Synthesis of Nitrogen-Containing Derivatives of (18α,19β)-19-Hydroxy-2,3-secooleanane-2,3,28-trioic Acid 28,19-Lactone

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The object of this study is the interaction of the cyclic anhydride **2** of (18α,19β)-19-hydroxy-2,3-secooleanane-2,3,28-trioic acid 28,19-lactone (**1**) with primary and secondary amines. It was shown that the products of steric control (the corresponding 2-amino-2-oxo-3-oic acids = 2-amides) were formed solely upon the opening of the anhydride cycle by secondary amines (*Scheme 2*), whereas the interaction with primary amines yielded a mixture of isomeric amides (*Scheme 10*). In the latter case, the solvent provided a noticeable effect on the reaction selectivity, which was demonstrated in the case of 4-methoxybenzylamine. The interaction between the resulting 3-amides and oxalyl chloride yielded the corresponding cyclic imides, whereas under these conditions, 2-amides formed spiropyrrolidinetriones (*Scheme 4*).

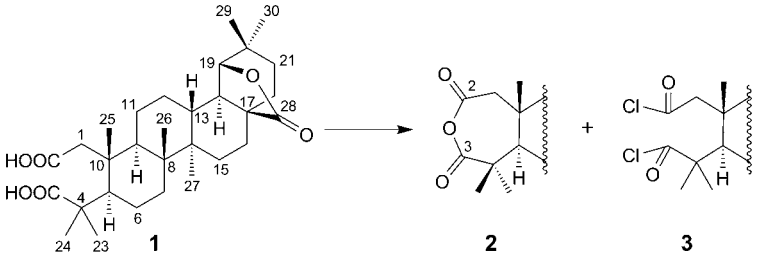
Introduction. – Pentacyclic triterpenoids of natural and semisynthetic origin are attracting increasing attention as a result of the fact that these compounds can be obtained from readily available sources, and are characterized by their high biological activity [1][2]. The production of various ring-*A*-seco derivatives, which are characterized by different biological activity [3–6], is an interesting application of the targeted chemical transformation of these compounds. Further modification of seco derivatives *via* the introduction of various pharmacophoric groups containing N-atoms (from amides, ketoximes, nitrile groups) usually results in the enhancement or variation of biological activity of the compounds obtained [7][8].

The data on 2,3-secooleananedioic acids and their cyclic anhydrides from the series of pentacyclic triterpenoids have been published [9–12]; however, there seem to be no data available on using them to produce amides and cyclic imides. The present study is devoted to the production of N-containing derivatives of pentacyclic triterpenoids based on (18α,19β)-19-hydroxy-2,3-secooleanane-2,3,28-trioic acid 28,19-lactone (**1**) which is readily accessible from allobetuline (= (3β,18α,19β)-19,28-epoxyoleanan-3-ol) [13].

Results and Discussion. – In the case of dicarboxylic acids, in which the carboxylic groups are spatially close to each other and can relatively easily form a cyclic anhydride, the synthesis of amides is usually carried out both *via* a cyclic anhydride or *via* a dicarbonyl dichloride. As reported earlier [14], the cyclic anhydride **2** can be obtained in a 90% yield *via* treatment of compound **1** with a twofold excess of oxalyl chloride in

CH_2Cl_2. With DMF as a catalyst and increasing both the excess of oxalyl chloride (to 1:30) and the reaction time (to 96 h), mixtures of anhydride **2** and 2,3-secooleanane-2,3-dioyl dichloride **3** were formed (*Scheme 1*), the amount of the latter being 25–56% (by ^{1}H-NMR). Dichloride **3** could be obtained *in situ via* interaction of **1** with a fourfold excess of phosphorus pentachloride in boiling CH_2Cl_2 for 30 min. However, compound **3** is unstable and could not be isolated from the mixture and used for further reactions. Therefore, to produce amides and cyclic imides of dioic acid **1** in further experiments, cyclic anhydride **2** was used as the starting material.

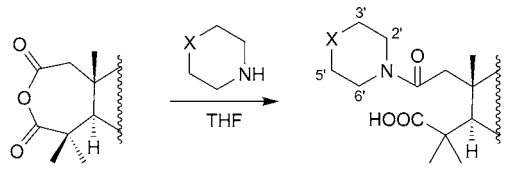
Scheme 1



1 **2** **3**

The acylation of amines with anhydride **2** occurred smoothly at room temperature in different solvents and did not require addition of catalysts, with the exception of aniline (=benzenamine) and *p*-anisidine (=4-methoxybenzenamine). For the latter compounds, refluxing in dioxane was required to accelerate the reaction. The interaction between cyclic anhydride **2** and secondary cyclic amines resulted solely in the formation of amides **4**–**7** *via* the sterically less hindered carboxy center C(2) of the initial acid **1** (*Scheme 2*).

Scheme 2



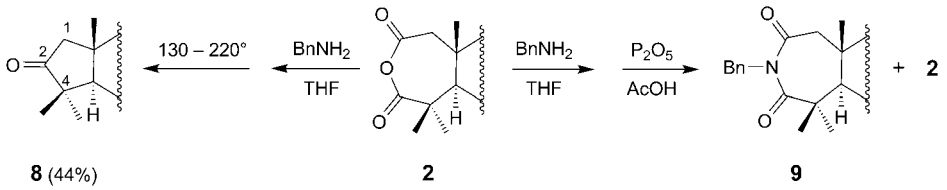
2

	X	Yield [%]
4	CH_2	90
5	Me–N	81
6	Et–N	83
7	O	75

The formation of the mixtures of isomeric amic acids at both possible positions *i.e.*, 2-amino-2-oxo-3-oic acid or 3-amino-3-oxo-2-oic acid, was observed upon interaction with primary amines. Since secondary amides are the major precursors of the corresponding cyclic imides, it appeared promising to produce the latter compounds without separation and isolation of the isomeric amic acids. Various methods of producing the desired compounds generally used in synthetic practice were tested; however, no efficient method could be found. Thus, when boiling the mixture of amic

acids obtained *via* reactions with benzylamine (= benzenemethanamine), or 4-methoxybenzyl amine (= 4-methoxybenzenemethanamine) in toluene with a *Dean-Stark* trap or by the action of AcCl or Ac_2O in boiling AcOH, no formation of the targetted products was observed. The known noroleanone **8** [15] was isolated when keeping the mixture of amic acids obtained from **2** and benzylamine at 130–220° under Ar (*Scheme 3*); yield of crude compound **8** (based on **2**) was 44%. When boiling the same mixture of amic acids in AcOH in the presence of P_2O_5, a fraction containing cyclic imide **9** and the initial cyclic anhydride **2** was isolated after a chromatographic separation, the ratio **9**/**2** being 72:28 (by ^{1}H-NMR). The formation of anhydride **2** is probably accounted for by the instability of the amide group under these conditions.

Scheme 3



8 (44%) **2** **9**

As reported earlier [16], the reaction of cyclic anhydride **2** and benzylamines and subsequent treatment with oxalyl chloride (one-pot conditions) yielded compounds with a triterpenoid noroleanone backbone, containing a spiropyrrolidinetrione fragment. During this reaction, the residue of oxalyl chloride was incorporated into the backbone as part of the pyrrolidinetrione moiety. It is known that pyrrolidinetriones can be produced by condensation of alkyl oxalates with primary amides under the action of alkali [17] or *via* the interaction of primary amides with oxalyl chloride [18–20]. In the latter case, when oxalyl chloride interacts with primary amides, oxazolidinediones are initially formed, which are rather unstable compounds with respect to nucleophilic agents and can easily isomerize to the corresponding pyrrolidinetriones, even upon recrystallization from EtOH [20] or boiling in a pyridine/EtOH mixture [21].

When studying the conversion described, the reaction of oxalyl chloride and individual isomeric amic acids isolated chromatographically after the reaction of the corresponding primary amines with anhydride **2** was investigated. Thus, the target cyclic imides **14**–**17** were obtained with a 6–10-fold excess of oxalyl chloride from the 3-amino-3-oxo-2-oic acids (= 3-amides) **10**–**13** in 64–84% yields (*Scheme 4*[1])). Spiropyrrolidinetriones **22** and **23** were formed in 76% and 74% yield, respectively, by the reaction with 2-amino-2-oxo-3-oic acids (= 2-amides) **18** and **19**. However, in the case of 2-anilide derivatives **20** and **21**, the reaction yielded a complex mixture of compounds, from which spiropyrrolidinetriones **24** and **25** were isolated in 27% and 23% yield, respectively.

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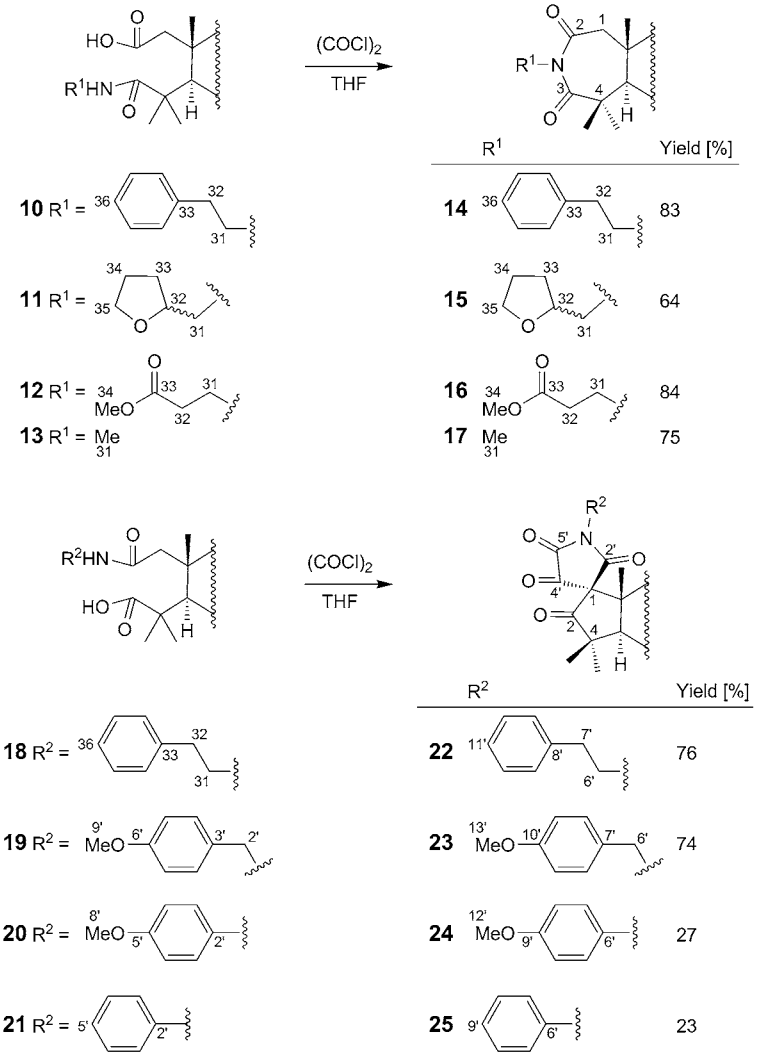
[1]) Arbitrary and/or trivial atom numberings; for systematic names, see *Exper. Part.*

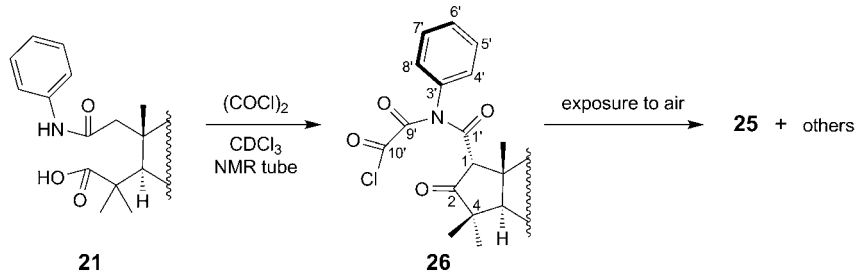
Scheme 4



The reactions of 2-[(4-methoxybenzyl)amino]-2-oxo-3-oic acid **19** and 2-(phenylamino)-2-oxo-3-oic acid **21** with an excess of oxalyl chloride in $CDCl_3$ were then carried out directly in a NMR tube. In the case of anilide derivative **21**, a mixture of compounds was formed, its composition remaining virtually constant for a week, upon being kept in the tube at room temperature. The major component **26** (*Scheme 5*[1])) was formed in *ca.* 80% yield; the corresponding spiropyrrolidinetrione was not observed. According to the NMR data, exposing the resulting mixture to air yielded a small amount of spiropyrrolidinetrione **25** and other compounds that contain the noroleanone backbone

in their structure (and have the characteristic cyclopentanone ^{13}C-signals in the $\delta(C)$ 200–230 range).

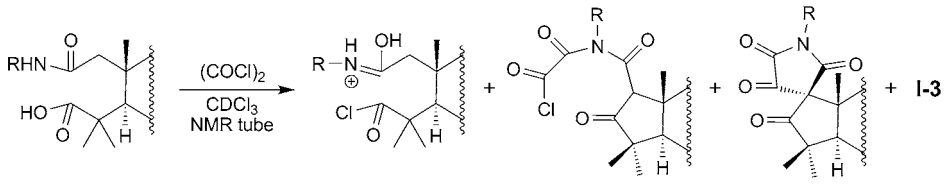
Scheme 5



It is worthy of note that the barrier to rotation of the Ph substituent around the N(2′)–C(3′) of **26** can be determined from the temperature-dependent NMR spectra. The rotational barrier estimated by the *Eyring* equation is equal to 14.6 kcal/mol at +29.4°. Comparatively high rotational barriers in cyclic and acyclic *N*,*N*-diacyl derivatives of *ortho*-substituted aromatic amines have been observed before [22][23]. The dependence of the rotational barrier on the electron effects of the acyl group was shown by *Murakami* and co-workers [24]. The presence of a relatively high barrier of rotation of the phenyl substituent in compound **26** can be accounted for by the presence of the strong π-acceptor C(=O)Cl in the acyl group. Based on the analysis of the NOESY 2D plot of **26**, in which the cross-peaks H–C(1)/Me(25) and Me(24) in β-position are present, the shown configuration of C(1) was proposed. The configuration was also confirmed by comparing the experimental chemical shifts with the calculated shifts that have the highest difference for both possible configurations of the stereogenic center C(1).

When performing the reaction in an NMR tube with 2-[(4-methoxybenzyl)amino]-2-oxo-3-oic acid **19**, the formation of three intermediates and product **23** was observed (*Scheme 6*), their ratio depending upon time (*Scheme 6*). Based on the analysis of 1D-

Scheme 6

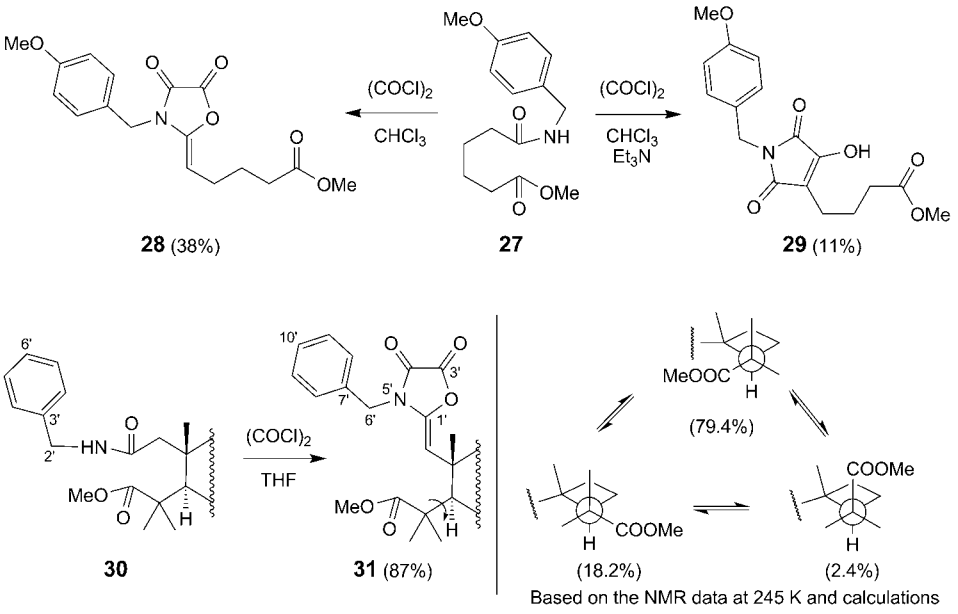


Reaction time (after addition of $(COCl)_2$) [min]	Ratio **I-1**/**I-2**/**23**/**I-3**
71	65.62 : 14.20 : 18.61 : 1.57
115	58.06 : 12.70 : 27.53 : 1.72
203	42.43 : 11.24 : 43.58 : 2.75
1093	4.51 : 1.76 : 90.29 : 3.44
1635	1.75 : 0.87 : 94.14 : 3.24

and 2D-NMR spectra (COSY, HMBC, HSQC) and comparing them with the spectra of compound **26**, the structures of compounds **I-1** and **I-2** were proposed. The structure of the 2-amino-2-oxo-3-oyl chloride of the initial aminooxooic acid **19** was proposed for compound **I-1**, the 2-amino-2-oxo moiety of **I-1** being almost completely protonated (broad *s* at δ(H) 14.85). A structure similar to that of compound **26** was proposed for compound **I-2**. Compound **I-3** is probably not an intermediate but a by-product that was formed at a noticeably lower rate, as attested to by its low amount that slowly changed with time. Taking into account the high excess (*ca.* 20-fold) of oxalyl chloride and neglecting the formation of compound **I-3**, calculations with the data of the table in *Scheme 6* can be made upon assumption of a kinetic scheme of two consecutive irreversible reactions, **I-1** $\xrightarrow{k_1}$ **I-2** $\xrightarrow{k_2}$ **23**. Thus, the variation of concentration of compound **I-1** in the mixture correlated well with a first-order reaction with the kinetic rate constant $k_1 = 3.9 \cdot 10^{-5}\ s^{-1}$. For the second reaction, the kinetic constant k_2 was equal to $2.1 \cdot 10^{-4}\ s^{-1}$. *Via* substitution of these constants into the function of content of the final product on time, which corresponds to the selected kinetic scheme, good agreement with the data on the amount of compound **23** in the mixture was achieved.

To test whether spiropyrrolidinetriones can be obtained from the derivatives of simple dicarboxylic acids, the model compound *N*-(4-methoxybenzyladipamic) acid was treated with excess of oxalyl chloride in chloroform; however, in this case, a complex mixture of products was formed. The use of the corresponding methyl ester **27** under the same conditions resulted in the formation of the corresponding oxazolidinedione **28** in 38% yield (*Scheme 7*). When conducting this reaction in the presence of Et_3N, a violent reaction was observed, yielding a complex mixture of products from which pyrrolidinetrione **29** was isolated in 11% yield. It should be noted that only the

Scheme 7

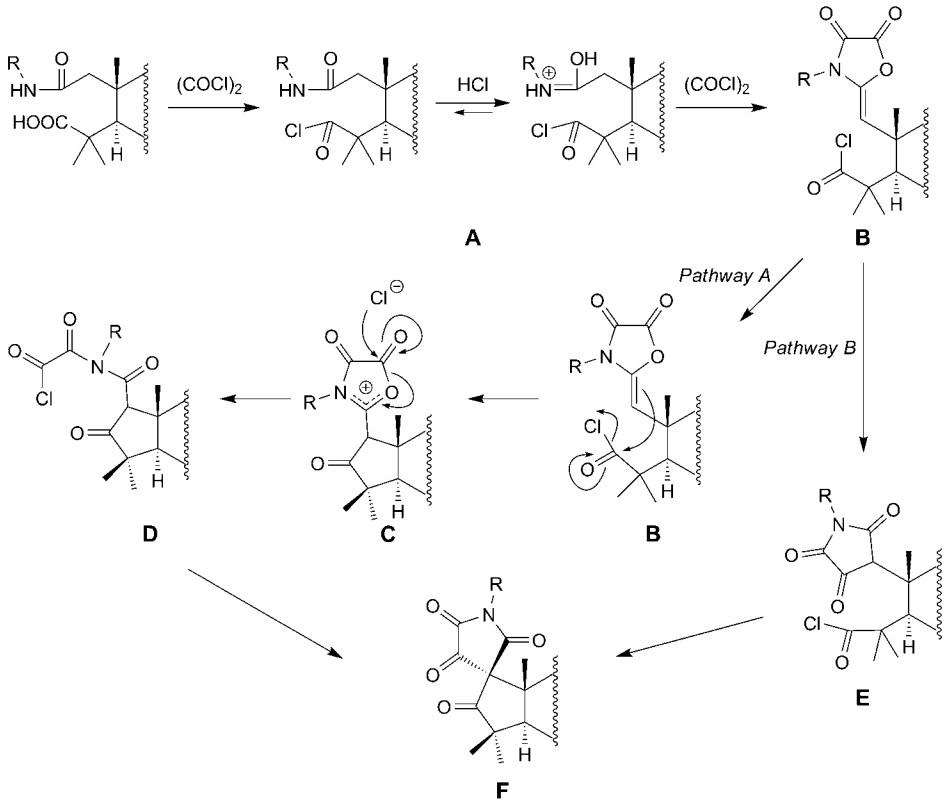


enol form of this compound was observed in the NMR spectra ($CDCl_3$). These data attest the assumption of instability of the oxazolidinedione ring system in the presence of nucleophiles, due to the presence of an 'activated' ester group and leave open the possibility of rearranging to the isomeric cyclic pyrrolidinetriones [20].

When methyl 2-(benzylamino)-2-oxo-3-oate **30**, corresponding to the model methyl ester **27**, was treated with oxalyl chloride, oxazolidinedione **31** was obtained in 87% yield (*Scheme 7*). Significantly broad signals were present in the NMR spectra of **31** at room temperature, and three inter-exchanging compounds were observed in the NMR spectra at 245 K. The quantum-chemical conformational analysis permitted the reasonable assumption that these compounds were three conformers, formed upon rotation around the C(5)–C(4) bond. Compound **31** contains six bonds, around which free rotation can take place. Based on the calculation results, this fact supposes the existence of one major conformer and 28 other conformers, their population having the capability to influence the NMR spectra. The fact that a conformational equilibrium was observed in **31**, unlike in other synthesized seco derivatives (*e.g.*, 2-amides), can be accounted for by the presence of a strong magnetically anisotropic Ph group in the structure of **31**. This magnetically anisotropic Ph group can adopt two positions: 'to the backbone' and 'from the backbone', resulting in an increased differentiation between the chemical shifts of the exchanging signals and shifting the exchange boundaries towards higher temperatures, due to the fact that the conformers have different populations. Moreover, compound **31**, as opposed to 2-amides, contains a COOMe group, which is incapable of reducing the energy of the most stable conformer by forming an intramolecular H-bond.

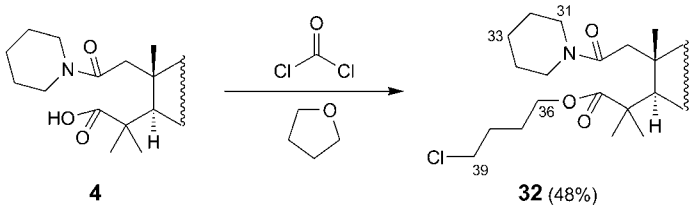
Hence, based on the published data on producing oxazolidinediones and pyrrolidinetriones and the conversions shown above, the following reaction mechanism of the formation of spiropyrrolidinetriones **22**–**25** can be proposed (*Scheme 8*): In a first step, oxalyl chloride reacts with a 2-amino-2-oxo-3-oic acid to give 2-amino-2-oxo-3-oyl chloride **A** wherein the amide moiety is protonated by HCl. Then the interaction between **A** and oxalyl chloride results in the formation of oxazolidinedione **B**. The reaction can then proceed *via* two pathways. The first one (*Scheme 8*, *Path A*) involves the intramolecular acylation of **B** with ring opening *via* a hypothetical intermediate **C** yielding **D**. The subsequent intramolecular acylation of the β-diketone moiety with the oxalyl chloride moiety of **D** yields the desired spiropyrrolidinetrione **F**. The second pathway (*Scheme 8*, *Path B*) involves the isomerization of the oxazolidinedione ring of **B** into the pyrrolidinetrione ring with the formation of **E**, followed by intramolecular acylation of the resulting β-diketone moiety with the acyl chloride moiety of **E**, which also yields **F**. However, *Path B* is less viable when the reaction is run in a base-free medium. A decrease in the yield of spiropyrrolidinetriones in the case of an aromatic substituent at the amide N-atom, indicates that the barrier of the reaction **D** $\rightarrow$ spiropyrrolidinetrione **F** is higher in this case, as established by the fact that the reaction of anilide derivative **21**, as opposed to that of amide derivative **19**, stopped at compound **26** (corresponding to compound **D** in *Scheme 8*) under conditions of the closed system in an NMR tube (*Scheme 5*). Under the preparative conditions (the concentration of HCl decreases because of its volatility), the formation of spiropyrrolidinetrione **F** from **D** in the case of an aromatic substituent is likely to be accompanied by side reactions, which results in the observed reduced yield.

Scheme 8



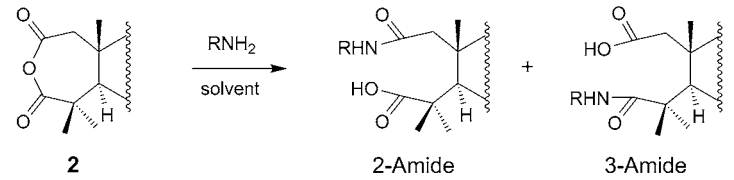
It is worthy of note that when conducting the reaction between 2-amino-2-oxo-3-oic acids and phosgene ($Cl_2C{=}O$) in THF, which is also used to obtain 2-amino-2-oxo-3-oyl chlorides, complex mixtures of products were obtained. According to the ^{1}H-NMR data, these mixtures included compounds containing a 4-chlorobutoxy fragment, which could be formed upon the opening of the solvent (THF) by the HCl formed. To verify this assumption, in a model reaction, the secondary-amide derivative **4** was treated with phosgene in THF, and indeed, compound **32** was isolated from the mixture (*Scheme 9*[1]). A complex mixture of products was also formed in the reaction of 2-amide derivatives and phosgene in $CHCl_3$.

Scheme 9



It was thus demonstrated that the reaction of oxalyl chloride and 2-amino-2-oxo-3-oic acids derived from 2,3-secooleanane-2,3-dioic acids **1** may yield spiropyrrolidine-triones, whereas 3-amino-3-oxo-2-oic acids form the corresponding cyclic imides under these conditions. However, as mentioned above, the isolation of the individual amic acids from the reaction mixture after treatment of cyclic anhydride **2** with primary amines presents some difficulties (*Scheme 10*[1])). We now established that the solvent used in this reaction has a considerable effect on the ratio of the formed isomeric amic acids. To the best of our knowledge, no systematic study of the effect of solvents on the acylation of amines with asymmetric cyclic anhydrides has been published yet. Thus a series of experiments with different solvents was carried out for the model reaction of

Scheme 10



2 2-Amide 3-Amide

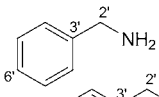
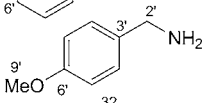
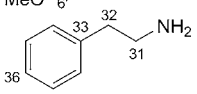
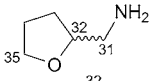
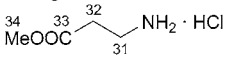
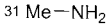
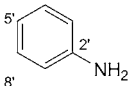
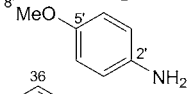
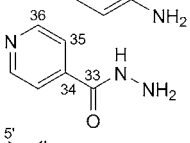
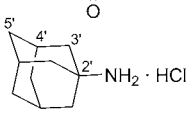
RNH_2	Solvent	2-Amide	Yield [%]	3-Amide	Yield [%]	Ratio 2-amide/3-amide (by NMR)
	THF	**33**	77	**34**	11	85:15
	MeOH	**19**	24	**35**	45	37:63
	$CHCl_3$	**18**	57	**10**	42	
	$CHCl_3$	**36**	28	**11**	42	
	CH_2Cl_2/Et_3N	**37**	13	**12**	49	
	DMF	–	–	**13**	70	27:73
	1,4-dioxane (reflux 6 h)	**21**	76	–	–	80:20
	1,4-dioxane/Et_3N (reflux 6 h)	**20**	80	–	–	90:10
	DMF	**38**	81	–	–	90:10
	THF/Et_3N	**39**	19	**40**	26	

Table 1. *Ratio of Isomeric Amic Acids in the Product Mixtures Obtained from Anhydride* **2** *and (4-Methoxybenzyl)amine*[a])

Entry	Solvent	Ratio 2-amide/3-amide[b])
1[c])	THF	93 : 7 (13.3 : 1.0)
2[d])	THF	88 : 12 (7.3 : 1.0)
3[e])	THF	87 : 13 (6.7: 1.0)
4	THF	85 : 15 (5.7 : 1.0)
5	1,4-dioxane	85 : 15 (5.7 : 1.0)
6[f])	THF	80 : 20 (3.8 : 1.0)
7	pyridine	80 : 20 (4.0 : 1.0)
8	MeCN	72 : 28 (2.6 : 1.0)
9	i-PrOH	71 : 29 (2.4 : 1.0)
10	DMF	69 : 31 (2.2 : 1.0)
11[g])	AcOH	68 : 32 (2.1 : 1.0)
12	$CHCl_3$	66 : 34 (1.9 : 1.0)
13	CH_2Cl_2	59 : 41 (1.4 : 1.0)
14	benzene	53 : 47 (1.1 : 1.0)
15	EtOH	50 : 50 (1.0 : 1.0)
16[d])	MeOH	48 : 52 (1.0 : 1.1)
17[c])	MeOH	47: 53 (1.0 : 1.1)
18[e])	MeOH	39 : 61 (1.0 : 1.6)
19	MeOH	38 : 62 (1.0 : 1.6)
20[h])	MeOH + H_2O (3 + 2 ml)	38 : 62 (1.0 : 1.6)
21[f])	MeOH	34 : 66 (1.0 : 1.9)

[a]) Reaction conditions: 0.10 mmol of **2**, 0.15 mmol of (4-methoxybenzyl)amine, 3 ml of solvent, at r.t. [b]) Ratio of 2-amide/3-amide (= 2-amino-2-oxo-3-oic acid/3-amino3-oxo-2-oic acid) as determined by HPLC analysis. [c]) Reactions were carried out in the presence of 0.2 ml of Et_3N. [d]) Reactions were carried out in the presence of 0.2 ml of Bu_3N. [e]) Catalytic amount of DMAP was added. [f]) Salt of amine and dehydroabietic acid was used. [g]) At 60°. [h]) Reflux.

anhydride **2** with (4-methoxybenzyl)amine, and the ratio of the isomeric amic acids (2-amide/3-amide) was determined by HPLC (*Table 1*). In the majority of cases, the amic acid resulting from attack at the sterically less hindered carboxy center C(2) predominated in the solvents under study (*Table 1*, *Entries 1–14*). In THF or dioxane, the ratio of the isomeric amic acids was 5.7 : 1.0 in favor of the 2-amide (*Entries 4* and *5*). In the case of benzene and EtOH, the ratio was close to 1 : 1 (*Entries 14* and *15*), whereas in MeOH, the prevalence of the product resulting from attack at the sterically more hidered carboxy center C(3) was observed (*Entry 19*). Within a series of alcohols, the amount of 3-amide increased with increasing polarity of the solvent (*Entries 9*, *15*, and *19*). The extreme ratios, obtained in MeOH and THF, were selected and the influence of various additions on these ratios were examined. Thus, when a salt of (4-methoxybenzyl)amine with dehydroabietic acid was acylated instead of the amine, a slight increase in content of 3-amide was observed in both cases (*Entries 6* and *21*). The addition of excess Et_3N or Bu_3N noticeably increased the content of 2-amide in both cases (*Entries 1* and *2*, and *17* and *16*). The addition of the catalytic amount of DMAP had no considerable effect on the reaction selectivity (*Entries 3* and *18*). Thus, to increase the content of 2-amide derivatives in the mixture, the reaction should be

performed in THF or dioxane with Et_3N added, whereas for a favored production of 3-amide derivatives, a polar protic solvent (MeOH) is recommended.

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Experimental Part

1. *General*. Yields of products are given in the corresponding *Schemes*. Anal. and spectroscopic studies were performed in the Chemical Service Center of collective use of the SB RAS. Column chromatography (CC): silica gel *Merck* (60–200 mesh). TLC: *Silufol* silica-gel plates. HPLC: *Milichrom-A02* (*EcoNova*). M.p.: *Kofler* stage and *Mettler-Toledo-FP-900* instrument. IR Spectra: *Vector-22* instrument; in KBr; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-DRX-500* (at 500.13 and 125.76 MHz, resp.), *AV-300* (at 300.13 MHz (^1H)), *AV-400* (at 400.13 and 100.78 MHz, resp.), and *AV-600* instrument (at 600.30 and 150.95 MHz, resp.); in $CDCl_3$, (D_6)DMSO, or $CDCl_3$/(D_6)DMSO 5:1; δ in ppm, J in Hz, with $CHCl_3$ as internal standard (δ(H) 7.24, δ(C) 76.90) or DMSO (δ(H) 2.50, δ(C) 39.50); assignments on a routine basis by a combination of 1D and 2D experiments (COSY, COLOC, HSCQ, and HMBC), most δ(H) as overlapping *m*; ^{13}C-NMR data in *Tables 2–5*; arbitrary and/or trivial atom numbering as given in the *Schemes*[1]); $H_a = H_{axial}$ and $H_e = H_{equatorial}$. MS: *Thermo-Electron-DFS* instrument; at 70 eV; in *m*/*z*.

Quantum-Chemical Calculations. The initial set of conformers was obtained by using *ChemAxon*'s Marvin (conformers plugin) [25] and Confab [26]; then structures were optimized by RM1 [27] with the MOPAC2009 program [28] and by the density functional theory (DFT; functional PBE [29], basis L1 (Λ01 [30], cc-pVDZ analog), with the PRIRODA program [31]). The chemical shifts were calculated by GIAO/DFT/PBE (basis L22 (Λ22, cc-pCVTZ analog), with the PRIRODA program. For quantum-chemical calculations, we used the cluster of the Information Computation Center, Novosibirsk State University. All results of calculations and selected NMR investigation are available from http://limor1.nioch.nsc.ru/quant/conformers/shern/spiro/.

2.1. *2-Amino-2-oxooleanan-3-oic Acids* **4**–**7**. *General Procedure*. To a soln. of the cyclic anhydride **2** (1.00 mmol) in THF (7–10 ml) was added a soln. of the corresponding amine (1.05–1.10 mmol) in THF (2 ml). After standing for 24 h, the mixture was extracted with $CHCl_3$ and the extract washed with dil. HCl soln. (pH 4–5), dried ($MgSO_4$), and concentrated.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-7-[2-oxo-2-(piperidin-1-yl)ethyl]-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**4**): IR: 1772 (lactone), 1695 (COOH), 1650 ($CONR^1R^2$). ^1H-NMR (500 MHz, (D_6)DMSO): 0.83 (*s*, Me(26)); 0.88 (*s*, Me(27)); 0.89 (*s*, Me(25)); 0.94 (*s*, Me(29), Me(30)); 1.11, 1.14 (2*s*, Me(23), Me(24)); 1.52–1.60 (*m*, CH_2(4′)); 1.62–1.71 (*m*, H_e–C(12), H_e–C(16), CH_2(22)); 1.86 (*d*, *J*(18,13) = 11.1, H–C(18)); 2.38 (*s*, CH_2(1)); 2.74 (*dd*, *J*(5a,6a) = 12.0, *J*(5a,6e) = 2.0, H_a–C(5)); 2.95 (*dd*, *J*(9a,11a) = 12.5, *J*(9a,11e) = 2.3, H_a–C(9)); 3.30–3.51 (*m*, CH_2(2′), CH_2(6′)); 3.96 (*s*, H–C(19)); 11.71 (br. *s*, COOH); others 0.77–1.53. Anal. calc. for $C_{35}H_{55}NO_5$ (569.81): C 73.77, H 9.73, N 2.46; found: C 73.55, 73.58, H 9.74, 9.79, N 2.60, 2.62.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-7-[2-(4-methylpiperazin-1-yl)-2-oxoethyl]-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**5**): M.p. 205°. IR: 1764 (lactone), 1726 (COOH), 1657 ($CONR^1R^2$). ^1H-NMR (500 MHz, $CDCl_3$): 0.85 (*s*, Me(27)); 0.86 (*s*, Me(26)); 0.89 (*s*, Me(30)); 0.90 (*s*, Me(25)); 0.97 (*s*, Me(29)); 1.08 (*s*, Me(24)); 1.17 (*s*, Me(23)); 0.84–0.92 (*m*, H_a–C(12)); 1.52–1.58 (*dm*, ^2J = 12.8, H_e–C(12)); 1.56–1.62 (*dm*, ^2J = 13.5, H_e–C(6)); 1.76 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.77–1.83 (*dm*, ^2J = 13.5, H_e–C(16)); 1.95–2.04 (*m*, H–C(3′), H–C(5′)); 2.22 (*s*, Me(7′)); 2.28, 2.31 (*AB*, *J* = 18.1, CH_2(1)); 2.72–2.87 (*m*, H–C(5), H–C(9), H–C(3′) or H–C(5′), H–C(2′) or H–C(6′)); 3.02–3.12 (*m*, H–C(5′) or H–C(3′), H–C(6′) or H–C(2′)); 3.68 (br. *d*, *J* = 12.5, H–C(2′) or H–C(6′)); 3.86 (*s*, H–C(19)); 4.35 (br. *d*, *J* = 12.5, H–C(6′) or H–C(2′)); others 1.13–1.52. HR-MS: 566.4061 ($[M - H_2O]^+$, $C_{35}H_{54}O_4N_2^+$; calc. 566.4184).

Table 2. *^{13}C-NMR Data* (125 MHz) *of Compounds* **4**–**8**[1]). δ in ppm.

C-Atom	**4** (in (D_6)DMSO)	**5** (in $CDCl_3$)	**6** (in $CDCl_3$/(D_6)DMSO 5 : 1)	**7** (in $CDCl_3$)	**8** (in $CDCl_3$)
C(1)	38.9 (*t*)	38.5 (*t*)	38.2 (*t*)	39.1 (*t*)	55.6 (*t*)
C(2)	168.8 (*s*)	169.5 (*s*)	168.9 (*s*)	170.4 (*s*)	224.0 (*s*)
C(3)	180.1 (*s*)	184.0 (*s*)	181.8 (*s*)	183.9 (br. *s*)	–
C(4)	46.0 (*s*)	45.3 (*s*)	44.5 (*s*)	46.3 (br. *s*)	45.7 (*s*)
C(5)	46.6 (*d*)	47.9 (*d*)	47.5 (*d*)	47.6 (*d*)	59.5 (*d*)
C(6)	20.9 (*t*)	19.2 (*t*)	18.9 (*t*)	20.5 (*t*)	17.8 (*t*)
C(7)	32.2 (*t*)	32.5 (*t*)	32.1 (*t*)	32.6 (*t*)	33.2 (*t*)
C(8)	39.8 (*s*)	40.3 (*s*)	39.9 (*s*)	40.4 (*s*)	41.3 (*s*)
C(9)	40.9 (*d*)	41.3 (*d*)	40.2 (*d*)	41.7 (*d*)	49.4 (*d*)
C(10)	42.1 (*s*)	43.0 (*s*)	42.1 (*s*)	42.9 (*s*)	41.2 (*s*)
C(11)	21.0 (*t*)	21.9 (*t*)	21.1 (*t*)	21.7 (*t*)	23.6 (*t*)
C(12)	26.0 (*t*)	26.4 (*t*)	26.1 (*t*)	26.5 (*t*)	26.1 (*t*)
C(13)	35.9 (*d*)	36.1 (*d*)	35.6 (*d*)	36.0 (*d*)	35.9 (*d*)
C(14)	39.7 (*s*)	40.2 (*s*)	39.7 (*s*)	40.1 (*s*)	40.0 (*s*)
C(15)	27.4 (*t*)	27.8 (*t*)	27.4 (*t*)	27.8 (*t*)	27.8 (*t*)
C(16)	25.0 (*t*)	25.3 (*t*)	25.0 (*t*)	25.4 (*t*)	25.4 (*t*)
C(17)	45.4 (*s*)	46.0 (*s*)	45.5 (*s*)	46.0 (*s*)	46.0 (*s*)
C(18)	45.5 (*d*)	46.5 (*d*)	46.0 (*d*)	46.5 (*d*)	46.6 (*d*)
C(19)	84.9 (*d*)	85.7 (*d*)	85.4 (*d*)	85.7 (*d*)	85.9 (*d*)
C(20)	33.0 (*s*)	33.4 (*s*)	33.0 (*s*)	33.4 (*s*)	33.4 (*s*)
C(21)	32.0 (*t*)	32.2 (*t*)	31.8 (*t*)	32.2 (*t*)	32.2 (*t*)
C(22)	30.8 (*t*)	31.7 (*t*)	31.3 (*t*)	31.7 (*t*)	31.8 (*t*)
C(23)	25.5[a]) (*q*)	30.9 (*q*)	29.9 (*q*)	27.6 (br. *q*)	27.6 (*q*)
C(24)	25.1[a]) (*q*)	21.3 (*q*)	21.1 (*q*)	23.9 (br. *q*)	20.9 (*q*)
C(25)	20.5 (*q*)	21.5 (*q*)	20.5 (*q*)	20.8 (*q*)	17.9 (*q*)
C(26)	15.1 (*q*)	15.2 (*q*)	15.0 (*q*)	15.5 (*q*)	15.5 (*q*)
C(27)	13.5 (*q*)	13.8 (*q*)	13.3 (*q*)	13.6 (*q*)	13.6 (*q*)
C(28)	178.7 (*s*)	179.6 (*s*)	179.4 (*s*)	179.7 (*s*)	179.5 (*s*)
C(29)	28.3 (*q*)	28.6 (*q*)	28.2 (*q*)	28.6 (*q*)	28.6 (*q*)
C(30)	23.2 (*q*)	23.8 (*q*)	23.3 (*q*)	23.8 (*q*)	23.8 (*q*)
C(2′)	41.4[b]) (br. *t*)	44.2[a]) (*t*)	41.5[a]) (br. *t*)	45.6[a]) (*t*)	
C(3′)	25.8[c]) (br. *t*)	53.5[b]) (*t*)	50.2 (br. *t*)	66.8[b]) (*t*)	
C(4′)	24.0 (*t*)	–	–	–	
C(5′)	25.3[c]) (br. *t*)	54.0[b]) (*t*)	50.2 (br. *t*)	66.3[b]) (*t*)	
C(6′)	*ca.* 39.7[b]) (br. *t*)	39.8[a]) (*t*)	37.4[a]) (br. *t*)	41.4[a]) (*t*)	
C(7′)	41.4[b]) (br. *t*)	44.2 (*q*)	51.3 (*t*)		
C(8′)	25.8[c]) (br. *t*)		8.9 (*q*)		

[a]) [b]) [c]) Interchangeable signals.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-7-[2-(4-Ethylpiperazin-1-yl)-2-oxoethyl]hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**6**): ^{1}H-NMR (500 MHz, $CDCl_3$): 0.81 (*s*, Me(26)); 0.84 (*s*, Me(27), Me(30)); 0.85 (*s*, Me(25)); 0.92 (*s*, Me(29)); 1.03 (*s*, Me(24)); 1.10 (*s*, Me(23)); 1.33 (*t*, J(8′,7′) = 7.0, Me(8′)); 1.72 (*dt*, ^2J = 13.8, J(16e,15) = 3.2, H_e–C(16)); 1.74 (*d*, J(18,13) = 11.1, H–C(18)); 2.18, 2.23 (*AB*, J = 18.7, CH_2(1)); 2.54 (*dd*, J(5,6a) = 11.8, J(5,6e) = 2.2, H–C(5)); 2.98 (*q*, J(7′,8′) = 7.0, CH_2(7′)); 3.03 (*dd*, J(9,11a) = 12.5, J(9,11e) = 2.5, H–C(9)); 3.83 (*s*, H–C(19)); signals of the piperazine moiety: 2.89–3.15 (*m*, 3 H); 3.15–3.30 (*m*, 1 H); 3.40 (br. *s*, 1 H); 3.53–3.70 (*m*, 2 H); 4.10 (br. *s*, 1 H); others 0.65–1.43. Anal. calc. for $C_{36}H_{58}N_2O_5$ (598.86): C 72.20, H 9.76, N 4.68; found: C 72.05, 72.11, H 9.73, 9.77, N 4.45, 4.55.

Table 3. *^{13}C-NMR Data* ($CDCl_3$) *of Compounds* **14**–**17**, **22**, **24**, **25**, *and* **32**[1]). δ in ppm.

C-Atom	**14** (125 MHz)	**15** (125 MHz)	**16** (125 MHz)	**17** (125 MHz)	**22** (125 MHz)	**24** (100 MHz)	**25** (100 MHz)	**32** (125 MHz)
C(1)	48.6 (*t*)	48.0, 48.2 (*t*)	48.7 (*t*)	48.8 (*t*)	76.6 (*s*)	76.6 (*s*)	76.6 (*s*)	39.3 (*t*)
C(2)	172.2 (*s*)	171.8, 172.3 (*s*)	171.9 (*s*)	172.3 (*s*)	209.6 (*s*)	209.7 (*s*)	209.5 (*s*)	169.2 (*s*)
C(3)	188.9 (*s*)	189.0, 188.8 (*s*)	188.5 (*s*)	189.0 (*s*)	–	–	–	179.5 (*s*)
C(4)	49.4 (*s*)	49.6, 49.6 (*s*)	49.6 (*s*)	50.0 (*s*)	48.4 (*s*)	48.5 (*s*)	48.6 (*s*)	46.1 (*s*)
C(5)	52.2 (*d*)	52.2, 52.3 (*d*)	52.5 (*d*)	52.9 (*d*)	53.2 (*d*)	53.2 (*d*)	53.1 (*d*)	48.0 (*d*)
C(6)	18.4 (*t*)	18.5, 18.5 (*t*)	18.5 (*t*)	18.7 (*t*)	17.0 (*t*)	17.1 (*t*)	17.0 (*t*)	20.6 (*t*)
C(7)	34.0 (*t*)	32.2, 34.1 (*t*)	34.0 (*t*)	34.0 (*t*)	32.3 (*t*)	32.3 (*t*)	32.3 (*t*)	32.6 (*t*)
C(8)	40.8 (*s*)	40.8, 40.8 (*s*)	40.8 (*s*)	40.9 (*s*)	41.7 (*s*)	41.8 (*s*)	41.8 (*s*)	40.3 (*s*)
C(9)	45.3 (*d*)	45.3, 45.3 (*d*)	45.3 (*d*)	45.5 (*d*)	42.7 (*d*)	42.8 (*d*)	42.3 (*d*)	41.3 (*d*)
C(10)	40.6 (*s*)	40.5, 40.5 (*s*)	40.7 (*s*)	40.9 (*s*)	56.4 (*s*)	57.1 (*s*)	57.2 (*s*)	42.5 (*s*)
C(11)	21.2 (*t*)	21.2, 21.2 (*t*)	21.2 (*t*)	21.3 (*t*)	24.9 (*t*)	25.2 (*t*)	25.8 (*t*)	21.6 (*t*)
C(12)	26.0 (*t*)	26.0, 26.0 (*t*)	26.0 (*t*)	26.1 (*t*)	25.7 (*t*)	25.8 (*t*)	25.2 (*t*)	26.6 (*t*)
C(13)	35.8 (*d*)	35.8, 35.8 (*d*)	35.8 (*d*)	35.9 (*d*)	35.7 (*d*)	35.7 (*d*)	35.7 (*d*)	36.1 (*d*)
C(14)	40.3 (*s*)	40.3, 40.3 (*s*)	40.3 (*s*)	40.3 (*s*)	40.7 (*s*)	40.7 (*s*)	40.7 (*s*)	40.1 (*s*)
C(15)	27.7 (*t*)	27.7, 27.7 (*t*)	27.7 (*t*)	27.7 (*t*)	27.8 (*t*)	27.8 (*t*)	27.8 (*t*)	27.8 (*t*)
C(16)	25.4 (*t*)	25.4, 25.4 (*t*)	25.4 (*t*)	25.4 (*t*)	25.2 (*t*)	25.2 (*t*)	25.2 (*t*)	25.4 (*t*)
C(17)	45.9 (*s*)	45.9, 45.9 (*s*)	45.9 (*s*)	45.9 (*s*)	45.9 (*s*)	45.9 (*s*)	45.9 (*s*)	46.0 (*s*)
C(18)	46.5 (*d*)	46.6, 46.6 (*d*)	46.5 (*d*)	46.5 (*d*)	46.4 (*d*)	46.4 (*d*)	46.4 (*d*)	46.5 (*d*)
C(19)	85.8 (*d*)	85.8, 85.8 (*d*)	85.8 (*d*)	85.8 (*d*)	85.8 (*d*)	85.7 (*d*)	85.7 (*d*)	85.8 (*d*)
C(20)	33.4 (*s*)	33.4, 33.4 (*s*)	33.4 (*s*)	33.4 (*s*)	33.4 (*s*)	33.4 (*s*)	33.4 (*s*)	33.4 (*s*)
C(21)	32.2 (*t*)	32.2, 32.2 (*t*)	32.2 (*t*)	32.2 (*t*)	32.1 (*t*)	32.1 (*t*)	32.0 (*t*)	32.2 (*t*)
C(22)	31.8 (*t*)	31.8, 31.8 (*t*)	31.8 (*t*)	31.8 (*t*)	31.7 (*t*)	31.7 (*t*)	31.7 (*t*)	31.8 (*t*)
C(23)	32.2 (*q*)	32.5, 33.1 (*q*)	32.5 (*q*)	32.7 (*q*)	27.3 (*q*)	27.2 (*q*)	27.2 (*q*)	27.6 (*q*)
C(24)	20.7 (*q*)	20.9, 21.1 (*q*)	20.5 (*q*)	20.2 (*q*)	22.0 (*q*)	22.1 (*q*)	22.1 (*q*)	24.4 (*q*)
C(25)	20.4 (*q*)	20.2, 20.4 (*q*)	20.3 (*q*)	20.4 (*q*)	16.7 (*q*)	16.8 (*q*)	16.8 (*q*)	20.8 (*q*)
C(26)	16.2 (*q*)	16.2, 16.2 (*q*)	16.1 (*q*)	16.2 (*q*)	16.0 (*q*)	16.0 (*q*)	16.0 (*q*)	15.5 (*q*)
C(27)	13.6 (*q*)	13.3, 13.5 (*q*)	13.4 (*q*)	13.5 (*q*)	13.7 (*q*)	13.7 (*q*)	13.7 (*q*)	13.9 (*q*)
C(28)	179.6 (*s*)	179.6, 179.6 (*s*)	179.6 (*s*)	179.6 (*s*)	179.3 (*s*)	179.3 (*s*)	179.3 (*s*)	179.7 (*s*)
C(29)	28.6 (*q*)	28.6, 28.6 (*q*)	28.6 (*q*)	28.6 (*q*)	28.6 (*q*)	28.5 (*q*)	28.5 (*q*)	28.6 (*q*)
C(30)	23.7 (*q*)	23.7, 23.7 (*q*)	23.7 (*q*)	23.8 (*q*)	23.7 (*q*)	23.7 (*q*)	23.7 (*q*)	23.8 (*q*)
C(31)	46.2 (*t*)	46.6, 48.8 (*t*)	40.8 (*t*)	31.8 (*q*)				42.1[a]) (br. *t*)
C(32)	34.8 (*t*)	76.4, 77.0 (*d*)	33.4 (*t*)					25.7[b]) (br. *t*)

Table 3 (cont.)

C-Atom	**14** (125 MHz)	**15** (125 MHz)	**16** (125 MHz)	**17** (125 MHz)	**22** (125 MHz)	**24** (100 MHz)	**25** (100 MHz)	**32** (125 MHz)
C(33)	138.6 (*s*)	28.9, 28.6 (*t*)	171.5 (*s*)					24.5 (*t*)
C(34)	128.9 (*d*)	25.2, 25.2 (*t*)	51.6 (*q*)					26.4[b]) (br. *t*)
C(35)	128.3 (*d*)	67.4, 67.1 (*t*)						46.2[a]) (br. *t*)
C(36)	126.3 (*d*)							63.2 (*t*)
C(37)	128.3 (*d*)							25.8 (*t*)
C(38)	128.9 (*d*)							29.1 (*t*)
C(39)								44.4 (*t*)
C(2′)					159.1 (*s*)	158.1 (*s*)	158.1 (*s*)	
C(4′)					188.7 (*s*)	188.8 (*s*)	188.9 (*s*)	
C(5′)					170.6 (*s*)	169.9 (*s*)	169.6 (*s*)	
C(6′)					40.6 (*t*)	122.9 (*s*)	130.3 (*s*)	
C(7′)					33.3 (*t*)	126.9 (*d*)	125.6 (*d*)	
C(8′)					136.8 (*s*)	114.5 (*d*)	129.3 (*d*)	
C(9′)					128.6 (*d*)	160.1 (*s*)	129.5 (*d*)	
C(10′)					128.6 (*d*)			
C(11′)					126.8 (*d*)			
C(12′)						55.4 (*q*)		

[a]) [b]) Interchangeable signals.

Table 4. *^{13}C-NMR Data* ($CDCl_3$) *of Compounds* **33**, **34**, **30**, **35**, **19**, **21**, *and* **20**[1]). δ in ppm.

C-Atom	**33** (125 MHz)	**34** (125 MHz)	**30** (125 MHz)	**19** (100 MHz)	**35** (100 MHz)	**21** (100 MHz)	**20** (125 MHz)
C(1)	44.6 (*t*)	44.7 (*t*)	44.6 (*t*)	44.5 (*t*)	44.6 (*t*)	45.8 (*t*)	45.5 (*t*)
C(2)	171.8 (*s*)	172.3 (*s*)	170.6 (*s*)	172.1 (*s*)	182.0 (*s*)	170.3 (*s*)	170.2 (*s*)
C(3)	183.6 (*s*)	182.1 (*s*)	181.8 (*s*)	183.7 (*s*)	172.4 (*s*)	185.3 (*s*)	185.0 (*s*)
C(4)	45.7 (*s*)	45.7 (*s*)	45.7 (*s*)	45.9[a]) (*s*)	45.6 (*s*)	45.5 (*s*)	46.1 (*t*)
C(5)	49.6 (*d*)	49.6 (*d*)	50.4 (*d*)	49.2 (*d*)	49.6 (*d*)	50.1 (*d*)	50.0 (*d*)
C(6)	20.3 (*t*)	20.0 (*t*)	20.3 (*t*)	20.4 (*t*)	19.9 (*t*)	20.1 (*t*)	20.2 (*t*)
C(7)	32.4 (*t*)	32.5 (*t*)	32.4 (*t*)	32.4 (*t*)	32.4 (*t*)	32.3 (*t*)	32.4 (*t*)
C(8)	40.1[a]) (*s*)	40.2 (*s*)	40.1 (*s*)	40.2 (*s*)	40.1[a]) (*s*)	40.1[a]) (*s*)	40.2[a]) (*s*)
C(9)	43.5 (*d*)	44.2 (*d*)	43.2 (*d*)	43.6 (*d*)	44.2 (*d*)	43.6 (*d*)	43.7 (*d*)
C(10)	43.3 (*s*)	43.0 (*s*)	43.1 (*s*)	43.2 (*s*)	42.9 (*s*)	43.6 (*s*)	43.6 (*s*)
C(11)	22.4 (*t*)	20.3 (*t*)	22.5 (*t*)	22.3 (*t*)	22.0 (*t*)	22.4 (*t*)	22.4 (*t*)
C(12)	25.8 (*t*)	25.8 (*t*)	25.8 (*t*)	25.8 (*t*)	25.8 (*t*)	25.9 (*t*)	26.0 (*t*)
C(13)	36.2 (*d*)	36.2 (*d*)	36.2 (*d*)	36.1 (*d*)	36.1 (*d*)	36.2 (*d*)	36.2 (*d*)
C(14)	40.1[a]) (*s*)	40.2 (*s*)	40.2 (*s*)	40.1 (*s*)	40.1[a]) (*s*)	40.1[a]) (*s*)	40.2[a]) (*s*)
C(15)	27.6 (*t*)	27.7 (*t*)	27.7 (*t*)	27.6 (*t*)	27.6 (*t*)	27.6 (*t*)	27.6 (*t*)
C(16)	25.3 (*t*)	25.4 (*t*)	25.4 (*t*)	25.3 (*t*)	25.3 (*t*)	25.3 (*t*)	25.4 (*t*)
C(17)	46.0 (*s*)	46.0 (*s*)	46.0 (*s*)	46.0[a]) (*s*)	46.0 (*s*)	46.1 (*s*)	45.6 (*s*)
C(18)	46.3 (*d*)	46.4 (*d*)	46.4 (*d*)	46.3 (*d*)	46.3 (*d*)	46.3 (*d*)	46.4 (*d*)
C(19)	85.7 (*d*)	85.8 (*d*)	85.8 (*d*)	85.7 (*d*)	85.8 (*d*)	85.9 (*d*)	85.9 (*d*)
C(20)	33.4 (*s*)	33.3 (*s*)	33.4 (*s*)	33.4 (*s*)	33.3 (*s*)	33.4 (*s*)	33.4 (*s*)
C(21)	32.2 (*t*)	32.2 (*t*)	32.2 (*t*)	32.1 (*t*)	32.1 (*t*)	32.1 (*t*)	32.2 (*t*)
C(22)	31.7 (*t*)	31.7 (*t*)	31.8 (*t*)	31.7 (*t*)	31.7 (*t*)	31.7 (*t*)	31.7 (*t*)
C(23)	29.5 (*q*)	31.2 (*q*)	29.6 (*q*)	29.1 (*q*)	31.2 (*q*)	30.1 (*q*)	29.9 (*q*)
C(24)	22.1 (*q*)	20.6 (*q*)	22.0 (*q*)	22.4 (*q*)	20.5 (*q*)	21.6 (*q*)	21.8 (*q*)
C(25)	19.5 (*q*)	20.3 (*q*)	19.5 (*q*)	19.6 (*q*)	20.3 (*q*)	19.6 (*q*)	19.6 (*q*)
C(26)	15.6 (*q*)	15.6 (*q*)	15.6 (*q*)	15.6 (*q*)	15.6 (*q*)	15.7 (*q*)	15.7 (*q*)
C(27)	13.3 (*q*)	13.4 (*q*)	13.4 (*q*)	13.3 (*q*)	13.4 (*q*)	13.3 (*q*)	13.4 (*q*)
C(28)	179.8 (*s*)	179.9 (*s*)	179.8 (*s*)	179.9 (*s*)	180.0 (*s*)	180.2 (*s*)	180.0 (*s*)
C(29)	28.6 (*q*)	28.6 (*q*)	28.6 (*q*)	28.6 (*q*)	28.6 (*q*)	28.6 (*q*)	28.6 (*q*)
C(30)	23.8 (*q*)	23.8 (*q*)	23.8 (*q*)	23.8 (*q*)	23.7 (*q*)	23.8 (*q*)	23.9 (*q*)
C(2′)	43.3 (*t*)	44.4 (*t*)	43.3 (*t*)	42.9 (*t*)	43.8 (*t*)	138.1 (*s*)	131.2 (*s*)
C(3′)	138.6 (*s*)	136.7 (*s*)	138.9 (*s*)	130.3 (*s*)	128.7 (*s*)	119.9 (*d*)	114.0 (*d*)

Table 4 (cont.)

C-Atom	**33** (125 MHz)	**34** (125 MHz)	**30** (125 MHz)	**19** (100 MHz)	**35** (100 MHz)	**21** (100 MHz)	**20** (125 MHz)
C(4′)	127.8 (*d*)	128.0 (*d*)	127.7 (*d*)	129.2 (*d*)	129.4 (*d*)	128.8 (*d*)	121.2 (*d*)
C(5′)	128.4 (*d*)	128.8 (*d*)	128.4 (*d*)	113.9 (*d*)	114.0 (*d*)	123.9 (*d*)	156.2 (*s*)
C(6′)	127.1 (*d*)	127.9 (*d*)	127.0 (*d*)	158.8 (*s*)	159.1 (*s*)		
C(8′)							55.4 (*q*)
C(9′)			52.1 (*q*)	55.1 (*q*)	44.1 (*q*)		

[a]) Interchangeable signals.

Table 5. *^{13}C-NMR Data* (125 MHz, $CDCl_3$) *of Compounds* **18**, **10**, **36**, **11**, **37**, **12**, *and* **13**[1]). δ in ppm.

C-Atom	**18**	**10**	**36** (major, minor)	**11** (major, minor)	**37**	**12**	**13**
C(1)	44.8 (*t*)	44.9 (*t*)	42.4, 43.2 (*t*)	44.8, 44.7 (*t*)	44.1 (*t*)	44.9 (*t*)	44.9 (*t*)
C(2)	172.6 (*s*)	172.3 (*s*)	172.1, 172.1 (*s*)	172.4, 172.3 (*s*)	172.2 (*s*)	172.2 (*s*)	172.2 (*s*)
C(3)	183.7 (*s*)	182.3 (*s*)	182.8, 182.5 (*s*)	182.3, 182.2 (*s*)	183.2 (*s*)	182.3 (*s*)	183.0 (*s*)
C(4)	45.8 (*s*)	45.6 (*s*)	45.3, 45.6 (*s*)	45.7, 45.7 (*s*)	45.8 (*s*)	45.7 (*s*)	45.6 (*s*)
C(5)	49.2 (*d*)	49.5 (*d*)	50.2, 49.8 (*d*)	49.6, 49.4 (*d*)	49.2 (*d*)	49.5 (*d*)	49.7 (*d*)
C(6)	20.2 (*t*)	19.9 (*t*)	19.2,19.7 (*t*)	20.0, 20.0 (*t*)	20.2 (*t*)	20.1 (*t*)	20.0 (*t*)
C(7)	32.4 (*t*)	32.4 (*t*)	33.0, 32.8 (*t*)	32.5, 32.5 (*t*)	32.5 (*t*)	32.5 (*t*)	32.5 (*t*)
C(8)	40.2 (*s*)	40.2 (*s*)	40.3, 40.3 (*s*)	40.2, 40.2 (*s*)	40.2 (*s*)	40.2[a]) (*s*)	40.3 (*s*)
C(9)	43.7 (*d*)	44.2 (*d*)	42.2, 42.9 (*d*)	44.1, 44.2 (*d*)	43.3 (*d*)	44.2 (*d*)	44.3 (*d*)
C(10)	43.1 (*s*)	42.9 (*s*)	43.8, 43.1 (*s*)	43.0, 43.0 (*s*)	43.1 (*s*)	43.0 (*s*)	43.1 (*s*)
C(11)	22.3 (*t*)	22.1 (*t*)	21.9, 22.0 (*t*)	22.1, 22.1 (*t*)	22.2 (*t*)	22.1 (*t*)	22.2 (*t*)
C(12)	26.0 (*t*)	25.8 (*t*)	26.2, 26.1 (*t*)	25.8, 25.8 (*t*)	26.0 (*t*)	25.8 (*t*)	25.9 (*t*)
C(13)	36.2 (*d*)	36.2 (*d*)	36.1, 36.1 (*d*)	36.2, 36.2 (*d*)	36.1 (*d*)	36.2 (*d*)	36.3 (*d*)
C(14)	40.1 (*s*)	40.2 (*s*)	40.2, 40.2 (*s*)	40.2, 40.2 (*s*)	40.2 (*s*)	40.2[a]) (*s*)	40.3 (*s*)
C(15)	27.6 (*t*)	27.7 (*t*)	27.8, 27.7 (*t*)	27.7, 27.7 (*t*)	27.6 (*t*)	27.7 (*t*)	27.7 (*t*)
C(16)	25.4 (*t*)	25.3 (*t*)	25.4, 25.4 (*t*)	25.3, 25.3 (*t*)	25.4 (*t*)	25.4 (*t*)	25.4 (*t*)
C(17)	46.0 (*s*)	46.0 (*s*)	46.0, 46.0 (*s*)	46.0, 46.0 (*s*)	46.0 (*s*)	46.0 (*s*)	46.0 (*s*)
C(18)	46.4 (*d*)	46.3 (*d*)	46.6, 46.5 (*d*)	46.3, 46.3 (*d*)	46.4 (*d*)	46.3 (*d*)	46.4 (*d*)
C(19)	85.8 (*d*)	85.8 (*d*)	85.8, 85.7 (*d*)	85.8, 85.8 (*d*)	85.7 (*d*)	85.8 (*d*)	85.8 (*d*)
C(20)	33.4 (*s*)	33.4 (*s*)	33.4, 33.4 (*s*)	33.4, 33.4 (*s*)	33.4 (*s*)	33.4 (*s*)	33.4 (*s*)
C(21)	32.2 (*t*)	32.2 (*t*)	32.2, 32.2 (*t*)	32.2, 32.2 (*t*)	32.2 (*t*)	32.2 (*t*)	32.3 (*t*)
C(22)	31.7 (*t*)	31.7 (*t*)	31.8, 31.8 (*t*)	31.7, 31.7 (*t*)	31.8 (*t*)	31.7 (*t*)	31.8 (*t*)
C(23)	29.2 (*q*)	31.3 (*q*)	29.8, 29.4 (*q*)	31.3, 31.1 (*q*)	29.1 (*q*)	31.1 (*q*)	31.3 (*q*)
C(24)	22.2 (*q*)	20.2 (*q*)	21.2, 21.7 (*q*)	20.5, 20.4 (*q*)	22.2 (*q*)	20.5 (*q*)	20.4 (*q*)
C(25)	19.7 (*q*)	20.2 (*q*)	20.9, 20.3 (*q*)	20.3, 20.3 (*q*)	19.8 (*q*)	20.2 (*q*)	20.3 (*q*)
C(26)	15.6 (*q*)	15.6 (*q*)	15.7, 15.7 (*q*)	15.6, 15.6 (*q*)	15.6 (*q*)	15.0 (*q*)	15.7 (*q*)
C(27)	13.4 (*q*)	13.4 (*q*)	13.8, 13.6 (*q*)	13.4, 13.4 (*q*)	13.3 (*q*)	13.4 (*q*)	13.5 (*q*)
C(28)	179.9 (*s*)	179.9 (*s*)	179.8, 179.8 (*s*)	179.8, 179.8 (*s*)	179.8 (*s*)	179.9 (*s*)	179.9 (*s*)
C(29)	28.6 (*q*)	28.6 (*q*)	28.6, 28.6 (*q*)	28.6, 28.6 (*q*)	28.6 (*q*)	28.6 (*q*)	28.6 (*q*)
C(30)	23.9 (*q*)	23.8 (*q*)	23.8, 23.8 (*q*)	23.8, 23.8 (*q*)	23.8 (*q*)	23.8 (*q*)	23.8 (*q*)
C(31)	40.6 (*t*)	41.4 (*t*)	43.5, 43.2 (*t*)	43.9, 43.7 (*t*)	35.0 (*t*)	35.5 (*t*)	27.2 (*q*)
C(32)	35.4 (*t*)	34.8 (*t*)	76.7, 78.0 (*d*)	76.9, 76.8 (*d*)	33.8 (*t*)	32.7 (*t*)	
C(33)	138.6 (*s*)	137.9 (*s*)	28.4, 28.8 (*t*)	28.7, 28.6 (*t*)	173.1 (*s*)	172.8 (*s*)	
C(34)	128.5 (*d*)	128.5 (*d*)	25.6, 25.4 (*t*)	25.7, 25.6 (*t*)	51.8 (*q*)	51.9 (*q*)	
C(35)	128.5 (*d*)	128.7 (*d*)	67.8, 67.9 (*t*)	68.1, 68.0 (*t*)			
C(36)	126.4 (*d*)	126.8 (*d*)					

[a]) Interchangeable signals.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-7-[2-(morpholin-4-yl)-2-oxoethyl]-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**7**): ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*s*, Me(26)); 0.87 (*s*, Me(27)); 0.89 (*s*, Me(30)); 0.90 (*s*, Me(25)); 0.97 (*s*, Me(29)); 1.19 (*s*, Me(24)); 1.21 (*s*, Me(23)); 0.90 – 0.99 (*m*, H_a–C(12)); 1.59 (*dddd*, ^2J = 12.8, *J*(12e,11a) = 4.2, *J*(12e,13a) = 3.1, *J*(12e,11e) = 2.8, H_e–C(12)); 1.78 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.81 (*ddd*, ^2J = 13.7, *J*(16e,15a) = *J*(16e,15e) = 3.4, H_e–C(16)); 2.27, 2.39 (*AB*, *J* = 17.9, CH_2(1)); 2.71 (*dd*, *J*(5,6a) = 9.3, *J*(5,6e) = 5.3, H–C(5)); 2.78 (*dd*, *J*(9,11a) = 12.5, *J*(9,11e) = 2.6, H–C(9)); 3.87 (*s*, H–C(19)); others 1.13 – 1.55. Anal. calc. for $C_{34}H_{53}NO_6$ (571.79): C 71.42, H 9.34, N 2.45; found: C 71.53, 71.50, H 9.29, 9.31, N 2.51, 2.47.

2.2. *Pyrolysis of an Amic Acid Mixture: (3a*R*,5a*R*,5b*R*,7a*R*,11*R*,11a*R*,11b*R*,13a*R*,13b*R*)-Octadecahydro-3,3,5a,5b,10,10,13b-heptamethyl-11,7a-(epoxymethano)-7a*H*-cyclopenta[*a*]chrysene-2,15(1*H*)-dione (=(18α,19β)-19-Hydroxy-3-oxo-2-noroleanan-28-oic Acid γ-Lactone*; **8**). The amic acid mixture obtained from anhydride **2** 0.523 g (1.08 mmol) with benzylamine (0.121 g, 1.13 mmol) in THF (7 ml) was heated under Ar at 130–220° for 3 h. CC (SiO_2, CH_2Cl_2/Et_2O) and recrystallization from EtOH/CH_2Cl_2 gave **8** (0.213 g, 44% from **2**). White powder. IR: 1757 (lactone), 1737 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.83 (*d*, *J*(25,1α) = 1.2, Me(25)); 0.90 (*s*, Me(27)); 0.91 (*s*, Me(26)); 0.93 (*s*, Me(30)); 0.94 (*s*, Me(24)); 0.98 (*s*, Me(23)); 1.00 (*s*, Me(29)); 1.04 (*dddd*, ^2J = *J*(12a,11a) = *J*(12a,13) = 12.8, *J*(12a,11e) = 4.2, H_a–C(12)); 1.17–1.22 (*m*, H_e–C(15)); 1.28 (*ddm*, ^2J = 13.0, *J*(11e,12a) = 4.2, H_e–C(11)); 1.63 (*dddd*, ^2J = 12.8, *J*(12e,11a) = 4.5, *J*(12e,13a) = 3.4, *J*(12e,11e) = 2.8, H_e–C(12)); 1.70 (*dd*, *J*(9a,11a) = 12.6, *J*(9a,11e) = 3.2, H_a–C(9)); 1.78 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.83–1.88 (*m*, H_e–C(16)); 1.86 (*dd*, ^2J = 15.8, *J*(1α,25) = 1.2, $H_α$–C(1)); 2.15 (*d*, ^2J = 15.8, $H_β$–C(1)); 3.90 (*s*, H–C(19)); others 1.30–1.56. Anal. calc. for $C_{29}H_{44}O_3$ (440.66): C 79.04, H 10.06; found: C 78.79, 78.86, H 9.88, 9.99.

2.3. *Cyclic Imides* **14**–**17** *and Spiro Derivatives* **22**–**25**: *General Procedure.* Oxalyl chloride (0.10–0.15 ml, 1.2–1.7 mmol) was added to a soln. of the corresponding amic acid (0.2 mmol) in THF (7–10 ml). After standing for 24–48 h, the solvent was evaporated and the residue subjected to CC (SiO_2, CH_2Cl_2/Et_2O): **14**–**17** and **22**–**25**.

*(5a*R*,7a*R*,7b*R*,9a*R*,13*R*,13a*R*,13b*R*,15a*R*,15b*R*)-Octadecahydro-5,5,7a,7b,12,12,15b-heptamethyl-3-(2-phenylethyl)-13,9a-(epoxymethano)-9a*H*-chryseno[1,2-*d*]azepine-2,4,17(1*H*,3*H*)-trione* (**14**): M.p. 259.4°. IR: 1772 (lactone), 1713, 1668 (CONRCO). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.90 (*s*, Me(26), Me(27)); 0.92 (*s*, Me(23)); 0.93 (*s*, Me(30)); 0.95 (*s*, Me(25)); 1.01 (*s*, Me(29)); 1.10–1.20 (*m*, H_a–C(12), H_e–C(15)); 1.18 (*s*, Me(24)); 1.67–1.73 (*dm*, ^2J = 12.8, H_e–C(12)); 1.74–1.82 (*m*, H_e–C(11), H_a–C(9)); 1.81 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.86 (*ddd*, ^2J = 13.5, *J*(16e,15a) = 3.5, *J*(16e,15e) = 3.0, H_e–C(16)); 2.03 (*d*, ^2J = 13.3, H–C(1)); 2.79 (*d*, ^2J = 13.3, H′–C(1)); 2.86 (*ddd*, ^2J = 13.4, *J*(32,31′) = 8.3, *J*(32,31) = 5.7, H–C(32)); 2.93 (*ddd*, ^2J = 13.4, *J*(32′,31) = 8.3, *J*(32′,31′) = 7.5, H′–C(32)); 3.76 (*ddd*, ^2J = 13.4, *J*(31,32′) = 8.3, *J*(31,32) = 5.7, H–C(31)); 3.93 (*s*, H–C(19)); 3.95 (*ddd*, ^2J = 13.4, *J*(31′,32) = 8.3, *J*(31′,32′) = 7.5, H′–C(31)); 7.16 (*tt*, *J*(36,35) = 7.0, *J*(36,34) = 1.7, H–C(36)); 7.20 (br. *d*, *J*(34,35) = 7.5, H–C(34), H–C(38)); 7.24 (*dd*, *J*(35,34) = 7.5, *J*(35,36) = 7.0, H–C(35), H–C(37)); others 1.21–1.58. Anal. calc. for $C_{38}H_{53}NO_4$ (587.83): C 77.64, H 9.09, N 2.38; found: C 77.77, 77.48, H 9.10, 9.07, N 2.00, 2.02.

*(5a*R*,7a*R*,7b*R*,9a*R*,13*R*,13a*R*,13b*R*,15a*R*,15b*R*)-Octadecahydro-5,5,7a,7b,12,12,15b-heptamethyl-3-[(tetrahydrofuran-2-yl)methyl]-13,9a-(epoxymethano)-9a*H*-chryseno[1,2-*d*]azepine-2,4,17(1*H*,3*H*)-trione* (**15**): Spectra were recorded for a 1:1 mixture of diastereoisomers. IR: 1774 (lactone), 1747, 1689 (CONRCO). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86, 0.87 (2*s*, 2 Me(27)); 0.92 (*s*, 2 Me(26), 2 Me(30)); 0.98 (*s*, 2 Me(25)); 1.00 (*s*, 2 Me(29)); 1.08–1.19 (*m*, 2 H_a–C(12), 2 H_e–C(15)); 1.22, 1.23 (2*s*, 2 Me(24))); 1.26, 1.29 (2*s*, 2 Me(23)); 1.62–1.72 (*m*, 2 H_e–C(12)); 1.79 (*d*, *J*(18,13) = 11.1, 2 H–C(18)); 2.09, 2.10 (2*d*, ^2J = 13.2, 2 H–C(1)); 2.79, 2.80 (2*d*, ^2J = 13.2, 2 H′–C(1)); 3.45 (*dd*, ^2J = 13.4, *J*(31,32) = 4.0, H–C(31)); 3.62–3.69 (*m*, 3 H–C(35)); 3.72–3.78 (*m*, 3 H–C(31)); 3.79–3.86 (*m*, 1 H–C(35)); 3.92 (*s*, 2 H–C(19)); 3.90–3.97 (*m*, 1 H–C(32)); 4.15–4.22 (*m*, 1 H–C(32)); others 1.20–1.60, 1.75–1.97.

*(5a*R*,7a*R*,7b*R*,9a*R*,13*R*,13a*R*,13b*R*,15a*R*,15b*R*)-Eicosahydro-5,5,7a,7b,12,12,15b-heptamethyl-2,4,17-trioxo-13,9a-(epoxymethano)-9a*H*-chryseno[1,2-*d*]azepine-3(4*H*)-propanoic Acid Methyl Ester* (**16**): M.p. 261.4°. IR: 1774 (lactone), 1740 (COOMe), 1718, 1671 (CONRCO). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*s*, Me(27)); 0.90 (*s*, Me(26)); 0.92 (*s*, Me(30)); 0.97 (*s*, Me(25)); 0.99 (*s*, Me(29)); 1.11 (*dddd*, ^2J = *J*(12a,11a) = *J*(12a,13) = 12.8, *J*(12a,11e) = 4.0, H_a–C(12)); 1.13–1.18 (*dm*, ^2J = 13.0, H_e–C(15)); 1.21 (*s*, Me(24)); 1.23 (*s*, Me(23)); 1.58 (*dd*, *J*(5,6a) = 11.5, *J*(5,6e) = 2.1, H–C(5)); 1.65–1.70 (*dm*, ^2J = 12.8, H_e–C(12)); 1.72–1.77 (*dm*, ^2J = 12.5, H_e–C(11)); 1.78 (*d*, *J*(18,13) = 11.0, H–C(18)); 1.78 (br. *d*, *J*(9a,11a) = 12.5, H_a–C(9)); 1.84 (*ddd*, ^2J = 13.5, *J*(16e,15a) = 3.5, *J*(16e,15e) = 3.0, H_e–C(16)); 2.06 (*d*, ^2J = 13.3, H–C(1)); 2.53 (*dd*, *J*(32,31) = 7.5, *J*(32,31′) = 7.0, H–C(32)); 2.80 (*d*, ^2J = 13.3, H′–C(1)); 3.63 (*s*, MeO); 3.75 (*dt*, ^2J = 13.5, *J*(31,32) = 7.5, H–C(31)); 3.91 (*s*, H–C(19)); 3.98 (*dt*, ^2J = 13.5, *J*(31′,32) = 7.0, H′–C(31)); others 1.18–1.58. Anal. calc. for $C_{34}H_{51}NO_6$ (569.77): C 71.67, H 9.02, N 2.46; found: C 71.45, 71.31, H 8.57, 8.55, N 2.58, 2.59.

*(5a*R*,7a*R*,7b*R*,9a*R*,13*R*,13a*R*,13b*R*,15a*R*,15b*R*)-Octadecahydro-5,5,7a,7b,12,12,15b-octamethyl-13,9a-(epoxymethano)-9a*H*-chryseno[1,2-*d*]azepine-2,4,17(1*H*,3*H*)-trione* (**17**): M.p. 256.4°. IR: 1775 (lactone), 1716, 1669 (CONRCO). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.87 (*s*, Me(27)); 0.92 (*s*, Me(26)); 0.93

(*s*, Me(30)); 0.98 (*s*, Me(25)); 1.00 (*s*, Me(29)); 1.09–1.19 (*m*, H_a–C(12), H_e–C(15)); 1.23 (*s*, Me(24)); 1.24 (*s*, Me(23)); 1.58 (*dd*, *J*(5,6a) = 11.5, *J*(5,6e) = 2.0, H–C(5)); 1.66–1.72 (*dm*, ^2J = 13.0, H_e–C(12)); 1.73–1.79 (*dm*, ^2J = 12.7, H_e–C(11)); 1.80 (*d*, *J*(18,13) = 11.2, H–C(18)); 1.80 (br. *d*, *J*(9a,11a) = 12.0, H_a–C(9)); 1.85 (*ddd*, ^2J = 13.5, *J*(16e,15a) = 3.5, *J*(16e,15e) = 2.8, H_e–C(16)); 2.08 (*d*, ^2J = 13.3, H–C(1)); 2.81 (*d*, ^2J = 13.3, H′–C(1)); 3.06 (*s*, Me(31)); 3.92 (*s*, H–C(19)); others 1.23–1.58. Anal. calc. for $C_{31}H_{47}NO_4$ (497.71): C 74.81, H 9.52, N 2.81; found: C 75.09, 75.21, H 9.27, 8.97, N 2.72, 2.78.

*(1*S*,3a*R*,5a*R*,5b*R*,7a*R*,11*R*,11a*R*,11b*R*,13a*S*,13b*R*)-Octadecahydro-3,3,5a,5b,10,10,13b-heptamethyl-1′-(2-phenylethyl)spiro[11,7a-(epoxymethano)-7a*H*-cyclopenta[a]chrysene-1(2*H*),3′-pyrrolidine]-2,2′,4′,5′,15-pentone* (**22**): M.p. 271.5°. IR: 1775 (lactone), 1740, 1718 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.53–0.59 (*dm*, ^2J = 13.2, H_e–C(11)); 0.79 (*dddd*, ^2J = *J*(12a,11a) = *J*(12a,13) = 13.0, *J*(12a,11e) = 4.3, H_a–C(12)); 0.84 (*s*, Me(27)); 0.90 (*s*, Me(30)); 0.92 (*s*, Me(26)); 0.98 (*s*, Me(29)); 1.11 (*s*, Me(24)); 1.14 (*s*, Me(23)); 1.29 (*s*, Me(25)); 1.70 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.82–1.87 (*dm*, ^2J = 13.0, H_e–C(16)); 2.04 (*dd*, *J*(9,11a) = 13.1, *J*(9,11e) = 3.0, H–C(9)); 2.70 (*dd*, *J*(5,6a) = 10.5, *J*(5,6e) = 4.4, H–C(5)); 2.96 (*t*, *J*(7′,6′) = 7.6, 2 H–C(7′)); 3.80 (*s*, H–C(19)); 3.92–4.06 (*m*, 2 H–C(6′)); 7.21 (*tt*, *J*(11′,10′) = 7.0, *J*(11′,9′) = 1.7, H–C(11′)); 7.24 (br. *d*, *J*(9′,10′) = 7.0, H–C(9′)); 7.28 (br. *t*, *J*(10′,9′(11′)) = 7.0, H–C(10′)); others 1.12–1.62. Anal. calc. for $C_{40}H_{51}NO_6$ (641.84): C 74.85, H 8.01, N 2.18; found: C 74.46, 74.56, H 8.18, 8.19, N 2.20, 2.21.

*(1*S*,3a*R*,5a*R*,5b*R*,7a*R*,11*R*,11a*R*,11b*R*,13a*S*,13b*R*)-Octadecahydro-1′-[(4-methoxyphenyl)methyl]-3,3,5a,5b,10,10,13b-heptamethylspiro[11,7a-(epoxymethano)-7a*H*-cyclopenta[a]chrysene-1(2*H*),3′-pyrrolidine]-2,2′,4′,5′,15-pentone* (**23**): Anal. data in [16].

*(1*S*,3a*R*,5a*R*,5b*R*,7a*R*,11*R*,11a*R*,11b*R*,13a*S*,13b*R*)-Octadecahydro-1′-(4-methoxyphenyl)-3,3,5a,5b,10,10,13b-heptamethylspiro[11,7a-(epoxymethano)-7a*H*-cyclopenta[a]chrysene-1(2*H*),3′-pyrrolidine]-2,2′,4′,5′,15-pentone* (**24**): ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*s*, Me(27)); 0.90 (*s*, Me(30)); 0.95 (*s*, Me(26)); 0.98 (*s*, Me(29)); 1.13 (*s*, Me(24)); 1.19 (*s*, Me(23)); 1.32 (*s*, Me(25)); 1.74 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.82–1.88 (*m*, H_e–C(16)); 2.14 (*dd*, *J*(9,11a) = 12.8, *J*(9,11e) = 2.4, H–C(9)); 2.76 (*dd*, *J*(5,6a) = 8.2, *J*(5,6e) = 6.8, H–C(5)); 3.82 (*s*, MeO); 3.83 (*s*, H–C(19)); 7.31 (*d*, *J*(7′,8′) = 8.9, H–C(7′), H–C(11′)); 7.24 (*d*, *J*(8′,7′) = 8.9, H–C(8′), H–C(10′)); others 0.81–1.71.

*(1*S*,3a*R*,5a*R*,5b*R*,7a*R*,11*R*,11a*R*,11b*R*,13a*S*,13b*R*)-Octahydro-3,3,5a,5b,10,10,13b-heptamethyl-1′-phenylspiro[11,7a-(epoxymethano)-7a*H*-cyclopenta[a]chrysene-1(2*H*),3′-pyrrolidine]-2,2′,4′,5′,15-pentone* (**25**): ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (*s*, Me(27)); 0.89 (*s*, Me(30)); 0.94 (*s*, Me(26)); 0.97 (*s*, Me(29)); 1.13 (*s*, Me(24)); 1.19 (*s*, Me(23)); 1.32 (*s*, Me(25)); 1.73 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.82–1.88 (*m*, H_e–C(16)); 2.15 (*dd*, *J*(9,11a) = 13.0, *J*(9,11e) = 2.6, H–C(9)); 2.76 (*dd*, *J*(5,6a) = 8.6, *J*(5,6e) = 6.4, H–C(5)); 3.83 (*s*, H–C(19)); 7.32 (br. *d*, *J*(7′,8′) = 7.2, H–C(7′), H–C(11′)); 7.44 (br. *t*, *J*(9′,8′) = 7.2, H–C(9′)); 7.50 (br. *tt*, *J*(8′,9′) = *J*(8′,7′) = 7.2, H–C(8′), H–C(10′)); others 0.80–1.70.

2.4. *Reaction of Amic Acids* **19** *and* **21** *with Oxalyl Chloride in an NMR Tube.* To the soln. of the corresponding amic acid (30–31 mg) in $CDCl_3$ (0.55 ml) was added $(COCl)_2$ (0.1 ml) and mixed with a thin glass rod. Spectra were recorded after the termination of gas evolution (30–60 min). Additional exper. data are available from http://limor1.nioch.nsc.ru/quant/conformers/shern/spiro/.

2.5. *Model Compounds from Adipic Acid* (= *Hexanedioic Acid*). A mixture of adipic acid (5 g), MeOH (1.2 ml), H_2SO_4 (3 drops), and $CHCl_3$ (30 ml) was refluxed for 6 h. The mixture was filtered and the filtrate washed with an aq. Na_2CO_3 soln., dried ($MgSO_4$), and concentrated to give 2.8 g of a liquid mixture of methyl and dimethyl adipates (ratio 85 : 15 by ^{1}H-NMR). Oxalyl chloride (0.85 ml) was added to a soln. of this ester mixture (1.1 g) in CH_2Cl_2 (10 ml). Two drops of dimethylformamide were added to the mixture as catalyst. After standing for 5 h, solvent and unreacted oxalyl chloride were evaporated, and the residue was dissolved in CH_2Cl_2 (12 ml) and added dropwise to a mixture of (4-methoxybenzyl)-amine (0.95 g) and Et_3N (0.8 ml) in CH_2Cl_2 (8 ml). After standing for 24 h, the mixture was washed with H_2O and dried ($MgSO_4$), the solvent evaporated, and the residue subjected to CC (SiO_2, $CHCl_3$/Et_2O, $CHCl_3$/MeOH): *methyl 6-[(4-methoxybenzyl)amino]-6-oxohexanoate* (**27**; 1.2 g, 70% with respect to the methyl adipate). Low-melting solid. IR: 1734 (COOMe), 1632, 1552 (CONHR). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.55–1.68 (*m*, CH_2(3), CH_2(4)); 2.16 (*t*, *J*(5,4) = 7.0, CH_2(5)); 2.28 (*t*, *J*(2,3) = 6.9, CH_2(2)); 3.61 (*s*, COOMe); 3.75 (*s*, MeO); 4.30 (*d*, *J*(CH_2,NH) = 5.6, CH_2–C_{ipso}); 5.97 (br. *t*, *J*(NH,CH_2) = 5.6, NH); 6.81 (*d*, *J*(*m*,*o*) = 8.6, 2 H_m); 7.15 (*d*, *J*(*o*,*m*) = 8.6, 2 H_o). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.7 (C(1)); 172.1

(C(6)); 158.8 (C_p); 130.3 (C_{ipso}); 129.0 (2 C_o); 113.9 (2 C_m); 55.1 (*Me*O–C_p); 51.4 (COO*Me*); 42.8 (CH_2–C_{ipso}); 36.0 (C(5)); 33.5 (C(2)); 24.9, 24.3 (C(4), C(3)).

Hydrolysis of **27** (0.290 g, 1.04 mmol) was carried out in THF/H_2O (30 ml/14 ml) with NaOH (0.146 g, 3.65 mmol) for 5 h. After neutralization the mixture was extracted with $CHCl_3$ and the extract dried ($MgSO_4$) and evaporated: *6-[(4-methoxybenzyl)amino]-6-oxohexanoic acid* (0.267g, 96%). Low-melting solid. IR: 3295 (COOH), 1690 (COOH), 1645, 1550 (CO-NHR). ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.42–1.56 (*m*, CH_2(3), CH_2(4)); 2.11 (*t*, *J*(5,4) = 6.9, CH_2(5)); 2.20 (*t*, *J*(2,3) = 6.9, CH_2(2)); 3.72 (*s*, MeO); 4.17 (*d*, *J*(CH_2,NH) = 5.8, CH_2–C_{ipso}); 6.84 (*d*, *J*(*m*,*o*) = 8.6, 2 H_m); 7.15 (*d*, *J*(*o*,*m*) = 8.6, 2 H_o); 8.24 (br. *t*, *J*(NH,CH_2) = 5.8, NH); 12.01 (br. *s*, COOH). ^{13}C-NMR (100 MHz, (D_6)DMSO): 174.4 (C(1)); 171.8 (C(6)); 158.2 (C_p); 131.6 (C_{ipso}); 128.5 (2 C_o); 113.7 (2 C_m); 55.0 (*Me*O–C_p); 41.4 (*C*H_2–C_{ipso}); 35.1 (C(5)); 33.4 (C(2)); 24.9, 24.2 (C(4), C(3)).

2.6. *Reaction of Model Compound* **27** *with Oxalyl Chloride.* 1. Oxalyl chloride (0.1 ml, 1.14 mmol) was added to a soln. of **27** (0.100 g, 0.36 mmol) in $CHCl_3$ (3 ml). After standing for 72 h, the mixture was concentrated and the residue subjected to CC (SiO_2, $CHCl_3$/Et_2O): **28** (0.045 g, 38%). 2. Oxalyl chloride (0.15 ml, 1.71 mmol) was added to **27** (0.150 g, 0.54 mmol) and Et_3N (0.2 ml) in $CHCl_3$ (5 ml) (violent reaction!). After standing for 72 h, the mixture was concentrated and worked up as described above: **29** (0.020 g, 11%).

Data of Methyl (5Z)-5-[3-(4-Methoxybenzyl)-4,5-dioxooxazolidin-2-ylidene)pentanoate (**28**): ^{1}H-NMR (300 MHz, $CDCl_3$): 1.67 (*tt*, *J*(3,2) = *J*(3,4) = 7.4, CH_2(3)); 2.21 (*dt*, *J*(4,5) = 7.9, *J*(4,3) = 7.4, CH_2(4)); 2.22 (*t*, *J*(2,3) = 7.4, CH_2(2)); 3.62 (*s*, COOMe); 3.76 (*s*, MeO); 4.47 (*t*, *J*(5,4) = 7.9, H–C(5)); 4.75 (*s*, ArCH_2); 6.84 (*d*, *J*(*m*,*o*) = 8.6, 2 H_m); 7.17 (*d*, *J*(*o*,*m*) = 8.6, 2 H_o). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.3 (C(1)); 159.6 (C_p); 154.5 (C(5) (ox.)); 150.4 (C(4) (ox.)); 140.7 (C(2) (ox.)); 129.0 (2 C_o); 125.3 (C_{ipso}); 114.3 (2 C_m); 90.8 (C(5)); 55.5 (MeO); 51.5 (COO*Me*); 44.3 (Ar*C*H_2); 32.9 (C(2)); 24.8, 23.1 (C(4), C(3)).

*Methyl 2,5-Dihydro-4-hydroxy-1-(4-methoxybenzyl)-2,5-dioxo-1*H*-pyrrole-3-butanoate* (**29**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.76 (*tt*, *J*(3,2) = *J*(3,4) = 7.5, CH_2(3)); 2.25 (*t*, *J*(4,3) = 7.5, CH_2(4)); 2.27 (*t*, *J*(2,3) = 7.5, CH_2(2)); 3.62 (*s*, COOMe); 3.77 (*s*, MeO); 4.73 (*s*, ArCH_2); 6.84 (*d*, *J*(*m*,*o*) = 8.7, 2 H_m); 7.22 (*d*, *J*(*o*,*m*) = 8.7, 2 H_o). ^{13}C-NMR (100 MHz, $CDCl_3$): 180.9 (C(4) (pyr.)); 173.2 (C(1)); 161.4 (C(2) (pyr.)); 159.4 (C_p); 156.5 (C(5) (pyr.)); 129.3 (2 C_o); 127.3 (C_{ipso}); 114.1 (2 C_m); 111.5 (C(3) (pyr.)); 55.2 (MeO); 51.5 (COO*Me*); 43.9 (ArCH_2); 33.1 (C(2)); 22.9 (C(3)); 21.2 (C(4)).

2.7. *Reaction of* **30** *with Oxalyl Chloride: (4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-7-{(*Z*)-[4,5-Dioxo-3-(phenylmethyl)oxazolidin-2-ylidene]methyl}-hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid Methyl Ester* (**31**). Oxalyl chloride (0.073 g, 0.56 mmol) was added to a soln. of **30** (0.140 g, 0.23 mmol) in THF (3 ml). After standing for 24 h, the mixture was subjected to CC (SiO_2, CH_2Cl_2/Et_2O): **31** (0.133 g, 87%). M.p. 205°. IR: 1824, 1766 (lactone), 1747, 1711. Major form in spectrum (content 79.4%, only characteristic signals): ^{1}H-NMR (600 MHz, −28.2°, $CDCl_3$): 0.63 (*s*, Me(27)); 0.78 (*s*, Me(26)); 0.93 (*s*, Me(30)); 0.95 (*s*, Me(23)); 0.98 (*s*, Me(29)); 1.19 (*s*, Me(25)); 1.12 (*s*, Me(24)); 0.23 (*dddd*, ^2J = *J*(12a,13) = *J*(12a,11a) = 12.8, *J*(12a,11e) = 3.6, H_a–C(12)); 0.59–0.63 (*m*, H_e–C(11)); 0.91 (*dm*, *J*(9,11a) = 13.0, H–C(9)); 1.50–1.54 (*m*, H–C(5)); 1.67 (*d*, *J*(18,13) = 11.2, H–C(18)); 1.78 (*dm*, ^2J = 14.0, H_e–C(16)); 3.46 (*s*, COOMe); 4.04 (*s*, H–C(1)); 4.49, 5.30 (*AB*, *J* = 15.3, CH_2(6′)); 7.21–7.35 (5 arom. H). ^{13}C-NMR (150 MHz, −28.2°, $CDCl_3$): 180.1 (*s*, C(28)); 179.2 (*s*, C(3)); 155.2 (*s*, C(3′)); 149.0 (*s*, C(4′)); 138.4 (*s*, C(1′)); 133.7 (*s*, C(7′)); 128.8 (*d*, C(9′), C(11′)); 128.2 (*d*, C(10′)); 127.2 (*d*, C(8′), C(12′)); 106.7 (*d*, C(1)); 85.6 (*d*, C(19)); 55.6 (*d*, C(5)); 51.7 (*q*, COO*Me*); 47.9 (*d*, C(9)); 46.2 (*s*, C(4)); 46.1 (*d*, C(18)); 45.8 (*s*, C(17)); 45.4 (*s*, C(10)); 44.2 (*t*, C(6′)); 39.8 (*s*, C(8)); 39.7 (*s*, C(14)); 35.5 (*d*, C(13)); 33.2 (*s*, C(20)); 32.1 (*t*, C(7)); 31.7 (*t*, C(21)); 31.4 (*t*, C(22)); 28.4 (*q*, C(29)); 27.3 (*t*, C(15)); 26.8 (br. *q*, C(24)); 25.7 (*t*, C(12)); 25.1 (*t*, C(16)); 23.6 (*q*, C(30)); 22.3 (br. *q*, C(23)); 22.2 (*t*, C(11)); 19.0 (*t*, C(6)); 15.4 (br. *q*, C(25)); 15.1 (*q*, C(26)); 13.0 (*q*, C(27)). MS: 659.3832 (M^+, $C_{40}H_{53}NO_7^+$; calc. 659.3817). Additional experimental data are available from http://limor1.-nioch.nsc.ru/quant/conformers/shern/spiro/.

2.8. *Reaction of* **4** *with Phosgene in THF: (4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-7-[2-oxo-2-(piperidin-1-yl)ethyl]-1*H*-4,12a-(epoxymethano)-chrysene-8-acetic Acid 4-Chlorobutyl Ester* (**32**). To a soln. of **4** (0.138 g, 0.24 mmol) in THF (7 ml) was added 20% phosgene soln. in toluene (1 ml) and refluxed. More 20% phosgene soln. in toluene (0.5 ml)

was added every 4 h (total amount: 2.5 ml (4.80 mmol)). The solvent was evaporated and the residue subjected to CC (SiO_2, CH_2Cl_2/Et_2O): **32**. M.p. 145.0°. IR: 1774 (lactone), 1719 (COOR), 1643 ($CONR^1R^2$). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*s*, Me(26)); 0.87 (*s*, Me(25)); 0.89 (*s*, Me(27)); 0.90 (*s*, Me(30)); 0.89 – 0.99 (*m*, H_a–C(12)); 0.98 (*s*, Me(29)); 1.16 (*s*, Me(24)); 1.18 (*s*, Me(23)); 1.69 – 1.76 (*m*, CH_2(37)); 1.78 (*d*, *J*(18,13) = 11.0, H–C(18)); 1.76 – 1.85 (*m*, H_e–C(16), CH_2(38)); 2.18; 2.31 (*AB*, *J* = 18.2, CH_2(1)); 2.74 – 2.79 (*m*, H–C(5)); 2.94 (*dd*, *J*(9a,11a) = 12.5, *J*(9a,11e) = 2.0, H_a–C(9)); 3.20 – 3.42, 3.61 – 3.70 (2*m*, CH_2(31), CH_2(35)); 3.53 (*t*, *J*(39,38) = 6.5, CH_2(39)); 3.81 (*dt*, ^2J = 11.0, *J*(36,37) = 6.0, H–C(36)); 3.88 (*s*, H–C(19)); 4.08 (*dt*, ^2J = 11.0, *J*(36′,37) = 6.3, H′–C(36)); others 1.10 – 1.65. Anal. calc. for $C_{39}H_{62}ClNO_5$ (660.37): C 70.93, H 9.46, N 2.12, Cl 5.37; found: C 71.51, 71.63, H 9.50, 9.27, N 2.26, 2.03, Cl 4.70, 4.46.

2.9. *Secondary Amides from Primary Amines and* **2**: *General Procedure.* The primary amine (1.05 – 1.10 mmol) was added to a soln. **2** (1.0 mmol) in the corresponding solvent (*Scheme 10*; 7 – 10 ml). After standing 24 – 72 h, the solvent was evaporated and residue subjected to CC (SiO_2, $CHCl_3$/MeOH, $CHCl_3$/AcOEt). If necessary, fractions were resubjected to CC again.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-7-{2-oxo-2-[(phenylmethyl)amino]ethyl}-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**33**): M.p. 170 °. IR: 3398 (COOH), 1774 (lactone), 1726 (COOH), 1639, 1547 (CONHR). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.68 (*s*, Me(27)); 0.86 (*s*, Me(26)); 0.90 (*s*, Me(30)); 0.94 (*s*, Me(25)); 0.98 (*s*, Me(29)); 1.18 (*s*, Me(23)); 1.19 (*s*, Me(24)); 0.83 – 0.92 (*m*, H_a–C(12)); 1.50 – 1.56 (*dm*, ^2J = 13.0, H_e–C(12)); 1.71 – 1.75 (*m*, H_e–C(11)); 1.75 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.76 – 1.79 (*m*, H–C(9)); 1.78 – 1.83 (*dm*, ^2J = 13.8, H_e–C(16)); 2.03 (*dd*, *J*(5a,6a) = 9.0, *J*(5a,6e) = 6.5, H_a–C(5)); 2.24, 2.35 (*AB*, ^2J = 14.8, CH_2(1)); 3.88 (*s*, H–C(19)); 4.34, 4.44 (2*dd*, ^2J = 14.8, *J*(2′,NH) = 5.6, CH_2(2′)); 7.20 (*tt*, *J* = 7.1, *J* = 1.6, H–C(6′)); 7.26 (br. *t*, *J* = 7.1, H–C(5′), H–C(7′)); 7.29 (br. *d*, *J* = 7.1, H–C(4′), H–C(8′)); 7.32 (*t*, *J*(NH,2′) = 5.6, NH); others 1.07 – 1.52. Anal. calc. for $C_{37}H_{53}NO_5$ (591.82): C 75.09, H 9.03, N 2.37; found: C 75.49, 75.13, H 9.14, 8.87, N 1.88, 1.94.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-8-{1,1-Dimethyl-2-oxo-2-[(phenylmethyl)amino]ethyl}-hexadecahydro-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-7-acetic Acid* (**34**): IR: 3401 (COOH), 1774 (lactone), 1715 (COOH), 1581, 1546 (CONHR). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.80 (*s*, Me(27)); 0.84 (*s*, Me(25)); 0.86 (*s*, Me(26)); 0.90 (*s*, Me(30)); 0.99 (*s*, Me(29)); 1.22 (*s*, Me(24)); 1.27 (*s*, Me(23)); 1.02 – 1.14 (*m*, H_a–C(11), H_a–C(12)); 1.54 – 1.62 (*m*, H_e–C(6), H_e–C(12)); 1.73 (*dd*, *J*(9a,11a) = 12.0, *J*(9a,11e) = 2.2, H_a–C(9)); 1.80 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.78 – 1.85 (*m*, H_e–C(11), H_e–C(16)); 1.99, 2.23 (*AB*, *J* = 14.0, H–C(1)); 2.00 (*dd*, *J*(5a,6a) = 11.8, *J*(5a,6e) = 3.0, H_a–C(5)); 3.90 (*s*, H–C(19)); 4.44 (*d*, *J*(2′,NH) = 5.5, CH_2(2′)); 6.80 (*t*, *J*(NH,2′) = 5.5, NH); 7.23 – 7.34 (5 arom. H); others 1.16 – 1.54. Anal calc. for $C_{37}H_{53}NO_5$ (591.82): C 75.09, H 9.03, N 2.37; found: C 74.87, 75.03, H 9.69, 9.72, N 2.74, 2.63.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-7-{2-{[(4-methoxyphenyl)methyl]amino}-2-oxoethyl}-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**35**): ^{1}H-NMR (400 MHz, $CDCl_3$): 0.65 (*s*, Me(27)); 0.86 (*s*, Me(26)); 0.92 (*s*, Me(30), Me(25)); 0.99 (*s*, Me(29)); 1.20 (*s*, Me(23)); 1.21 (*s*, Me(24)); 1.74 (*d*, *J*(18,13) = 11.1, H–C(18)); 2.12 (*dd*, *J*(5a,6a) = 8.5, *J*(5a,6e) = 6.6, H_a–C(5)); 2.18, 2.32 (*AB*, *J* = 15.1, CH_2(1)); 3.75 (*s*, Me(9′)); 3.87 (*s*, H–C(19)); 4.27, 4.35 (2*dd*, ^2J = 14.4, *J*(2′,NH) = 5.6, CH_2(2′)); 6.80 (*d*, *J*(5′,4′) = 8.6, H–C(5′), H–C(7′)); 6.98 (*t*, *J*(NH,2′) = 5.6, NH); 7.21 (*d*, *J*(4′,5′) = 8.6, H–C(4′), H–C(8′)); others 0.78 – 1.85.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-8-{2-{[(4-methoxyphenyl)methyl]amino}-1,1-dimethyl-2-oxoethyl}-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-7-acetic Acid* (**19**): ^{1}H-NMR (400 MHz, $CDCl_3$): 0.78 (*s*, Me(27)); 0.82 (*s*, Me(25)); 0.84 (*s*, Me(26)); 0.88 (*s*, Me(30)); 0.97 (*s*, Me(29)); 1.19 (*s*, Me(24)); 1.24 (*s*, Me(23)); 1.70 (*dd*, *J*(9a,11a) = 11.3, *J*(9a,11e) = 2.1, H_a–C(9)); 1.78 (*d*, *J*(18,13) = 11.2, H–C(18)); 1.76 – 1.85 (*m*, H_e–C(11), H_e–C(16)); 1.96, 2.20 (*AB*, *J* = 14.0, CH_2(1)); 1.97 (*dd*, *J*(5a,6a) = 11.7, *J*(5a,6e) = 2.8, H_a–C(5)); 3.75 (*s*, MeO); 3.90 (*s*, H–C(19)); 4.33, 4.38 (*dd*, ^2J = 14.5, *J*(2′,NH) = 5.7, CH_2(2′)); 6.82 (*d*, *J*(5′,4′) = 8.7, H–C(5′), H–C(7′)); 6.84 (*t*, *J*(NH,2′) = 5.7, NH); 7.18 (*d*, *J*(4′,5′) = 8.7, H–C(4′), H–C(8′)); 11.90 (br. *s*, COOH); others 1.16 – 1.54.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-7-{2-oxo-2-[(2-phenylethyl)amino]ethyl}-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**18**): IR: 1774 (lactone), 1728 (COOH), 1626, 1546 (CONH). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.76 (*s*, Me(27)); 0.87

(*s*, Me(26)); 0.92 (*s*, Me(30)); 0.93 (*s*, Me(25)); 0.89–1.00 (*m*, H_a–C(12)); 1.00 (*s*, Me(29)); 1.15 (*s*, Me(23)); 1.19 (*s*, Me(24)); 1.58 (*dddd*, ^2J = 12.8, *J*(12e,11a) = 3.4, *J*(12e,11e) = *J*(12e,13) = 3.2, H_e–C(12)); 1.66–1.74 (*m*, H_a–C(9), H_e–C(11)); 1.79 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.82 (*ddd*, ^2J = 13.5, *J*(16e,15a) = 3.8, *J*(16e,15e) = 3.2, H_e–C(16)); 1.97–2.01 (*m*, H–C(5)); 2.16, 2.28 (*AB*, *J* = 15.2, CH_2(1)); 2.77–2.87 (*m*, CH_2(32)); 3.40 (*dtd*, ^2J = 13.4, *J*(31,32) = 7.0, *J*(31,NH) = 5.0, 1 H of CH_2(31)); 3.65 (*dtd*, ^2J = 13.4, *J*(31′,32) = 7.0, *J*(31′,NH) = 6.2, H′–C(31)); 3.90 (*s*, H–C(19)); 6.73 (*dd*, *J*(NH,31′) = 6.2, *J*(NH,31) = 5.0, NH); 7.17–7.22 (*m*, H–C(34), H–C(36), H–C(38)); 7.27 (br. *t*, *J*(35,34(36)) = 7.5, H–C(35), H–C(37)); others 1.10–1.55. Anal. calc. for $C_{38}H_{55}NO_5$ (605.85): C 75.33, H 9.15, N 2.31; found: C 75.15, 75.03, H 9.27, 8.97, N 2.21, 1.93.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-8-{1,1-Dimethyl-2-oxo-2-[(2-phenylethyl)amino]ethyl}-hexadecahydro-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-7-acetic Acid* (**10**): M.p. 263.8°. IR: 1772 (lactone), 1714 (COOH), 1576, 1551 (CONH). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.75 (*s*, Me(25)); 0.80 (*s*, Me(27)); 0.84 (*s*, Me(26)); 0.89 (*s*, Me(30)); 0.98 (*s*, Me(29)); 1.08 (*s*, Me(24)); 1.03–1.13 (*m*, H_a–C(11), H_a–C(12)); 1.19 (*s*, Me(23)); 1.70 (*dd*, *J*(9a,11a) = 11.5, *J*(9a,11e) = 2.2, H_a–C(9)); 1.81 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.77–1.86 (*m*, H_e–C(11), H_e–C(16)); 1.94 (*dd*, *J*(5,6a) = 12.0, *J*(5,6e) = 3.0, H–C(5)); 2.00, 2.27 (*AB*, *J* = 13.9, CH_2(1)); 2.80–2.87 (*m*, CH_2(32)); 3.50–3.63 (*m*, CH_2(31)); 3.91 (*s*, H–C(19)); 6.38 (br. *t*, *J*(NH,31) = 5.6, NH); 7.16 (br. *d*, *J*(34,35) = 7.5, H–C(34), H–C(38)); 7.22 (*tt*, *J*(36,35) = 7.5, *J*(36,34) = 1.8, H–C(36)); 7.29 (br. *t*, *J*(35,34(36)) = 7.5, H–C(35), H–C(39)); 12.08 (br. *s*, COOH); others 1.14–1.64. Anal. calc. for $C_{38}H_{55}NO_5$ (605.85): C 75.33, H 9.15, N 2.31; found: C 75.94, 76.17, H 9.20, 9.33, N 2.29, 2.26.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-7-{2-oxo-2-[[(tetrahydrofuran-2-yl)methyl]amino}ethyl}-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**36**): Diastereoisomer mixture 1.0:0.4. Major in the mixture: ^{1}H-NMR (500 MHz, $CDCl_3$): 0.87 (*s*, Me(26)); 0.88 (*s*, Me(25)); 0.89 (*s*, Me(30)); 0.91 (*s*, Me(27)); 0.98 (*s*, Me(29)); 1.13 (*s*, Me(24)); 1.18 (*s*, Me(23)); 1.81 (*d*, *J*(18,13) = 11.0, H–C(18)); 1.80–1.85 (*m*, H_e–C(16)); 1.87–1.95 (*m*, CH_2(34)); 1.95–2.03 (*m*, H–C(33)); 2.13–2.17 (*m*, H–C(5)); 2.19, 2.33 (*AB*, *J* = 17.1, CH_2(1)); 2.66 (*ddd*, ^2J = 14.0, *J*(31,32) = 9.3, *J*(31,NH) = 4.5, H–C(31)); 2.81 (*dd*, *J*(9a,11a) = 12.0, *J*(9a,11e) = 2.0, H_a–C(9)); 3.72 (*ddd*, ^2J = 14.0, *J*(31′,NH) = 7.5, *J*(31′,32) = 3.0, H′–C(31)); 3.79 (*dt*, ^2J = 8.0, *J*(35,34) = 6.5, H–C(35)); 3.90 (*s*, H–C(19)); 3.89–3.95 (*m*, H′–C(35)); 4.16–4.23 (*m*, H–C(32)); 6.09 (*dd*, *J*(NH,31′) = 7.5, *J*(NH,31) = 4.5, NH). Minor in the mixture: ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*s*, Me(27)); 0.88 (*s*, Me(26), Me(30)); 0.90 (*s*, Me(25)); 0.98 (*s*, Me(29)); 1.16 (*s*, Me(24)); 1.21 (*s*, Me(23)); 1.80 (*d*, *J*(18,13) = 11.0, H–C(18)); 1.80–1.85 (*m*, H_e–C(16)); 1.86–1.94 (*m*, CH_2(34)); 1.95–2.03 (*m*, H–C(31)); 2.15–2.19 (*m*, H–C(5)); 2.26, 2.32 (*AB*, *J* = 16.7, CH_2(1)); 2.51 (*dd*, *J*(9a,11a) = 12.0, *J*(9a,11e) = 2.0, H_a–C(9)); 3.20 (*ddd*, ^2J = 14.0, *J*(31,NH) = 3.8, *J*(31,32) = 2.8, H–C(31)); 3.47 (*ddd*, ^2J = 14.0, *J*(31′,32) = 9.0, *J*(31′,NH) = 7.0, H′–C(31)); 3.77 (*dt*, ^2J = 8.0, *J*(35,34) = 6.5, H–C(35)); 3.86–3.91 (*m*, H′–C(35)); 3.90 (*s*, H–C(19)); 3.97–4.04 (*m*, H–C(32)); 6.06 (*dd*, *J*(NH,31′) = 7.0, *J*(NH,31) = 3.8, NH). Others for both isomers 1.05–1.65.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-8-{1,1-Dimethyl-2-oxo-2-[[(tetrahydrofuran-2-yl)methyl]amino}ethyl}hexadecahydro-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-7-acetic Acid* (**11**): Diastereoisomer mixture 1:1. M.p. 233°. IR: 1774 (lactone), 1716 (COOH), 1584, 1545 (CONH). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.80 (*s*, 2 Me(27)); 0.87 (*s*, 2 Me(26)); 0.89 (*s*, 2 Me(30), Me(25)); 0.90 (*s*, Me(25)); 0.97 (*s*, 2 Me(29)); 1.02–1.16 (*m*, 2 H_a–C(11), 2 H_a–C(12)); 1.21 (*s*, Me(24)); 1.22 (*s*, Me(24)); 1.23 (*s*, Me(23)); 1.24 (*s*, Me(23)); 1.80 (*d*, *J*(18,13) = 11.1, 2 H–C(18)); 1.74–1.86 (*m*, 2 H_a–C(9), 2 H_e–C(11), 2 H_e–C(16)); 1.84–1.92 (*m*, 2 CH_2(34)); 1.94–2.00 (*m*, 2 H–C(33)); 2.01 (*dd*, *J*(5,6a) = 12.2, *J*(5,6e) = 3.0, H–C(5)); 2.02 (*dd*, *J*(5,6a) = 12.2, *J*(5,6e) = 3.0, H–C(5)); 2.15, 2.18, 2.37, 2.38 (2*AB*, *J* = 14.2, 2 CH_2(1)); 3.07–3.15 (*m*, 2 H–C(31)); 3.54–3.65 (*m*, 2 H′–C(31)); 3.68–3.75, 3.79–3.85 (*m*, 2 CH_2(35)); 3.90 (*s*, 2 H–C(19)); 3.89–3.98 (*m*, 2 H–C(32)); 6.72 (*dd*, *J*(NH,31′) = 6.2, *J*(NH,31) = 4.6, NH); 6.75 (*dd*, *J*(NH,31′) = 6.2, *J*(NH,31) = 4.6, NH); 11.94 (br. *s*, 2 COOH), others 1.15–1.63. Anal. calc. for $C_{35}H_{55}NO_6$ (585.81): C 71.76, H 9.46, N 2.39; found: C 71.47, 71.60, H 9.32, 9.38, N 2.52, 2.53.

N-*{2-[(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-8-(1-Carbonyl-1-methylethyl)hexadecahydro-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysen-7-yl]acetyl}-β-alanine Methyl Ester* (**37**): IR: 1773 (lactone), 1739 (COOMe), 1702 (COOH), 1630, 1542 (CONH). ^{1}H-NMR (500 MHz,

$CDCl_3$): 0.81 (*s*, Me(27)); 0.88 (*s*, Me(26)); 0.90 (*s*, Me(30)); 0.92 (*s*, Me(25)); 0.98 (*s*, Me(29)); 1.00 (*dddd*, $^2J = J$(12a,11a) = J(12a,13) = 12.7, J(12a,11e) = 3.4, H_a–C(12)); 1.20 (*s*, Me(24)); 1.25 (*s*, Me(23)); 1.61 (*dddd*, $^2J = 12.7$, J(12e,11a) = 3.4, J(12e,11e) = J(12e,13) = 3.2, H_e–C(12)); 1.63 – 1.69 (*dm*, $^2J = 12.7$, H_e–C(11)); 1.80 (*d*, J(18,13) = 11.1, H–C(18)); 1.82 (*ddd*, $^2J = 13.5$, J(16e,15a) = 3.8, J(16e,15e) = 3.2, H_e–C(16)); 2.09 – 2.15 (*m*, H–C(5)); 2.22, 2.29 (*AB*, $J = 15.5$, CH_2(1)); 2.50 (*ddd*, $^2J = 16.8$, J(32,31′) = 6.7, J(32,31) = 4.7, H–C(32)); 2.59 (*ddd*, $^2J = 16.8$, J(32′,31) = 8.2, J(32′,31′) = 4.7, H′–C(32)); 3.36 (*dddd*, $^2J = 13.7$, J(31,32′) = 8.2, J(31,NH) = 5.5, J(31,32) = 4.7, H–C(31)); 3.62 (*dddd*, $^2J = 13.7$, J(31′,32) = 6.7, J(31′,NH) = 6.3, J(31′,32′) = 4.7, H′–C(31)); 3.67 (*s*, MeO); 3.90 (*s*, H–C(19)); 6.81 (*dd*, J(NH,31′) = 6.3, J(NH,31) = 5.5, NH); others 1.09 – 1.55.

N-*{2-[(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-7-(Carboxymethyl)hexadecahydro-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysen-8-yl]-2-methyl-1-oxopropyl}-β-alanine Methyl Ester* (**12**): M.p. 254.6°. IR: 1768 (lactone), 1745 (COOMe), 1707 (COOH), 1574, 1553 (CONH). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.81 (*s*, Me(27)); 0.87 (*s*, Me(25), Me(26)); 0.90 (*s*, Me(30)); 0.98 (*s*, Me(29)); 1.03 – 1.15 (*m*, H_a–C(11), H_a–C(12)); 1.20 (*s*, Me(24)); 1.22 (*s*, Me(23)); 1.76 (*dd*, J(9a,11a) = 11.5, J(9a,11e) = 2.1, H_a–C(9)); 1.81 (*d*, J(18,13) = 11.1, H–C(18)); 1.78 – 1.86 (*m*, H_e–C(11), H_e–C(16)); 1.99 (*dd*, J(5,6a) = 12.0, J(5,6e) = 3.0, H–C(5)); 2.10, 2.38 (*AB*, $J = 13.9$, CH_2(1)); 2.55 (*dd*, J(32,31) = 7.0, J(32,31′) = 5.3, CH_2(32)); 3.51 – 3.58 (*m*, CH_2(31)); 3.68 (*s*, MeO); 3.90 (*s*, H–C(19)); 7.12 (br. *t*, J(NH,31) = 5.6, NH); 11.78 (br. *s*, COOH); others 1.16 – 1.64. Anal. calc. for $C_{34}H_{53}NO_7$ (587.79): C 69.47, H 9.09, N 2.38; found: C 69.34, 69.62, H 8.70, 8.76, N 2.52, 2.60.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-8-[1,1-Dimethyl-2-(methylamino)-2-oxoethyl]hexadecahydro-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-7-acetic Acid* (**13**): M.p. 277.2°. IR: 1770 (lactone), 1713 (COOH). 1578 (CONH). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.83 (*s*, Me(27)); 0.89 (*s*, Me(26)); 0.90 (*s*, Me(25)); 0.91 (*s*, Me(30)); 0.99 (*s*, Me(29)); 1.05 – 1.17 (*m*, H_a–C(11), H_a–C(12)); 1.22 (*s*, Me(24)); 1.25 (*s*, Me(23)); 1.76 (*dd*, J(9a,11a) = 11.5, J(9a,11e) = 2.1, H_a–C(9)); 1.83 (*d*, J(18,13) = 11.1, H–C(18)); 1.80 – 1.90 (*m*, H_e–C(11), H_e–C(16)); 2.00 (*dd*, J(5,6a) = 12.0, J(5,6e) = 3.0, H–C(5)); 2.07, 2.39 (*AB*, $J = 13.8$, CH_2(1)); 2.86 (*d*, J(31,NH) = 4.6, Me(31)); 3.92 (*s*, H–C(19)); 6.44 (br. *q*, J(NH,31) = 4.6, NH); 12.0 (br. *s*, COOH); others 1.18 – 1.65. Anal. calc. for $C_{31}H_{49}NO_5$ (515.72): C 72.20, H 9.58, N 2.72; found: C 72.75, 72.87, H 9.57, 9.65, N 2.31, 2.63.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-7-[2-oxo-2-(phenylamino)ethyl]-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**21**): ^{1}H-NMR (400 MHz, $CDCl_3$): 0.74 (*s*, Me(27)); 0.87 (*s*, Me(26)); 0.91 (*s*, Me(30)); 0.93 (*s*, Me(25)); 0.89 (*s*, Me(29)); 1.20 (*s*, Me(24)); 1.27 (*s*, Me(23)); 1.80 (*d*, J(18,13) = 11.1, H–C(18)); 1.93 (br. *d*, J(9a,11a) = 11.3, H_a–C(9)); 2.10 (*dd*, J(5,6a) = 10.2, J(5,6e) = 4.6, H–C(5)); 2.29, 2.37 (*AB*, $J = 15.1$, CH_2(1)); 3.92 (*s*, H–C(19)); 7.06 (br. *t*, J(5′,4′(6′)) = 7.4, H–C(5′)); 7.27 (br. *dd*, J(4′,3′) = 7.8, J(4′,5′) = 7.4, H–C(4′), H–C(6′)); 7.52 (br. *d*, J(3′,4′) = 7.8, H–C(3′), H–C(7′)); 8.81 (*s*, NH); others 1.02 – 1.84. ^{13}C-NMR (100 MHz, $CDCl_3$): 185.3 (C(3)); 180.2 (C(28)); 170.3 (C(2)); 138.1 (C(2′)); 128.8 (C(6′), C(4′)); 123.9 (C(5′)); 119.9 (C(3′), C(7′)); 85.9 (C(19)); 50.1 (C(5)); 46.3 (C(18)); 46.1 (C(17)); 45.8 (C(1)); 45.5 (C(4)); 43.6 (C(10)); 43.6 (C(9)); 40.1, 40.1 (C(8), C(14)); 36.2 (C(3)); 33.4 (C(20)); 32.3 (C(7)); 32.1 (C(21)); 31.7 (C(22)); 30.1 (C(23)); 28.6 (C(29)); 27.6 (C(15)); 25.9 (C(12)); 25.3 (C(16)); 23.8 (C(30)); 22.4 (C(11)); 21.6 (C(24)); 20.1 (C(6)); 19.6 (C(25)); 15.7 (C(26)); 13.3 (C(27)).

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-7-{2-[(4-methoxyphenyl)amino]-2-oxoethyl}-α^8,α^8,3,3,7,10a,10b-heptamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**20**): ^{1}H-NMR (500 MHz, $CDCl_3$): 0.75 (*s*, Me(27)); 0.88 (*s*, Me(26)); 0.91 (*s*, Me(30)); 0.94 (*s*, Me(25)); 0.99 (*s*, Me(29)); 1.22 (*s*, Me(24)); 1.28 (*s*, Me(23)); 1.76 – 1.84 (*m*, H_e–C(16), H_e–C(11)); 1.80 (*d*, J(18,13) = 11.1, H–C(18)); 1.93 (*dd*, J(9a,11a) = 11.9, J(9a,11e) = 2.0, H_a–C(9)); 2.14 (*dd*, J(5,6a) = 10.4, J(5,6e) = 4.8, H–C(5)); 2.30, 2.38 (*AB*, $J = 15.1$, CH_2(1)); 3.75 (*s*, MeO)); 3.91 (*s*, H–C(19)); 6.80 (*d*, J(4′,3′) = 8.9, H–C(4′), H–C(6′)); 7.40 (*d*, J(3′,4′) = 8.9, H–C(3′), H–C(7′)); 8.53 (*s*, NH); others 1.02 – 1.64. ^{13}C-NMR (125 MHz, $CDCl_3$): 185.0 (C(3)); 180.0 (C(28)); 170.2 (C(2)); 156.2 (C(5′)); 131.2 (C(2′)); 121.7 (C(4′), C(6′)); 114.0 (C(3′), C(7′)); 85.9 (C(19)); 55.4 (C(8′)); 50.0 (C(5)); 46.4 (C(18)); 46.1 (C(4)); 45.6 (C(1)); 43.7 (C(9)); 43.6 (C(10)); 40.2, 40.2 (C(8), C(14)); 36.2 (C(13)); 33.4 (C(20)); 32.4 (C(7)); 32.2 (C(21)); 31.7 (C(22)); 29.9 (C(23)); 28.6 (C(29)); 27.6 (C(15)); 26.0 (C(12)); 25.4 (C(16)); 23.9 (C(30)); 22.4 (C(11)); 21.8 (C(24)); 20.2 (C(6)); 19.6 (C(25)); 15.7 (C(26)); 13.4 (C(27)).

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α*^{8}*,α*^{8}*,3,3,7,10a,10b-heptamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-7,8-diacetic Acid 7-[2-(Pyridin-4-ylcarbonyl)hydrazide* (**38**): IR: 1773 (lactone), 1724 (COOH), 1657, 1573 (CO-NHR). ^{1}H-NMR (500 MHz, $CDCl_3$/(D_6)DMSO): 0.81 (*s*, Me(27)); 0.84 (*s*, Me(26)); 0.85 (*s*, Me(30)); 0.92 (*s*, Me(25)); 0.93 (*s*, Me(29)); 0.99 (*dddd*, ^{2}J = 12.8, *J*(11a,12a) = 12.8, *J*(11a,9a) = 12.2, *J*(11a,12e) = 3.7, H_a–C(11)); 1.13 (*s*, Me(24)); 1.20 (*s*, Me(23)); 1.62 (*dm*, ^{2}J = 12.8, H_e–C(11)); 1.72 (*ddd*, ^{2}J = 13.5, *J*(16e,15a) = 4.0, *J*(16e,15e) = 3.1, H_e–C(16)); 1.74 (*d*, *J*(18,13) = 11.1, H–C(18)); 2.31 (dd, *J*(5,6a) = 12.0, *J*(5,6e) = 3.1, H–C(5)); 2.34, 2.39 (*AB*, *J* = 16.8, CH_2(1)); 3.84 (*s*, H–C(19)); 7.71 (*d*, *J* = 6.1, H–C(35)); 8.62 (*d*, *J* = 6.1, H–C(36)); 9.48 (*d*, *J*(31,32) = 2.1, H–N(31)); 8.48 (*d*, *J*(32,31) = 2.1, H–N(32)). ^{13}C-NMR (125 MHz, $CDCl_3$/(D_6)DMSO): 182.42 (C(3)); 179.24 (C(28)); 170.03 (C(2)); 164.18 (C(33)); 149.65 (C(36), C(38)); 138.87 (C(34)); 121.09 (C(35), C(39)); 85.25 (C(19)); 49.18 (C(5)); 45.93 (C(18)); 45.47 (C(17)); 44.87 (C(4)); 42.64 (C(10)); 42.05 (C(9)); 40.80 (C(1)); 39.85 (C(8)); 39.74 (C(14)); 35.68 (C(13)); 32.93 (C(20)); 32.09 (C(7)); 31.76 (C(21)); 31.25 (C(22)); 28.93 (C(23)); 28.18 (C(29)); 27.27 (C(15)); 25.66 (C(12)); 24.95 (C(16)); 23.31 (C(30)); 21.49 (C(11)); 21.42 (C(24)); 19.76 (C(25)); 19.43 (C(6)); 15.13 (C(26)); 13.10 (C(27)). Anal. calc. for $C_{36}H_{51}N_3O_6$ (621.81): C 69.54, H 8.27, N 6.76; found: C 69.76, 69.86, H 8.10, 8.30, N 6.37, 6.43.

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α*^{8}*,α*^{8}*,3,3,7,10a,10b-heptamethyl-13-oxo-7-[2-oxo-2-(tricyclo[3.3.1.1^{3,7}]dec-1-ylamino)ethyl]-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid* (**39**): ^{1}H-NMR (500 MHz, $CDCl_3$): 0.80 (*s*, Me(27)); 0.87 (*s*, Me(26)); 0.91 (*s*, Me(30), Me(25)); 0.97 (*s*, Me(29)); 1.19 (*s*, Me(24)); 1.25 (*s*, Me(23)); 1.64 (br. *s*, CH_2(5′), CH_2(7′), CH_2(11′)); 1.80 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.99 (br. *s*, CH_2(3′), CH_2(10′), CH_2(9′)); 2.03 (br. *s*, H–C(4′), H–C(6′), H–C(8′)); 2.06, 2.21 (*AB*, *J* = 14.9, CH_2(1)); 3.89 (*s*, H–C(19)); 6.48 (*s*, NH); others 1.00–2.12. ^{13}C-NMR (125 MHz, $CDCl_3$): 184.1 (C(3)); 179.8 (C(28)); 171.4 (C(2)); 85.8 (C(19)); 51.9 (C(2′)); 49.5 (C(5)); 46.3 (C(18)); 46.0 (C(17)); 45.8 (C(1)); 45.7 (C(4)); 43.5 (C(9)); 43.2 (C(10)); 41.4 (C(3′), C(10′), C(9′)); 40.2 (C(8)); 40.1 (C(14)); 36.2 (C(5′), C(7′), C(11′)); 36.12 (C(13)); 33.4 (C(20)); 32.5 (C(7)); 32.2 (C(21)); 31.7 (C(22)); 29.7 (C(23)); 29.2 (C(4′), C(6′), C(8′)); 28.6 (C(29)); 27.6 (C(15)); 25.9 (C(12)); 25.3 (C(16)); 23.8 (C(30)); 22.4 (C(11)); 22.0 (C(24)); 20.3 (C(6)); 19.5 (C(25)); 15.7 (C(26)); 13.2 (C(27)).

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-8-[1,1-Dimethyl-2-oxo-2-(tricyclo[3.3.1.1^{3,7}]dec-1-ylamino)ethyl]hexadecahydro-3,3,7,10a,10b-pentamethyl-13-oxo-1*H*-4,12a-(epoxymethano)chrysene-7-acetic Acid* (**40**): M.p. 281.4°. IR: 1776 (lactone), 1721 (COOH), 1586, 1536 (CO-NHR). ^{1}H-NMR (500 MHz, $CDCl_3$/(D_6)DMSO): 0.58 (*s*, Me(27)); 0.64 (*s*, Me(26)); 0.68 (*s*, Me(25)); 0.69 (*s*, Me(30)); 0.75 (*s*, Me(29)); 0.90, 1.02 (2*s*, Me(23), Me(24)); 0.80 (*dddd*, ^{2}J = 12.7, *J*(12a,11a) = *J*(12a,13) = 12.7, *J*(12a,11e) = 3.3, H_a–C(12)); 1.36–1.42 (*dm*, ^{2}J = 12.7, H_e–C(12)); 1.41 (br. *s*, CH_2(5′), CH_2(7′), CH_2(11′)); 1.52–1.58 (*m*, H_e–C(11), H_e–C(16)); 1.57 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.73 (*d*, *J* = 2.7, CH_2(3′), CH_2(9′), CH_2(10′)); 1.78–1.82 (*m*, H–C(4′), H–C(6′), H–C(8′)); 1.90 (*dd*, *J*(5a,6a) = 11.5, *J*(5a,6e) = 3.4, H–C(5)); 2.17, 2.30 (*AB*, *J* = 14.5, CH_2(1)); 3.66 (*s*, H–C(19)); 5.85 (*s*, NH); others 0.88–1.34. MS: 635.4533 (M^+, $C_{40}H_{61}NO_5^+$; calc. 635.4544).

*(4*R*,4a*R*,4b*R*,6a*R*,7*R*,8*R*,10a*R*,10b*R*,12a*R*)-Hexadecahydro-α*^{8}*,α*^{8}*,3,3,7,10a,10b-heptamethyl-13-oxo-7-{2-oxo-2-[(phenylmethyl)amino)ethyl}-1*H*-4,12a-(epoxymethano)chrysene-8-acetic Acid Methyl Ester* (**30**): To a soln. of **33** 0.279 g (0.47 mmol) in $CHCl_3$ (10 ml) was added freshly prepared CH_2N_2 soln. in Et_2O (6.5 ml; obtained from *N*-nitrosomethylurea (0.6 g), KOH (1.7 g), H_2O (3 ml), and Et_2O (10 ml). When the excess CH_2N_2 was decomposed of the solvent was evaporated: **30** 0.286 g (100%). Colorless powder. M.p. 175–176°. IR: 1775 (lactone), 1723 (COOMe), 1663, 1531 ($CONHR_2$). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.74 (*s*, Me(27)); 0.87 (*s*, Me(26)); 0.90 (*s*, Me(30)); 0.91 (*s*, Me(25)); 0.99 (*s*, Me(29)); 1.15 (*s*, Me(23)); 1.17 (*s*, Me(24)); 1.04 (*dddd*, ^{2}J = 12.8, *J*(12a,11a) = *J*(12a,13) = *J*(12a,11e) = 12.8, H_a–C(12)); 1.57 (*dm*, ^{2}J = 12.8, H_e–C(12)); 1.80 (*d*, *J*(18,13) = 11.1, H–C(18)); 1.81 (*m*, H_e–C(11)); 1.90 (*dd*, *J*(9a,11a) = 12.0, *J*(9a,11e) = 2.2, H_a–C(9)); 1.91, 2.23 (*AB*, *J* = 14.8, CH_2(1)); 1.97 (*m*, H_a–C(5)); 3.90 (*s*, MeO); 3.90 (*s*, H–C(19)); 4.28 (*dd*, ^{2}J = 14.6, *J*(2′,NH) = 5.1, H–C(2′)); 4.56 (*dd*, ^{2}J = 14.6, *J*(2′,NH) = 6.2, H–C(2′)); 7.06 (*dd*, *J* = 6.2, *J* = 5.1, NH); 7.22 (*tt*, *J*(6′,5′) = 7.1, *J*(6′,4′) = 1.5, H–C(6′)); 7.29 (*tt*, *J* = 7.1, *J* = 1.5, H–C(5′), H–C(7′)); 7.32 (br. *d*, *J* = 7.1, H–C(4′), H–C(8′)); others 1.08–1.54. MS: 605.4068 (M^+, $C_{38}H_{55}NO_5^+$; calc. 605.4075).

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