# 70. Synthesis of Medium- and Large-Ring Compounds Initiated by Photochemical Decarboxylation of ω-Phthalimidoalkanoates

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Dedicated to Prof. *Waldemar Adam* and Prof. *Dieter Seebach* on the occasions of their 60th birthdays on July 26th and October 31st 1997, respectively

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The synthesis of a variety of hydroxylactams from ω-phthalimidoalkanoates using a triplet-sensitized photodecarboxylation reaction initiated by intramolecular photo electron transfer is described. Ring sizes available by this method span from 4 (benzazepine-1,5-dione **7**) to 26 (cyclodipeptide **26e**). Ground-state template formation is proposed as the explanation for the high efficiency of this reaction and for the decrease in reactivity in the presence of organic bases instead of metal carbonates. The crucial step in this macrocyclization reaction seems to be the protonation of the intermediary ketyl radials (*Scheme 4*). Spacer groups investigated were alkyl chains ($C_3$-$C_{11}$: **5c–h**, **11a**, **12**), ether (**16**, **18**), ester (**20**, **22**), and amide (**26a–f**) linkages. Within the detection limits, no dimeric (= decarboxylative coupling) products were observed, indicating the high preference for intra- *vs.* intermolecular photoelectron transfer. The C,C radical combination step proceeds with low stereoselectivity (*cf.* products **11** and **12**) in contrast to comparable singlet reactions. Except for the lactones **22**, all products were stable under the photolysis conditions. Prolonged irradiation of **22** led to the formation of the spiro compounds **23**, probably *via* an intermediary acyliminium betaine (*Scheme 8*). One serious limitation of the decarboxylative macrocyclization is its incompatibility with the glycine spacer (as in **27a** and **27b**), probably the consequence of a strong intramolecular H-bond (*Scheme 10*).

**Introduction.** – Enantiomerically pure α-amino acids are substrates for photochemical reactions when activated by specific chromophoric groups introduced at the C- or N-terminus. We have investigated these reactions in the last years [1] taking advantage of the well-studied and synthetically easily accessible phthalimido chromophore [2]. The alkyl-substituted amino acids such as valine, leucine, isoleucine, or *tert*-leucine always had to be transformed into the corresponding esters prior to photolysis, otherwise efficient decarboxylation was observed [3]. In contrast to the chain-modification steps

[1]) Part of the Ph.D. thesis of *A. H.*, University of Würzburg, 1996.
[2]) Part of the projected Ph.D. theses of *W. K.*, *F. N.*, and *M. O.*
[3]) X-Ray structure analyses.

(isomerization, cyclization, ring enlargement[4])), this α-decarboxylation proceeds from the first excited singlet state as well as from the triplet state with relatively high quantum yields. It also resembles the photochemical silyl transfer reaction of *N*-[(trialkylsilyl)methyl]imides developed by *Yoon et al.* [4]. In both cases, azomethine ylides were formed which could be trapped by protonation or by reaction with dipolarophiles. An advantageous aspect of this reaction is its regioselectivity: COOH groups at other positions of the molecule were completely stable under the photolysis conditions. Thus, *N*-phthaloylglutamic or *N*-phthaloylaspartic acid were transformed into the corresponding β- and γ-amino acids, respectively [3]. Even prolonged irradiation of these products did not lead to further decarboxylation, *i.e.*, the 'remote' COOH groups were completely inert.

Parallel to our investigations of the photochemistry of alkyl-substituted amino acids, we have also studied heteroatom-substituted amino acids (serine [5], threonine [5], methionine [6], cysteine [7]) and aryl-substituted amino acids (phenylalanine, tyrosine, DOPA (= 3-hydroxytyrosine) [5]). The presence of easily oxidizable groups in the substrates led to significant changes in the chemoselectivity: the C-terminal-unprotected α-amino acids were decarboxylated only partially when directly excited or triplet-sensitized. Competing photo-induced electron transfer (PET) reactions diminished the $CO_2$ extrusion and led to isomerization products with intact COOH groups. An extreme example was found in the photochemistry of DOPA derivatives where PET occurred without any decarboxylation. We noticed, however, that the addition of $K_2CO_3$ to the reaction mixture substantially altered the product composition and favored again the decarboxylation reaction. *E.g.*, the photolysis of *N*-phthaloyl-*S*-methyl-L-cysteine (**1**) in a suspension of 10 equiv. of $K_2CO_3$ in acetone resulted mainly in the formation of the annulation product **3**, whereas the reaction without carbonate gave 60% of the thiazino isoindole **2** in its free acid form (*Scheme 1*) [8]. Obviously the base activated the COOH group and additionally protected the hydroxy-lactam against acid-catalyzed dehydration. Thus, it appeared that also remote COOH groups should become reactive when applied as the corresponding carboxylates. In a recent publication [9], we have described our first successful experiments in the area of photochemical macrocyclization using this concept [10].

Herein we report our approaches to a straightforward synthesis of macrocyclic ring systems with a remarkable flexibility concerning ring size (ring sizes 4–9, 12, 13, 16–18, 20, and 26), substituent pattern, nature of the spacer group and configuration, as well as reaction conditions.

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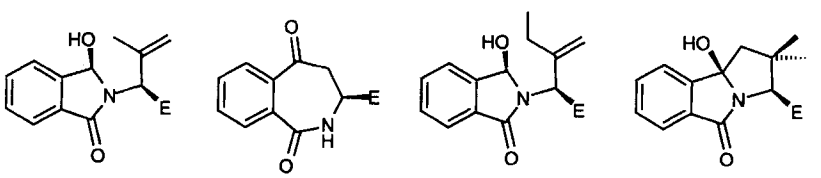
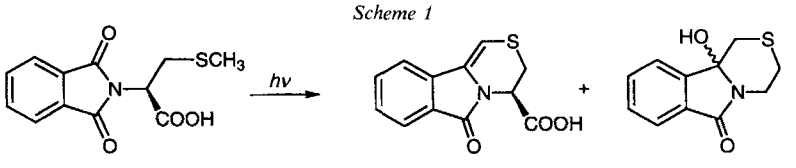
[4]) Products of direct irradiation of valine, leucine, isoleucine, and *tert*-leucine derivatives (E = COOMe) [3]:



*Scheme 1*




**1** **2** **3**

| | | |
|---|---|---|
| acetone | 60% | 40% |
| acetone/$K_2CO_3$ | 0% | 87% |

**Results and Discussion.** – To elaborate the scope and limitations of this new cyclization reaction, we focused on the synthesis of medium- and large-ring compounds[5]) testing a variety of ring sizes (from 4 to 26) and spacer groups. Firstly, alkyl chains were used to separate the phthalimido and the carboxylate part. There was no trace of a cyclization product when *N*-phthaloylglycine (**4a**) was irradiated under standard conditions, only *N*-methylphthalimide (**6a**) was formed. The homologous substrate, 3-phthalimidobutanoic acid (**4b**) did already give 10% (relative yield from NMR analysis of the crude product mixture) of the benzazepine-1,5-dione **7**, a rearrangement product of the primarily formed azetoisoindole **5b** (*Scheme 2*).

Substrates with longer alkyl chains did result in the formation of the corresponding annulation products **5** in yields not lower than 61%. In all cases, also small amounts (*ca.* 5–10%) of the 'simple' decarboxylation products **6** were detected. Only the starting material **4h** with a *trans*-cyclohexane-1,4-diyl spacer did show a slightly higher degree of decarboxylation leading to the mono-substitued cyclohexane **6h**. But also in this case, the cyclization product **5h** was formed in good yield. The latter example already indicated that a loss in conformational flexibility of the connecting hydrocarbon chain is not crucial for the efficiency of the ring formation. Furthermore, the conversion of **4h** into **6h** showed that also α-branched carboxylic acids can be used as substrates in the title reaction. All medium- and large-ring hydroxy-lactams **5** could be easily crystallized from acetone, and the X-ray structures were determined for the macrocycles **5f** [9] and **5g**[6]) (*Fig. 1*).

Neither dimeric products nor '*Kolbe* dimers', nor cross-cyclization products[7]) could be detected by NMR of MS analysis.

Initially, we used an experimental procedure which was developed on the basis of empirical facts and further optimization rather than on the basis of mechanistic understanding. Acetone proved to be the solvent of choice, $K_2CO_3$ the ideal base, and a small amount of $H_2O$ was crucial for the rate of conversion and for the chemoselectivity. The reaction could not be performed in the presence of organic bases such as amines or

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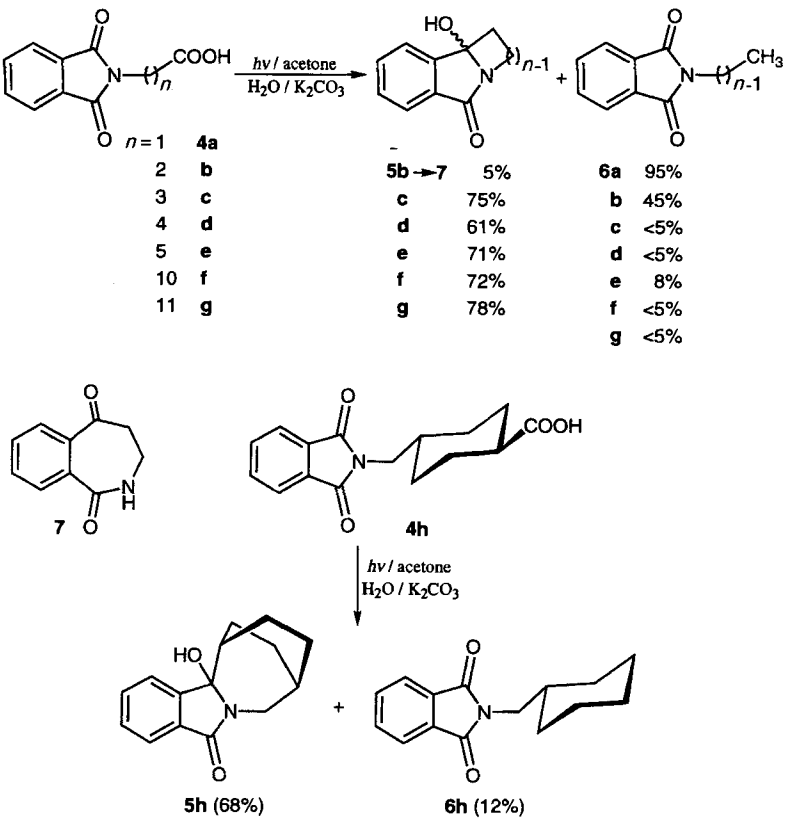
[5]) For a definition of these terms, see [11].

[6]) *Data Collection: Enraf-Nonius-CAD*4 diffractometer (**5f, 27b**) and *Siemens R3m/V* diffractometer (**11b**, *cis*-**12**, **16, 20**). Mo$K_\alpha$, graphite monochromator; *Wyckoff* scan, $\theta$ range 1.75–27.5°. *Structural analysis and refinement*: solution by direct phase determination; method of refinement, full-matrix least squares H-atom positions of riding model with fixed isotropic $U$; program used, *Siemens* SHELXL-93 and SHELXTL PLUS. Data in *Table 2*.

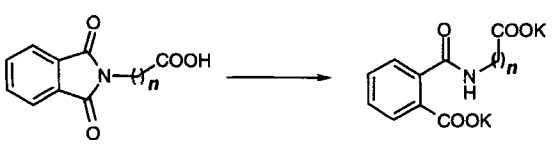
[7]) *Yoon et al.* have reported the formation of dimeric products in the PET macrocyclization using the (trialkylsilyl)methoxy group as electron donor [15b]. Within a detection limit of *ca.* 5%, we did not detect dimers when using comparable substrates in the photo-decarboxylation route.

*Scheme 2*




alkoxides, indicating the specific function of the alkali metal. Of all carbonate additives investigated, the potassium salt led to the highest degree of ring formation. It was striking to see that small changes in the concentration of $H_2O$ strongly influenced the ratio of cyclization *vs.* 'simple' decarboxylation. Thus, protonation constitutes a crucial step during the course of the reaction and influences the behavior of the C radicals which are formed after decarboxylation. We examined these influences using 6-phthalimidohexanoic acid (**4e**) as the model substrate (*Table 1, Scheme 3*). The maximum amount of cyclization product **5e** was found when 4 vol-% of $H_2O$ were used in the presence of 1 mol-equiv. of $K_2CO_3$ with acetone as solvent[8]). MeCN could likewise be used as

[8]) A serious side reaction is the ring opening of the phthalimide to give the corresponding *N*-(2-carboxybenzoyl)amino acids. This (reversible) reaction occurs in the presence of higher amounts of inorganic base *and* higher concentrations of $H_2O$ in the reaction mixture. The benzoylamino acids were photochemically unreactive.



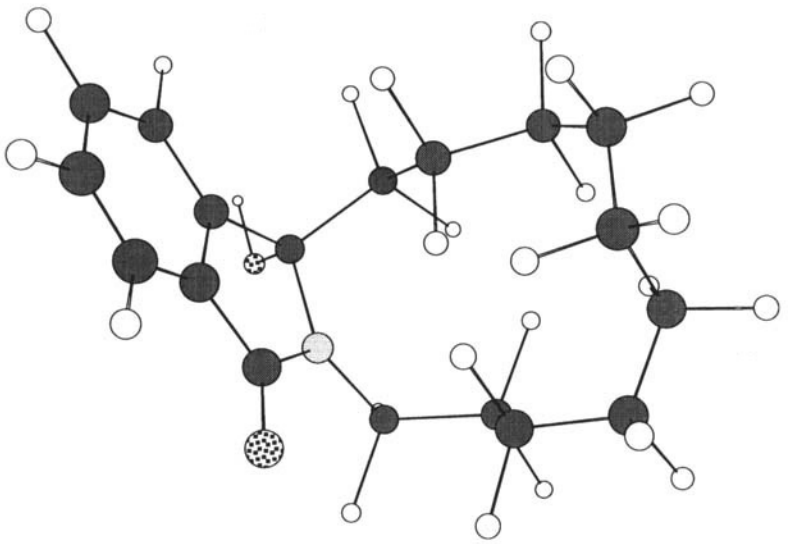


Fig. 1. *Structure of* **5f** *in the crystal: Chem 3D plot*

*Scheme 3*

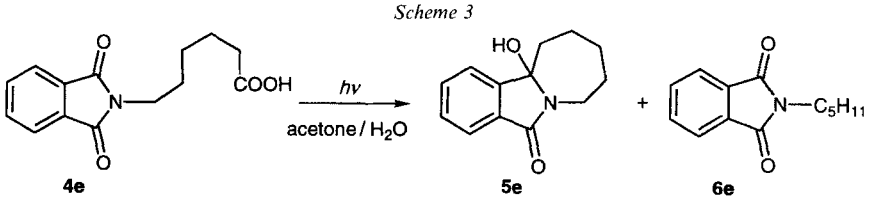



Table 1. *Photodecarboxylation of* **4e**: *Conversion and Product Composition*

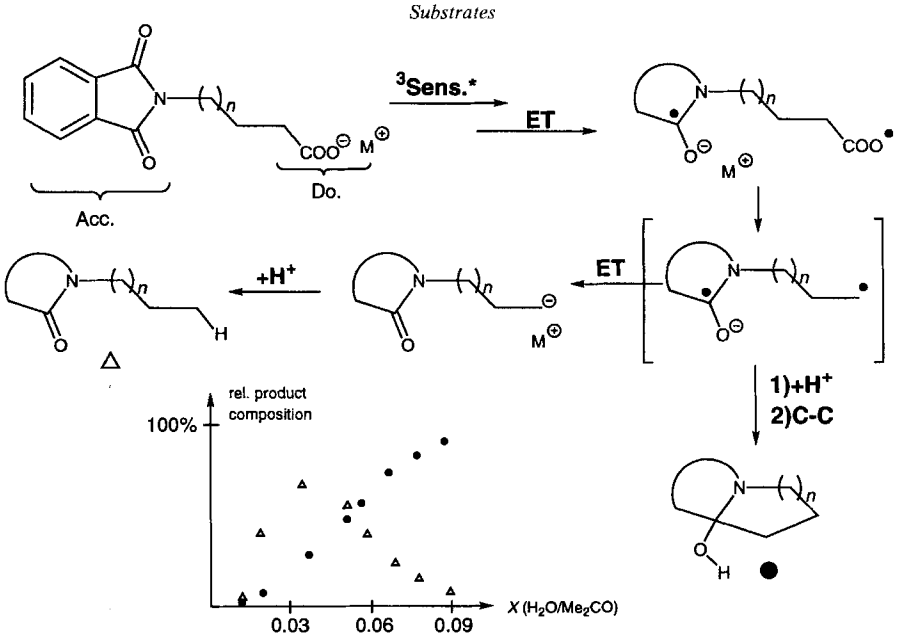
| Additive[a]) | Water [vol%] | Conversion [%][b]) | **5e**/**6e**[b]) |
|---|---|---|---|
| $Li_2CO_3$ | 2.0 | 90 | 30:70 |
| $Na_2CO_3$ | 2.0 | 100 | 60:40 |
| $K_2CO_3$ | 2.0 | 100 | 81:19 |
| $Cs_2CO_3$ | 2.0 | 100 | 61:39 |
| NaOMe | 2.0 | 0 | – |
| Pyridine | 2.0 | 5 | – |
| $K_2CO_3$ | 0.2 | 100 | 47:53 |
| $K_2CO_3$ | 0.5 | 100 | 54:46 |
| $K_2CO_3$ | 1.3 | 100 | 69:31 |
| $K_2CO_3$ | 3.0 | 100 | 85:15 |
| $K_2CO_3$ | 4.0 | 100 | 96:4 |

[a]) 1 equiv. of additive in acetone solution (10 mM **4e**), *hv* (300 nm), r.t., 24 h.
[b]) Determined by $^1$H-NMR (250 MHz) directly from the crude reaction mixture.

solvent but led to a decrease in conversion. We, therefore, assume that the excited triplet is the reactive species, similar by to other PET reactions with the phthalimide chromophore as the electron-accepting part and acetone as the triplet sensitizer [5] [7]. In a

relatively broad concentration window, the amount of $H_2O$ did not influence the rate of substrate conversion, but strongly the product ratio **5e/6e**. We interpret this fact by assuming that PET from the carboxylate ion to the excited triplet phthalimide must be followed by rapid protonation of the radical anion to give a high degree of cyclization, *i.e.*, biradical combination reaction. Otherwise, the radical anion operates as an efficient reductant and converts the C radical (formed after $CO_2$ extrusion from the carboxy radical) into the corresponding carbanion. The latter process is less probable for secondary radicals which also explains the high yield for the cyclization product **5h** (*Scheme 4*).

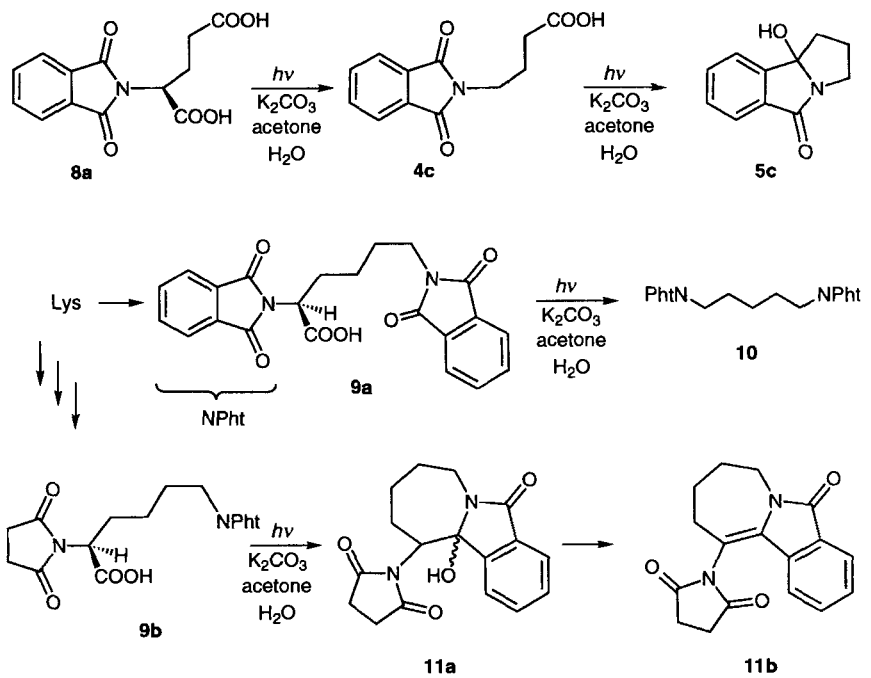
Scheme 4. *Mechanism of the PET Photodecarboxylation: Averaged Product Composition for Unfunctionalized Substrates*




Two other important questions concern the regio- and stereoselectivity of the PET decarboxylation and the biradical combination, respectively. Apparently, there is a substantial difference between α- and ω-decarboxylation with respect to spin selectivity (*vide supra*) and the secondary processes. Two illustrative examples were the *N*-phthaloyl derivatives **8a** and **9a** of L-glutamic acid and L-lysine respectively (*Scheme 5*). The first substrate when irradiated under salt conditions (excess $K_2CO_3$ in acetone/$H_2O$) was rapidly converted into the γ-amino butanoic acid derivative **4c**. The subsequent cyclization step to **5c** was *ca.* 10 times slower. This ratio of > 10:1 for α- *vs.* ω-decarboxylation was also observed for the $N^2$,$N^6$-diphthaloyl derivative **9a** of lysine. In this case, only the pentane-1,5-diamine derivative **10** was formed, indicating that the quantum yields for α- *vs.* ε-decarboxylation differ by at least a factor of 5 (assuming identical probability for excitation of each of the chromophoric groups). When the mixed protected lysine **9b** was irradiated, a clean formation of the azepinoisoindole **11a** was observed. This reaction was another example where an α-branched carboxylate underwent photocyclization (*cf.* sub-

strate **4h**). In the case of **11a** a 1:1 mixture of two diastereoisomers was isolated. When trying to crystallize one of them, we obtained the dehydration product **11b** (see *Fig. 2* for X-ray structure[6])). We could show independently that this acid-catalyzed dehydration proceeds with remarkable ease and efficiency with both stereoisomers **11a**.

*Scheme 5*




The low diastereoselectivity observed in the reaction of the lysine derivative **9b** was also apparent in the photocyclization of the glutamic-acid derivative **8b** (*Scheme 6*). In this case, a 1:1 mixture of *cis*- and *trans*-**12** resulted after a relatively short irradiation time. When directly using the potassium salt of **8b**, no trace of the simple decarboxylation product was observed after quantitative conversion in acetone/$H_2O$ 1:1. The two diastereoisomeric benzopyrrolizidinones (= pyrroloisoindoles) were easily distinguishable by $^1$H-NMR (*cis*-**12**: both $^3J$(H,H) couplings to H–C(α) were 8.5 Hz, *trans*-**12**: only one $^3J$(H,H) coupling was detectable). Treatment of this 1:1 product mixture with catalytic amounts of trifluoroacetic acid ($CF_3COOH$) led to near quantitative epimerization of *trans*-**12** into the *cis*-**12**. By this method, we were able to isolate diastereoisomerically pure *cis*-**12** which was also identified by X-ray crystal-structure analysis (*Fig. 3*)[6]). This compound crystallized as a 2:2 cluster of *cis*-**12** with two molecules of $H_2O$ which forms a network of three independent H-bonds each.

Epimerization at the stereogenic center of hydroxy-lactams resulting in an 1:1 equilibrium mixture has already been reported by us for the product of the *N*-phthaloylvaline ester photolysis [1b]. In the glutamic-acid case reported herein, however, the epimerization equilibrium mixture is > 9:1 in favor of *cis*-**12**. Further treatment of *cis*-**12**

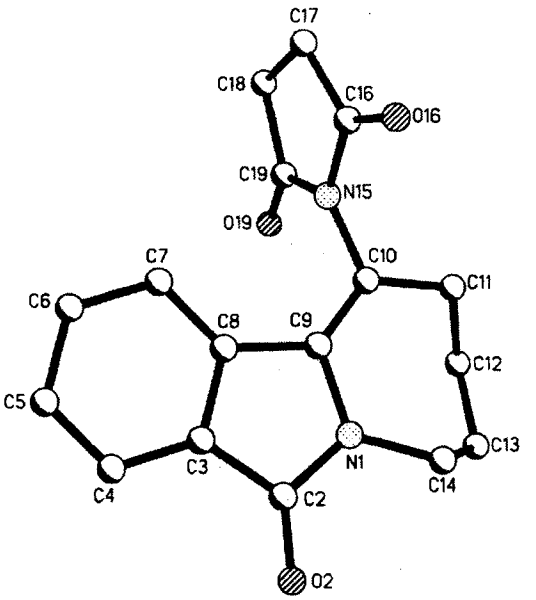
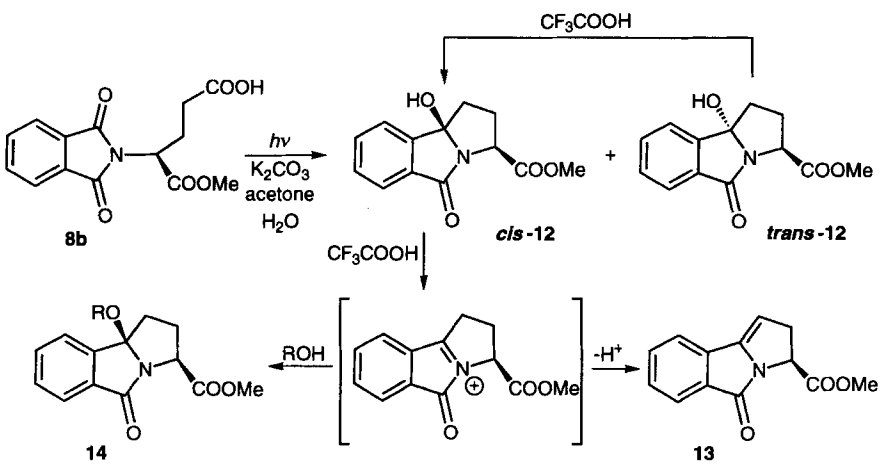



Fig. 2. *Structure of* **11b** *in the crystal.* Arbitrary numbering.

*Scheme 6*




with $CF_3COOH$ in an inert solvent led to the enamide **13**, whereas in the presence of alcohols, the *cis*-alkoxy-lactams **14** were formed in high (> 95:5) diastereoselectivity [12]. These reactions proceed *via* intermediary acyliminium cations which are known to be reactive with a multitude of nucleophiles [13]. Benzopyrrolizidines of this type have also been synthesized using the azomethine ylide route developed for *N*-[(trialkylsilyl)-methyl]imides [4].

The low diastereoselectivity observed for the photocyclization of **8b** is typical for a triplet 1,5-biradical combination (in contrast to triplet 1,4-biradical reactions [14]). The

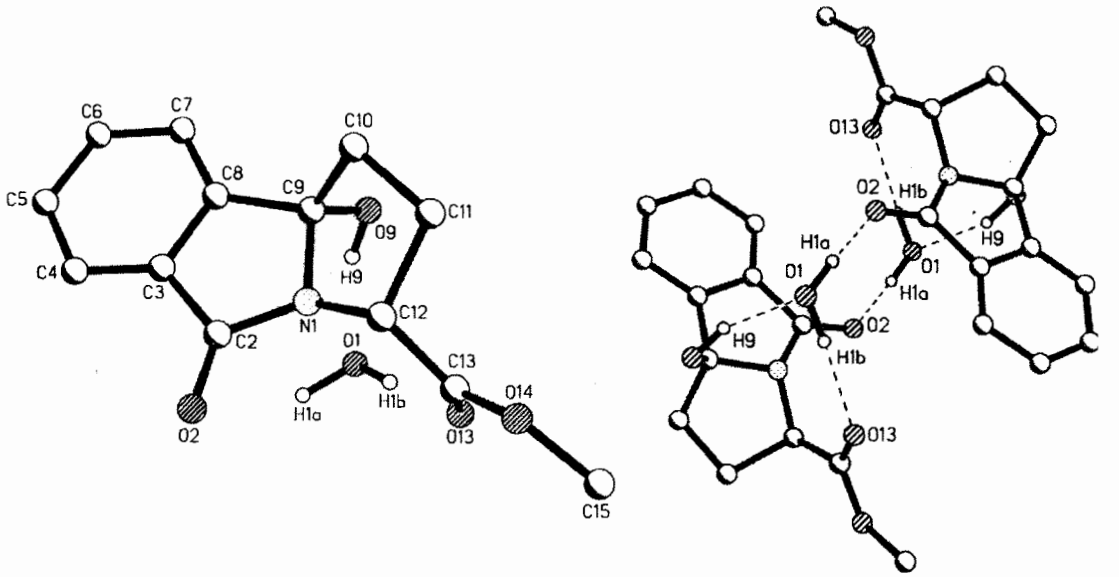
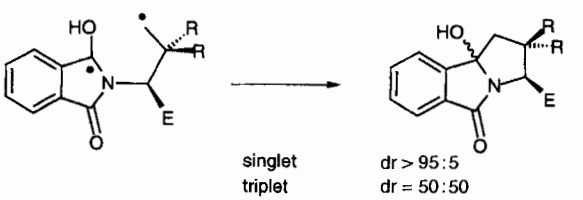



Fig. 3. *Structure of* cis-**12** *in the crystal.* Arbitrary numbering.

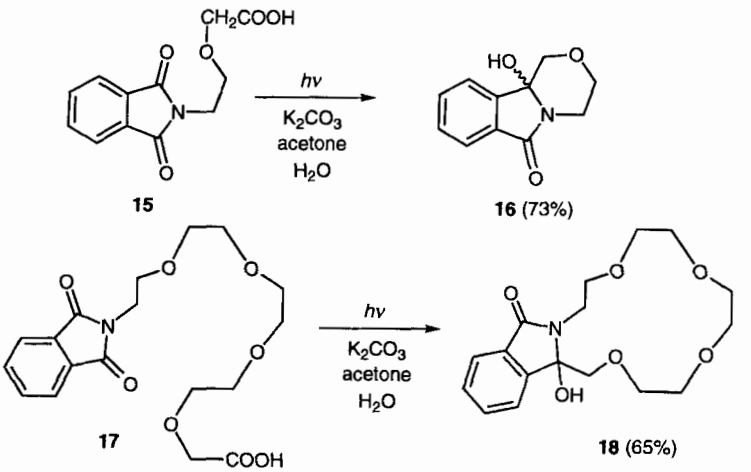
corresponding singlet reactions which also lead to the benzopyrrolizidine skeleton, *e.g.*, for the *N*-phthaloyl-*tert*-leucine substrate, proceed with high diastereoselectively [1a, b][9]).

To elaborate this photocyclization methodology further, we investigated other spacers connecting the electron-donating carboxylate and the electron-accepting phthalimide groups. The use of ether linkers was tested for substrate **15** and the crown ether precursor **17** (*Scheme 7*). In both examples, the oxyacetic-acid moiety serves as the terminal building block. Alternatively, the (trimethylsilyl)methoxy substituent has been developed by *Yoon*, *Mariano*, and coworkers as a versatile electron-donor group which, after oxidation *via* PET and desilylation, was converted into an α-oxy-stabilized C radical [15]. Thus, the intermediate biradicals are identical in both approaches; however, the PET-decarboxylation route is not limited to substrates with a terminal alkyl group substituted by an electron-donor group at the α-position [16]. The photocycliza-

[9]) For examples, the asymmetric induction by the methoxycarbonyl group is > 9:1 when the reaction is conducted by direct excitation (singlet pathway) and 1:1 when the reaction is triplet-sensitized. The first case is based on a (ground state) conformational memory effect [1b] which does no longer exist in the triplet case.



*Scheme 7*




tion products **16** and **18**[10]) were formed from **15** and **17** in high yields (73 and 65%, resp., after recrystallization) and essentially without by-products.

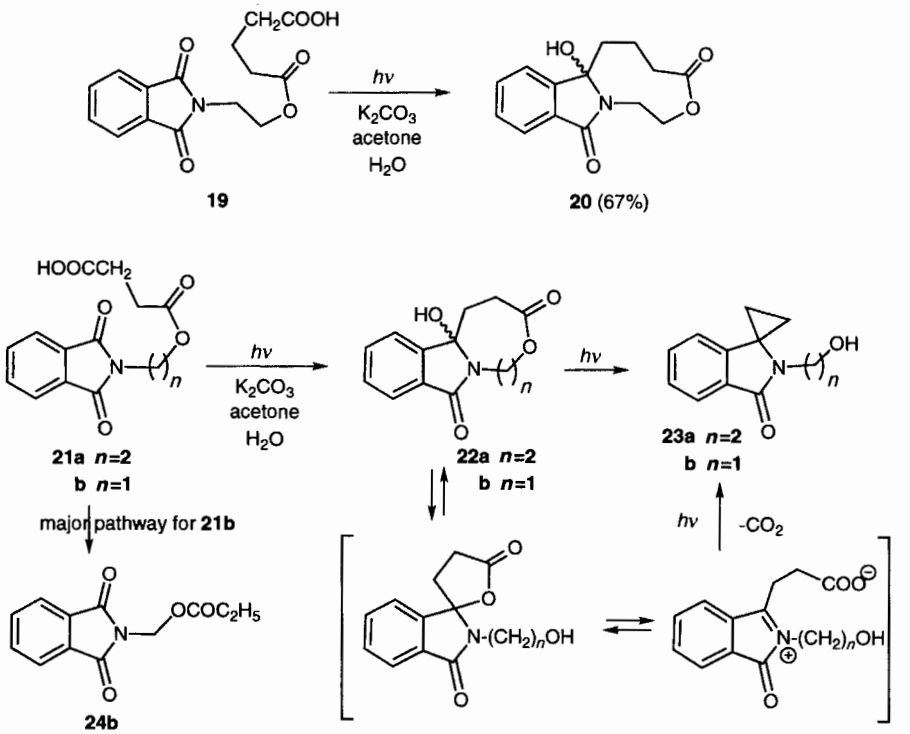
Medium- and large-ring lactones (macrolides) also constitute an interesting class of compounds which should be accessible by our method. Thus, the glutaric-acid derivative **19** could be successfully photocyclized, and the nine-membered azalactone **20** was formed in 67% yield and characterized by an X-ray structure analysis (*Scheme 8*, *Fig. 4*)[6]). When using the succinic acid derivative **21a** as lower homologue, much to our surprise, the spirocyclopropane **23a** was isolated as the sole product after prolonged photolysis.

When repeating this experiment under the same conditions but for a shorter irradiation time, we could detect and isolate the eight-membered azalactone **22a**. After purification and repetition of the liquid-phase photolysis, **22a** was completely converted into **23a**. Thus, we postulate as the key step an isomerization of **22a** into a corresponding spirolactone (see *Scheme 8*). This intermediate can ring-open under the basic reaction conditions to give an acyliminium betaine. The latter can be electronically excited and, after electron transfer and decarboxylation, gives the C,C coupling product **23a**. This interpretation is based on the assumption that the ring size of the intermediary spirolactone is a critical criterion for the second decarboxylation step. We, therefore, also investigated substrates with only one $CH_2$ group separating the ester from the phthalimido substituent. As expected, the corresponding succinic acid **21b** derivative gave the spirocyclopropane **23b** after longer irradiation beside appreciable amounts of the reductive decarboxylation product **24b**, whereas the homologous glutaric-acid derivative **19** gave nearly exclusively the product of simple decarboxylation.

Another highly important class of macrocyclic compounds are cyclic oligopeptides. To optimize the procedure for the preparation of these targets, we investigated six substrates **25a–f** with different spacer patterns (*Scheme 9*). The N-terminal spacer

[10]) In this case, the formation of a ground-state template with the potassium cation complexed by the polyether chain is highly probable and explains the remarkable efficiency of this macrocyclization.

*Scheme 8*




groups used in compounds **25a–c** were glycine, β-alanine, and 4-aminobutanoic acid. Similarly as already described for the methylene-linked ester **21b**, the glycine derivative **25a** gave mainly reductive decarboxylation and only 26% of cyclization product **26a**. A functional group which is linked in close proximity to the phthalimide chromophore seems to reduce the cyclization propensity of the 1,*x*-biradical formed after PET decar-

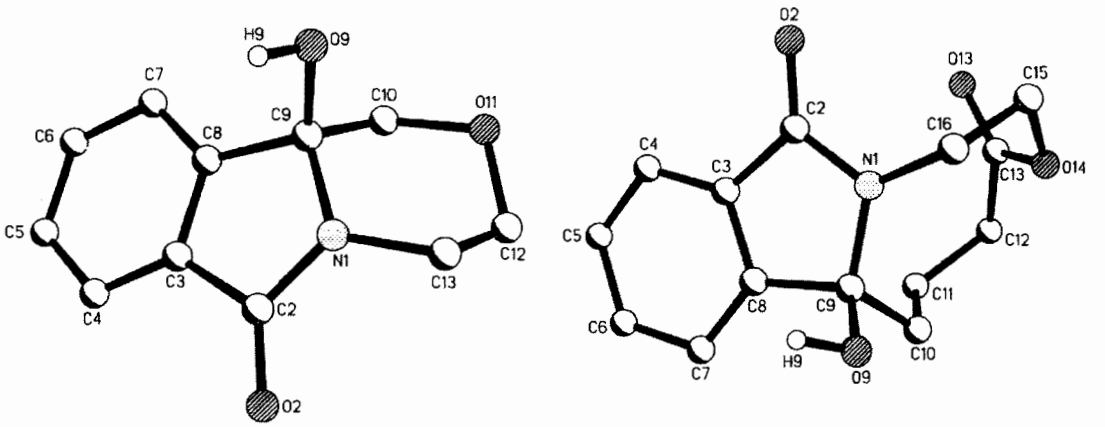
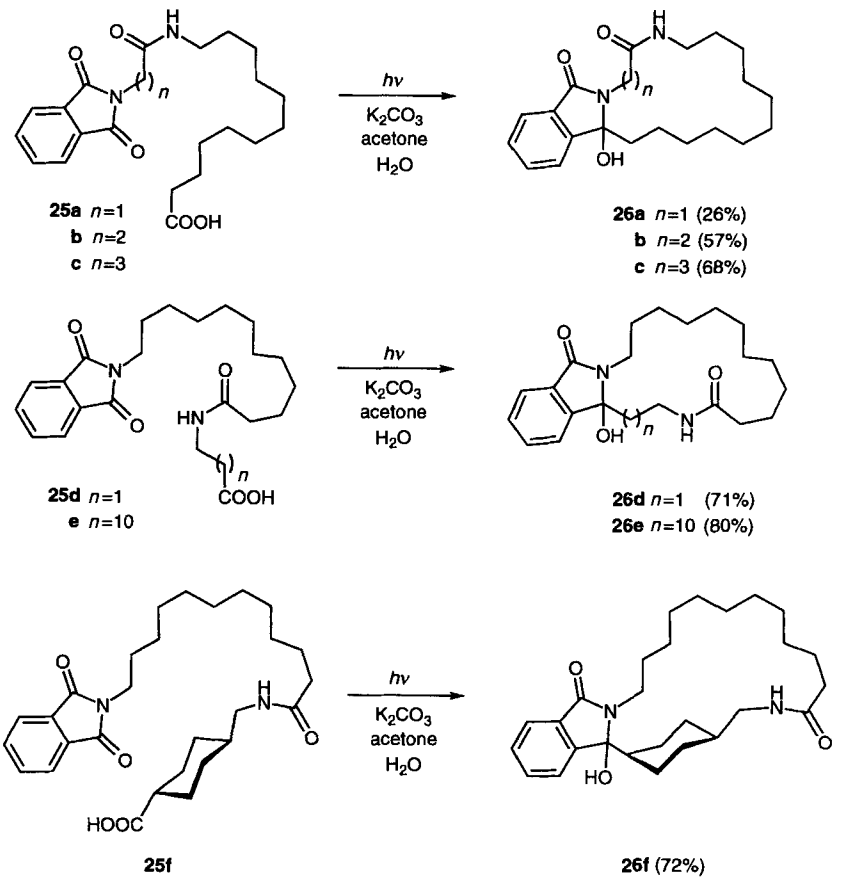



Fig. 4. *Structure of* **16** *and* **20** *in the crystal.* Arbitrary numbering.

*Scheme 9*

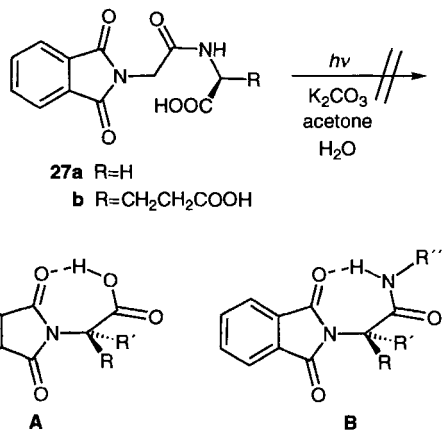



boxylation. When using the 'more flexible' substrates **25b** and **25c**, the yields for the macrocycles **26b, c** were very good (57 and 68%, resp.). Increasing the chain length of the N-terminal spacer to $C_{11}$ additionally lead to an increase in cyclization efficiency as shown for the two examples **25d** and **25e**. It is remarkable that the substrate with the longest and most flexible spacer between donor and acceptor gave the highest yield of cyclization product (**26e**, 80%). Even the *trans*-cyclohexane-1,4-diyl-linked dipeptide **25f** gave the macrocycle **26f** in excellent yields (comparable with the directly connected donor-acceptor pair in **4h** see above, *Scheme 2*).

It was this last series of experiments in combination with the results obtained for the variation of the countercation (*vide supra*) which led to the idea of a ground-state intramolecular stabilization of the ω-phthalimido-substituted alkanoates, similar to template effects in other macrocyclization reactions. An alternative concept would involve a long-lived excited phthalimide triplet state and the formation of a triplet exciplex; however, this does not explain the high tendency for the intramolecular reaction with essentially no intermolecular electrontransfer competition. Another hint for the role of ground-state stabilization came from the fact, that the 'real' dipeptides **27a**

(Pht=Gly-Gly) and **27b** (Pht=Gly-Glu) were unreactive under the given reaction conditions, *i.e.*, did neither give cyclization nor reductive decarboxylation. It is highly probable that the same effect which makes the α-decarboxylation exceedingly effective (see **A**) also deactivates the glycine-linked dipeptides (see **B**). This assumption was confirmed by an X-ray structure analysis of the *N*-phthaloyldipeptide **27b** (*Fig. 5*). This compound crystallized with four molecules of $H_2O$ in the elementary cell. With these $H_2O$ molecules, **27b** forms a H-bonded network where every $H_2O$ molecule shows three H-bonds (two to the α- and γ-carboxy groups and one H-bond to the amide carbonyl group). The only direct intermolecular H-bond between two molecules of **27b** is formed between the amide group and the phthalimide carbonyl group in agreement with our assumption, that this interaction in its intramolecular version is strongly deactivating the electron-transfer step.

*Scheme 10*




**Conclusions.** – Decarboxylation reactions are highly important in organic chemistry and have been applied for numerous syntheses. Electrochemical processes have been developed using decarboxylative coupling (*Kolbe* process [17]) as well as oxidative decarboxylation (*Hofer-Moest* process [18]) steps for the synthesis of complex target molecules. Non-electrochemical processes which have similar efficiency in producing C-centered radicals are the 'photo-*Kolbe* process' [19], the *Barton* decarboxylation using thiohydroxamic esters as radical precursors [20], the intermolecular PET reduction of *N*-(acyloxy)phthalimides [21], and (for special cases) the direct photolytic decarboxylation [22]. The intramolecular PET of ω-phthalimidoalkanoates with concomitant decarboxylation and C,C combination proceeds analogously to the PET of ω-(alkylthio)- [23], ω-(alkylamino)- [24], or ω-[(trimethylsilyl)methoxy]-substituted [15] phthalimides. A major advantage of our method is the extrusion of the former electron-donating part during the course of the reaction. Thus, the macrocyclic ring system is formed only with incorporation of the original electron-accepting part. To circumwent also this effect, we are currently investigating acyclic donor-acceptor substrates.

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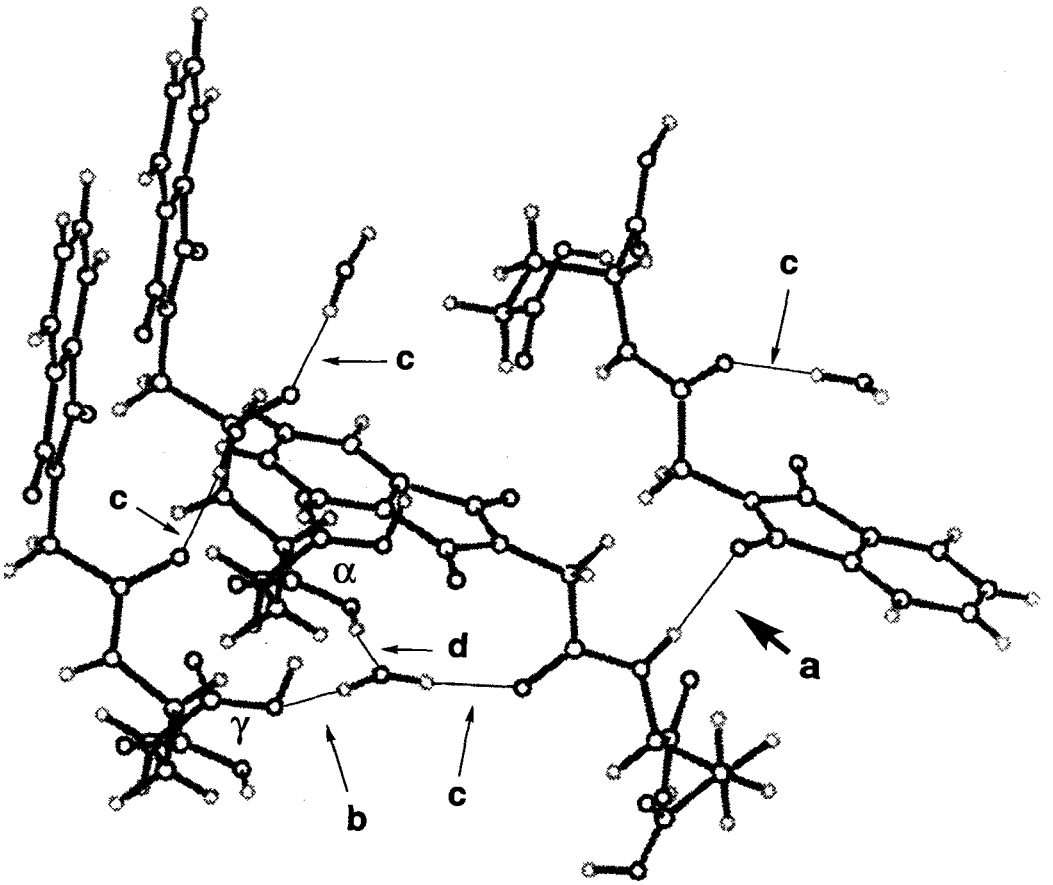


Fig. 5. *Structure of* **27b** *in the crystal: SCHAKAL plot* with *H-bonds indicated.* Light circles: H-atoms; a–d: H-bonds.

## Experimental Part

1. *General.* For special procedures for the synthesis of starting materials, see below. For standard procedures for the synthesis of α-(phthaloylamino) acids (**4a**, **8a**, **9a**), see [25] and [26]. *Rayonet®* chamber photoreactors *RPR-208* (8 × 3000 Å lamps, *ca.* 800 W, $\lambda$ 300 ± 10 nm) and *RPR-100* (16 × 3500 Å lamps, *ca.* 400 W, $\lambda$ = 350 ± 20 nm) and immersion-wall reactors ($\lambda$ > 280 nm) were used for irradiations. Column chromatography: silica gel (*Merck*) 60–230 mesh; petroleum ether 40–60° (p.e.). M.p.: *Büchi* melting-point apparatus, type No. *535*; uncorrected. IR: *Perkin-Elmer-1605*, FT-IR spectrophotometer; $\tilde{\nu}$ in $cm^{-1}$. $^1$H-NMR: *AC-200* (200 MHz), *Bruker AC 250* (250 MHz), *Bruker AC 300* (300 MHz), *Bruker DMX 600* (600 MHz). $^{13}$C-NMR: *Bruker AC 200* (50.3 MHz), *Bruker AC 250* (63.4 MHz), *Bruker AC 300* (75 MHz), C multiplicities were determined by DEPT; $\delta$ in ppm, $J$ in Hz. Mass spectroscopy (EI): *Finnigan MAT 8200* and *Finnigan MAT 312*; *m/Z* (rel. %). Combustion analyses: Institut für Anorganische Chemie der Universität Würzburg and Institut für Anorganische Chemie der Universität zu Köln.

2. *Unfunctionalized ω-(Phthaloylamino) Acids: General Procedure.* A mixture of phthalic anhydride (= isoindol-1,3-dione; 14.81 g, 100 mmol) and 4-aminobutanoic acid (10.31 g, 100 mmol) was heated in an open flask (500 ml) to 150° for 45 min. After complete evaporation of the $H_2O$ and cooling to 50°, the mixture was poured into $H_2O$ (150 ml). Filtration of the solid material and second filtration after reduction of the remaining soln. to *ca.* 20% gave 20.60 g (88%) of *1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-butanoic acid* (**4c**) as a

Table 2. *Crystallographic Data for Compounds* **5f**, **11b**, cis-**12**, **16**, **20**, *and* **27b**

| | **5f** | **11b** | *cis*-**12** | **16** | **20** | **27b** |
|---|---|---|---|---|---|---|
| Formula | $C_{18}H_{25}NO_2$ | $C_{17}H_{16}N_2O_3$ | $C_{13}H_{15}NO_5$ | $C_{11}H_{11}NO_3$ | $C_{14}H_{15}NO_4$ | $C_{15}H_{16}N_2O_8$ |
| Molecular mass | 287.39 | 296.33 | 265.27 | 205.21 | 261.28 | 352.30 |
| Crystal dim. [mm] | 0.35 × 0.3 × 0.28 | 0.2 × 0.45 × 0.7 | 0.4 × 0.75 × 0.35 | 0.2 × 0.55 × 0.75 | 0.7 × 1.25 × 0.25 | 0.2 × 0.08 × 0.06 |
| *a* [pm] | 829.8(2) | 921.1(2) | 993.2(2) | 794.1(1) | 2274.6(6) | 892.3(2) |
| *b* [pm] | 990.4(3) | 960.5(1) | 1043.7(2) | 1583.3(2) | 744.2(1) | 1205.8(4) |
| *c* [pm] | 1127.7(3) | 1682.3(3) | 1239.8(2) | 776.0(1) | 1695.8(4) | 1560.2(5) |
| $\alpha$ [°] | 66.23(2) | | | | | |
| $\beta$ [°] | 72.44(2) | | 94.23(2) | | 116.18(2) | |
| $\gamma$ [°] | 80.51(2) | | | | | |
| $V$ [$10^6$pm$^3$] | 807.7(4) | 1488.3(3) | 1281.6(3) | 975.6(2) | 2576(1) | 1678.7(9) |
| $Z$ | 2 | 4 | 4 | 4 | 8 | 4 |
| $\rho$(calc.) | 1.182 | 1.322 | 1.375 | 1.397 | 1.374 | 1.394 |
| Crystal system | triclinic | orthorhombic | monoclinic | orthorhombic | monoclinic | orthorhombic |
| Space group *P*1 | $P\bar{1}$ | $Pna2_1$ | $P2_1/n$ | $Pna2_1$ | $C2/c$ | $P2_12_12_1$ |
| No. refl. measured | 5358 | 2609 | 3276 | 3307 | 3267 | 3096 |
| No. unique refl. | 4677 | 1877 | 2936 | 1368 | 2956 | 2936 |
| No. obs. refl. | 3598[a]) | 1391[b]) | 2502[b]) | 1333[b]) | 2490[b]) | 1808[a]) |
| $R$ | 0.051 | 0.057 | 0.061 | 0.038 | 0.061 | 0.068 |
| $R_w$[c]) | 0.136 | 0.052 | 0.060 | 0.039 | 0.059 | 0.152 |
| Largest diff. Peak/hole [eÅ$^{-3}$] | 0.41/−0.40 | 0.26/0.24 | 0.33/0.19 | 0.22/0.20 | 0.31/0.19 | 0.23/−0.34 |

[a]) For $F > 2\sigma(F)$. [b]) For $F > 3\sigma(F)$. [c]) Weight for **5f** and **27b**, $R_w = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; weight for **11b**, **12**, **16**, and **20**: $w = 1/\sigma^2(F)$.

colorless powder with m.p. 118–120° ([27]: 117–188°). Substrates **4a**, **b**, **d**–**h**, and **8a** were likewise prepared in yields of 65–90%.

*1-Methyl 5-Hydrogen (2S)-2-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)pentanedioate* (**8b**). To a soln. of *N*-phthaloyl-L-glutamic acid (**8a**; 27.72 g, 100 mmol) and $Et_3N$ (14 ml, 100 mmol) in $CHCl_3$ (150 ml) was added dimethyl sulfate (10.5 ml, 110 mmol) at r.t. After stirring ar r.t. for 40 h, the solvent was removed and the residue treated with $H_2O$ (150 ml) and extracted with AcOEt (3 × 100 ml). The combined org. extract was extracted with sat. $NaHCO_3$ soln. (3 × 100 ml). The combined aq. soln. was acidified with conc. HCl soln. The colorless precipitate was dried ($MgSO_4$), dissolved in MeOH, and crystallized by adding hexane: 17.4 g (60%) of **8b**. Colorless crystals. M.p. 134–136° (from acetone; [28]: 134–136°). IR (KBr): 2936, 2905, 2837, 1743*m*, 1704*s*, 1373, 710. $^1$H-NMR (250 MHz, $CD_3OD$): 2.39–2.49 (*m*, 2H); 2.52–2.70 (*m*, 2H); 2.76 (*s*, 3H, MeO); 5.02 (*dd*, *J* = 4.9, 10.0, 1H); 7.85–8.05 (*m*, 4 arom. H). $^{13}$C-NMR (63 MHz, $CD_3OD$): 25.2 ($CH_2$); 29.2 ($CH_2$); 50.3 (CH); 51.0 (Me); 122.3 (CH); 130.8 (C); 133.6 (CH); 166.8 (C); 168.9 (C); 173.8 (C).

*(2S)-6-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)-2-(2,5-dioxopyrrolidin-1-yl)hexanoic Acid* (**9b**). To a soln. of L-lysine hydrochloride (27.4 g, 150 mmol) and NaOH (12 g) in $H_2O$ (250 ml) was added a soln. of $CuSO_4 \cdot H_2O$ (19 g) in $H_2O$ (250 ml) and stirred for 30 min. During 10 min $NaHCO_3$ (15 g) was added and then the soln. stirred for 10 min. During 20 min, ethyl 1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-carboxylate (37.5 g, 150 mmol) was added and the soln. stirred for additional 2 h. The precipitate was filtered and dried. The resulting copper complex (32.67 g) was stirred in 6N HCl (175 ml) and filtered. After drying, the hydrochloride salt was dissolved in $H_2O$ (150 ml), and $KHCO_3$ (15 g) was added. Neutralization with AcOH gave 7.05 g of $N^6$-phthaloyl-L-lysine [29] as a colorless powder (overall yield: 30%). A mixture of $N^6$-phthaloyl-L-lysine (2.67 g, 10 mmol) and succinic anhydride (1.02 g, 10 mmol) was heated to 145° for 10 min. After cooling to r.t., the resulting viscous oil was dissolved in MeOH (200 ml), cooled to 0°, treated twice with gaseous HCl, and stirred for 5 h. After column chromatography (silica gel, MeOH/$CH_2Cl_2$ 1:10), the resulting material was treated with 20 ml of AcOH/HCl 10:1. Extraction with AcOEt (2 × 100 ml), drying, and evaporation resulted in 1.05 g (29%) of **9b**. Colorless powder. M.p. > 210°. IR (KBr): 3260*m* (br.), 2944, 1760*m*, 1712*s*, 1395, 1188, 710. $^1$H-NMR (250 MHz, $CDCl_3$): 1.32 (*m*, 2H); 1.70 (*m*, 2H); 2.20 (*sept.*, *J* = 8.2, 2H); 2.89 (*s*, 4H); 3.70 (*t*, *J* = 7.0, 2H); 4.70 (*dd*, *J* = 6.2, 8.9, 1H); 7.77 (*dd*, *J* = 3.0, 5.5, 2H); 7.88 (*dd*, *J* = 3.0, 5.5, 2H); 9.77 (*s*, COOH). $^{13}$C-NMR (63 MHz, $CDCl_3$): 23.3 ($CH_2$); 27.0 ($CH_2$); 27.7 ($CH_2$); 28.0 ($CH_2$); 37.4 ($CH_2$); 53.5 (CH); 123.4 (CH); 131.7 (CH); 134.3 (CH); 169.0 (C); 174.0 (C); 177.5 (C). Anal. calc. for $C_{18}H_{18}N_2O_6$ (358.1): C 60.33, H 5.06, N 7.82; found: C 60.06, H 4.97, N 7.44.

*[2-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)ethoxy]acetic Acid* (**15**). A mixture of 2-(2-aminoethoxy)ethanol (3.15 g, 30 mmol) and phthalic anhydride (4.45 g, 30 mmol) was heated to 150° in an open flask (250 ml) for 20 min to give 6.79 g (94%) of crude *2-[2-(2-hydroxyethoxy)ethyl]-1*H*-isoindole-1,3-(2*H*)-dione* colorless powder. To a soln. of this material (3.53 g, 15 mmol) in acetone (50 ml) cooled to 0° was added a soln. of $CrO_3$ (4.20 g, 36 mmol) in 35% $H_2SO_4$ soln. (75 ml) in 1 h. After 4 h stirring at r.t., the mixture was carefully poured into $H_2O$ (500 ml) and extracted with AcOEt (3 × 150 ml). After drying ($Na_2SO_4$) and evaporation, 2.53 g (68%) of **15** were isolated. Colorless powder. M.p. 126–129° ([39]: 127–129°). IR (KBr): 3526, 3393*s* (br.), 2953, 2920, 2560, 1772*s*, 1706*s*, 1612, 1464, 1396, 1258, 1139, 720, 529. $^1$H-NMR (250 MHz, $CDCl_3$): 3.80 (*t*, *J* = 5.2, 2H); 3.92 (*t*, *J* = 5.2, 2H); 4.10 (*s*, 2H); 7.40 (*s*, COOH); 7.70 (*dd*, *J* = 3.1, 5.5, 2H); 7.83 (*dd*, *J* = 3.1, 5.5, 2H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 37.3 ($CH_2$); 67.4 ($CH_2$); 68.5 ($CH_2$); 123.3 (CH); 131.9 (C); 134.0 (CH); 168.3 (C); 173.8 (C).

*14-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)-3,6,9,12-tetraoxatetradecanoic Acid* (**17**). To a soln. of methyl 14-hydroxy-3,6,9,12-tetraoxatetradecanoate (5.33 g, 20 mmol), diethyl diazenedicarboxylate (3.83 g, 22 mmol), and phthalimide (= 1*H*-isoindole-1,3(2*H*)-dione; 3.23 g, 22 mmol) in HF (30 ml) cooled to 0°, triphenylphosphine (5.55 g, 22 mmol) in THF (30 ml) was added. After stirring for 24 h at r.t., the solvent was evaporated at 30°/18 Torr. The residue was suspended in $CHCl_3$ (60 ml) and filtrated. The $CHCl_3$ soln. was dried and evaporated. After column chromatography, the methyl ester (2.93 g, 37%) was isolated. A soln. of the methyl ester (1.47 g, 3.9 mmol) in AcOH (15 ml) and 10N HCl (3 ml) was subsequently heated to reflux for 1 h. Evaporation and crystallization from acetone gave 1.38 g (97%) of **17**. Colorless solid. M.p. 76–77°. IR (KBr): 3456*s*, 3060, 2963, 2882, 2567, 1774*s*, 1720*s*, 1614*s*, 1452, 1250, 1091, 723, 533. $^1$H-NMR (250 MHz, $CDCl_3$): 3.52–3.61 (*m*, 10H); 3.65–3.70 (*m*, 2H); 3.68 (*t*, *J* = 5.6, 2H); 3.84 (*t*, *J* = 5.6, 2H); 4.08 (*s*, 2H); 7.65 (*dd*, *J* = 3.1, 5.5, 2H); 7.78 (*dd*, *J* = 3.1, 5.5, 2H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 30.9 ($CH_2$); 67.9 ($CH_2$); 68.9 ($CH_2$); 70.1 ($CH_2$); 70.2–70.6 ($CH_2$); 71.3 ($CH_2$); 132.2 (CH); 132.1 (C); 133.9 (CH); 168.1 (C); 172.3 (C). Anal. calc. for $C_{18}H_{23}NO_8$ (381.1): C 56.69, H 6.08, N 3.67; found: C 56.50, H 6.09, N 3.61.

*[2-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)ethyl] Hydrogen Pentanedioate* (**19**). A mixture of 2-(2-hydroxyethyl)-1*H*-isoindole-1,3(2*H*)-dione (9.56 g, 50 mmol) and glutaric anhydride (8.50 g, 75 mmol) was heated to 150° for 30 min in an open flask (250 ml). Cooling to r.t. and purification by column chromatography (silica gel, MeOH/$CH_2Cl_2$ 1:30) gave 9.51 g (62%) of **19**. Slightly brownish oil. IR (KBr): 3450*s* (br.), 2955, 1775*s*, 1714*s*,

1616, 1429, 1395, 1190, 720. $^1$H-NMR (250 MHz, $CDCl_3$): 1.82 (*m*, 2H); 2.22–2.39 (*m*, 4H); 3.95 (*t*, *J* = 5.5, 2H); 4.31 (*t*, *J* = 5.5, 2H); 7.73 (*dd*, *J* = 3.0, 5.4, 2H); 7.85 (*dd*, *J* = 3.0, 5.4, 2H); 9.50 (*s*, COOH). $^{13}$C-NMR (63 MHz, $CDCl_3$): 19.4 ($CH_2$); 32.8 ($CH_2$); 37.0 ($CH_2$); 61.5 ($CH_2$); 123.4 (CH); 131.9 (C); 134.1 (CH); 168.1 (C); 172.6 (C); 178.5 (C). Anal. calc. for $C_{15}H_{15}NO_6$ (305.1): C 59.01, H 4.95, N 4.59; found: C 59.22, H 4.90, N 4.31.

*2-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)ethyl Hydrogen Butanedioate* (**21a**). As described for **19**, from 2-(2-hydroxyethyl)-1*H*-isoindole-1,3(2*H*)-dione (9.56 g, 50 mmol) and succinic anhydride (5.00 g, 65 mmol): 2.21 g (16%) of **21a**. Colorless powder. M.p. 111–112° (from acetone). IR (KBr): 3050*s* (br.), 3037, 2949, 2650, 2545, 1697*s*, 1424, 1424, 1317, 1200*s*, 922, 722. $^1$H-NMR (250 MHz, $CDCl_3$): 2.63 (*m*, 4H); 3.96 (*t*, *J* = 5.3, 2H); 4.35 (*t*, *J* = 5.3, 2H); 7.74 (*dd*, *J* = 3.1, 5.4, 2H); 7.90 (*dd*, *J* = 3.1, 5.4, 2H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 28.6 ($CH_2$); 28.7 ($CH_2$); 36.9 ($CH_2$); 62.0 ($CH_2$); 123.4 (CH); 131.9 (C); 134.1 (CH); 168.1 (C); 171.8 (C); 177.4 (C). Anal. calc. for $C_{14}H_{13}NO_6$ (291.1): C 57.73, H 4.50, N 4.81; found: C 57.78, H 4.39, N 4.80.

*2-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)methyl Hydrogen Butanedioate* (**21b**). A mixture of (2-hydroxymethyl-1*H*-isoindole-1,3(2*H*)-dione (4.96 g, 28 mmol) and succinic anhydride (2.82 g, 28 mmol) was heated to 140° for 3 h in an open flask (250 ml). Cooling to r.t. and repetitive crystallization from acetone/$H_2O$ and AcOEt/cyclohexane gave 2.10 g (27%) of colorless powder. M.p. 130–133° (from AcOEt/cyclohexane). IR (KBr): 3261*s* (br.), 1783*s*, 1733*s*, 1709*s*, 1419, 1359, 1157, 717. $^1$H-NMR (200 MHz, $CDCl_3$): 2.63 (*m*, 4H); 7.72 (*s*, 2H); 7.76 (*dd*, *J* = 3.3, 5.5, 2H); 7.90 (*dd*, *J* = 3.0, 5.5, 2H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 28.5 ($CH_2$); 28.6 ($CH_2$); 60.9 ($CH_2$); 124.0 (CH); 131.7 (C); 134.6 (CH); 166.6 (C); 171.0 (C); 176.9 (C).

3. *C-Terminal-Unprotected* N*-Phthaloyl Dipeptides: General Procedure* [31]. *12-{[(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)acetyl]amino}dodecanoic Acid* (**25a**). To a suspension of *N*-phthaloylglycine (8.21 g, 40 mmol; *vide supra*) in THF (60 ml) and DMF (30 ml) was added $Et_3N$ (4.65 g, 46 mmol). The mixture was then cooled to −35°, and a soln. of isobutyl chloroformate (= 2-methylpropyl carbonochloridate; 6.28 g, 46 mmol) in THF (40 ml) was added in 10 min under vigorous stirring. After 1 h, a precooled (0°) soln. of methyl 12-aminododecanoate hydrochloride (12.23 g, 46 mmol; prepared from the amino acid and MeOH/HCl) and $Et_3N$ (4.65 g, 46 mmol) in $CH_2Cl_2$ (100 ml) was added over 1 h at −35°. After 2 h, the mixture was warmed to r.t. and stirred for 1 h at r.t. After evaporation, the residue was treated with $H_2O$ (300 ml) and extracted with $CHCl_3$ (3 × 200 ml). The combined org. extract was washed with 5% aq. $NaHCO_3$ soln. (200 ml), brine (200 ml), 2N HCl (200 ml), and additionally with half-sat. aq. NaCl soln. (200 ml), dried, and evaporated. The crude methyl ester was directly saponified by treating with conc. HCl soln. (20 ml) and AcOH (100 ml) and heating to reflux for 1 h. After evaporation, the product was crystallized from $H_2O$/MeOH resulting in 10.77 g (89%) of **25a**. Colorless powder. M.p. 109–111°. IR (KBr): 3290*s*, 3086*s*, 2922, 2880, 2684, 1772*s*, 1702, 1675*s*, 1560*s*, 1614, 1188, 743, 628. $^1$H-NMR (250 MHz, $CDCl_3$): 1.18–1.30 (*m*, 14H); 1.48 (*t*, *J* = 7.2, 2H); 1.61 (*t*, *J* = 7.5, 2H); 2.37 (*t*, *J* = 7.5, 2H); 3.26 (*dt*, *J* = 6.5, 7.0, 2H); 4.41 (*s*, 2H (Gly)); 6.33 (*s*, NH); 7.76 (*dd*, *J* = 3.0, 5.5, 2H); 7.86 (*dd*, *J* = 3.0, 5.5, 2H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 24.5 ($CH_2$); 26.6 ($CH_2$); 28.7–29.3 (7 $CH_2$); 33.9 ($CH_2$); 40.6 ($CH_2$); 40.8 ($CH_2$); 124.0 (CH); 131.4 (C); 134.8 (CH); 168.2 (C); 168.4 (C); 181.3 (C). Anal. calc. for $C_{22}H_{30}N_2O_5$ (402.2): C 65.65, H 7.51, N 6.96; found: C 65.34, H 7.85, N 7.06.

*12-{[3-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)propanoyl]amino}dodecanoic Acid* (**25b**). As described for **25a**, from *N*-phthaloyl-β-alanin and methyl 12-aminododecanoate hydrochloride in 91% yield. M.p. 135–136° (from $H_2O$/MeOH). IR (KBr): 3287*s*, 3074*m*, 2927, 2850, 1768*s*, 1709*s*, 1625, 1550, 1400, 1004, 720. $^1$H-NMR (250 MHz, $CDCl_3$/$CF_3COOH$ (*ca.* 10%)): 1.24–1.35 (*m*, 14H); 1.52 (*m*, 2H); 1.66 (*t*, *J* = 7.5, 2H); 2.44 (*t*, *J* = 7.5, 2H); 2.92 (*t*, *J* = 6.7, 2H); 3.31 (*m*, 2H); 4.06 (*t*, *J* = 6.7, 2H); 7.55 (*s*, NH); 7.82 (*dd*, *J* = 3.2, 5.5, 2H); 7.89 (*dd*, *J* = 3.2, 5.5, 2H); 11.70 (*s*, COOH). $^{13}$C-NMR (63 MHz, $CDCl_3$/$CF_3COOH$ (*ca.* 10%)): 24.7 ($CH_2$); 26.7 ($CH_2$); 28.4 ($CH_2$); 29.0–29.5 (7 $CH_2$); 34.1 ($CH_2$); 34.4 ($CH_2$); 41.8 ($CH_2$); 124.5 (CH); 131.0 (C); 135.6 (CH); 170.3 (C); 174.4 (C); 182.9 (C). Anal. calc. for $C_{23}H_{32}N_2O_5$ (416.2): C 66.32, H 7.74, N 6.73; found: C 66.09, H 7.80, N 6.60.

*12-{[4-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)butanoyl]amino}dodecanoic Acid* (**25c**). As described for **25a**, from **4c** and methyl 12-aminododecanoate hydrochloride in 90% yield. M.p. 96–97° (from $H_2O$/MeOH). IR (KBr): 3522*s*, 3371, 3070, 2920, 2890, 1770*s*, 1709, 1680*s*, 1541*s*, 1405, 1012, 890, 723. $^1$H-NMR (250 MHz, $CDCl_3$/$CF_3COOH$ (*ca.* 10%)): 1.25 (br., 14H); 1.50–1.65 (*m*, 4H); 2.03 (*m*, 2H); 2.35–2.45 (*m*, 2H); 2.38 (*t*, *J* = 7.4, 2H); 3.30 (*s*, 2H); 3.74 (*t*, *J* = 6.2, 2H); 7.48 (*s*, NH); 7.76 (*dd*, *J* = 3.1, 5.5, 2H); 7.89 (*dd*, *J* = 3.1, 5.5, 2H); 11.55 (*s*, COOH). $^{13}$C-NMR (63 MHz, $CDCl_3$/$CF_3COOH$ (*ca.* 10%)): 24.5 ($CH_2$); 25.9 ($CH_2$); 26.6 ($CH_2$); 28.7–29.2 (7 $CH_2$); 32.7 ($CH_2$); 34.0 ($CH_2$); 37.1 ($CH_2$); 41.0 ($CH_2$); 123.7 (CH); 131.4 (C); 134.7 (CH); 169.5 (C); 175.5 (C); 181.3 (C). Anal. calc. for $C_{24}H_{34}N_2O_5$ (430.3): C 66.95, H 7.96, N 6.51; found: C 66.68, H 7.85, N 6.33.

*3-{[12-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)dodecanoyl]amino}propanoic Acid* (**25d**). As described for **25a**, from 1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-dodecanoic acid and methyl 3-aminopropanoate hydrochloride

in 87% yield. M.p. 128–129° (from $H_2O$/MeOH). IR (KBr): 3470*s*, 2910, 2840, 1770*m*, 1695vs, 1650*m*, 1515*m*, 1390, 1140. $^1$H-NMR (250 MHz, $CDCl_3$): 1.15–1.27 (*m*, 14 H); 1.50–1.66 (*m*, 4 H); 2.13–2.22 (*m*, 2 H); 2.55 (*t*, *J* = 6.0, 2 H); 3.49 (*dt*, *J* = 5.9, 6.0, 2 H); 3.64 (*t*, *J* = 7.3, 2 H); 6.45 (*t*, *J* = 6.0, NH); 7.68 (*dd*, *J* = 3.1, 5.4, 2 H); 7.81 (*dd*, *J* = 3.1, 5.5, 2 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 25.5 ($CH_2$); 26.7 ($CH_2$); 28.5 ($CH_2$); 29.0 ($CH_2$); 29.1–29.4 (5 $CH_2$); 33.9 ($CH_2$); 34.9 ($CH_2$); 36.6 ($CH_2$); 38.0 ($CH_2$); 123.1 (CH); 132.0 (C); 133.8 (CH); 168.5 (C); 174.0 (C); 175.6 (C). Anal. calc. for $C_{23}H_{32}N_2O_5$ (416.2): C 66.32, H 7.74, N 6.73; found: C 66.14, H 7.56, N 6.69.

*12-{[12-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)dodecanoyl]amino}dodecanoic Acid* (**25e**). As described for **25a**, from 1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-dodecanoic acid and methyl 12-aminododecanoate hydrochloride in 82% yield. M.p. 121–122° (from $H_2O$/MeOH). IR (KBr): 3299*s*, 3048, 2904, 1770*s*, 1720*s*, 1634*s*, 1537*s*, 1200, 1055, 877, 723, 531. $^1$H-NMR (250 MHz, $CDCl_3$): 1.24 (br., 28 H); 1.48–1.61 (*m*, 8 H); 2.35 (*t*, *J* = 7.4, 4 H); 3.26 (br. *s*, 2 H); 3.66 (*t*, *J* = 7.2, 2 H); 6.15 (*s*, NH); 7.75 (*dd*, *J* = 3.9, 5.5, 1 H); 7.90 (*dd*, *J* = 3.0, 5.5 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 24.6 ($CH_2$); 25.9 ($CH_2$); 26.7 ($CH_2$); 26.8 ($CH_2$); 28.5 ($CH_2$); 29.0–29.4 (13 $CH_2$); 34.0 ($CH_2$); 36.0 ($CH_2$); 38.1 ($CH_2$); 40.5 ($CH_2$); 123.3 (CH); 131.8 (C); 134.1 (CH); 169.0 (C); 179.8 (C). Anal. calc. for $C_{32}H_{50}N_2O_5$ (542.5): C 70.81, H 9.29, N 5.16; found: C 70.50, H 9.52, N 5.05.

*trans 4-{{[12-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)dodecanoyl]amino}methyl}cyclohexanecarboxylic Acid* (**25f**). As described for **25a**, from 1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-dodecanoic acid and methyl 4-(aminomethyl)cyclohexanoate hydrochloride in 87% yield. M.p. 136–138° (from $H_2O$/MeOH). IR (KBr): 2910, 2840, 1770*m*, 1695*s*, 1650vs, 1565*m*, 1390, 1180, 720. $^1$H-NMR (250 MHz, $CDCl_3$): 0.89 (*dt*, *J* = 3.4, 12.9, 2 H); 1.19–1.25 (*m*, 14 H); 1.32 (*dd*, *J* = 3.4, 12.9, 2 H); 1.43–1.56 (*m*, 1 H); 1.56 (*m*, 4 H); 1.75 (*m*, 2 H); 1.87–1.94 (*m*, 2 H); 2.10 (*t*, *J* = 7.6, 2 H); 2.20–2.36 (br. *m*, 1 H); 3.03 (*t*, *J* = 6.4, 2 H); 3.58 (*t*, *J* = 7.2, 2 H); 6.07 (*t*, *J* = 5.9, NH); 7.68 (*dd*, *J* = 3.1, 5.5, 2 H); 7.70 (*dd*, *J* = 3.1, 5.5, 2 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 24.0 ($CH_2$); 25.6 ($CH_2$); 26.6 ($CH_2$); 28.2–29.6 (10 $CH_2$); 36.6 ($CH_2$); 37.2 (CH): 37.8 ($CH_2$); 42.9 (CH); 45.1 ($CH_2$); 123.1 (CH); 132.1 (C); 133.8 (CH); 168.4 (C); 173.5 (C); 180.8 (C). Anal. calc. for $C_{28}H_{40}N_2O_5$ (484.3): C 69.39, H 8.32, N 5.78; found: C 69.12, H 8.49, N 5.60.

*2-{[(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)acetyl]amino}pentanedioic Acid* (**27b**). Prepared from Pht=Gly–Glu(OMe)$_2$ in 91% yield [32]: A soln. of *N*-phthaloyl-glycyl-L-glutamic acid dimethyl ester (7.8 g, 20 mol) in 40 ml of conc. HCl soln. (40 ml) was stirred for 2 h at r.t. The clear soln. was evaporated and the residue recrystallized twice from $H_2O$, 5.8 g (91%) of colorless crystals. $^1$H-NMR (300 MHz, $CDCl_3$/$CF_3COOH$ (*ca.* 10%)): 2.08 (*m*, 1 H); 2.28 (*m*, 1 H); 2.55 (*dd*, *J* = 6.7, 6.7, 2 H); 4.49 (*d*, *J* = 16.9, 1 H); 4.52 (*d*, *J* = 16.9, 1 H); 4.71 (*dd*, *J* = 7.6, 12.6, 1 H); 7.47 (*d*, *J* = 7.6, NH); 7.75 (*dd*, *J* = 3.0, 5.5, 2 H); 7.85 (*dd*, *J* = 3.0, 5.5, 2 H). $^{13}$C-NMR 75 MHz, $CDCl_3$/$CF_3COOH$ (*ca.* 10%)): 26.3 ($CH_2$); 26.7 ($CH_2$); 40.3 ($CH_2$); 52.1 (CH): 124.1 (CH); 131.2 (C); 135.1 (CH); 168.7 (C); 175.4 (C); 178.8 (C).

4. *Photodecarboxylation of ω-(Phthaloylamino)alkanoic Acid Derivatives: General Procedure.* 4.1. A suspension of $K_2CO_3$ (10 mmol) and the substrate (2 mmol) in $H_2O$ (3 ml) and acetone (200 ml) was prepared and irradiated ($\lambda$ 300 nm ± 5 nm) in *Pyrex* tube for 12–24 h while purging with a slow stream of $N_2$ and cooling to *ca.* 15°. After decantation, the solvent was evaporated at 40°/10 Torr and the residue washed with cold $Et_2O$. The resulting light-yellow precipitate was (if not indicated otherwise) crystallized from acetone.

4.2. A mixture fo $K_2CO_3$ (1 mmol) and the substrate (2 mmol) in $H_2O$ (2 ml) was heated to 60–70° for 1 min and dissolved in $H_2O$/acetone 1:1 (*v*/*v* 100 ml). A homogeneous soln. resulted which was irradiated ($\lambda$ 300 nm ± 5 nm) in a *Pyrex* tube for 12–24 h while purging with a slow stream of $N_2$ and cooling to *ca.* 15°. After evaporation of most of the acetone, the residual soln. was extracted with $CHCl_3$ (3 × 100 ml). After drying ($MgSO_4$) and evaporation, the resulting product was (if not indicated otherwise) crystallized from acetone.

*1,2,3,9b-Tetrahydro-9b-hydroxy-5*H*-pyrrolo[2,1-a]isoindol-5-one* (**5c**): Oil. IR (KBr): 3394, 2926*m*, 1773*m*, 1700*s*, 1605, 1466, 692. $^1$H-NMR (250 MHz, $CDCl_3$): 1.45 (*dd*, *J* = 8.8, 12.1, 12.1, 1 H); 2.19–2.30 (br. *m*, 2 H); 2.46–2.66 (*m*, 1 H); 3.22 (*ddd*, *J* = 2.9, 9.3, 11.5, 1 H); 3.47 (*ddd*, *J* = 8.4, 8.4, 11.5, 1 H); 4.15 (br. *s*, OH); 7.33–7.53 (*m*, 4 arom. H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 27.7 ($CH_2$); 34.6 ($CH_2$); 41.1 ($CH_2$); 96.3 (C); 122.5 (CH); 123.3 (CH); 129.4 (CH); 131.4 (C); 132.6 (CH); 147.3 (C); 170.1 (C). Anal. calc. for $C_{11}H_{11}NO_2$ (189.1): C 69.83, H 5.86, N 7.40; found: C 69.56, H 5.79, N 7.12.

*1,3,4,10b-Tetrahydro-10b-hydroxypyridol[2,1-a]isoindol-6-(2*H*)-one* (**5d**): M.p. 171–172° (from acetone). IR (KBr): 3396, 3293, 3045, 2940, 1773*m*, 1701, 1670*s*, 1612, 1467, 1399, 695. $^1$H-NMR (250 MHz, $CDCl_3$): 1.10–1.27 (*m*, 2 H); 1.62–178 (*m*, 2 H); 2.00 (*tt*, *J* = 3.3, 13.4, 1 H); 2.37 (*d*, *J* = 13.4, 1 H); 2.96 (*ddd*, *J* = 3.2, 12.9, 12.9, 1 H); 3.87 (*dd*, *J* = 4.7, 12.9, 1 H); 4.38 (*s*, OH); 7.35 (*m*, 2 arom. H); 7.55 (*m*, 2 arom. H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 19.6 ($CH_2$); 25.0 ($CH_2$); 35.4 ($CH_2$); 36.2 ($CH_2$); 85.2 (C); 121.3 (CH); 123.1 (CH); 129.0 (CH); 130.3 (C); 133.9 (CH); 148.5 (C); 165.2 (C). MS (70 eV): 203.1 (4, $M^+$), 185.1 (100), 170.1 (29), 156.1 (22), 129.1 (13), 104.1 (6), 40.1 (8). Anal. calc. for $C_{12}H_{13}NO_2$ (203.1): C 70.92, H 6.45, N 6.89; found: C 70.56, H 6.68, N 6.86.

*7,8,9,10,11,11a-Hexahydro-11a-hydroxy-5*H*-azepino[2,1-a]isoindol-5-one* (**5e**): M.p. 163–164° (from ace-

tone). IR (KBr): 3290, 3058, 2940*m*, 1772*m*, 1670*s*, 1614, 1421, 776, 696. $^1$H-NMR (250 MHz, $CDCl_3$): 0.51–0.70 (*m*, 1 H); 1.20–1.71 (*m*, 5 H); 2.00–2.16 (*m*, 1 H); 2.49 (*dd*, *J* = 8.2, 14.8, 1 H); 2.95 (*ddd*, *J* = 2.5, 11.5, 14.0, 1 H); 3.31 (*m*, 1 H); 4.45 (*s*, OH); 7.37 (*ddd*, *J* = 2.8, 5.8, 7.2, 1 H); 7.46–7.55 (*m*, 3 arom. H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 22.1 ($CH_2$); 27.0 ($CH_2$); 29.7 ($CH_2$); 38.5 ($CH_2$); 38.6 ($CH_2$); 91.1 (C); 21.9 (CH); 122.8 (CH); 129.1 (CH); 131.0 (C); 132.4 (CH); 147.9 (C); 167.8 (C). Anal. calc. for $C_{13}H_{15}NO_2$ (217.1): C 71.87, H 6.96, N 6.45; found: C 72.01, H 6.81, N 6.45.

*8,9,10,11,12,13,14,15,16,16a-Decahydro-16a-hydroxy-7*H*-azacyclododecino[2,1-*a*]isoindol-5-one* (**5f**): M.p. 175–176° (from acetone). IR (KBr): 3267, 2927, 2844, 1722*m*, 1670*s*, 1616*w*, 1420, 1090, 767, 705. $^1$H-NMR (250 MHz, $CDCl_3$): 0.43 (*m*, 1 H); 0.86 (*m*, 1 H); 1.04–1.54 (*m*, 14 H); 1.91 (*ddd*, *J* = 1.6, 12.1, 14.0, 1 H); 2.49 (*ddd*, *J* = 6.7, 12.9, 13.8, 1 H); 3.24–3.31 (*m*, 2 H); 4.12 (*s*, OH); 7.34 (*ddd*, *J* = 1.3, 7.6, 7.6, 1 H); 7.42–7.48 (*m*, 2 H); 7.52 (*ddd*, *J* = 1.3, 7.6, 7.6 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 18.7 ($CH_2$); 20.5 ($CH_2$); 20.6 ($CH_2$); 23.0 ($CH_2$); 24.5 ($CH_2$); 25.1 ($CH_2$); 25.7 ($CH_2$); 26.5 ($CH_2$); 36.6 ($CH_2$); 37.2 ($CH_2$); 92.2 (C); 121.3 (CH); 123.1 (CH); 129.2 (CH); 130.9 (C); 132.1 (CH); 146.8 (C); 169.0 (C). Anal. calc. for $C_{18}H_{25}NO_2$ (287.2): C 75.22, H 8.77, N 4.87; found: C 75.08, H 8.77, N 4.72.

*7,8,9,10,11,12,13,14,15,16,17,17a-Dodecahydro-17a-hydroxy-5*H*-azacyclotridecino[2,1-*a*]isoindol-5-one* (**5g**): M.p. 169–172° (from acetone). IR (KBr): 3271, 2927, 2844, 1773*w*, 1670*s*, 1615, 1420, 1090, 767, 705. $^1$H-NMR (250 MHz, $CDCl_3$): 0.69 (*m*, 1 H); 1.01–1.65 (*m*, 16 H); 1.77 (*m*, 1 H); 1.91 (*ddd*, *J* = 1.6, 12.1, 10.0, 1 H); 1.97–2.22 (*m*, 1 H); 2.13 (*m*, 2 H); 3.84 (*s*, OH); 7.35 (*ddd*, *J* = 1.3, 7.6, 7.6, 1 H); 7.47–7.52 (*m*, 2 H); 7.54 (*ddd*, *J* = 1.3, 7.6, 7.6, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 21.3 ($CH_2$); 24.9 ($CH_2$); 25.6 ($CH_2$); 26.1 ($CH_2$); 26.6 ($CH_2$); 26.7 ($CH_2$); 26.8 ($CH_2$); 27.0 ($CH_2$); 28.5 ($CH_2$); 36.4 ($CH_2$); 38.5 ($CH_2$); 91.6 (C); 121.5 (CH); 123.1 (CH); 129.2 (CH); 130.0 (C); 132.1 (CH); 147.1 (C); 168.4 (C). Anal. calc. for $C_{19}H_{27}NO_2$ (301.2); C 75.71, H 9.03, N 4.65; found: C 75.56, H 8.86, N 4.58.

*7,8,9,10,11,11a-Hexahydro-11a-hydroxy-8,11-ethano-5*H*-azepino[2,1-*a*]isoindol-5-one* (**5h**): M.p. 198–199° (from acetone). IR (KBr): 3267, 2903, 1688*s*, 1615*w*, 1415, 1075, 761, 693. $^1$H-NMR (250 MHz, $CDCl_3$): 0.82 (*m*, 1 H); 1.26–191 (*m*, 6 H); 2.01 (*m*, 1 H); 2.45 (*m*, 1 H); 2.58 (*m*, 1 H); 2.96 (*d*, *J* = 13.5, 1 H); 3.86 (*s*, OH); 4.10 (*dd*, *J* = 6.9, 13.5, 1 H); 7.35 (*ddd*, *J* = 1.2, 7.5, 7.5, 1 H); 7.42–7.48 (*m*, 2 arom. H); 7.52 (*ddd*, *J* = 1.2, 7.5, 7.5, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 19.0 ($CH_2$); 20.2 ($CH_2$); 21.1 ($CH_2$); 27.2 ($CH_2$); 28.8 (CH); 37.6 (CH); 44.6 ($CH_2$); 93.1 (C); 121.3 (CH); 123.0 (CH); 129.1 (CH); 131.5 (C); 132.2 (CH); 148.2 (C); 167.2 (C). MS (70 eV): 243.2 (100, $M^+$), 225 (53), 214 (52), 196 (49), 182 (45), 161 (47), 147 (55), 130 (29), 40 (17). Anal. calc. for $C_{15}H_{17}NO_2$ (243.1): C 74.05, H 7.04, N 5.76; found: C 73.81, H 6.96, N 5.75.

*2-(Cyclohexylmethyl)-2*H*-isoindole-1,3-dione* (**6h**): M.p. 58–59° (from MeOH/$CH_2Cl_2$ 1:30). IR (KBr): 2924, 2851, 1773*m*, 1718*s*, 1617*w*, 1396, 1361, 721. $^1$H-NMR (250 MHz, $CDCl_3$): 0.89–1.20 (*m*, 4 H); 1.56–183 (*m*, 7 H); 3.51 (*d*, *J* = 7.2, 2 H); 7.68 (*dd*, *J* = 3.0, 5.4, 2 H); 7.81 (*dd*, *J* = 3.0, 5.4, 2 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 25.6 ($CH_2$); 26.2 ($CH_2$); 30.7 ($CH_2$); 37.0 (CH); 44.1 ($CH_2$); 123.1 (CH); 132.0 (C); 133.8 (CH); 168.7 (C). Anal. calc. for $C_{15}H_{17}NO_2$ (243.1): C 74.05, H 7.04, N 5.76; found: C 73.84, H 6.92, N 5.56.

*11-(2,5-Dioxopyrrolidin-1-yl)-7,8,9,10,11,11a-hexahydro-11a-hydroxy-5*H*-azepino[2,1-*a*]isoindol-5-one* (*trans*-**11a**): M.p. > 220° (from acetone). IR (KBr): 3273, 2938, 2855, 1772*m*, 1707, 1677*s*, 1613*m*, 1366, 1177, 767, 664. $^1$H-NMR (250 MHz, $CDCl_3$): 1.36–1.90 (*m*, 5 H); 2.15 (*s*, 4 H); 2.68 (*s*, OH); 2.65–2.76 (*m*, 1 H); 3.08 (*ddd*, *J* = 3.8, 10.6, 14.3, 1 H); 3.38 (*m*, 1 H); 4.70 (*dd*, *J* = 1.5, 10.0, 1 H); 7.05–7.09 (*m*, 1 H); 7.36–7.46 (*m*, 2 H); 7.50–7.53 (*m*, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 26.1 ($CH_2$); 28.0 ($CH_2$); 28.1 ($CH_2$); 28.8 ($CH_2$); 29.2 ($CH_2$); 38.8 ($CH_2$); 61.5 (CH); 91.5 (C); 122.9 (CH); 123.4 (CH); 129.9 (CH); 131.5 (C); 131.8 (CH); 144.6 (C); 167.4 (C); 176.5 (C). Anal. calc. for $C_{16}H_{16}N_2O_4$ (300.3): C 63.99, H 5.37, N 9.33; found: C 63.77, H 5.14, N 9.03.

*Isomer* **11a**: $^1$H-NMR (250 MHz, $CDCl_3$ mixture with *trans*-**11a**): 1.51–1.98 (*m*, 8 H); 2.76 (*s*, OH); 3.18 (*ddd*, *J* = 3.0, 11.9, 14.3, 1 H); 3.67 (*m*, 1 H); 4.74 (*dd*, *J* = 1.5, 10.4, 1 H); 7.10–7.12 (*m*, 1 H); 7.42–7.46 (*m*, 2 H); 7.65–7.69 (*m*, 1 H).

*11-(2,5-Dioxopyrrolidin-1-yl)-7,8,9,10-tetrahydro-5*H*-azepino[2,1-*a*]isoindol-5-one* (**11b**): M.p. > 220° (from acetone). IR (KBr): 2950, 1778*m*, 1709*s*, 1396, 118. $^1$H-NMR (250 MHz, $CDCl_3$): 2.06–2.17 (*m*, 8 H); 2.70 (*m*, 2 H); 4.17 (*t*, *J* = 5.9, 2 H); 7.05 (*m*, 1 H); 7.54–7.63 (*m*, 2 H); 7.90 (*m*, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 24.2 ($CH_2$); 25.0 ($CH_2$); 28.8 ($CH_2$); 30.8 ($CH_2$); 41.6 ($CH_2$); 118.5 (C); 121.0 (C); 124.5 (CH); 128.6 (CH); 130.7 (CH); 133.1 (C); 133.8 (CH); 138.7 (C); 169.9 (C); 178.9 (C). Anal. calc. for $C_{16}H_{14}N_2O_4$ (282.1): C 67.08, H 5.05, N 9.02; found: C 66.73, H 5.52, N 9.16.

*(3S,9bR)-Methyl 2,3,5,9b-Tetrahydro-9b-hydroxy-5-oxo-1*H*-pyrrolo[2,1-*a*]isoindole-3-carboxylate* (*cis*-**12**): M.p. 153–154° (from acetone). IR (KBr): 3504, 3411, 3234, 2926, 2858, 1724, 1695*s*, 1612, 1442, 1231*s*, 1075, 764. $^1$H-NMR (250 MHz, $CDCl_3$): 1.55 (*ddd*, *J* = 9.3, 11.2, 12.5, 1 H); 2.33 (*ddd*, *J* = 2.3, 5.8, 12.5, 1 H); 2.65 (*m*, 2 H); 3.73 (*s*, MeO); 4.53 (*dd*, *J* = 8.5, 8.6, 1 H); 7.40–7.51 (*m*, 3 H); 7.65 (*d*, *J* = 7.4, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 33.0 ($CH_2$); 35.6 ($CH_2$); 52.7 (Me); 55.5 (CH); 96.7 (C); 122.7 (CH); 124.1 (CH); 130.0 (CH); 131.0 (C); 133.3

(CH); 146.8 (C); 169.5 (C); 173.1 (C). Anal. calc. for $C_{13}H_{13}NO_4$ (265.1): C 58.86, H 5.70, N 5.28; found: C 58.78, H 5.65, N 5.19.

*(3S,9bS)-Isomer* (trans-**12**): $^1$H-NMR (250 MHz, $CDCl_3$; mixture with *cis*-**12**): 1.93 (*m*, 1 H); 2.08–2.22 (*m*, 2 H); 2.95 (*m*, 1 H); 3.64 (*s*, MeO); 4.23 (*d*, *J* = 8.9, 1 H); 4.25 (*s*, OH); 7.60–7.71 (*m*, 4 H). $^{13}$C-NMR (63 MHz, $CDCl_3$; mixture with *cis*-**12**): 32.7 ($CH_2$); 33.4 ($CH_2$); 52.2 (Me); 55.7 (CH); 97.0 (C); 122.6 (CH); 123.4 (CH); 129.5 (CH); 131.9 (C); 132.9 (CH); 146.9 (C); 169.0 (C); 171.4 (C).

*(3S)-Methyl 3,5-Dihydro-5-oxo-2*H*-pyrrolo[2,1-*a*]isoindole-3-carboxylate* (**13**): $^1$H-NMR (250 MHz, $CDCl_3$; mixture with *cis*-**12**): (*ddd*, *J* = 3.3, 4.0, 10.2, 1 H); 3.51 (*ddd*, *J* = 2.9, 4.0, 10.2, 1 H); 3.68 (*s*, MeO); 3.70 (*dd*, *J* = 4.0, 10.4, 1 H); 5.60 (*dd*, *J* = 2.9, 2.9, 1 H); 7.31–7.58 (*m*, 4 arom. H). $^{13}$C-NMR (63 MHz, $CDCl_3$; mixture with *cis*-**12**): 40.5 ($CH_2$); 52.3 (Me); 53.2 (CH); 103.2 (CH); 120.7 (CH); 122.5 (CH); 128.4 (CH); 130.0 (C); 131.2 (CH); 135.7 (C); 141.4 (C); 170.5 (C); 173.8 (C).

*1,3,4,10b-Tetrahydro-10b-hydroxy-6*H*-[1,4]oxazino[3,4-*a*]isoindol-6-one* (**16**): M.p. 156–157° (from acetone). IR (KBr): 3263*s* (br.), 3060*w*, 2970, 2858*m*, 1655 (br.), 1615*m*, 1412, 1288, 1069, 940, 760. $^1$H-NMR (250 MHz, $CDCl_3$): 3.12 (*d*, *J* = 11.5, 1 H); 3.14–3.30 (*m*, 2 H); 3.92 (*m*, 2 H); 4.33 (*d*, *J* = 11.5, 1 H); 7.46 (*ddd*, *J* = 0.7, 2.1, 6.6, 1 arom. H); 7.54 (*m*, 2 arom. H); 7.61 (*ddd*, *J* = 1.0, 1.0, 6.6, 1 arom. H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 37.0 ($CH_2$); 66.4 ($CH_2$); 74.3 ($CH_2$); 84.4 (C); 122.1 (CH); 123.7 (CH); 130.0 (CH); 131.2 (C); 132.3 (CH); 144.3 (C); 165.3 (C). HR-MS: 205.0740 (calc. 205.0739). Anal. calc. for $C_{11}H_{11}NO_3$ (205.1): C 64.38, H 5.40, N 6.83; found: C 64.56, H 5.26, N 6.68.

*1,3,4,6,7,9,10,12,13,19b-Decahydro-19b-hydroxy-5*H*-[1,4,7,10,13]tetraoxaazacyclopentadecino[12,13-*a*]isoindole-15-one* (**18**): M.p. 115–117° (from acetone). IR (KBr): 3265*s* (br.), 2879, 1701*m*, 1674*s*, 1617*m*, 1131, 1087, 767, 705. $^1$H-NMR (250 MHz, $CDCl_3$): 3.56–3.78 (*m*, 15 H); 3.82 (*d*, *J* = 10.3, 1 H); 4.02 (*m*, 1 H); 4.09 (*d*, *J* = 10.3, 1 H); 5.35 (*s*, OH); 7.44 (*ddd*, *J* = 1.3, 7.3, 7.3, 1 H); 7.51 (*ddd*, *J* = 1.3, 7.4, 7.4, 1 H); 7.63 (*m*, 1 H); 7.71 (*m*, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 46.0 ($CH_2$); 70.0 ($CH_2$); 70.1 ($CH_2$); 70.3 ($CH_2$); 70.4 ($CH_2$); 70.5 ($CH_2$); 71.0 ($CH_2$); 71.3 ($CH_2$); 75.4 ($CH_2$); 88.4 (C); 123.9 (CH); 123.1 (CH); 129.4 (CH); 131.1 (C); 132.0 (CH); 145.5 (C); 167.8 (C). MS (70 eV): 337.2 (7, $M^+$), 319 (30), 187 (18), 174 (100), 160 (21), 147 (24), 131 (21), 104 (28), 45 (40). Anal. calc. for $C_{17}H_{13}NO_6$ (337.2): C 60.52, H 6.87, N 4.15; found: C 60.19, H 6.73, N 3.92.

*1,2,5,6,7,7a-Hexahydro-7a-hydroxy[1,4]oxazonino[5,4-*a*]isoindole-4,12-dione* (**20**): M.p. 149–151° (fom acetone). IR (KBr): 3263*s* (br.), 3050*w*, 2955, 2849*m*, 1743, 1671*s* (br.), 1614*s*, 1404, 1137, 1057, 760. $^1$H-NMR (250 MHz, $CDCl_3$): 0.65 (*m*, 1 H); 1.61 (*m*, 1 H); 2.09 (*m*, 2 H); 2.24 (*ddd*, *J* = 2.4, 6.5, 15.4, 1 H); 2.47 (*ddd*, *J* = 2.4, 11.1, 15.4, 1 H); 3.02 (*ddd*, *J* = 3.1, 11.1, 14.5, 1 H); 3.38 (*ddd*, *J* = 4.5, 12.5, 14.5, 1 H); 3.80 (*ddd*, *J* = 4.5, 6.5, 11.1, 1 H); 4.56 (br. *s*, OH); 4.95 (*ddd*, *J* = 3.1, 11.1, 12.4, 1 H); 7.34 (*ddd*, *J* = 1.2, 7.3, 7.3, 1 arom. H); 7.48 (*m*, 2 arom. H); 7.52 (*ddd*, *J* = 1.2, 7.3, 7.3, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 20.9 ($CH_2$); 33.1 ($CH_2$); 35.5 ($CH_2$); 39.2 ($CH_2$); 60.5 ($CH_2$); 92.2 (C); 121.9 (CH); 123.2 (CH); 129.4 (CH); 130.7 (C); 132.6 (CH); 147.1 (C); 169.0 (C); 174.4 (C). HR-MS: (calc. 261.1001). Anal. calc. for $C_{14}H_{15}NO_4$ (261.1): C 64.36, H 5.79, N 5.36; found: C 64.61, H 5.62, N 5.22.

*1,2,6,6a-Tetrahydro-6a-hydroxy-4*H*-[1,4]oxazocino[5,4-*a*]isoindole-4,11(5*H*)-dione* (**22a**): Oil. IR (KBr): 3448*s* (br.), 2934*w*, 1774*m*, 1718*s*, 1596*m*, 1400, 1181, 1042, 766, 700. $^1$H-NMR (250 MHz, $CDCl_3$): 2.83 (*m*, 2 H); 3.04 (*m*, 2 H); 3.55 (*ddd*, *J* = 3.7, 6.4, 15.0, 1 H); 3.72 (*ddd*, *J* = 3.7, 6.4, 15.0, 1 H); 3.86 (*ddd*, *J* = 3.7, 6.6, 11.7, 1 H); 4.00 (*ddd*, *J* = 3.6, 6.6, 11.7, 1 H); 7.46 (*ddd*, *J* = 1.3, 1.3, 7.4, 1 arom. H); 7.54 (*ddd*, *J* = 1.3, 7.4, 7.4, 1 arom. H); 7.62 (*ddd*, *J* = 1.3, 7.4, 7.4, 1 arom. H); 7.78 (*ddd*, *J* = 1.3, 1.3, 7.4, 1 arom. H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 29.3 ($CH_2$); 29.8 ($CH_2$); 42.6 ($CH_2$); 61.4 ($CH_2$); 97.8 (C); 121.3 (CH); 123.7 (CH); 129.4 (C); 130.7 (CH); 133.2 (CH); 144.6 (C); 168.2 (C); 174.3 (C). Anal. calc. for $C_{13}H_{13}NO_4$ (247.1): C 63.15, H 5.30, N 5.66; found: C 62.9, H 5.17, N 5.54.

*2'-(2-Hydroxyethyl)spiro[cyclopropan-1,1'-[1*H*]isoindol]-3'(2'*H*)-one* (**23a**): M.p. 100–101° (from MeOH/$CH_2CCl_2$ 1:30). IR (KBr): 3384*m* (br.), 3083*w*, 2934, 2861*m*, 1664*s*, 1405, 1340*s*, 1053, 758. $^1$H-NMR (250 MHz, $CDCl_3$): 1.36 (*m*, 2 H); 1.53 (*m*, 2 H); 3.23 (*t*, *J* = 4.8, 2 H); 3.82 (*t*, *J* = 4.8, 2 H); 3.98 (br. *s*, OH); 7.02 (*ddd*, *J* = 1.0, 1.0, 7.4, 1 H); 7.41 (*ddd*, *J* = 1.1, 7.4, 7.4, 1 H); 7.50 (*ddd*, *J* = 1.1, 7.4, 7.4, 1 H); 7.85 (*ddd*, *J* = 1.0, 1.0, 7.5, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 10.9 ($CH_2$); 42.3 ($CH_2$); 45.1 (C); 62.3 ($CH_2$); 117.6 (CH); 123.5 (CH); 127.5 (CH); 130.8 (C); 131.7 (CH); 147.5 (C); 169.9 (C). Anal. calc. for $C_{12}H_{13}NO_2$ (203.1): C 70.92, H 6.45, N 6.89; found: C 70.63, H 6.19, N 6.82.

*2'-(Hydroxymethyl)spiro[cyclopropan-1,1'-[1*H*]isoindol]-3'(2'*H*)-one* (**23b**): Data from the product mixture **23b**/**22b**/**21b**. $^1$H-NMR (300 MHz, $(CD_3)_2SO$): 1.49 (*dd*, *J* = 5.6, 7.9, 2 H); 1.78 (*dd*, *J* = 5.8, 8.2, 2 H); 5.44 (*s*, 2 H); 7.37–8.02 (*m*, 4 arom. H). $^{13}$C-NMR (75 MHz, $(CD_3)_2SO$): 11.4 ($CH_2$); 43.8 (C); 54.9 ($CH_2$); 119.0 (CH); 123.4 (CH); 127.5 (CH); 130.9 (C); 132.5 (CH); 147.7 (C); 169.9 (C).

*4,5,6,7,8,9,10,11,12,13,14,14a-Dodecahydro-14a-hydroxy[1,4]diazacyclohexadecino[16,1-*a*]isoindole-2,19(1*H*,3*H*)-dione* (**26a**): M.p. 188–190° (from acetone/$H_2O$). IR (KBr): 3292, 3086, 2928, 2854*s*, 1707, 1658*s*, 1550*m*,

1419, 1247, 764. $^1$H-NMR (250 MHz, $CDCl_3$): 0.67 (*m*, 1 H); 1.00–1.52 (*m*, 17H); 2.10 (*m*, 2 H); 2.92 (*dt*, *J* = 5.3, 13.5, 1 H); 3.64 (*m*, 1 H); 3.91 (*d*, *J* = 15.8, 1 H); 4.12 (*d*, *J* = 15.8, 1 H); 4.25 (*s*, OH); 7.01 (*t*, *J* = 5.3, 1 H); 7.48 (*ddd*, *J* = 1.4, 7.1, 7.1, 1 H); 7.45–7.63 (*m*, 2 H); 7.73 (*ddd*, *J* = 1.1, 1.1, 7.4, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 22.8 ($CH_2$); 24.5 ($CH_2$); 25.0 ($CH_2$); 25.1 ($CH_2$); 25.7 ($CH_2$); 26.4 ($CH_2$); 27.1 ($CH_2$); 27.2 ($CH_2$); 29.0 ($CH_2$); 36.8 ($CH_2$); 38.9 ($CH_2$); 43.9 ($CH_2$); 91.6 (C); 122.1 (CH); 123.4 (CH); 129.6 (CH); 130.3 (C); 132.8 (CH); 147.3 (C); 169.2 (C); 172.9 (C). MS (70 eV): 358.3 (9, $M^+$), 198.3 (71), 188.1 (14), 161.1 (100), 160.1 (48), 104.1 (11), 41.1 (12). Anal. calc. for $C_{21}H_{30}N_2O_3$ (358.2): C 70.36, H 8.44, N 7.81; found: C 70.09, H 8.14, N 7.59.

*1,2,5,6,7,8,9,10,11,12,13,14,15,15a-Tetradecahydro-15a-hydroxy-3*H*-[1,5]diazacycloheptadecino[17,1-a]isoindole-3,20(4*H*)-dione* (**26b**): M.p. 173–174° (from acetone/$H_2O$). IR (KBr): 3501, 3260*s*, 2929, 2854*s*, 1688, 1635*s*, 1566, 1446, 1368, 1078, 763. $^1$H-NMR (250 MHz, $CDCl_3$): 0.84 (*m*, 2 H); 1.18–1.40 (*m*, 14 H); 1.47 (*m*, 2 H); 2.16 (*m*, 2 H); 2.66 (*m*, 2 H); 2.93 (*m*, 1 H); 3.46 (*m*, 1 H); 3.68 (*m*, 1 H); 3.95 (*dt*, *J* = 6.3, 14.5, 1 H); 5.45 (*s*, OH); 6.64 (*dd*, *J* = 3.2, 5.5, 1 H); 7.44 (*ddd*, *J* = 3.2, 4.4, 1 H); 7.4 (*ddd*, *J* = 1.8, 7.4, 7.4, 1 H); 7.52–7.57 (*m*, 2 H); 7.69 (*ddd*, *J* = 1.8, 1.8, 7.4, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 22.0 ($CH_2$); 25.4 ($CH_2$); 27.0–27.4 (7 $CH_2$); 35.4 ($CH_2$); 35.6 ($CH_2$); 36.4 ($CH_2$); 39.0 ($CH_2$); 91.6 (C); 121.8 (CH); 123.0 (CH); 129.3 (CH); 130.9 (C); 132.5 (C); 147.0 (C); 168.5 (C); 171.9 (C).

*2,3,6,7,8,9,10,11,12,13,14,15,16a-Tetradecahydro-16a-hydroxy[1,6]diazacyclooctadecino[18,1-a]isoindole-4,21(1*H*,5*H*)-dione* (**26c**): M.p. 118–119° (from acetone/$H_2O$). IR (KBr): 3364, 2929, 2859*s*, 1693*s*, 1548*s*, 1430, 1244, 702. $^1$H-NMR (250 MHz, $CDCl_3$): 0.64 (*m*, 2 H); 1.04–1.32 (*m*, 14 H); 1.44 (*m*, 2 H); 1.80–2.31 (*m*, 6 H); 2.90 (*m*, 2 H); 3.10 (*m*, 1 H); 3.17 (*t*, *J* = 7.0, 1 H); 3.45–3.61 (*m*, 2 H); 5.96 (*s*, OH); 7.13 (*dd*, *J* = 3.4, 7.8, 1 H); 7.36 (*ddd*, *J* = 1.5, 7.3, 7.3, 1 H); 7.44 (*m*, 2 H); 7.60 (*d*, *J* = 5.6, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 22.2 ($CH_2$); 25.7 ($CH_2$); 26.0 ($CH_2$); 26.8 ($CH_2$); 26.9 ($CH_2$); 27.1 ($CH_2$); 27.2 ($CH_2$); 27.4 ($CH_2$); 27.8 ($CH_2$); 29.0 ($CH_2$); 34.2 ($CH_2$); 36.1 ($CH_2$); 37.5 ($CH_2$); 39.0 ($CH_2$); 91.7 (C); 121.6 (CH); 122.7 (CH); 129.0 (CH); 131.1 (C); 132.2 (CH); 147.0 (C); 168.2 (C); 173.0 (C). MS (70 eV): 368.2 (100, $M^+$), 198 (23), 184 (14), 172 (13), 170 (12), 86 (10).

*1,2,3,6,7,8,9,10,11,12,13,14,15,21b-Tetradecahydro-21b-hydroxy-17*H*-[1,5]diazacycloheptadecino[2,1-a]isoindole-4,17(5*H*)-dione* (**26d**): M.p. 161–162° (from acetone/$H_2O$). IR (KBr): 3292, 3078, 2930, 2856*s*, 1678, 1640*s*, 1552, 1407, 1049, 706. $^1$H-NMR (250 MHz, $CDCl_3$): 1.19–1.42 (*m*, 14 H); 1.45–1.78 (*m*, 4 H); 1.89 (*m*, 1 H); 2.14 (*m*, 2 H); 2.40 (*m*, 1 H); 3.05–3.29 (*m*, 4 H); 4.56 (*s*, OH); 5.98 (*t*, *J* = 5.4, 1 H); 7.39 (*ddd*, *J* = 3.2, 5.3, 7.4, 1 H); 7.49–7.56 (*m*, 2 H); 7.60 (*d*, *J* = 7.4, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 25.4 ($CH_2$); 25.5 ($CH_2$); 26.0 ($CH_2$); 16.2 ($CH_2$); 26.3 ($CH_2$); 26.5 ($CH_2$); 26.8 ($CH_2$); 26.9 ($CH_2$); 35.3 ($CH_2$); 36.2 ($CH_2$); 37.2 ($CH_2$); 38.6 ($CH_2$); 81.1 (C); 122.1 (CH); 123.4 (CH); 129.6 (CH); 131.7 (C); 132.1 (CH); 146.2 (C); 167.2 (C); 173.3 (C).

*8,9,10,11,12,13,14,15,16,17,20,21,22,23,24,25,26,27,28,29,30,30a-Docosahydro-30a-hydroxy[1,14]diazacyclohexacosino[2,1-a]isoindole-5,18(7*H*,19*H*)-dione* (**26e**): M.p. 174–175° (from acetone/$H_2O$). IR (KBr): 3400*s* (br.), 3302, 2923, 2850, 1731, 1635*s*, 1543, 1466, 1061, 714. $^1$H-NMR (250 MHz, $CDCl_3$): 0.59 (*m*, 1 H); 0.85 (*m*, 1 H); 1.15–1.34 (*m*, 30 H); 1.46 (*m*, 2 H); 1.60 (*m*, 2 H); 2.02 (*m*, 1 H); 2.13 (*t*, *J* = 6.9, 1 H); 3.07–3.31 (*m*, 4 H); 3.68 (*s*, OH); 5.56 (*t*, *J* = 5.8, 1 H); 7.39 (*ddd*, *J* = 1.3, 7.2, 7.2, 1 H); 7.44 (*m*, 1 H); 7.51 (*ddd*, *J* = 1.3, 7.2, 7.2, 1 H); 7.57 (*m*, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 23.0 ($CH_2$); 25.8 ($CH_2$); 26.5 ($CH_2$); 27.4 ($CH_2$); 28.6–29.5 (14 $CH_2$); 36.3 ($CH_2$); 36.3 ($CH_2$); 38.6 ($CH_2$); 39.3 ($CH_2$); 91.4 (C); 121.5 (CH); 123.0 (CH); 129.2 (CH); 131.1 (C); 132.1 (CH); 146.8 (C); 167.8 (C); 173.2 (C). HR-MS: 498.3829 (calc. 498.3821). Anal. calc. for $C_{31}H_{50}N_2O_3$ (498.4): C 74.65, H 10.10, N 5.62; found: C 74.35, H 9.56, N 5.43.

*8,9,10,11,12,13,14,15,16,17,20,21,22,23,24,24a-Hexadecahydro-24a-hydroxy-21,24-ethano[1,8]diazacycloeicosino[2,1-a]isoindole-5,18(7*H*,19*H*)-dione* (**26f**): M.p. 155–157° (from acetone/$H_2O$). IR (KBr): 3293*s* (br.), 3082, 2928, 2853*s*, 1716, 1677, 1647*s*, 1551, 1418, 1098, 732. $^1$H-NMR (250 MHz, $CDCl_3$): 0.30–0.45 (*m*, 1 H); 0.85–0.94 (*m*, 1 H); 1.05–1.30 (*m*, 18 H); 1.30 (*d*, *J* = 4 H); 1.67–1.88 (*m*, 4 H); 2.10–2.15 (*m*, 2 H); 2.18–2.26 (*m*, 1 H); 2.88 (*m*, 1 H); 3.17 (*m*, 2 H); 3.19 (*s*, OH); 5.40 (*t*, *J* = 6.0, 1 H); 7.38 (*ddd*, *J* = 2.3, 7.3, 7.3, 1 H); 7.45–7.55 (*m*, 2 H); 7.60 (*m*, 1 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 25.6 ($CH_2$); 26.1 ($CH_2$); 26.5 ($CH_2$); 26.9 ($CH_2$); 27.5 ($CH_2$); 27.8 ($CH_2$); 27.9 ($CH_2$); 28.1 ($CH_2$); 28.1 ($CH_2$); 28.2 ($CH_2$); 28.3 ($CH_2$); 28.5 ($CH_2$); 29.2 ($CH_2$); 36.8 ($CH_2$); 37.0 (CH); 38.7 ($CH_2$); 43.8 ($CH_2$); 44.4 (CH); 93.2 (C); 122.8 (CH); 123.1 (CH); 129.3 (CH); 131.6 (C); 131.7 (CH); 146.1 (C); 167.9 (C); 173.3 (C). Anal. calc. for $C_{27}H_{40}N_2O_3$ (440.3): C 73.60, H 9.15, N 6.36; found: C 73.28, H 9.15, N 5.90. HR-MS: 440.3028 (calc. 440.3039).

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