMR spectrum, δ_C, ppm: 14.00 (C^{18}), 14.15 (C^{19}), 15.88, 20.35 (C^{14}, C^{15}), 16.86 (C^6), 21.79 (C^9), 23.41 (C^4), 32.58 (C^{13}), 34.41 (C^{10}), 35.65 (C^3), 36.75 (C^7), 37.25 (C^{4b}), 37.48 (C^5), 41.12 (C^{10a}), 46.80 (C^8), 48.56 (C^2), 48.99 (C^{8a}), 54.16 (C^1), 54.45 (C^{4a}), 60.06, 60.53 ($2OCH_2CH_3$), 124.17 (C^{11}), 148.00 (C^{12}), 173.56 (CO), 174.18 (CO), 185.23 (CO). Found, %: C 70.98; H 12.69. $C_{28}H_{42}O_6$. Calculated, %: C 70.85; H 12.59.

5,9-Dimethyl-13β,14β-diethoxycarbonyl-16-isopropyl-5-chlorocarbonyltetracyclo-[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (XV). A mixture of 2 g (4.2 mmol) of compound **XIV** and 1.64 g (12 mmol) of PCl_3 was kept at 20°C for 24 h, the excess PCl_3 was distilled off, the residue was diluted with toluene and evaporated. We obtained 2.1 g of crude oily acyl chloride **XV**. IR spectrum, cm^{-1}: 1725, 1795.

5,9-Dimethyl-13β,14β-diethoxycarbonyl-16-isopropyl-5-morpholinocarbonyltetracyclo-[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (XVI). To a stirred mixture of 7.4 g (15 mmol) of acyl chloride **XV** and 100 ml of toluene at 5°C was slowly (within 0.5 h) added 5.31 g (61 mmol) of morpholine. The stirring at

20°C was continued for 16 h. The separated precipitate was filtered off, the filtrate was diluted with 100 ml of ethyl acetate, washed with 50 ml of 10% HCl, with water, the organic layer was separated, dried on Na_2SO_4, evaporated, the residue was subjected to chromatography (SiO_2, hexane–ethyl acetate, 1:1). We obtained 7.52 g (95%) of oily compound **XVI**, $[\alpha]_D^{20}$ 4.8° (*c* 3.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.53 s (3H, $C^{18}H_3$), 0.99 d (6H, $C^{14}H_3$, $C^{15}H_3$, 6.8), 1.13 s (3H, $C^{19}H_3$), 1.17 m (6H, $2OCH_2CH_3$), 0.68–1.90 m (14H, C^4H_2, H^{4a}, C^5H_2, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$), 2.33 d.sept. (1H, H^3, $J_{13,11}$ 1.3), 2.48 d.d.d (1H, H^2, $J_{2,1}$ 5.9, $J_{2,3}$ 2.7, $J_{2,4\beta}$ 2.7), 2.68 d (1H, H^1, $J_{1,2}$ 5.9), 2.80 q.d. (1H, H^3, $J_{3,2}$ 2.7, $J_{3,4\alpha}$= $J_{3,4\beta}$ 2.8, $J_{3,11}$ 1.5), 3.58 br.s (8H, $4CH_2$), 3.96 q (2H, OCH_2CH_3, 7), 4.07 q (2H, OCH_2CH_3), 5.31 s (1H, H^{11}). ^{13}C NMR spectrum, δ_C, ppm: 13.95 (C^{18}, $2OCH_2CH_3$), 16.09 (C^{19}), 16.22 (C^6), 18.63, 20.26 (C^{14}, C^{15}), 21.86 (C^9), 23.27 (C^4), 32.48 (C^{13}), 34.56 (C^{10}), 35.58 (C^3), 37.10 (C^7), 37.47 (C^{4b}), 37.64 (C^5), 41.10 (C^{10a}), 45.90 [$(CH_2)_2N$], 46.40 (C^{10a}), 48.92 (C^2), 49.50 (C^{8a}), 54.06 (C^1), 54.86 (C^{4a}), 59.89, 60.37 ($2OCH_2CH_3$), 66.70 [$(CH_2)_2O$], 124.34 (C^{11}), 147.82 (C^{12}) 173.51 (CO), 174.18 (CO), 177.33 (CO). Found, %: C 72.74; H 9.41; N 2.52. $C_{32}H_{49}NO_5$. Calculated, %: C 72.83; H 9.36; N 2.52.

5,9-Dimethyl-13β,14β-dihydroxymethyl-16-isopropyl-5-morpholinomethyltetracyclo-[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (XVII). To a suspension of 1.1 g (28 mmol) of $LiAlH_4$ in 20 ml of ether at 20°C was added a solution of 7.4 g (14 mmol) of compound **XVI** in 100 ml of ether. The reaction mixture was stirred for 8 h and was left overnight at room temperature, then was added 10 ml of ethyl acetate and 5 ml of 50% NaOH solution. The separated precipitate was filtered off, washed with 20 ml of hot dioxane, filtrate was evaporated, the residue was subjected to chromatography (SiO_2, hexane–ethyl acetate, 1:2). We obtained 5.8 g (93%) of oily compound **XVII**, $[\alpha]_D^{20}$ –7.0° (*c* 4.4, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.56 s (3H, $C^{18}H_3$), 0.59 s (3H, $C^{19}H_3$), 0.73 m (1H, H^5), 0.97 d (6H, $C^{14}H_3$, $C^{15}H_3$, 6.8), 1.10–1.63 m (14H, H^2, C^4H_2, H^{4a}, H^5, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$), 1.82 d (2H, $C^{20}H_2$, 7), 2.15 m (1H, H^1), 2.26 d.sept. (1H, H^{13}, $J_{13,11}$ 1.3), 2.34 m (1H, H^3), 2.43 m [4H, $(CH_2)_2N$)], 2.83 t (1H, H^{16}, $J_{16A,2}$ = $J_{16A,16B}$ 10), 3.44 t (1H, H^{17}, $J_{17A,1}$ = = $J_{17A,17B}$ 10), 3.57 m (1H, H^{16}), 3.62 m [4H, $(CH_2)_2O$], 3.83 m (1H, H^{17}), 5.25 s (1H, H^{11}). ^{13}C NMR spectrum, δ_C, ppm: 16.01 (C^{18}), 17.27 (C^6), 18.97 (C^{19}), 19.25 (C^9), 20.82 (C^{14}, C^{15}), 23.29 (C^4), 32.45 (C^{13}), 35.40 (C^3), 35.62 (C^{10}), 36.53 (C^7), 37.93 (C^{4b}), 38.25 (C^5), 38.34 (C^{10a}), 39.76 (C^8), 44.69 (C^2), 48.53 (C^{8a}), 55.47 (C^1), 55.77 (C^{4a}), 56.26 [$(CH_2)_2N$], 63.95 (C^{17}), 66.63 (C^{16}), 67.28 [$(CH_2)_2O$], 69.62 (C^{20}), 124.05 (C^{11}), 149.75 (C^{12}). Found, %: C 75.58; H 10.71; N 3.02. $C_{28}H_{47}NO_5$. Calculated, %: C 75.46; H 10.63; N 3.14.

5,9-Dimethyl-13β,14β-ditosyloxymethyl-16-isopropyl-5-morpholinomethyltetracyclo-[10.2.2.0^{1,10}.0^{4,9}]hexadec-15-ene (XVIII). To a mixture of 5.5 g (12 mmol) of diol **XVII** and 50 ml of pyridine at –20°C in an argon flow was added by small portions 9.34 g (49 mmol) of tosyl chloride. The stirring at –20°C was continued for 16 h. Then to the reaction mixture was added 40 ml of ice water, 10 ml of ether, and the separated thick oily substance was ground till crystallization. The crystals were filtered off, washed on filter with 20 ml of ice water, 10 ml of cold ether, and dried in a vacuum (1 mm Hg, 40°C). We obtained 4.52 g (50%) of compound **XVIII**, mp 89–92°C, $[\alpha]_D^{20}$ –2.4° (*c* 4.0, $CHCl_3$). ^{1}H NMR spectrum,δ, ppm (*J*, Hz): 0.48 s (3H, $C^{18}H_3$), 0.62 s (3H, $C^{19}H_3$), 0.79 d (3H, $C^{14}H_3$, 6.8), 0.81 d (3H, $C^{15}H_3$, 6.8), 0.85–2.22 m (20H, H^1, H^2, H^3, C^4H_2, H^{4a}, C^5H_2, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$, H^{13}, $C^{20}H_2$), 2.39 s (3H, $CH_3C_6H_4$), 2.40 s (3H, $CH_3C_6H_4$), 2.40 m [4H, $(CH_2)N$], 3.24 t (1H, H^{16}, $J_{16A,2}$ = $J_{16A,16B}$ 10), 3.62 m [4H, $(CH_2)O$], 3.76 t (1H, H^{17}, $J_{17A,1}$ = $J_{17A,17B}$ 10), 4.04 m (2H, H^{16}, H^{17}), 5.13 s (1H, H^{11}), 7.26–7.78 m (8H, $2C_6H_4$). ^{13}C NMR spectrum, δ_C, ppm: 15.79 (C^{18}), 17.19 (C^6), 18.90 (C^{19}), 18.97 (C^9), 20.14, 20.28 (C^{14}, C^{15}), 21.42 ($2CH_3C_6H_4$), 21.65 (C^4), 32.32 (C^{13}), 32.77 (C^3), 35.17 (C^{10}), 36.47 (C^7), 37.81 (C^{4b}), 38.20 (C^5), 38.45 (C^{10a}), 39.49 (C^8), 40.82 (C^2), 48.81 (C^{8a}), 49.57 (C^1), 54.95 (C^{4a}), 56.29 [$(CH_2)N$], 67.23 [$(CH_2)O$], 69.59 (C^{20}), 71.45 (C^{17}), 71.64 (C^{16}), 123.70 (C^{11}), 127.65, 127.75, 129.65, 129.75, 132.65, 132.83, 144.64 ($2C_6H_4$), 149.79 (C^{12}).

X-ray diffraction study of the single crystal of compound **XVIII** was carried out by standard procedure on a diffractometer Bruker P4 (MoK_α-irradiation, graphite monochromator). Crystallographic parameters of compound **XVIII**: monoclinic crystal, *a* 11.544(2), *b* 11.192(2), *c* 15.857(3) Å, β 105.90(1)°, *V* 1970.3(6) Å^3. $C_{42}H_{59}N_1O_7S_2$. *M* 754.02, *Z* 2, *d* 1.271 g/cm^3, μ 0.186 mm^{-1}, crystal size $0.70 \times 0.17 \times 0.12$ mm. Intensities of 3646

Table 3. Coordinates ($\times 10^4$) and equivalent thermal factors ($Å^2$, $\times 10^3$) of nonhydrogen atoms in molecule **XVIII**

Atom	*x*	*y*	*z*	U_{eq}
S^1	3668(1)	3024(2)	2411(1)	53(1)
S^2	573(2)	4952(2)	4884(1)	57(1)
N^1	–3855(4)	–2032(6)	2366(3)	49(1)
O^1	–3572(5)	–3756(5)	3776(3)	68(2)
O^2	2529(4)	3640(5)	2604(3)	54(1)
O^3	4252(4)	3987(6)	2102(3)	76(2)
O^4	3289(4)	2002(6)	1881(3)	70(2)
O^5	448(4)	3770(5)	4350(3)	57(1)
O^6	–24(5)	5875(5)	4330(4)	76(2)
O^7	1830(4)	5019(7)	5308(3)	84(2)
C^1	–1697(5)	–183(7)	590(4)	45(2)
C^2	–2609(6)	–1080(7)	54(4)	55(2)
C^3	–3362(6)	–1598(6)	618(4)	54(2)
C^4	–4020(6)	–679(6)	1036(4)	47(2)
C^5	–3074(5)	255(5)	1528(4)	36(2)
C^6	–3573(5)	1250(6)	2004(4)	43(2)
C^7	–2574(5)	1862(6)	2672(4)	40(2)
C^8	–1632(5)	2415(6)	2265(4)	35(2)
C^9	–1237(5)	1511(6)	1664(3)	34(2)
C^{10}	–2262(5)	827(6)	997(4)	37(2)
C^{11}	–310(5)	2127(6)	1264(4)	43(2)
C^{12}	–64(5)	3422(6)	1597(4)	40(2)
C^{13}	458(5)	3415(6)	2600(3)	37(2)
C^{14}	–446(5)	2747(6)	3001(4)	38(2)
C^{15}	–2033(5)	3538(6)	1761(4)	37(2)
C^{16}	–1251(5)	4084(6)	1406(4)	40(2)
C^{17}	–1467(6)	5206(7)	880(4)	54(2)
C^{18}	–1524(6)	4961(9)	–80(4)	67(2)
C^{19}	–531(8)	6157(8)	1270(6)	80(3)
C^{20}	–2944(5)	1659(6)	256(4)	46(2)
C^{21}	–5093(6)	–126(8)	318(4)	63(2)
C^{22}	–4621(6)	–1319(6)	1661(5)	52(2)
C^{23}	1709(5)	2873(7)	2919(4)	45(2)
C^{24}	–706(6)	3447(7)	3741(4)	50(2)
C^{25}	–4016(7)	–1735(7)	3225(4)	60(2)
C^{26}	–3301(7)	–2533(7)	3942(5)	67(2)
C^{27}	–3352(7)	–4060(8)	2963(5)	69(2)
C^{28}	–4111(7)	–3327(7)	2222(5)	61(2)
C^{29}	4548(5)	2570(7)	3435(4)	45(2)
C^{30}	5149(6)	3409(7)	4044(5)	61(2)
C^{31}	5845(6)	3043(8)	4843(5)	66(2)
C^{32}	6001(6)	1856(8)	5066(4)	56(2)
C^{33}	5417(6)	1031(8)	4455(5)	59(2)
C^{34}	4692(6)	1407(7)	3642(4)	52(2)
C^{35}	6783(7)	1469(9)	5956(5)	81(3)
C^{36}	–215(6)	4675(6)	5663(4)	47(2)
C^{37}	325(6)	3976(7)	6375(5)	59(2)
C^{38}	–258(7)	3745(8)	7001(4)	62(2)
C^{39}	–1385(7)	4239(8)	6934(5)	62(2)
C^{40}	–1897(6)	4928(8)	6217(5)	62(2)
C^{41}	–1327(6)	5146(7)	5576(5)	59(2)
C^{42}	–2001(8)	4006(10)	7657(5)	96(3)

independent reflections with $2\theta < 50°$ were measured, scanning by $\theta/2\theta$. A correction for crystal faces was introduced by integration method (transmission 0.97–0.99). The structure was solved by the direct method using SHELXS-97 program. The final refinement of parameters was carried out by least-squares procedure in the full-matrix anisotropic for nonhydrogen atoms (isotropic for hydrogen atoms) approximation along all F^2. The positions of hydrogen atoms were determined from geometrical considerations (rider model). The final values of *R*-factors are as follows: wR_2 0.1192, *S* 0.976 for all reflections (*R* 0.0566 for 2254 $I > 2\sigma$). The absolute structure parameter (Fluk parameter) equals to 0.08(14) indicating that the structure is sufficiently reliably solved. The coordinates of nonhydrogen atoms of the molecule of compound **XVIII** are listed in Table 3,the structure of the molecule is presented in Fig. 2.

13β,14β-Bis(diphenylphosphanylmethyl)-5,9-dimethyl-16-isopropyl-5-morpholinomethyltetracyclo-[10.2.2.$0^{1,10}$.$0^{4,9}$]hexadec-15-ene (XIX). A mixture of 9 ml of dioxane, 0.69 g (30 mmol) of sodium metal, and 1.29 g (5.8 mmol) of diphenylchlorophosphine were refluxed at vigorous stirring in an argon flow for 5 h. The orange dispersion obtained was cooled to room temperature, and 1.96 g (2.6 mmol) of ditosylate **XVIII** was added thereto in one portion. The reaction mixture was stirred for 2 h, and a dispersion of 30 g of Al_2O_3 in 70 ml of anhydrous benzene was added. The mixture was filtered, the filtrate was evaporated, the residue was ground in 10 ml of methanol till crystallization. The solvent was decanted, the precipitate was recrystallized from ethanol–benzene, 4 : 1. We obtained 0.65 g (32%) of compound **XIX**, mp 154–156°C, R_f 0.70 (benzene– ethyl acetate, 9 : 1), $[\alpha]_D^{20}$ –32.7° (*c* 1.0, $CHCl_3$), mp 154–156°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.63 s (3H, $C^{18}H_3$), 0.71 s (3H, $C^{19}H_3$), 0.90 d (6H, $C^{14}H_3$, $C^{15}H_3$, 6.8), 0.65–2.85 m (22H, H^1, H^2, H^3, C^4H_2, H^{4a}, C^5H_2, C^6H_2, C^7H_2, H^{8a}, C^9H_2, $C^{10}H_2$, H^{13}, $C^{16}H_2$, $C^{17}H_2$), 1.82 d (2H, $C^{20}H_2$, 7), 2.45 m [4H, (CH_2)N], 3.70 m [4H, (CH_2)O], 5.30 s (1H, H^{11}), 7.22– 7.76 m (20H, $4C_6H_5$). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 15.87 s (C^{18}), 17.35 s (C^6), 19.13 s (C^{19}), 19.43 s (C^9), 20.34, 20.57 2s (C^{14}, C^{15}), 22.12 s (C^4), 32.55 s (C^{13}), 32.90 d (C^{10a}, $J_{10A,P(2)}$ 13), 35.28 d (C^3, $J_{3,P(1)}$ 12), 35.90 s (C^{10}), 36.46 s (C^7), 37.74 s (C^{4b}), 39.25 s (C^5), 39.71 s (C^8), 41.69 d (C^{16}, C^{17}, $J_{16,P(1)} = J_{17,P(2)}$ 9), 42.70 q (C^2, $J_{2,P(1)}$ 8, $J_{2,P(2)}$ 12), 48.32 s (C^{8a}), 54.38 q (C^1, $J_{1,P(2)} = J_{1,P(1)}$ 8), 55.32 s (C^{4a}), 56.22 s [($\underline{C}H_2$)N], 67.21 s [($\underline{C}H_2$)O], 69.29 s (C^{20}), 126.73 (C^{11}), 127.71, 128.61 2d ($8C_{ortho}$, $4PC_6H_5$, $J_{C,P}$ 28), 127.99, 128.17 2d ($4C_{para}$,

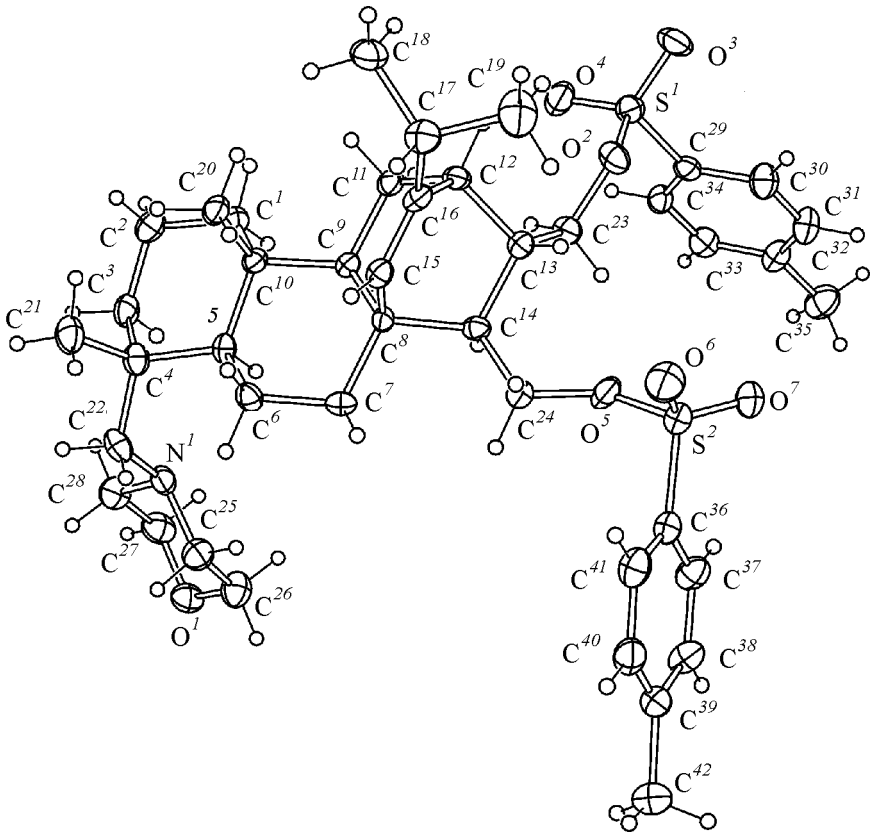


Fig. 2. Crystal structure of compound **XVIII** according to X-ray diffraction analysis.

$4PC_6H_5$, $J_{C,P}$ 7), 131.69, 132.20, 133.61, 134.08 4d ($8C_{meta}$, $4PC_6H_5$, $J_{C,P}$ 19), 137.13, 137.57, 140.55, 140.96 4d ($4C_{ipso}$, $4PC_6H_5$, $J_{C,P}$ 15), 149.92 s (C^{12}). ^{31}P NMR spectrum, δ_P, ppm: –18.91, –21.96. Found, %: C 79.97; H 8.45; N 1.84. $C_{52}H_{65}NOP_2$. Calculated, %: C 79.86; H 8.38; N 1.79.

Complex XX. A mixture of 0.06 g (0.12 mmol) of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium, 20 μl of 1,5-cyclooctadiene, and 15 ml of dichloromethane was boiled for 1 h, cooled to room temperature, and 0.16 g (0.024 mmol) of bisphosphine **IX** was added. The reaction mixture was stirred for 2 h, and a solution of 1 g of $NaBF_4$ in 5 ml of water was added. After stirring for 3 h the water layer was separated, the organic phase was dried with Na_2SO_4 and evaporated. To the residue was added 5 ml of methanol, 10 ml of water, the mixture was stirred for 1 h at 20°C, the precipitate was filtered off, washed with 5 ml of water, and dried in a vacuum (1 mm Hg, 40°C). We obtained 0.17 g of complex **XX**, orange crystals, mp 200°C (decomp.). ^{31}P NMR spectrum, δ_P, ppm (*J*, Hz): 35.57 d.d (1P, $J_{Rh,P}$ 116, $J_{P,P}$ 28), 39.49 d.d (1P, $J_{Rh,P}$ 121). Found, %: Rh 9.48. $C_{63}H_{76}ßF_4OP_2Rh$. Calculated, %: Rh 9.35.

Complex XXI. Under the conditions used in preparation of complex **XX** from 0.06 g (0.12 mmol) of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium, 0.16 g (0.24 mmol) of bisphosphine **XIII**, and 1 g of $NaBF_4$ we obtained 0.16 g (64%) of compound **XXI**, orange crystals, mp 218°C (decomp.). ^{31}P NMR spectrum, δ_P, ppm (*J*, Hz): 14.26 d.d (1P, $J_{Rh,P}$ 138, $J_{P,P}$ 30), 19.05 d.d (1P, $J_{Rh,P}$ 143). Found, %: Rh 9.23. $C_{63}H_{76}ßF_4OP_2Rh$. Calculated, %: Rh 9.35.

Complex XXII. Under the conditions used in preparation of complex **XX** from 0.06 g (0.12 mmol) of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium, 0.18 g (0.24 mmol) of bisphosphine **XIX**, and 1 g of $NaBF_4$ we obtained 0.15 g (56%) of compound **XXII**, dark-yellow crystals, mp 220°C (decomp.). ^{31}P NMR spectrum, δ_P, ppm (*J*, Hz): 19.88 d.d (1P, $J_{Rh,P}$ 142, $J_{P,P}$ 37), 24.29 d.d (1P, $J_{Rh,P}$ 144). Found, %: Rh 9.45.$C_{60}H_{77}ßF_4NOP_2Rh$. Calculated, %: Rh 9.53.

Hydrogenation of (*Z*)-2-acetylaminocinnamic acid XXIII. To a solution of 0.62 g (3 mmol) of acid **XXIII** in 10 ml of anhydrous ethanol was added under hydrogen flow 0.03 mmol of complex **XX**. The mixture was shaken at $p(H_2)$ 1.5 at, then the solvent was evaporated, and the residue was subjected to

chromatography (SiO_2, chloroform–methanol, 15 : 1, then 10 : 1, 1 : 1). Similarly was carried out the hydrogenation in the presence of complexes **XXI, XXII**. The hydrogenation results are given in Table 1.

Hydrogenation of 2-acetylamino-3-(3,4-dimethoxy-1-phenyl)-2-propenoic acid (XXIV). To a solution of 0.82 g (3 mmol) of acid **XXIV** in 10 ml of anhydrous tetrahydrofuran was added under hydrogen flow 0.03 mmol of one of the complexes **XX–XXII**. The mixture was shaken at $p(H_2)$ 1.5 at, then the solvent was evaporated, and the residue was subjected to chromatography (SiO_2, chloroform–methanol, 10 : 1, then ethyl acetate). The hydrogenation results are given in Table 1.

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