Synthesis of *N*-Aryl-5-alkylidene-2,5-dihydropyrrol-2-ones by "Cyclization/Dimroth Rearrangement" Reactions of 1,3-Dicarbonyl Dianions with Diimidoyl Dichlorides of Oxalic Acid

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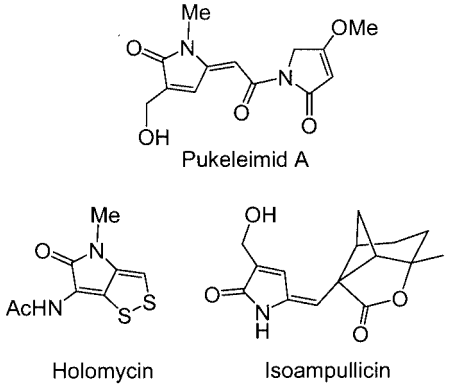
The reaction of dilithiated dicarbonyl compounds with oxaldiimidoyl dichlorides resulted in regio- and (*E*)/(*Z*)-diastereoselective formation of 5-alkylidene-3-arylamino-2,5-dihydropyrrol-2-ones. The products were formed by a domino "cyclization/Dimroth rearrangement" reaction. The mechanism and preparative scope of the cyclization was studied. The arylamino groups of the products were removed chemoselectively under mild conditions and in high yields by hydrolytic cleavage. The products, *N*-aryl-5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-ones, are of considerable interest from pharmacological and synthetic viewpoints.

Introduction

5-Alkylidene-2,5-dihydropyrrol-2-ones, which are of considerable pharmacological relevance, occur in a variety of natural products, such as amaryllidacae alkaloids[1a−1c] α-lycorane and 4,5-dehydroanhydrolycorine,[1c−1d] the pukeleimides A−G,[2a−2c,3] holomycin,[4] and isoampullicin (Scheme 1).[5] 5-Alkylidene-2,5-dihydropyrrol-2-ones represent synthetic precursors to γ-lactam and tetramic acid antibiotics[6] and to γ-lactam analogues of carbapenems.[7] 2-Alkylidenepyrrolidines represent key intermediates during the synthesis of mitomycin antitumor agents possessing antibacterial activity.[8] They are potent inhibitors of serine protease and have been used for the treatment of tumors and arthritis.[9] In addition, 2-alkylidenepyrrolidines have been used as peptide mimics,[9] angiotensin II antagonists,[10] and prostaglandin analogues.[11] An unsubstituted 2-alkylidenepyrrolidine has been used during the synthesis of cancerostatic camptothecin.[12] 5-Alkylidene-2,5-dihydropyrrol-2-ones and 2-alkylidenepyrrolidines represent precursors to functionalized pyrroles[13] that are building blocks of natural tetrapyrrol pigments, such as porphobilinogen or bilirubin,[14,15] and other natural products.[16]



Scheme 1. 5-Alkylidene-2,5-dihydropyrrol-2-one natural products

5-Alkylidene-2,5-dihydropyrrol-2-ones have been prepared by Wittig reactions of imides with stabilized ylides.[17] Alternative syntheses rely, for example, on 1,3-dipolar cycloadditions of nitrones with alkenes and alkynes to give isoxazolidines, which can be transformed into α-hydroxy-γ-lactams by hydrogenolysis,[18] and on the reaction of amines with alkylidenetetronic acids[19] and dimethyl-β-oxoalkanedioates.[20] 5-Alkylidenepyrrolidin-2-ones have been prepared, for example, by the reactions of cyclic enol lactones with amines[9] and protected 2,2-diethoxypyrrolidines with ketones.[21]

A few years ago we reported a new approach to γ-alkylidenebutenolides by cyclization of 1,3-dicarbonyl dianions with *N*,*N*′-dimethoxy-*N*,*N*′-dimethylethanediamide, the bis-Weinreb amide of oxalic acid.[22,23] Recently, we developed a new synthesis of 5-alkylidene-3-amino-2,5-dihydropyrrol-2-ones, aza-analogous γ-alkylidenebutenolides,[24] by cyclization reactions[25] of 1,3-dicarbonyl dianions[26] with oxaldiimidoyl dichlorides, which can be regarded as aza-analogues of oxalyl chloride.[27] Herein, we report the full details, the extension of the preparative scope, and studies re-

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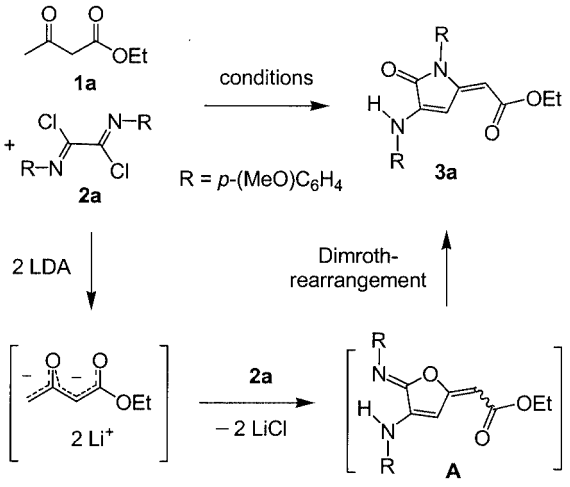
lated to the mechanism of this reaction. In addition, we describe a mild and efficient hydrolytic transformation of the cyclization products into *N*-aryl-5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-ones.

Results and Discussion

Optimization: The reaction of dilithiated ethyl acetoacetate **1a** with cyanogen[28] resulted in formation of a complex mixture. The reaction of the dianion of **1a** with diethyl *N*,*N*′-bis(*p*-methoxyphenyl)oxaldiimidoate, $C_2[N(PMP)]_2(OEt)_2$ [PMP = *p*-$MeOC_6H_4$], resulted in formation of a complex mixture. In contrast, the reaction of the dianion of **1a** with *N*,*N*′-bis(*p*-methoxyphenyl)oxaldiimidoyl dichloride (**2a**), which is more reactive than the corresponding diester, afforded the 5-alkylidene-2,5-dihydropyrrol-2-one **3a** (Scheme 2). Similar to the observations made concerning the synthesis of γ-alkylidenebutenolides from 1,3-dicarbonyl dianions,[23] matching the reactivity of the dianion and dielectrophile is an important parameter for optimization.



Scheme 2. Mechanism of the formation of **3a**. Conditions: 1) 2.2 equiv. LDA, 2) **2a**, THF, −78 then 20 °C, 56%

The formation of **3a** can be explained by a regioselective attack of the terminal carbon atom of the dianion onto the dielectrophile and cyclization mediated by the oxygen atom to give intermediate **A**. The latter underwent a Dimroth rearrangement to give the final product. The domino "cyclization/Dimroth rearrangement" reaction proceeded with excellent (*E*)/(*Z*)-diastereoselectivity, due to the stereodirecting effect of the substituent attached to the pyrrole nitrogen atom.

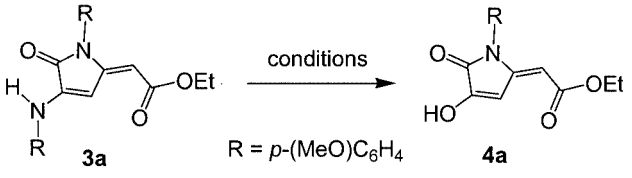
Oligomerization and isocyanide formation proved to be major side reactions. (*p*-Methoxyphenyl)isocyanide could be isolated in up to 10% yield and was formed presumably by reduction of **2a** by the dianion. The formation of small amounts of isocyanide was observed even under optimized conditions. Optimal yields were obtained when the dianion was added within 5 min to a 0.075 M THF solution of **2a** at −78 °C. The solution was warmed to 20 °C during 1 h and then stirred at 20 °C for 5 h. The yield decreased and significant amounts of isocyanide and oligomers were formed when a) the reaction was carried out at 0 °C rather than −78 °C, b) a more concentrated solution of **2a** was used (0.2 M), c) the inverse addition protocol was employed, and d) the dianion was added too rapidly (0.3 min). The dianion was prepared by addition of **1a** to a THF solution of LDA. The use of NaH/*n*BuLi resulted in a minor decrease of the yield.

Next, we studied the deprotection of the 5-alkylidene-2,5-dihydropyrrol-2-one **3a** (Table 1). The *p*-methoxyphenyl (PMP) protective group is frequently used in the chemistry of *N*-heterocycles such as β-lactams.[29] Our initial attempts, however, to achieve cleavage of the enamine moiety of **3a** were unsuccessful. An attempted oxidative cleavage of the PMP group by CAN in CH_3CN resulted in decomposition. Only starting material was recovered in the reaction of **3a** with an aqueous solution (1 M) of sulfuric acid. The use of an aqueous solution of sodium hydroxide also proved unsuccessful. Treatment of **3a** with BBr_3 and subsequent addition of methanol resulted in hydrolytic cleavage and formation of the desired *N*-aryl-5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-one **4a**, but in low yield. After much experimentation, we found that the enamine moiety could be removed in high yield (87%) by treatment of **3a** with a 5:3 mixture of THF and 1 M aqueous hydrochloric acid (Scheme 3). The use of less- or more-concentrated solutions of HCl resulted in a decrease of the yield; the presence of THF was mandatory.

Table 1. Optimization of the synthesis of **4a**

Entry	Conditions	*t* [h]	(%)[a]
1	BBr_3, MeOH	12	22
2	NaOH, H_2O	120	0
3	CAN, CH_3CN	120	0
4	H_2SO_4/H_2O (1M)	4	0
5	HCl/H_2O (37%), THF	1	50
6	HCl/H_2O (10%), THF	1	49
7	HCl/H_2O (1 M), THF	1	87
8	HCl/H_2O (1 M), THF	12	86
9	HCl/H_2O (0.1 M), THF	12	48

[a] Isolated yield

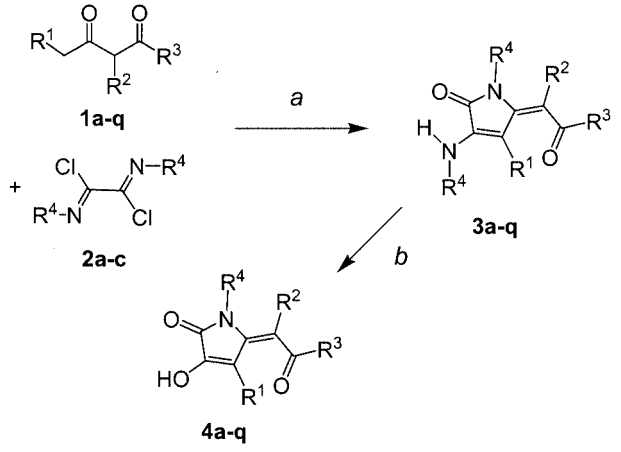


Scheme 3. Hydrolytic cleavage of the enamine moiety 3a. For conditions see Table 1.

In all experiments, **4a** was obtained as a single isomer, containing an (*E*)-configured exocyclic double bond. The reaction proceeded with very good chemoselectivity: no cleavage of either the ester group or the heterocyclic moiety was observed. The transformation of **3a** into **4a** has preparative value because the hydroxy group of α-hydroxy-γ-alkylidenebutenolides can be functionalized by palladium-catalyzed cross-coupling reactions via their corresponding enol triflates.[23c,30]

Variation of the substituent attached to the diimidoyl dichloride (R = Ph, Tol) had no major effect on the yield of heterocycles **3** and **4** (vide infra). To date, however, the methodology is limited to aryl-substituted oxaldimidoyl dichlorides. The cyclization of *N*,*N*′-bis(*p*-tolylsulfonyl)oxaldiimidoyl dichloride (**2d**)[27] with dilithiated **1a** resulted in the formation of a complex mixture (vide infra). We are currently studying the removal of the second PMP group of **4a** and also working on the synthesis of bis(imidoyl) dichlorides containing other protective groups, which is an important feature for applications in natural product syntheses. We believe, however, that *N*-aryl-5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-ones, such as **4a**, represent interesting and useful molecules for their own sake from both a synthetic and pharmacological viewpoint. Therefore, herein we report the results of our efforts that we believe constitute a significant expansion of the methods known today for the synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones.

Preparative Scope: To study the preparative scope of our methodology, we varied the substituents of the starting materials systematically. The reactions of oxaldiimidoyl dichlorides **2a**−**c** with the 1,3-dicarbonyl compounds **1** afforded a large variety of 5-alkylidene-2,5-dihydropyrrol-2-ones (**3a**−**q**; Scheme 4, Table 2).



Scheme 4. Synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones **4a**−**q**, a: 1) 2.2 equiv. LDA, 2) **2a**−**c**, THF, −78 to 20 °C; b: 1 M HCl, THF, 1 h, 20 °C.

The reaction of diimidoyl dichlorides with the dianions of ethyl acetoacetate, *N*,*N*-diethylacetylacetic amide, and *N*-(*o*-tolyl)acetylacetic amide gave the 5-alkylidene-2,5-dihydropyrrol-2-ones **3a**−**e** with very good regio- and (*E*)-diastereoselectivities. The cyclization of dilithiated ethyl 2-methylacetoacetate (**1f**) and ethyl 2-ethylacetoacetate (**1g**) with *N*,*N*′-diphenyloxaldiimidoyl dichloride (**2b**) afforded the (*E*)-configured heterocycles **3f**−**g**, each of which contains a substituent at the exocyclic double bond. Starting with the dianions of methyl 3-oxopentanoate and ethyl 3-oxohexanoate, the (*Z*)-configured 5-alkylidene-2,5-dihydropyrrol-2-ones **3h**−**i** were obtained. The change from the (*E*) to (*Z*) configuration can be explained by the relative steric influence of the methyl and ethyl group, respectively.

Heterocycles **3j**−**m** were prepared with very good regio- and (*E*)-diastereoselectivities from α-acetyl-γ-butyrolactones **1j**−**m**. 5-Alkylidene-2,5-dihydropyrrol-2-ones **3n**−**o** were prepared with very good (*E*) diastereoselectivities from 3-acetyl-2,3-dihydrobenzofuran-2-one and *N*-methyl-3-acetylindol-2-one. The reaction of **2a** with dilithiated cyclohexane-1,3-diones afforded the bicyclic 5-alkylidene-2,5-dihydropyrrol-2-ones **3p**−**q**.

As described above, esters (e.g., ethyl acetoacetate) and amides have been used mainly as the 1,3-dicarbonyl compounds and gave the desired 5-alkylidene-2,5-dihydropyrrol-2-ones **3a**−**q**. The hydrolytic deprotection of heterocycles **3a**−**q** proceeded uneventfully in most cases and afforded a variety of *N*-aryl-5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-ones **4a**−**q** in moderate to excellent yields (Scheme 4).

Heterocycles **4a**−**q** were obtained as colorless or slightly yellow solids. Inspection of the UV/Vis spectra (Table 2) showed that the influence of both the aryl group attached to the nitrogen atom (**4a**−**c**) and the presence of an alkyl group attached to the heterocyclic moiety or to the exocyclic double bond was relatively low (cf. **4b**, **4f**, **4h** and **4i**). A small bathochromic effect was observed for dinuclear esters with respect to mononuclear ones (**4b**/**4j**). The influence of an amide group was relatively low. A bathochromic shift was observed for the oxindole-derived product **4o**, as well as for the bicyclic product **4q**. The strongest effect was observed for the dihydrobenzofuranone **4n** because of its larger conjugated π-electron system. In contrast to the other 2-alkylidene-2,5-dihydropyrrol-2-ones, which are yellow, **4n** has a deep-red color.

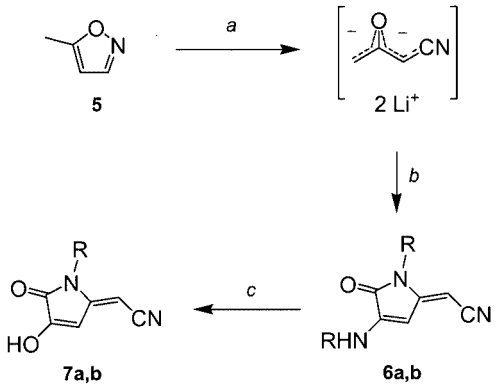
Treatment of 5-methylisoxazole with two equivalents of LDA afforded the dianion of α-cyanoacetone.[31] Treatment of the latter with **2b**,**c** afforded the cyano-substituted 5-alkylidene-2,5-dihydropyrrol-2-ones **6a**,**b** as 10:1 mixtures of (*E*)/(*Z*)isomers (Scheme 5). Treatment of **6a**,**b** with HCl/H_2O afforded the desired products **7a**,**b**.

Structure: The structures of **3c** and **4c** were established by NOESY experiments and, independently, by crystal structure analyses (Figure 1). The exocyclic double bond possesses an *E* configuration. The ester group and the heterocyclic moiety are in-plane. Inspection of the crystal lattice exhibits the presence of a dimeric structure (Figure 2). The configuration of the exocyclic double bonds of **3c** and of other derivatives was established by NOESY experiments and by comparison of the ^{1}H NMR spectroscopic chemical shifts (Scheme 6, Table 2). The chemical shifts of the signals of the hydrogen atoms located at the pyrrole moiety and at the exocyclic double bond are generally higher for (*E*)- than for (*Z*)-configured isomers (by ca. 0.3 ppm). A related trend

Table 2. Synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones **3a**−**q** and **4a**−**q** [PMP = *p*-(MeO)C_6H_4]

3, **4**	R^1	R^3	R^2	R^4	δ (**3**)[a]	(*E*)/(*Z*)[b]	**3** (%)[c]	**4** (%)[c]	UV (**4**)[d]
a	H	OEt	H	PMP	5.46, 7.20	> 98:2	56	87	389
b	H	OEt	H	Ph	5.50, 7.20	> 98:2	55	92	376
c	H	OEt	H	Tol	5.46, 7.20	> 98:2	60	66	386
d	H	NH(*o*-Tol)	H	Tol	5.74,[e]	> 98:2	40	63	385
e	H	NEt_2	H	Ph	5.80,[e] (*E*)	97:3	59	94	
					5.35, 6.25 (*Z*)	1:5	21	−	
f	H	OEt	Me	Ph	−, 7.20	> 98:2	58	96	373
g	H	OEt	Et	Ph	−, 7.35	> 98:2	57	70[f]	−
h	Me	OMe	H	Ph	5.16, −	< 2:98	54	100	376
i	Et	OEt	H	Ph	5.19, −	< 2:98	48	63	374
j	H	$-OCH_2CH_2-$		Ph	−, 7.08	> 98:2	56	100	384
k	Me	$-OCH_2CH_2-$		Ph	−, −	> 98:2	36	52	391
l	H	$-OCH(CH_3)CH_2-$		Ph	−, 7.20	> 98:2	52	100	384
m	H	$-OCH(CH_2CH_3)CH_2-$		Ph	−,[e]	> 98:2	49	99	384
n	H	$-O(C_6H_4)-$		PMP	−, 7.40	> 98:2	47	42	470
o	H	$-NMe(C_6H_4)-$		Ph	−,[e]	> 98:2	38	97	425
p	$-CH_2CH_2-$		H	PMP	5.64, −	−	44	50	382
q	$-C(CH_3)_2CH_2-$		H	PMP	5.65, −	−	40	60	394

[a] ^{1}H NMR spectroscopic signals (CH) of the exocyclic double bond and the pyrrole moiety (ppm). [b] Isomeric ratio of isolated products (^{1}H NMR). [c] Isolated yields. [d] UV/Vis (CH_3CN, nm), $\lambda_{max.}$ [e] Signal overlap in the aromatic region. [f] Mixture of isomers (1:1).



Scheme 5. Synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones **7a**,**b**. a: 2.2 equiv. LDA [**6a** (R = Tol), 44%; **6b** (R = Ph), 40%]; b: **2b**,**c**, THF, −78 to 20 °C; c: 1 M HCl, THF, 1 h, 20 °C [**7a** (R = Tol), 63%; **7b** (R = Ph), 52%]

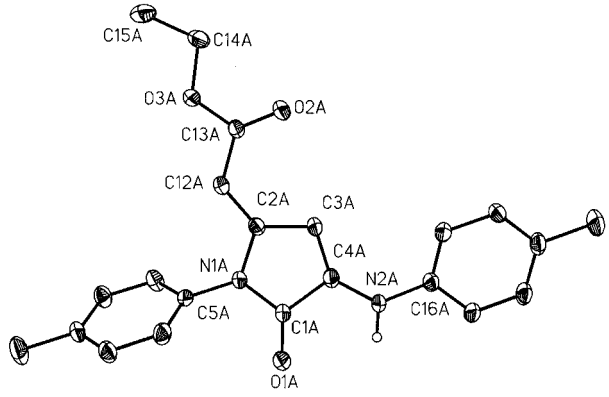


Figure 1. ORTEP plot of **3c**. The thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths (Å) and angles (°): O(1)−C(1) 1.212(5), N(1A)−C(1A) 1.371(5), C(2A)−C(12A) 1.342(5), N(1A)−C(2A) 1.414(5), C(2A)−C(3A) 1.450(5), C(1A)−C(4A) 1.504(5); C(1A)−N(1A)−C(5A) 124.2(3), O(1A)−C(1A)−C(4A) 127.5(3), N(1A)−C(1A)−C(4A) 106.0(3), C(4A)−C(3A)−C(2A) 108.4(3)

has been noted previously for γ-alkylidenebutenolides[23,30] and for 2-alkylidenetetrahydrofurans.[32,33] The *Z* configurations of **3h**,**i** were proven by NOESY measurements with **3h** and by comparison of the chemical shifts of the hydrogen atoms located at each exocyclic double bond. The configurations of **3j** and **3f**,**g** were established by NOESY experiments and by comparison of the chemical shifts of the pyrrole hydrogen atoms with those of (*E*)-configured 5-alkylidene-2,5-dihydropyrrol-2-ones.

Mechanism: The reaction of dilithiated 4-(phenylimino)pentan-2-one (**8**)[34] with **2c** resulted in regioselective C/O-cyclization and formation of product **9** as an inseparable 1:1 mixture of (*E*)/(*Z*) isomers (Scheme 7). Upon standing, a solution of yellow-colored **9** isomerized slowly into the red-colored 5-alkylidene-2,5-dihydropyrrol-2-one **10** by Dimroth rearrangement (12%, low conversion). The yield of **10** was improved (56%) by addition of 2 equiv. of lithium chloride to the reaction mixture. The rearrangement proceeded stereoselectively and afforded the *E*-configured isomer exclusively. This result suggests that the stereoselectivity for all 5-alkylidene-2,5-dihydropyrrol-2-ones **3** was established during the Dimroth rearrangement. The selectivity can be explained by the steric effect of the *N*-aryl group, which can operate only in products **10** and **3**, but not in **9** and intermediate **A**. The rate of the Dimroth rearrangement[35] is enhanced by the presence of a Lewis acid. In fact, a Lewis acid, lithium chloride, was formed during the cyclization of 1,3-dicarbonyl dianions **1** with bis(imidoyl)dichlorides **2**.

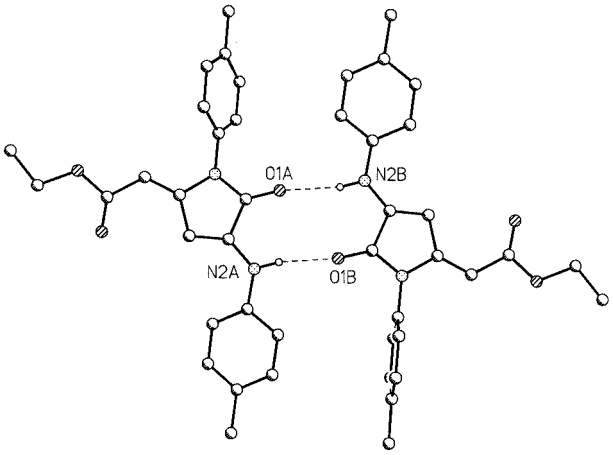
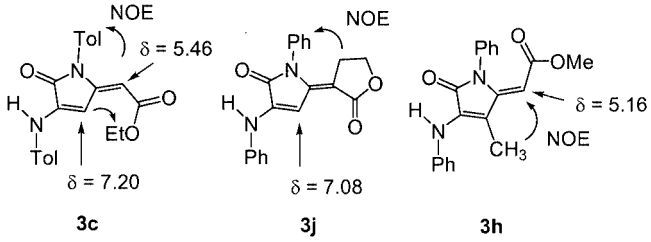
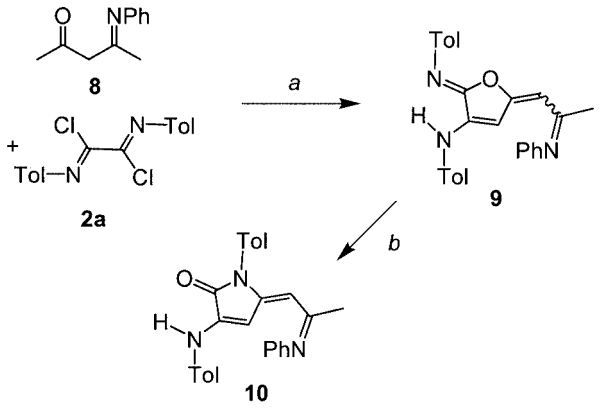


Figure 2. Dimeric structure of **3c**



Scheme 6. Chemical shifts and NOESY experiments



Scheme 7. Cyclization of dilithiated **8** with **2c**: a: 1) 2.2 equiv. LDA, 2) **2c**, THF, −78 to 20 °C, 45% [(*E*)/(*Z*)= 1:1, the product contains ca. 20% of an unknown isomer]; b: THF, 72 h, 20 °C, 12% (low conversion); alternatively: THF, LiCl, 72 h, 56%.

The structure of 5-alkylidene-2,5-dihydropyrrol-2-one **10** was confirmed independently by crystal structure analysis (Figure 3). The exocyclic double bond exhibits an (*E*) configuration. The *p*-tolyl group of the enamine is in-plane with the pyrrole moiety. In contrast, the other *p*-tolyl group is twisted out of the plane. Similar to **3c**, a dimeric structure is present in the crystal lattice (Figure 4).

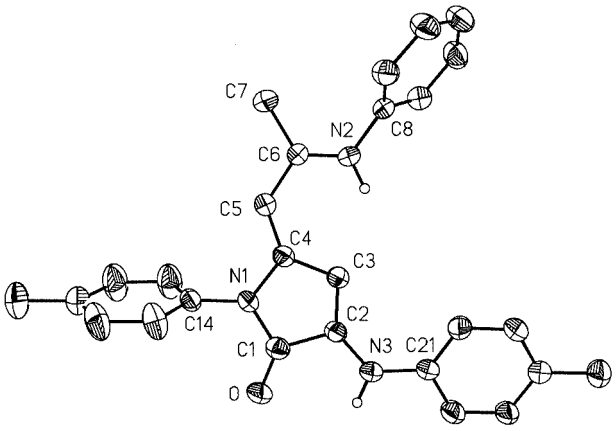


Figure 3. ORTEP plot of **10**. The thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths (Å) and angles (°): O−C(1) 1.211(4), N(1)−C(1) 1.368(5), C(2)−C(3) 1.352(5), C(3)−C(4) 1.439(5), N(1)−C(4) 1.417(4), C(2)−N(3) 1.349(4), C(4)−C(5) 1.341(5); C(1)−N(1)−C(4) 110.2(3), O−C(1)−C(2) 127.8(4), N(3)−C(2)−C(3) 136.7(4), N(2)−C(6)−C(5) 121.3(4), C(2)−C(3)−C(4) 109.2(3), O−C(1)−N(1) 126.1(4)

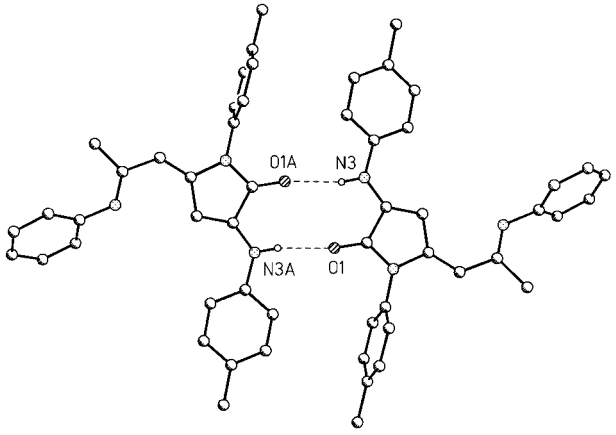
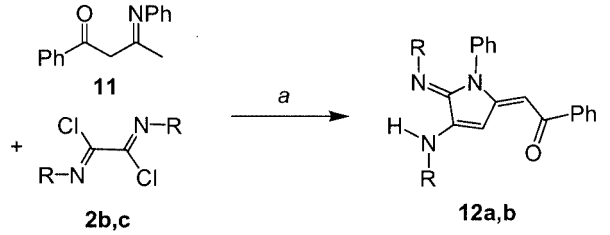


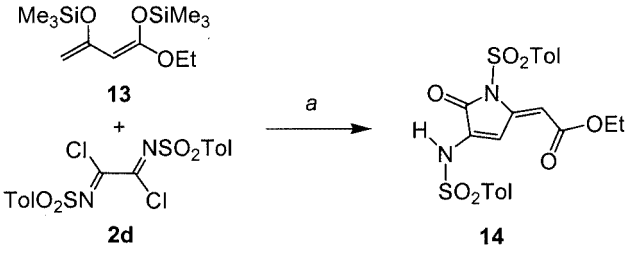
Figure 4. Dimeric structure of **10**

The cyclization of the dianion of **1** with oxaldiimidoyl dichlorides **2b** and **2c** afforded the 5-alkylidene-2-arylimino-2,5-dihydropyrroles **12a** and **12b**, respectively (Scheme 8). These products were formed with very good *C*/*N* regioselectivities and (*E*) diastereoselectivities. Because of the lack of a structural driving force, a Dimroth rearrangement of the amidine moiety is unlikely, but cannot be ruled out. In the case of **12b**, the rearrangement would represent an identity-reaction.

Lewis Acid-Mediated Cyclization: The tolylsulfonyl group represents a useful protective group for pyrrole and indole nitrogen atoms. The cyclization of dilithiated ethyl acetoacetate with bis(imidoyl)dichloride **2d** resulted in formation of a complex mixture. In contrast, the $TiCl_4$-mediated reaction of **2d** with 1,3-bis(silyl enol ether) **13**, which can be regarded as an electroneutral dianion equivalent, afforded the desired product **14**, albeit in low yield



Scheme 8. Cyclization of dilithiated **11** with **2b**,**c**: *a*: 1) 2.2 equiv. LDA, 2) **2b**,**c**, THF, −78 to 20 °C [**12a** (R = Tol), 35%; **12b** (R = Ph), 32%].



Scheme 9. Lewis acid-mediated cyclization of 1,3-bis(silyl enol ether) **13** with **2d**, a: 2.0 equiv. $TiCl_4$, CH_2Cl_2, −78 to 20 °C, 15%

(Scheme 9). Only starting materials were recovered when TMSOTf was employed in place of $TiCl_4$.

Conclusion

We have developed a new and efficient domino reaction of 1,3-dicarbonyl dianions with oxaldiimidoyl dichlorides that affords 5-alkylidene-3-arylamino-2,5-dihydropyrrol-2-ones. The cyclizations proceed with excellent regio- and *E*/*Z*-diastereoselectivity. The arylamino group of each product can be hydrolyzed in high yields to give a variety of *N*-aryl-5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-ones.
These products are of pharmacological and synthetic interest. The chemistry reported constitutes an expansion of the methods known today for the synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones.

Experimental Section

General: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. All solvents were distilled prior to use. ^{1}H NMR: Bruker AM 250 (250 MHz), Varian VXR-200 (200 MHz), Varian Mercury 200 (200 MHz), Varian Unity 300 (300 MHz), Bruker AMX 300 (300 MHz), or Varian Inova 500 (500 MHz) spectrometers. For ^{1}H NMR spectrosopy, we used the solvents $CDCl_3$ (δ = 7.26 ppm), [D_8]THF (δ = 1.73, 3.58 ppm), [D_6]acetone (δ = 2.04 ppm), [D_6]dimethyl sulfoxide (δ = 2.50 ppm), and [D_4]methanol (δ = 3.30 ppm). Tetramethylsilane (TMS) was used as the internal standard. ^{13}C NMR: Bruker AM 250 (62.9 MHz), Varian VXR-200 (50.3 MHz), Varian Mercury 200 (50.3 MHz), Varian Unity 300 (75.5 MHz), Bruker AMX 300 (75.5 MHz), or Varian Inova 500 (125.7 MHz) spectrometers. As solvents, we used $CDCl_3$ (δ = 77.0 ppm), [D_6]acetone (δ = 29.8 ppm), [D_6]DMSO (δ = 39.5 ppm), [D_4]methanol (δ = 49.0 ppm), and [D_8]THF (δ = 25.5, 67.7 ppm). The multiplicity of each carbon atom was determined by the DEPT 135 (DEPT = Distortionless Enhancement by Polarization Transfer) and APT techniques (APT = Attached-Proton Test); they and quoted as CH_3, CH_2, CH, and C for primary, secondary, tertiary, and quaternary carbon atoms, respectively. IR: Perkin−Elmer 2000 FT-IR, FT-IR Bruker Vector 22, Bruker IFS 66, or Nicolett 205 FT-IR spectrometers. UV spectroscopy: Perkin−Elmer UV/Vis/NR − Spectrometer Lambda 19; CH_3CN was used as solvent. Mass spectroscopy: Finnigan MAT 95 spectrometer [electron ionization (EI): 70 eV], Finnigan LC-Q (electrospray ionization, ESI). Chemical ionization (CI): H_2O. For preparative scale chromatography we used silica gel (60−200 mesh); solvents: petroleum ether (PE, b.p. 40−70 °C) and diethyl ether. Melting points are uncorrected and were measured using a Büchi apparatus. Elemental analyses: microanalytical laboratory of the University of Göttingen (Leco CHN 2000, Heraeus Mikro U/D).

General Procedure for the Synthesis of 5-Alkylidene-3-arylamino-2,5-dihydropyrrol-2-ones (3): A THF solution of LDA was prepared by addition of *n*BuLi (8.25 mL, 13.2 mmol, 1.6 M solution in hexane) to a THF solution (20 mL) of diisopropylamine (1.34 g, 1.86 mL, *d* = 0.722, 13.2 mmol). A THF solution (20 mL) of ethyl acetoacetate (0.72 g, *d* = 1.021, 0.71 mL, 5.7 mmol) was added at 0 °C to the LDA solution. The yellow-colored solution was stirred at 0 °C for 60 min and was then transferred to a THF solution (80 mL) of *N*,*N*′-bis[(*p*-methoxyphenyl)oxaldiimidoyl dichloride (2.02 g, 6.0 mmol) at −78 °C. The solution was warmed to 20 °C within 1 h, stirred for 5 h, and then1 M aqueous ammonium chloride was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (4 × 150 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and then the filtrate was concentrated in vacuo. The residue was purified by chromatography (SiO_2; diethyl ether/PE, 1:10 → 1:1) to give **3a** [1.26 g, 56%, (*E*)/(*Z*) > 98:2] as yellow crystals.

(*E*)-5-(Ethoxycarbonylmethylidene)-1-(4-methoxyphenyl)-3-(4-methoxyphenylamino)-2,5-dihydropyrrol-2-one (3a): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.32 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 3.82, 3.85 (2 × s, 2 × 3 H, OCH_3), 4.21 (q, *J* = 7 Hz, 2 H, CH_2), 5.46 (s, 1 H, =CH), 6.95 (d, *J* = 11 Hz, 4 H, Ar), 7.05 (s, 1 H, 4-H), 7.15, 7.51 (2 × d, *J* = 11 Hz, 2 × 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.41 (CH_2CH_3), 55.29, 55.40 (OCH_3), 59.76 (OCH_2), 90.45, 95.53 (CH), 114.04, 114.69, 120.08, 126.90 (CH, Ar), 132.59, 136.31, 140.39, 149.50, 155.85, 158.01, 167.07, 167.56 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3385 (w), 3285 (w), 2978 (w), 2957 (w), 2933 (w), 2836 (w), 1696 (s), 1605 (s), 1524 (s), 1508 (s), 1462 (m), 1445 (m), 1418 (w), 1400 (w), 1296 (m), 1248 (s), 1229 (s), 1172 (m), 1133 (s), 1074 (s), 1038 (m), 935 (w), 834 (m), 812 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 379.9 (4.46), 298.1 (3.98), 248.7 (4.36) nm. MS (EI, 70 eV): *m*/*z* (%) = 394 (100) [M^+]; the exact molecular mass *m*/*z* = 394.1528 (±2 mD) [M^+] of $C_{22}H_{22}N_2O_5$ was confirmed by HRMS (EI, 70 eV). $C_{22}H_{22}N_2O_5$ (394.42): calcd. C 66.99, H 5.62; found C 67.17, H 5.84.

(*E*)-5-(Ethoxycarbonylmethylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3b): Starting from ethyl acetoacetate (0.76 mL, 6.0 mmol) and *N*,*N*′-bis[(*p*-methoxyphenyl)oxaldiimidoyl dichloride (1.66 g, 6.0 mmol), **3b** was isolated as a yellow solid [1.10 g, 55%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.29 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 4.20 (q, *J* = 7 Hz, 2 H, CH_2CH_3), 5.50 (s, 1 H, $CHCO_2Et$), 7.00−7.50 (m, 12 H, 4-H, Ph, NH) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.39 (CH_2CH_3), 59.95 (CH_2CH_3),

92.03, 97.61 (CH, *C*HCO$_2$Et, C-4), 118.23, 123.42, 124.56, 126.09, 128.94, 129.61 (CH, Ph), 139.14, 139.33, 143.45 (C, C-3, Ph), 151.26 (C, C-2), 166.50, 167.33 (C, C-5, *C*O$_2$Et) ppm. IR (KBr): $\tilde{\nu}$ = 3356 (m), 2976 (w), 2932 (w), 1704 (s), 1616 (s), 1596 (s), 1532 (s), 1380 (m), 1236 (s), 1132 (s), 1072 (s), 1040 (m) cm^{-1}. MS-FAB: *m*/*z* (%) = 335 [M + 1]$^+$, 250 [M − TolNC]$^+$. $C_{20}H_{18}N_2O_3$ (334.36): calcd. C 71.84, H 5.43, N 8.37; found C 71.42, H 5.71, N 8.68.

(*E*)-5-(Ethoxycarbonylmethylidene)-1-(4-tolyl)-3-(4-tolylamino)-2,5-dihydropyrrol-2-one (3c): Starting from ethyl acetoacetate (0.76 mL, 6.0 mmol) and *N*,*N*′-di(*p*-tolyl)oxaldiimidoyl dichloride (1.83 g, 6.0 mmol), **3c** was isolated as a yellow solid [1.30 g, 60%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.29 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 2.30, 2.33 (s, 6 H, Tol-CH_3), 4.19 (q, *J* = 7 Hz, 2 H, CH_2CH_3), 5.46 (s, 1 H, *C*HCO$_2$Et), 7.00−7.40 (m, 10 H, 4-H, Tol, NH) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.40 (CH_2CH_3), 20.79, 21.12 (Tol-CH_3), 59.84 (CH_2CH_3), 91.25, 96.76 (CH, *C*HCO$_2$Et, C-4), 118.27, 124.77, 129.55, 130.06 (CH, Tol), 133.02, 136.04, 136.84 (C, C-3, Tol-C to CH_3), 139.57, 140.80 (C, Tol-C to N), 150.70 (C, C-2), 166.82, 167.48 (C, C-5, *C*O$_2$Et) ppm. IR (KBr): $\tilde{\nu}$ = 3360 (w), 2980 (w), 2928 (w), 1702 (s), 1638 (s), 1605 (s), 1532 (s), 1232 (s), 1130 (m), 1075 (s), 1043 (m) cm^{-1}. MS (CI, H_2O): *m*/*z* (%) = 363 [M + 1]$^+$, 250 [M − TolNC]$^+$. $C_{22}H_{22}N_2O_3$ (362.42): calcd. C 72.91, H 6.12, N 7.73; found C 72.53, H 6.73, N 8.11.

(*E*)-1-(4-Tolyl)-3-(4-tolylamino)-5-[*N*-(2-tolyl)carbamoylmethylidene]-2,5-dihydropyrrol-2-one (3d): Starting from *N*-(*o*-tolyl-)acetoacetic amide (1.15 g, 6.0 mmol) and *N*,*N*′-di(*p*-tolyl)oxaldiimidoyl dichloride (1.83 g, 6.0 mmol), **3d** was isolated as a yellow solid [1.02 g, 40%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ = 2.26, 2.30, 2.33 (s, 9 H, Tol-CH_3), 5.74 (s, 1 H, C*H*CONHTol), 6.40−7.70 (m, 13 H, 4-H, Tol), 8.05 (br., 1 H, NH), 8.29 (br., 1 H, NH) ppm. ^{13}C NMR ([D$_8$]THF, 50 MHz): δ = 18.00, 20.76, 21.01 (Tol-CH_3), 94.72, 98.38 (CH, C-4, *C*HCONHTol), 119.55, 125.04, 126.66, 126.67, 129.95, 129.96, 130.51, 130.74 (CH, Tol), 133.10, 135.71, 138.09 (C, Tol-C to CH_3), 138.28 (C, C-3), 138.90, 140.28, 142.86 (C, Tol-C to N), 152.15 (C, C-2), 164.88, 165.21 (C, C-5, *C*ONHTol) ppm. IR (KBr): $\tilde{\nu}$ = 3360 (w), 3025 (w), 1690 (m), 1655 (m), 1630 (s), 1605 (s), 1524 (s), 1450 (m), 1290 (m), 1245 (m), 1078 (m) cm^{-1}. MS (CI, H_2O): *m*/*z* (%) = 424 [M + 1]$^+$. $C_{27}H_{25}N_3O_2$ (423.50): calcd. C 76.58, H 5.95, N 9.92; found C 76.24, H 5.93, N 9.88.

(*E*)- and (*Z*)-5-(*N*,*N*-Diethylcarbamoylmethylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3e): Starting from *N*,*N*-diethylacetoacetic amide (314 mg, 0.32 mL, 2.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (544 mg, 2.0 mmol), **3e** was isolated as a yellow solid [(*E*) isomer: 428 mg, 59%, (*E*)/(*Z*) = 97:3; (*Z*) isomer: 153 mg, 21%, (*E*)/(*Z*) = 1:5]. After 2 months of storage at room temperature, 80% of the isolated (*Z*) isomer had turned to (*E*). ^{1}H NMR ($CDCl_3$, 250 MHz): (*E*) isomer, δ = 1.20 (t, ^3J = 7.4 Hz, 6 H, NCH_2CH_3), 3.34−3.52 (m, 4 H, NCH_2CH_3), 5.83 (s, 1 H, CH−CO), 7.03−7.45 (m, 12 H, NH, C-4, 2 Ph) ppm; (*Z*) Isomer, δ = 1.17 (t, ^3J = 7.1 Hz, 6 H, NCH_2CH_3), 3.37−3.49 (m, 4 H, NCH_2CH_3), 5.35 (s, 1 H, CH-CO), 6.25 (s, 1 H, C-4), 7.03−7.45 (m, 10 H, NH, Ph), 7.65 (d, ^3J = 7.4 Hz, 1 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): (*E*) and (*Z*) isomers: δ = 13.42, 14.85 (NCH_2CH_3), 40.71, 42.56 (NCH_2CH_3), 92.18 (*C*H-CO), 98.98 (C-4), 117.93, 122.94, 124.11, 125.60, 128.89, 129.53 (CH, Ph), 138.05, 139.54, 143.99, 151.98 (C), 164.68, 165.69 (NCO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 361 (91) [M$^+$], 289 (100); the exact molecular mass *m*/*z* = 361.1790 (±2 mD) [M$^+$] of $C_{22}H_{23}N_3O_2$ was confirmed by HRMS (EI, 70 eV).

(*E*)-5-[1-(Ethoxycarbonyl)ethylidene]-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3f): Starting from ethyl 2-methylacetoacetate (0.58 g, 0.56 mL, 4.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (1.11 g, 4.0 mmol), **3f** was isolated as a yellow solid [806 mg, 58%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.38 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 2.05 (s, 3 H, CH_3), 4.32 (q, *J* = 7 Hz, 2 H, CH_2), 7.20 (s, 1 H, CH), 7.05−7.25 (m, 4 H, Ph), 7.38 (t, *J* = 9 Hz, 4 H, Ph), 7.70 (d, *J* = 9 Hz, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.00, 14.50 (CH_3), 60.63 (OCH_2), 97.61 (CH, Ring), 99.62 (C), 118.07, 123.13, 125.45, 126.16, 128.99, 129.63 (CH, Ph), 137.38, 139.76, 143.36, 152.12, 158.30, 166.72 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3352 (m), 3305 (w), 3061 (w), 3009 (w), 2983 (w), 2932 (w), 1778 (w), 1671 (s), 1620 (s), 1596 (s), 1533 (s), 1495 (m), 1445 (m), 1326 (m), 1293 (m), 1210 (s), 1132 (m), 1080 (m), 1027 (m), 873 (w), 762 (m), 753 (m), 688 (w), 589 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 376.1 (4.34), 248.1 (4.28) nm. MS (EI, 70 eV): *m*/*z* (%) = 348 (68) [M$^+$], 240 (100); the exact molecular mass *m*/*z* = 348.1473 (±2 mD) [M$^+$] of $C_{21}H_{20}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{21}H_{20}N_2O_3$ (348.39): calcd. C 72.40, H 5.79; found C 72.18, H 5.75.

(*E*)-5-[1-(Ethoxycarbonyl)propylidene]-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3g): Starting from ethyl 2-ethylacetoacetate (0.63 g, 0.64 mL, 4.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (1.11 g, 4.0 mmol), **3g** was isolated as a yellow solid [825 mg, 57%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.13, 1.38 (2 × t, *J* = 7 Hz, 2 × 3 H, CH_3), 2.59 (q, *J* = 7 Hz, 2 H, CCH_2), 4.29 (q, *J* = 7 Hz, 2 H, OCH_2), 7.05 (d, *J* = 11 Hz, 2 H, Ph), 7.15−7.50 (m, 9 H, Ph, NH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.40, 14.47 (CH_3), 20.33 (CCH_2), 60.23 (OCH_2), 99.67 (CH), 114.01 (C), 117.78, 122.75, 125.03, 125.92, 128.95, 129.51 (CH, Ar), 137.68, 139.89, 143.78, 151.45, 161.79, 167.64 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3366 (m), 3317 (w), 3160 (w), 3060 (w), 2976 (w), 2935 (w), 2874 (w), 1775 (w), 1695 (s), 1628 (s), 1595 (s), 1527 (s), 1494 (m), 1447 (m), 1330 (m), 1253 (m), 1227 (s), 1126 (m), 1083 (s), 1030 (m), 981 (w), 805 (w), 752 (m), 692 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 378.0 (4.34), 248.7 (4.27), 202.9 (4.29) nm. MS (EI, 70 eV): *m*/*z* (%) = 362 (100) [M$^+$], 347 (43); the exact molecular mass *m*/*z* = 362.1630 (±2 mD) [M$^+$] of $C_{22}H_{22}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{22}H_{22}N_2O_3$ (362.42): calcd. C 72.91, H 6.12; found C 73.12, H 5.97.

(*Z*)-5-(Methoxycarbonylmethylidene)-4-methyl-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3h): Starting from methyl 3-oxopentanoate (0.52 g, 0.50 mL, 4.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (1.11 g, 4.0 mmol), **3h** was isolated as a yellow solid [720 mg, 54%, (*E*)/(*Z*) < 2:98]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.65 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 5.16 (s, 1 H, C=CH), 6.80 (s, 1 H, NH), 7.00−7.50 (m, 8 H, Ph), 7.74 (d, *J* = 10 Hz, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 10.42 (CH_3), 51.34 (OCH_3), 88.83 (C=*C*H), 109.56 (*C*CH_3), 121.79, 124.06, 125.84, 126.46, 128.96, 129.04 (CH, Ph), 136.13, 139.15, 143.24, 151.60, 164.39, 165.29 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3320 (s), 3058 (w), 3030 (w), 3020 (w), 2950 (w), 2921 (w), 1678 (s), 1616 (s), 1592 (s), 1517 (s), 1493 (m), 1441 (s), 1339 (s), 1313 (m), 1275 (s), 1253 (m), 1148 (s), 1029 (m), 956 (w), 915 (w), 869 (w), 846 (w), 818 (m), 771 (m), 747 (m), 697 (m), 505 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 376.7 (4.32), 247.4 (4.34) nm. MS (EI, 70 eV): *m*/*z* (%) = 334 (100) [M$^+$], 301 (16), 275 (28); the exact molecular mass *m*/*z* = 334.1317 (±2 mD) [M$^+$] of $C_{20}H_{18}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{20}H_{18}N_2O_3$ (334.36): calcd. C 71.84, H 5.43; found C 72.08, H 5.52.

(*Z*)-5-(Ethoxycarbonylmethylidene)-4-ethyl-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3i): Starting from ethyl 3-oxohexanoate

(0.63 mL, 4.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (1.11 g, 4.0 mmol), **3i** was isolated as a yellow solid [695 mg, 48%, (*E*)/(*Z*) < 2:98). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, *J* = 7 Hz, 3 H, CCH_2CH_3), 1.36 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 2.15 (q, *J* = 7 Hz, 2 H, CCH_2), 4.32 (q, *J* = 7 Hz, 2 H, OCH_2), 5.19 (s, 1 H, =CH), 6.73 (s, 1 H, NH), 7.10−7.45 (m, 8 H, Ph), 7.72 (d, *J* = 10 Hz, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 12.51, 14.50 (CH_3), 17.24 (CCH_2), 60.10 (OCH_2), 89.61 (=CH), 115.25 (CCH_2), 122.43, 124.51, 125.85, 126.36, 128.96, 128.99 (CH, Ph), 135.60, 139.12, 143.37, 151.80, 163.15, 165.10 (C) ppm. IR (KBr): ṽ = 3350 (m), 3304 (w), 3060 (w), 3016 (w), 2979 (m), 2937 (w), 2877 (w), 1690 (s), 1640 (s), 1613 (s), 1593 (s), 1528 (s), 1492 (m), 1451 (m), 1363 (m), 1328 (m), 1265 (s), 1250 (m), 1165 (s), 1143 (s), 1054 (m), 1039 (m), 989 (m), 807 (m), 770 (m), 692 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 375.3 (4.30), 246.9 (4.34) nm. MS (EI, 70 eV): *m*/*z* (%) = 362 (100) [M$^+$], 289 (46); the exact molecular mass *m*/*z* = 362.1630 (±2 mD) [M$^+$] of $C_{22}H_{22}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{22}H_{22}N_2O_3$ (362.42): calcd. C 72.91, H 6.12; found C 72.71, H 6.07.

(*E*)-5-(2-Oxotetrahydrofuran-3-ylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3j): Starting from 2-acetyl-γ-butyrolactone (0.43 mL, 4.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (1.11 g, 4.0 mmol), **3j** was isolated as a yellow solid [744 mg, 56%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.18 (t, *J* = 7 Hz, 2 H, CH_2), 4.25 (t, *J* = 7 Hz, 2 H, OCH_2), 7.08 (s, 1 H, 4-H), 7.20−7.50 (m, 10 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 25.82, 65.53 (CH_2), 96.26 (C), 96.55 (CH, C-4), 118.08, 123.36, 124.72, 126.22, 128.97, 129.65 (CH, Ph), 137.89, 139.22, 143.25, 151.06, 160.61, 171.66 (C) ppm. IR (KBr): ṽ = 3448 (w), 3354 (w), 3333 (m), 1731 (s), 1691 (m), 1657 (s), 1621 (s), 1596 (s), 1537 (s), 1491 (m), 1446 (m), 1373 (m), 1325 (m), 1291 (m), 1226 (s), 1208 (s), 1091 (m), 1074 (m), 1022 (m), 1000 (s), 955 (m), 773 (m), 750 (m), 691 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 388.1 (4.39), 249.4 (4.30) nm. MS (EI, 70 eV): *m*/*z* (%) = 332 (100) [M$^+$]; the exact molecular mass *m*/*z* = 332.1160 (±2 mD) [M$^+$] of $C_{20}H_{16}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{20}H_{16}N_2O_3$ (332.35): calcd. C 72.28, H 4.85; found C 72.04, H 4.73.

(*E*)-4-Methyl-5-(2-oxotetrahydrofuran-3-ylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3k): Starting from 2-propionyl-γ-butyrolactone (0.43 g, 3.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (831 mg, 3.0 mmol), **3k** was isolated as a yellow solid [372 mg, 36%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.12 (s, 3 H, CH_3), 3.21, 4.39 (2 × t, *J* = 8 Hz, 2 × 2 H, CH_2), 6.65 (s, 1 H, NH), 6.90−7.55 (m, 10 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 13.85 (CH_3), 28.19, 65.44 (CH_2), 100.42, 113.13 (C), 120.67, 123.45, 124.71, 125.89, 128.93, 129.04 (CH, Ph), 137.69, 139.47, 143.82, 151.28, 160.70, 170.11 (C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 346 (100) [M$^+$]; the exact molecular mass *m*/*z* = 346.1317 (±2 mD) [M$^+$] of $C_{21}H_{18}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{21}H_{18}N_2O_3$ (346.38): calcd. C 72.82, H 5.24; found C 74.00, H 5.83.

(*E*)-5-(5-Methyl-2-oxotetrahydrofuran-3-ylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3l): Starting from 2-acetyl-4-methyl-γ-butyrolactone (0.38 g, 3.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (831 mg, 3.0 mmol), **3l** was isolated as a yellow solid [540 mg, 52%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.50 (d, *J* = 7 Hz, 3 H, CH_3), 2.75 (dd, *J* = 7, *J* = 16 Hz, 1 H, CH_2), 3.31 (dd, *J* = 8, *J* = 16 Hz, 1 H, CH_2), 4.73 (m, 1 H, $CHCH_3$), 7.05−7.30 (m, 5 H, Ph, 4-H), 7.45 (m, 5 H, Ph), 7.70 (d, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 22.28 (CH_3), 33.47 (CH_2), 74.19, 96.79 (CH), 97.55 (C), 118.11, 119.80, 124.68, 128.98, 129.27, 129.69 (CH, Ph), 137.87, 139.28, 143.33, 151.17, 160.38, 171.14 (C) ppm. IR (KBr): ṽ = 3338 (m), 3307 (s), 3061 (w), 2973 (w), 2927 (w), 1731 (s), 1693 (m), 1664 (s), 1621 (s), 1622 (s), 1596 (s), 1533 (s), 1494 (m), 1441 (s), 1343 (m), 1318 (m), 1225 (s), 1088 (m), 1004 (m), 941 (w), 871 (w), 797 (w), 774 (w), 751 (s), 689 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 387.5 (4.18), 256.5 (4.26) nm. MS (EI, 70 eV): *m*/*z* (%) = 346 (100) [M$^+$], 240 (70); the exact molecular mass *m*/*z* = 346.1317 (±2 mD) [M$^+$] of $C_{21}H_{18}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{21}H_{18}N_2O_3$ (346.38) C 72.82, H 5.24; found C 71.57, H 5.32.

(*E*)-5-(5-Ethyl-2-oxotetrahydrofuran-3-ylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3m): Starting from 2-acetyl-4-ethyl-γ-butyrolactone (0.47 g, 3.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (831 mg, 3.0 mmol), **3m** was isolated as a yellow solid [530 mg, 49%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.02 (t, *J* = 7 Hz, 3 H, CH_3), 1.75 (m, 2 H, CH_2CH_3), 2.72 (dd, *J* = 6, 16 Hz, 1 H, CH_2), 3.25 (dd, *J* = 8, 16 Hz, 1 H, CH_2), 4.52 (m, 1 H, $CHCH_2$), 7.00−7.25 (m, 6 H, Ph, CH, NH), 7.30−7.50 (m, 6 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 9.16 (CH_3), 29.33, 31.33 (CH_2), 78.95, 96.76 (CH), 97.53 (C), 118.05, 123.30, 124.76, 126.19, 129.00, 129.66 (CH, Ph), 137.78, 139.29, 143.33, 151.14, 160.31, 171.25 (C) ppm. IR (KBr): ṽ = 3355 (w), 3336 (m), 2972 (w), 2937 (w), 1733 (s), 1694 (m), 1659 (s), 1621 (s), 1596 (s), 1536 (s), 1493 (m), 1447 (m), 1351 (m), 1324 (m), 1294 (w), 1223 (s), 1212 (s), 1089 (m), 1074 (m), 1005 (s), 795 (w), 775 (w), 751 (m), 691 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 388.6 (4.40), 249.3 (4.30) nm. MS (EI, 70 eV): *m*/*z* (%) = 360 (100) [M$^+$]; the exact molecular mass *m*/*z* = 360.1473 (±2 mD) [M$^+$] of $C_{22}H_{20}N_2O_3$ was confirmed by HRMS (EI, 70 eV). $C_{22}H_{20}N_2O_3$ (360.40): calcd. C 73.32, H 5.59; found C 72.17, H 5.90.

(*E*)-1-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)-5-(2-oxo-2,3-dihydrobenzofuran-3-ylidene)-2,5-dihydropyrrol-2-one (3n): Starting from 3-acetyl-2,3-dihydrobenzofuran-2-one (0.35 g, 2.0 mmol) and *N*,*N*′-bis(*p*-methoxyphenyl)oxaldiimidoyl dichloride (674 mg, 2.0 mmol), **3n** was isolated as a yellow solid [412 mg, 47%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.83, 3.90 (2 × s, 2 × 3 H, OCH_3), 6.87−7.25 (m, 11 H, Ar, CH), 7.32 (s, 1 H, NH), 7.59 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 55.45, 55.50 (OCH_3), 95.05 (CH), 110.05 (C), 114.30, 114.93, 120.59, 121.33, 123.59, 123.71, 126.88, 127.06 (CH, Ar), 128.21, 131.67, 135.67, 141.64, 148.25, 151.04, 156.55, 158.65, 163.83, 168.75 (C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 440 (4) [M$^+$], 322 (100); the exact molecular mass *m*/*z* = 440.1372 (±2 mD) [M$^+$] of $C_{26}H_{20}N_2O_5$ was confirmed by HRMS (EI, 70 eV). $C_{26}H_{20}N_2O_5$ (440.45): calcd. C 70.90, H 4.58; found C 69.74, H 5.14.

(*E*)-5-(1-Methyl-2-oxo-2,3-dihydroindol-3-ylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3o): Starting from 3-acetyl-1-methyl-2,3-dihydroindol-2-one (0.57 g, 3.0 mmol) and *N*,*N*′-diphenyloxaldiimidoyl dichloride (831 mg, 3.0 mmol), **3o** was isolated as a yellow solid [448 mg, 38%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.22 (s, 3 H, CH_3), 6.69, 6.95 (2 × m, 2 × 1 H, Ar), 7.08 (m, 2 H, Ar), 7.22−7.65 (m, 12 H, Ar, CH, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 25.76 (CH_3), 97.99 (CH), 101.47 (C), 107.53, 118.24, 121.87, 122.32, 123.60, 124.39, 126.39, 127.03, 129.02, 129.64 (CH, Ph), 121.69, 138.95, 139.06, 140.86, 143.37, 151.04, 160.57, 168.17 (C) ppm. IR (KBr): ṽ = 3354 (w), 3239 (w), 3150 (w), 3126 (w), 3056 (m), 1689 (s), 1683 (s), 1636 (s), 1611 (s), 1575 (s), 1537 (s), 1486 (s), 1470 (m), 1449 (m), 1418 (m), 1374 (s), 1347 (m), 1284 (m), 1268 (s), 1230 (m), 1180 (m), 1140 (m), 1077 (s), 975 (m), 957 (m), 771 (m), 746 (m), 690 (m), 547 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 429.2 (4.37), 242.1 (4.40) nm. MS (EI, 70 eV): *m*/*z* (%) = 393 (100) [M$^+$]; the exact molecular mass *m*/*z* = 393.1477 (±2 mD) [M$^+$] of $C_{25}H_{19}N_3O_2$ was con-

firmed by HRMS (EI, 70 eV). $C_{25}H_{19}N_3O_2$ (394.28): calcd. C 76.32, H 4.87; found C 76.55, H 5.04.

1-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)-2,4,5,6-tetrahydro-1*H*-indole-2,6-dione (3p): Starting from 1,3-cyclohexanedione (0.34 g, 3.0 mmol) and *N*,*N*′-bis(*p*-methoxyphenyl)oxaldiimidoyl dichloride (1.01 g, 3.0 mmol), **3p** was isolated as a yellow solid (495 mg, 44%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.42 (t, *J* = 4 Hz, 4 H, CH_2), 3.80 (s, 6 H, OCH_3), 5.64 (s, 1 H, CH), 6.66 (s, 1 H, NH), 6.92 (m, 4 H, Ar), 7.10 (d, *J* = 12 Hz, 2 H, Ar), 7.48 (d, *J* = 12 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 20.07, 35.74 (CH_2), 55.42, 55.49 (OCH_3), 99.85 (CH), 104.61 (C), 114.18, 114.28, 125.59, 126.72 (CH, Ar), 131.13, 135.11, 136.13, 149.62, 157.658, 158.13, 170.49, 197.59 (C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 376 (12) [M^+], 361 (6), 268 (22), 69 (100); the exact molecular mass *m*/*z* = 376.1423 (±2 mD) [M^+] of $C_{22}H_{20}N_2O_4$ was confirmed by HRMS (EI, 70 eV). $C_{22}H_{20}N_2O_4$ (376.40): calcd. C 70.20, H 5.36; found C 70.10, H 5.38.

1-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)-4,4-dimethyl-2,4,5,6-tetrahydro-1*H*-indole-2,6-dione (3q): Starting from 5,5-dimethylcyclohexane-1,3-dione (0.42 g, 3.0 mmol) and *N*,*N*′-bis(*p*-methoxyphenyl)oxaldiimidoyl dichloride (1.01 g, 3.0 mmol), **3q** was isolated as a yellow solid (485 mg, 40%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.94 (s, 6 H, OCH_3), 2.28 (s, 2 H, CH_2), 3.79 (s, 6 H, OCH_3), 5.65 (s, 1 H, CH), 6.57 (s, 1 H, NH), 6.85 (m, 4 H, Ar), 7.12 (d, *J* = 12 Hz, 2 H, Ar), 7.45 (d, *J* = 12 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 27.17 (CH_3), 33.14 (C), 54.14 (CH_2), 55.38, 55.47 (OCH_3), 99.54 (CH), 114.13, 114.33 (CH, Ar), 116.43 (C), 126.77, 127.57 (CH, Ar), 134.20, 136.15, 136.45, 150.53, 158.09, 158.11, 169.76, 197.69 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3264 (s), 3004 (w), 2954 (w), 2932 (w), 2835 (w), 1695 (s), 1650 (s), 1586 (s), 1523 (s), 1509 (s), 1462 (m), 1385 (s), 1295 (s), 1250 (s), 1170 (s), 1129 (m), 1042 (s), 977 (w), 842 (m), 800 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 386.1 (4.35), 295.3 (4.01), 251.8 (4.22), 243.4 (4.21) nm. MS (EI, 70 eV): *m*/*z* (%) = 404 (100) [M^+], 389 (24); the exact molecular mass *m*/*z* = 404.1736 (±2 mD) [M^+] of $C_{24}H_{24}N_2O_4$ was confirmed by HRMS (EI, 70 eV). $C_{24}H_{24}N_2O_4$ (404.46): calcd. C 71.27, H 5.98; found C 71.13, H 5.94.

General Procedure for the Synthesis of 5-Alkylidene-3-hydroxy-2,5-dihydropyrrol-2-ones (4): 3a (44.5 mg, 112.8 μmol) was dissolved in THF (25 mL) at room temperature. 1 M Aqueous hydrochloric acid (15 mL,) was added to this solution under vigorous stirring. The temperature of the mixture rose to ca. 40 °C during the addition and the color changed from yellow to orange. After stirring for 1 h at 25 °C, the solution was poured into water (150 mL). The organic and aqueous layers were separated and the latter was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and then the filtrate was concentrated in vacuo. The residue was purified by chromatography (SiO_2; diethyl ether/PE, 1:10 → 1:1) to give **4a** [28.5 mg, 98.5 μmol, 87%, (*E*)/(*Z*) > 98:2] as yellow crystals.

(*E*)-5-(Ethoxycarbonylmethylidene)-3-hydroxy-1-(4-methoxyphenyl)-2,5-dihydropyrrol-2-one (4a): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.30 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 3.79 (s, 3 H, OCH_3), 4.20 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 5.62 (s, 1 H, CH-CO), 6.85 (br. s, 1 H, OH), 6.90 (d, *J* = 8.9 Hz, AA′, 2 H, Ar), 7.12 (d, *J* = 9.0 Hz, XX′, 2 H, Ar), 7.21 (s, 1 H, C-4) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.24 (OCH_2CH_3), 55.50 (OCH_3), 60.32 (OCH_2CH_3), 96.16 (C=*C*H-CO), 99.66 (C-4), 114.90 (C-3′, C-5′), 120.16 (C-2′, C-6′), 131.81 (C-1′), 134.42 (C-3), 156.35 (C-4′), 162.05 (C-5), 166.20 (C-2), 166.48 (CO_2Et) ppm. IR (KBr): $\tilde{\nu}$ = 3151 (w), 3070 (w), 2981 (w), 2934 (w), 2839 (w), 1777 (s), 1708 (s), 1645 (s), 1622 (s), 1619 (s), 1531 (s), 1512 (s), 1464 (m), 1443 (m), 1400 (m), 1351 (m), 1299 (m), 1261 (s), 1230 (s), 1176 (m), 1140 (s), 1083 (s), 1036 (s), 933 (w), 816 (m), 772 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 388.6 (4.25), 287.4 (3.92), 236.2 (4.23) nm. MS (EI, 70 eV): *m*/*z* (%) = 289 (100) [M^+], 244 (20), 217 (44), 174 (8); the exact molecular mass *m*/*z* = 289.0950 (±2 mD) [M^+] of $C_{15}H_{15}NO_5$ was confirmed by HRMS (EI, 70 eV). $C_{15}H_{15}NO_5$ (289.29): calcd. C 62.28, H 5.23, N 4.84; found C 62.44, H 5.00, N 4.69.

(*E*)-5-(Ethoxycarbonylmethylidene)-3-hydroxy-1-phenyl-2,5-dihydropyrrol-2-one (4b): Starting from **3b** (31 mg, 92.7 μmol), **4b** was isolated as a yellow solid (22 mg, 84.9 μmol, 92%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.32 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 4.23 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 5.69 (s, 1 H, CH-CO), 6.92 (br. s, 1 H, OH), 7.00−7.24 (m, 3 H, Ar), 7.30−7.41 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.27 (OCH_2CH_3), 60.46 (OCH_2CH_3), 97.03 (*C*H-CO), 101.27 (C-4), 118.18, 124.05, 129.76 (CH, Ph), 133.59, 138.67, 161.77 (C), 166.22 (NCO), 166.38 (CO_2Et) ppm. IR (KBr): $\tilde{\nu}$ = 3341 (s), 3299 (w), 3076 (w), 2927 (w), 2853 (w), 1782 (s), 1707 (s), 1647 (s), 1620 (s), 1597 (s), 1542 (m), 1499 (m), 1448 (w), 1403 (w), 1381 (w), 1274 (s), 1235 (w), 1143 (s), 1083 (s), 1040 (m), 804 (m), 752 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 376.2 (4.27), 278.0 (3.79), 241.7 (4.06) nm. MS (EI, 70 eV): *m*/*z* (%) = 259 (100) [M^+], 214 (35), 187 (72); the exact molecular mass *m*/*z* = 259.0845 (±2 mD) [M^+] of $C_{14}H_{13}NO_4$ was confirmed by HRMS (EI, 70 eV).

(*E*)-5-(Ethoxycarbonylmethylidene)-3-hydroxy-1-(4-tolyl)-2,5-dihydropyrrol-2-one (4c): Starting from **3c** (36 mg, 99.3 μmol), **4c** was isolated as a yellow solid (18 mg, 65.9 μmol, 66%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.32 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.33 (s, 3 H, Me_{Tol}), 4.23 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 5.67 (s, 1 H, CH-CO), 6.82 (br. s, 1 H, OH), 7.05−7.31 (m, 5 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.28 (OCH_2CH_3), 20.82 (CH_3, Tol), 60.40 (OCH_2CH_3), 96.62 (*C*H-CO), 100.61 (C-4), 118.28, 130.25 (CH, Tol), 133.85, 133.93, 133.96, 136.13 (C), 161.95 (NCO), 161.97 (CO_2Et) ppm. IR (KBr): $\tilde{\nu}$ = 3131 (w), 3067 (w), 3038 (w), 2977 (w), 2924 (w), 2857 (w), 1779 (s), 1710 (s), 1610 (s), 1540 (s), 1516 (s), 1427 (m), 1399 (m), 1342 (m), 1270 (s), 1232 (s), 1161 (m), 1140 (s), 1109 (m), 1081 (s), 1038 (m), 821 (m), 803 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 385.6 (4.18), 286.4 (3.77), 245.1 (4.14) nm. MS (EI, 70 eV): *m*/*z* (%) = 273 (100) [M^+], 228 (24), 201 (50); the exact molecular mass *m*/*z* = 273.1001 (±2 mD) [M^+] of $C_{15}H_{15}NO_4$ was confirmed by HRMS (EI, 70 eV).

(*E*)-3-Hydroxy-1-(4-tolyl)-5-[*N*-(2-tolyl)carbamoylmethylidene]-2,5-dihydropyrrol-2-one (4d): Starting from **3d** (73 mg, 172.4 μmol), **4d** was isolated as a yellow solid (36 mg, 107.7 μmol, 63%). ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 2.28 (s, 3 H, Me-Tol), 2.30 (s, 3 H, Me-Tol), 6.04 (s, 1 H, CH-CO), 7.03−7.31 (m, 7 H, Tol), 7.53 (s, 1 H, C-4), 7.77 (d, 1 H, Ar), 8.25 (br. s, 1 H, OH), 8.74 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]acetone, 50.3 MHz): δ = 18.08, 20.74 (Me_{Tol}), 99.30 (*C*H-CO), 101.64 (C-4), 119.34 (*p*-Tol), 124.15, 125.49, 126.71 (*o*-Tol), 130.60 (*p*-Tol), 131.00 (*o*-Tol), 133.56, 134.69, 137.29, 138.28, 160.76, 164.30, 165.12, 166.01 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3336 (s), 3298 (m), 3035 (w), 2960 (w), 2924 (m), 2855 (w), 1781 (s), 1638 (s), 1612 (s), 1527 (s), 1454 (s), 1297 (m), 1263 (s), 1220 (m), 1087 (s), 815 (m), 799 (m), 748 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 384.7 (4.36), 286.4 (3.93), 245.7 (4.27) nm. MS (EI, 70 eV): *m*/*z* (%) = 334 (42) [M^+], 228 [M − NHTol]$^+$ (100), 107 (40); the exact molecular mass *m*/*z* = 334.1317 (±2 mD) [M^+] of $C_{20}H_{18}N_2O_3$ was confirmed by HRMS (EI, 70 eV).

(*E*)-5-(*N*,*N*-Diethylcarbamoylmethylidene)-3-hydroxy-1-phenyl-2,5-dihydropyrrol-2-one (4e): Starting from the (*E*)-isomer of **3e** (43 mg,

119 μmol), **4e** was isolated as a yellow solid [32 mg, 111.8 μmol, 94%, (*E*)/(*Z*) > 98:2]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.14−1.25 (m, 6 H, NCH_2CH_3), 3.34−3.50 (m, 4 H, NCH_2CH_3), 6.01 (s, 1 H, CH-CO), 6.87 (br. s, 1 H, OH), 7.03−7.36 (m, 5 H, Ph), 7.55 (s, 1 H, C-4) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 13.26, 14.85 (NCH_2CH_3), 40.83, 42.75 (NCH_2CH_3), 96.90 (*C*H-CO), 102.71 (C-4), 117.88, 123.49, 129.60 (CH, Ph), 132.80, 138.96, 160.04 (C), 164.74, 166.50 (NCO) ppm. IR (KBr): $\tilde{\nu}$ = 3058 (w), 2978 (w), 2931 (w), 1783 (s), 1626 (s), 1595 (s), 1542 (m), 1496 (m), 1483 (m), 1463 (m), 1445 (m), 1377 (m), 1363 (m), 1266 (s), 1185 (m), 1135 (w), 1087 (m), 1072 (m), 820 (w), 753 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 370.5 (4.23), 278.0 (3.79), 242.3 (4.06) nm. MS (EI, 70 eV): *m*/*z* (%) = 286 (100) [M$^+$], 214 [M − NEt_2]$^+$ (78), 187 [M − $CONEt_2$]$^+$ (28). $C_{16}H_{18}N_2O_3$ (286.32): calcd. C 67.12, H 6.34, N 9.78; found C 66.88, H 6.64, N 9.71.

(*E*)-5-[1-(Ethoxycarbonyl)ethylidene]-3-hydroxy-1-phenyl-2,5-dihydropyrrol-2-one (4f): Starting from **3f** (44 mg, 126.3 μmol), **4f** was isolated as a yellow solid (33 mg, 120.8 μmol, 96%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.34 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.05 (s, 3 H, Me), 4.28 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.61 (s, 1 H, CH-CO), 6.85 (br. s, 1 H, OH), 7.07−7.15 (m, 3 H, Ar), 7.36−7.42 (m, 2 H, Ar), 7.67 (d, ^3J = 7.8 Hz, 1 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 13.78, 14.27 (CH_3), 60.99 (OCH_2CH_3), 101.37 (C-4), 105.51 (C), 117.96, 123.65, 129.72 (CH, Ph), 131.94, 139.17, 152.71 (C), 165.91 (NCO), 166.84 (CO_2Et) ppm. IR (KBr): $\tilde{\nu}$ = 3136 (w), 3060 (w), 3020 (w), 2980 (w), 2929 (w), 2905 (w), 1772 (s), 1702 (s), 1670 (s), 1628 (s), 1619 (s), 1600 (s), 1532 (m), 1504 (m), 1446 (m), 1366 (w), 1304 (s), 1262 (m), 1232 (m), 1219 (m), 1129 (m), 1076 (s), 770 (w), 749 (m), 687 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 372.8 (4.17), 284.2 (3.78), 242.0 (4.06) nm. MS (EI, 70 eV): *m*/*z* (%) = 273 (100) [M$^+$], 228 (20), 201 (20); the exact molecular mass *m*/*z* = 273.1001 (±2 mD) [M$^+$] of $C_{15}H_{15}NO_4$ was confirmed by HRMS (EI, 70 eV). $C_{15}H_{15}NO_4$ (273.29): calcd. C 65.93, H 5.53, N 5.13; found C 65.77, H 5.62, N 4.97.

(*Z*)-3-Hydroxy-5-(methoxycarbonylmethylidene)-4-methyl-1-phenyl-2,5-dihydropyrrol-2-one (4h): Starting from **3h** (67 mg, 200.0 μmol), **4h** was isolated as a yellow solid (51.7 mg, 200.0 μmol, 100%, pure compound without purification). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.72 (s, 3 H, Ar-CH_3), 3.77 (s, 3 H, OMe), 5.30 (s, 1 H, CH-CO), 6.47 (br. s, 1 H, OH), 7.01 (d, ^3J = 8.0 Hz, 2 H, Ph), 7.12 (t, ^3J = 7.4 Hz, 2 H, Ph), 7.33 (t, ^3J = 7.5 Hz, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 10.25 (CH_3), 51.55 (OCH_3), 93.71 (*C*H-CO), 115.14 (C), 122.00, 124.73, 129.18 (CH, Ph), 130.70, 138.59, 159.37 (C), 164.33 (NCO), 166.13 (CO_2Me) ppm. IR (KBr): $\tilde{\nu}$ = 3264 (s), 3119 (w), 3050 (w), 3036 (w), 2947 (w), 2927 (w), 1785 (s), 1696 (s), 1662 (m), 1620 (s), 1595 (s), 1532 (s), 1493 (m), 1451 (m), 1427 (m), 1344 (s), 1299 (m), 1191 (s), 1151 (s), 1035 (m), 831 (m), 755 (w), 697 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 375.5 (4.16), 272.2 (3.92), 246.2 (4.06) nm. MS (EI, 70 eV): *m*/*z* (%) = 259 (100) [M$^+$], 228 (16), 199 (50), 130 (30), 77 (44); the exact molecular mass *m*/*z* = 259.0845 (±2 mD) [M$^+$] of $C_{14}H_{13}NO_4$ was confirmed by HRMS (EI, 70 eV). $C_{14}H_{13}NO_4$ (259.26): calcd. C 64.86, H 5.05, N 5.40; found C 65.05, H 5.33, N 5.22.

(*Z*)-5-(Ethoxycarbonylmethylidene)-4-ethyl-3-hydroxy-1-phenyl-2,5-dihydropyrrol-2-one (4i): Starting from **3i** (128 mg, 353 μmol), **4i** was isolated as a yellow solid (64 mg, 223 μmol, 63%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.84 (t, ^3J = 7.5 Hz, 3 H, CCH_2CH_3), 1.30 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.15 (q, ^3J = 7.5 Hz, 2 H, CCH_2CH_3), 4.23 (q, ^3J = 7.1 Hz, 2 H, CCH_2CH_3), 5.32 (s, 1 H, CH-CO), 6.42 (br. s, 1 H, OH), 7.05 (d, ^3J = 7.8 Hz, 2 H, Ph), 7.15 (t, ^3J = 7.4 Hz, 1 H, Ph), 7.34 (t, ^3J = 7.8 Hz, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 12.54 (CCH_2CH_3), 14.23 (OCH_2CH_3), 17.21 (CCH_2CH_3), 60.44 (OCH_2CH_3), 94.17 (*C*H-CO), 120.69 (C), 122.43, 125.07, 129.13 (CH, Ph), 129.99, 138.44, 158.35 (C), 163.92 (NCO), 166.31 (CO_2Et) ppm. IR (KBr): $\tilde{\nu}$ = 3356 (s), 3069 (w), 3039 (w), 2980 (m), 2939 (w), 2877 (w), 1776 (s), 1718 (s), 1696 (s), 1662 (s), 1626 (s), 1596 (s), 1528 (s), 1497 (m), 1448 (m), 1385 (w), 1366 (m), 1331 (s), 1261 (m), 1172 (s), 1145 (s), 1046 (s), 824 (m), 778 (w), 753 (m), 699 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 373.7 (4.16), 272.4 (3.92), 234.0 (4.18) nm. MS (EI, 70 eV): *m*/*z* (%) = 287 (100) [M$^+$], 242 (20), 213 (76); the exact molecular mass *m*/*z* = 287.1158 (±2 mD) [M$^+$] of $C_{15}H_{15}NO_4$ was confirmed by HRMS (EI, 70 eV). $C_{16}H_{17}NO_4$ (287.31): calcd. C 66.89, H 5.96, N 4.88; found C 66.57, H 6.21, N 4.77.

(*E*)-3-Hydroxy-5-(2-oxotetrahydrofuran-3-ylidene)-1-phenyl-2,5-dihydropyrrol-2-one (4j): Starting from **3j** (62 mg, 187 μmol), **4j** was isolated as a yellow solid (48 mg, 187 μmol, 100%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.20 (t, ^3J = 7.3 Hz, 2 H, OCH_2CH_2), 4.46 (t, ^3J = 7.4 Hz, 2 H, OCH_2CH_2), 6.82 (br. s, 1 H, OH), 7.09−7.18 (m, 3 H, Ar), 7.36−7.42 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 25.95 (OCH_2CH_2), 65.83 (OCH_2CH_2), 100.47 (C-4), 101.90 (C), 118.06, 123.99, 129.81 (CH, Ph), 132.23, 138.64, 155.87 (C), 166.23 (NCO), 170.81 (CO_2R) ppm. IR (KBr): $\tilde{\nu}$ = 3284 (s), 3137 (m), 3086 (w), 2974 (w), 2916 (w), 2907 (w), 1795 (s), 1739 (s), 1665 (s), 1632 (s), 1615 (s), 1595 (s), 1550 (m), 1501 (m), 1446 (m), 1376 (m), 1324 (m), 1296 (w), 1248 (m), 1229 (s), 1207 (s), 1182 (m), 1090 (m), 1030 (s), 1002 (s), 954 (m), 814 (m), 770 (m), 751 (m), 695 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 383.9 (4.38), 287.0 (3.77), 238.1 (4.22) nm. MS (EI, 70 eV): *m*/*z* (%) = 257 (100) [M$^+$], 199 (24), 117 (20); the exact molecular mass *m*/*z* = 257.0688 (±2 mD) [M$^+$] of $C_{14}H_{11}NO_4$ was confirmed by HRMS (EI, 70 eV). $C_{14}H_{11}NO_4$ (257.24): calcd. C 65.37, H 4.31, N 5.44; found C 65.60, H 4.21, N 5.30.

(*E*)-3-Hydroxy-4-methyl-5-(2-oxotetrahydrofuran-3-ylidene)-1-phenyl-2,5-dihydropyrrol-2-one (4k): Starting from **3k** (663 mg, 1.914 mmol), **4k** was isolated as a yellow solid (267.2 mg, 985 μmol, 52%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.12 (s, 3 H, CH_3), 3.25 (t, ^3J = 7.3 Hz, 2 H, OCH_2CH_2), 4.43 (t, ^3J = 7.4 Hz, 2 H, OCH_2CH_2), 6.22 (br. s, 1 H, OH), 6.95 (d, ^3J = 7.9 Hz, 2 H, Ph), 7.09 (t, ^3J = 7.4 Hz, 1 H, Ph), 7.32 (d, ^3J = 7.6 Hz, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 14.10 (CH_3), 28.32 (OCH_2CH_2), 65.63 (OCH_2CH_2), 106.29, 118.76 (C), 120.54, 123.96, 129.14 (CH, Ph), 132.01, 138.78, 155.70 (C), 165.43 (NCO), 168.10 (CO_2R) ppm. IR (KBr): $\tilde{\nu}$ = 3336 (s), 3053 (w), 3009 (w), 2966 (w), 2926 (m), 2853 (w), 1783 (s), 1739 (s), 1647 (s), 1609 (s), 1593 (s), 1521 (s), 1493 (m), 1450 (m), 1374 (m), 1253 (m), 1209 (s), 1179 (s), 1101 (m), 1047 (s), 1015 (s), 990 (s), 955 (m), 757 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 391.0 (4.14), 286.5 (3.96), 244.0 (4.13) nm. MS (EI, 70 eV): *m*/*z* (%) = 271 (100) [M$^+$], 226 (16), 131 (16); the exact molecular mass *m*/*z* = 271.0845 (±2 mD) [M$^+$] of $C_{15}H_{13}NO_4$ was confirmed by HRMS (EI, 70 eV). $C_{15}H_{13}NO_4$ (271.27): calcd. C 66.41, H 4.83, N 5.16; found C 66.31, H 5.00, N 4.99.

(*E*)-3-Hydroxy-5-(5-methyl-2-oxotetrahydrofuran-3-ylidene)-1-phenyl-2,5-dihydropyrrol-2-one (4l): Starting from **3l** (64 mg, 185 μmol), **4l** was isolated as a yellow solid (50 mg, 185 μmol, 100%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.46 (d, ^3J = 6.3 Hz, 3 H, CH_3), 2.71 & 2.79 (2 d, *J* = 5.9 Hz, 1 H, CH_2), 3.30 & 3.36 (2 d, *J* = 7.8 Hz, 1 H, CH_2), 4.76 (m, 1 H, C*H*-CH_3), 6.81 (br. s, 1 H, OH), 7.09−7.24 (m, 3 H, Ar), 7.36−7.69 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 22.13 (CH_3), 33.63 (CH_2),

74.55 (*C*H-CH_3), 100.81 (C-4), 103.20 (C), 118.21, 124.04, 129.82 (CH, Ph), 132.43, 138.86, 155.68 (C), 166.22 (NCO), 170.14 (CO_2R) ppm. IR (KBr): $\tilde{\nu}$ = 3342 (s), 3138 (w), 2981 (w), 1776 (s), 1730 (s), 1666 (s), 1628 (s), 1597 (s), 1519 (m), 1445 (m), 1343 (m), 1225 (s), 1205 (s), 1075 (m), 1000 (m), 940 (w), 819 (w), 770 (w), 755 (w), 700 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 384.0 (4.00), 279.9 (3.72), 246.6 (3.85) nm. MS (EI, 70 eV): *m*/*z* (%) = 271 (75) [M^+], 240 (84), 199 (55), 154 (10), 121 (40), 93 (100), 77 (60); the exact molecular mass *m*/*z* = 271.0845 (±2 mD) [M^+] of $C_{15}H_{13}NO_4$ was confirmed by HRMS (EI, 70 eV).

(*E*)-5-(5-Ethyl-2-oxotetrahydrofuran-3-ylidene)-3-hydroxy-1-phenyl-2,5-dihydropyrrol-2-one (4m): Starting from **3m** (70 mg, 194 μmol), **4m** was isolated as a yellow solid (55 mg, 192 μmol, 99%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.96 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.70 (m, 2 H, CH_2CH_3), 2.68 & 2.77 (2 d, *J* = 5.8 Hz, 1 H, CCH_2CH), 3.17 & 3.26 (2 d, *J* = 7.9 Hz, 1 H, CCH_2CH), 4.51 (quint., ^3J = 6.6 Hz, 1 H, CCH_2CH), 6.70 (br. s, 1 H, OH), 7.02−7.19 (m, 3 H, Ar), 7.30−7.40 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 8.85 (CH_2CH_3), 29.17 (CH_2CH_3), 31.40 (CCH_2CH), 79.21 (CH_2CH), 100.69 (C-4), 103.06 (C), 118.14, 123.88, 129.70 (CH, Ph), 132.33, 138.82, 155.50 (C), 166.12 (NCO), 170.16 (CO_2R) ppm. IR (KBr): $\tilde{\nu}$ = 3281 (m), 3137 (w), 2965 (w), 2935 (w), 1794 (s), 1738 (s), 1666 (s), 1634 (s), 1599 (s), 1547 (m), 1501 (m), 1447 (m), 1351 (s), 1324 (m), 1300 (w), 1283 (w), 1250 (m), 1228 (s), 1210 (s), 1182 (m), 1088 (m), 1070 (m), 1006 (s), 965 (m), 811 (w), 770 (w), 752 (m), 688 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 384.0 (4.31), 274.7 (4.14) nm. MS (EI, 70 eV): *m*/*z* (%) = 285 (100) [M^+], 256 (8), 228 (12), 199 (100), 154 (20); the exact molecular mass *m*/*z* = 285.1001 (±2 mD) [M^+] of $C_{16}H_{15}NO_4$ was confirmed by HRMS (EI, 70 eV). $C_{16}H_{15}NO_4$ (285.30): calcd. C 67.36, H 5.30, N 4.91; found C 67.23, H 5.52, N 5.03.

(*E*)-3-Hydroxy-1-(4-methoxyphenyl)-5-(2-oxo-2,3-dihydrobenzofuran-3-ylidene)-2,5-dihydropyrrol-2-one (4n): Starting from **3n** (64 mg, 144 μmol), **4n** was isolated as a red solid (20 mg, 60 μmol, 42%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.82 (s, 3 H, OMe), 6.90−7.00 (m, 3 H, Ar & OH), 7.03−7.35 (m, 6 H, Ar), 7.80 (d, ^3J = 7.4 Hz, 1 H, Ar) ppm. ^{13}C NMR ([D_6]DMSO, 50.3 MHz): δ = 55.43 (OCH_3), 96.05 (C-4), 110.29 (CH, Ar), 114.92, 121.60 (PMP), 122.40 (CH, Ar), 122.61 (C), 123.85, 128.21 (CH, Ar), 132.18, 137.14, 137.41, 150.70, 155.83, 155.99 (C), 160.01 (NCO), 164.17 (CO_2R) ppm. IR (KBr): $\tilde{\nu}$ = 3273 (m), 3068 (w), 3001 (w), 2960 (m), 2924 (m), 2853 (m), 1795 (s), 1739 (s), 1654 (m), 1625 (s), 1577 (s), 1509 (s), 1461 (m), 1349 (m), 1328 (m), 1265 (m), 1244 (s), 1142 (s), 1092 (m), 1035 (m), 982 (s), 829 (m), 802 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 469.5 (4.44), 247.5 (4.18) nm. MS (EI, 70 eV): *m*/*z* (%) = 335 (100) [M^+], 291 (4), 174 (6), 147 (38); the exact molecular mass *m*/*z* = 335.0794 (±2 mD) [M^+] of $C_{19}H_{13}NO_5$ was confirmed by HRMS (EI, 70 eV).

(*E*)-3-Hydroxy-5-(1-methyl-2-oxo-2,3-dihydroindol-3-ylidene)-1-phenyl-2,5-dihydropyrrol-2-one (4o): Starting from **3o** (85 mg, 215 μmol), **4o** was isolated as a red solid (66 mg, 207 μmol, 97%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.26 (s, 3 H, nme), 6.81 (d, ^3J = 7.7 Hz, 1 H, Ar), 6.98 (br. s, 1 H, OH), 7.02−7.27 (m, 6 H, Ar), 7.37−7.43 (m, 2 H, Ar), 7.71 (s, 1 H, Ar, C-4), 7.81 (d, ^3J = 7.3 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 25.90 (NMe), 101.81 (C-4), 105.73 (C), 107.87, 118.15 (CH), 120.99 (C), 122.42, 124.14, 124.44, 128.60, 129.82 (CH, Ar), 132.73, 138.59, 141.90, 155.52 (C), 166.16, 167.79 (NCO) ppm. IR (KBr): $\tilde{\nu}$ = 3330 (s), 3263 (m), 3057 (w), 1781 (s), 1698 (s), 1644 (s), 1619 (s), 1587 (s), 1539 (m), 1499 (m), 1485 (m), 1470 (m), 1447 (m), 1374 (m), 1274 (s), 1231 (m), 1179 (m), 1137 (m), 1080 (s), 972 (m), 952 (m), 746 (s) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 425.3 (4.39), 274.1 (4.24) nm. MS (EI, 70 eV): *m*/*z* (%) = 318 (100) [M^+], 272 (4), 173 (32), 117 (24); the exact molecular mass *m*/*z* = 318.1004 (±2 mD) [M^+] of $C_{19}H_{14}N_2O_3$ was confirmed by HRMS (EI, 70 eV).

3-Hydroxy-1-(4-methoxyphenyl)-2,4,5,6-tetrahydro-1*H*-indole-2,6-dione (4p): Starting from **3p** (39 mg, 103 μmol), **4p** was isolated as an orange solid (14 mg, 52 μmol, 50%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.82 (s, 3 H, OMe), 6.90−7.00 (m, 3 H, Ar + OH), 7.03−7.35 (m, 6 H, Ar), 7.80 (d, ^3J = 7.4 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 20.35 (CH_2), 35.89 (CH_2), 55.55 (OCH_3), 104.14 (*C*H−CO), 110.14 (C), 114.54 (PMP), 125.56 (PMP), 129.65, 130.44, 158.08, 165.22 (C), 165.45 (NCO), 196.85 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3273 (m), 3038 (w), 3009 (w), 2955 (m), 2923 (m), 2852 (m), 1798 (s), 1745 (w), 1645 (s), 1605 (s), 1520 (s), 1465 (m), 1417 (m), 1393 (s), 1317 (m), 1287 (m), 1242 (s), 1206 (m), 1184 (m), 1166 (s), 1028 (m), 990 (m), 827 (m), 763 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 382.0 (3.99), 281.0 (3.82), 247.5 (3.98) nm. MS (EI, 70 eV): *m*/*z* (%) = 271 (100) [M^+], 256 (12), 214 (4), 200 (8); the exact molecular mass *m*/*z* = 271.0845 (±2 mD) [M^+] of $C_{15}H_{13}NO_4$ was confirmed by HRMS (EI, 70 eV).

3-Hydroxy-1-(4-methoxyphenyl)-4,4-dimethyl-2,4,5,6-tetrahydro-1*H*-indole-2,6-dione (4q): Starting from **3q** (63 mg, 156 μmol), **4q** was isolated as an orange solid (28 mg, 93 μmol, 60%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.08 (s, 6 H, Me), 2.35 (s, 2 H, CH_2), 3.74 (s, 3 H, OMe), 5.75 (s, 1 H, CH-CO), 6.05 (br. s, 1 H, OH), 6.81 (d, ^3J = 8.8 Hz, 2 H, AA′, PMP), 7.00 (d, ^3J = 8.9 Hz, 2 H, XX′, PMP) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 27.40 (CH_3), 29.64 (CH_2), 53.51 (CMe_2), 55.46 (OCH_3), 103.56 (*C*H−CO), 114.43 (PMP), 123.73 (C), 125.84 (PMP), 130.11, 132.42, 157.91, 163.75 (C), 164.79 (NCO), 196.94 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3334 (m), 3295 (m), 2959 (m), 2925 (s), 2853 (m), 1798 (s), 1660 (s), 1617 (s), 1513 (s), 1464 (m), 1418 (m), 1396 (m), 1382 (m), 1365 (m), 1295 (s), 1240 (s), 1179 (m), 1108 (m), 1031 (s), 1012 (s), 953 (w), 827 (m), 750 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 393.5 (3.93), 289.0 (3.92), 247.2 (3.94) nm. MS (EI, 70 eV): *m*/*z* (%) = 299 (100) [M^+], 284 (24), 256 (16), 228 (12); the exact molecular mass *m*/*z* = 299.1158 (±2 mD) [M^+] of $C_{17}H_{17}NO_4$ was confirmed by HRMS (EI, 70 eV).

(*E*)-5-(Cyanomethylidene)-1-(4-tolyl)-3-(4-tolylamino)-2,5-dihydropyrrol-2-one (6a): Starting from 5-methylisoxazole (499 mg, 0.49 mL, 6.0 mmol), **6a** was isolated as a yellow solid (830 mg, 44%, *E*/*Z* = 10:1). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.33, 2.36 (s, 6 H, Tol-CH_3), 4.47 (s, 1 H, C*H*CN), 6.11 (s, 1 H, 4-H), 7.00−7.60 (m, 8 H, Tol) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 20.82, 21.20 (Tol-CH_3), 66.77 (CH, *C*HCN), 95.20 (CH, C-4), 116.18 (C, CN), 118.70, 125.63, 129.79, 130.20 (CH, Tol), 133.79, 136.46, 137.10 (C, C-3, Tol-C to CH_3), 139.75, 140.42 (C, Tol-C to N), 148.92 (C, C-2), 167.89 (C, C-5) ppm. IR (KBr): $\tilde{\nu}$ = 3360 (s), 3202 (m), 3075 (s), 3030 (s), 2920 (s), 2202 (s, CN), 1697 (m), 1639 (s), 1610 (s), 1531 (s), 1430 (m), 1321 (m), 1239 (m), 1080 (m), 952 (m) cm^{-1}. MS-FAB: *m*/*z* (%) = 316 [M + 1]$^+$. $C_{20}H_{17}N_3O$ (315.36): calcd. C 76.17, H 5.43, N 13.32; found C 76.00, H 5.53, N 13.00.

(*E*)-5-(Cyanomethylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (6b): Starting from 5-methylisoxazole (499 mg, 0.49 mL, 6.0 mmol), **6b** was isolated as a yellow solid (688 mg, 40%, *E*/*Z* = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.52 (s, 1 H, C*H*CN), 6.21 (s, 1 H, 4-H), 7.10−7.60 (m, 10 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 67.60 (CH, C*H*CN), 96.02 (CH, C-4), 115.89 (C, CN), 118.52, 124.03, 125.63, 127.02, 129.21, 129.90 (CH, Ph), 138.91, 140.10, 142.30 (C, C-3, Ph), 149.50 (C, C-2), 167.59 (C, C-5) ppm. IR (KBr): $\tilde{\nu}$ = 3366 (m), 3306 (w), 3070 (w), 2202 (s, CN), 1696 (s), 1669 (m), 1619 (s), 1592 (s), 1515 (s),

1492 (m), 1447 (m), 1320 (m), 1238 (m), 1174 (m), 1074 (m), 1027 (w), 996 (w), 950 (m), 794 (m), 773 (m), 747 (m), 691 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 370.3 (4.36), 245.4 (4.30) nm. MS-FAB: *m*/*z* (%) = 288 $[M + 1]^+$. $C_{18}H_{13}N_3O$ (287.30): calcd. C 75.25, H 4.56, N 14.62; found C 75.27, H 4.74, N 14.43.

(*E*)-5-(Cyanomethylidene)-3-hydroxy-1-(4-tolyl)-2,5-dihydropyrrol-2-one (7a): Starting from **6a** (22 mg, 69.8 μmol), **7a** was isolated as a yellow solid (10 mg, 44 μmol, 63%). ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.32 (s, 3 H, Me-Tol), 4.74 (s, 1 H, CH-CN), 6.33 (s, 1 H, C-4), 6.82 (br. s, 1 H, OH), 7.04 (d, ^3J = 8.5 Hz, 2 H, AA′, *p*-Tol), 7.20 (d, ^3J = 8.5 Hz, 2 H, XX′, *p*-Tol) ppm. ^{13}C NMR ($CDCl_3$, 150.8 MHz): δ = 20.87 (CH_3), 73.04 (*C*H-CN), 99.27 (C-4), 114.46 (CN), 118.73 (*p*-Tol), 130.40 (*p*-Tol), 134.66, 134.78, 135.66, 163.16 (C), 164.78 (NCO) ppm. IR (KBr): $\tilde{\nu}$ = 3353 (s), 3066 (w), 3033 (w), 2959 (w), 2922 (w), 2852 (w), 2211 (s, CN), 1785 (s), 1652 (m), 1630 (s), 1526 (m), 1512 (m), 1412 (w), 1330 (m), 1257 (m), 1235 (m), 1082 (m), 943 (m), 827 (w), 804 (s) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 380.0 (3.23), 282.5 (2.65), 228.5 (3.15), 200.5 (3.19) nm. MS (EI, 70 eV): *m*/*z* (%) = 226 (100) $[M^+]$, 221 (12), 198 (10), 182 (16), 167 (20), 131 (20), 116 (12), 91 (12); the exact molecular mass *m*/*z* = 226.0742 (±2 mD) $[M^+]$ of $C_{13}H_{10}N_2O$ was confirmed by HRMS (EI, 70 eV).

(*E*)- and (*Z*)-5-(Cyanomethylidene)-3-hydroxy-1-phenyl-2,5-dihydropyrrol-2-one (7b): Starting from **6b** (92 mg, 318 μmol), **7b** was isolated as a yellow solid [35 mg, 165 μmol, 52%, (*E*)/(*Z*)= 1:1]. ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.91 [s, 1 H, CH-CN, (*Z*) isomer], 5.24 [s, 1 H, CH-CN, (*E*) isomer], 6.55 [s, 1 H, C-4, (*Z*) isomer], 6.82 [s, 1 H, C-4, (*E*) isomer], 7.13−7.40 (m, 4 H, Ph & OH), 7.40−7.60 (m, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, (*E*)/(*Z*) = 1:1): δ = 73.48, 74.86 (*C*H−CN), 98.79, 99.92 (C-4), 114.05, 115.80 (CN), 118.59, 118.66 (Ph), 124.77, 124.92 (Ph), 129.90, 129.97 (Ph), 134.10, 134.15 (C), 138.20, 138.30 (C), 163.01, 164.90 (C), 165.10, 165.30 (NCO) ppm. IR (KBr): $\tilde{\nu}$ = 3330 (m), 3073 (m), 3021 (w), 2961 (w), 2923 (w), 2853 (w), 2219 (m, CN), 2209 (m, CN), 1789 (s), 1625 (s), 1592 (s), 1543 (m), 1501 (m), 1492 (w),1447 (m), 1323 (m), 1295 (m), 1282 (m), 1234 (m), 1181 (m), 1110 (m), 1092 (m), 949 (m), 795 (m), 755 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 374.0 (4.35), 280.0 (3.73), 228.0 (4.23), 199.5 (4.26) nm. MS (EI, 70 eV): *m*/*z* (%) = 212 (100) $[M^+]$, 184 (12), 167 (8), 117 (32); the exact molecular mass *m*/*z* = 212.0586 (±2 mD) $[M^+]$ of $C_{12}H_8N_2O_2$ was confirmed by HRMS (EI, 70 eV). $C_{12}H_8N_2O_2$ (212.20): calcd. C 67.92, H 3.80, N 13.20; found C 67.63, H 4.07, N 13.18.

(*E*/*Z*)-5-(2-Phenyliminopropylidene)-3-(4-tolylamino)-2-(4-tolylimino)-2,5-dihydrofuran (9): Starting from 4-(phenylimino)pentan-2-one (1.04 g, 6.0 mmol), **9** was isolated as a deep-yellow solid [1.10 g, 45%, 1:1 mixture of (*E*)/(*Z*)*Z* isomers]. ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.14, 2.24, 2.33/2.28, 2.33, 2.54 [s, 9 H, C(NPh)CH_3, Tol-CH_3], 5.19/5.61 [s, 1 H, C*H*(NPh)CH_3, both isomers], 5.89/6.16 (s, 1 H, 4-H, both isomers), 6.70−7.50 (m, 14 H, Ar, NH) ppm. ^{13}C NMR ([D$_8$]THF, 50 MHz): δ = 19.68/20.71, 20.99/21.03, 21.41/27.51 [Tol-CH_3, C(NPh)*C*H_3], 95.89/97.89, 100.60/100.75 [CH, C-4, *C*HC(NPh)CH_3], 120.45/120.54, 123.13/123.21, 124.91/125.07, 129.20/129.31, 129.36/129.95, 130.04/130.37, 130.42/130.47 (CH, Ar), 132.60/132.68, 132.69/132.96 (C, Tol-C to CH_3), 135.62/135.87, 137.45/137.95, 138.93/139.01 (C, Ph and Tol to N), 142.63/142.65 (C-3), 153.27/153.30 (C, C-2), 159.73/158.32 (C, C-5), 163.97/164.05 [C, *C*(NPh)CH_3] ppm. IR (KBr): $\tilde{\nu}$ = 3362 (m), 3068 (w), 1640 (w); 1620 (s), 1598 (m), 1590 (s), 1450 (m), 1322 (m), 1239 (m), 1172 (m), 1074 (m) cm^{-1}. MS (CI, H_2O): *m*/*z* (%) = 408 $[M + 1]^+$. $C_{27}H_{25}N_3O$ (407.50): calcd. C 79.58, H 6.18, N 10.31; found C 79.18, H 6.56, N 10.95.

(*E*)-5-(2-Phenyliminopropylidene)-1-(4-tolyl)-3-(4-tolylamino)-2,5-dihydropyrrol-2-one (10): A THF solution of **9** (250 mg, 0.61 mmol) was stirred in the presence of LiCl (2 equiv.) for 72 h. The solvent was evaporated in vacuo and the residue was purified by chromatography to give **10** as a red solid (140 mg, 56%). ^1H NMR ([D$_8$]THF, 200 MHz): δ = 1.87, 2.26, 2.41 [s, 9 H, C(NPh)CH_3, Tol-CH_3], 5.49 (s, 1 H, H-3), 6.60−7.35 [m, 14 H, C*H*(NPh)CH_3, Ar], 8.10 (br., 1 H, NH) ppm. ^{13}C NMR ([D$_8$]THF, 50 MHz): δ = 20.65, 21.07, 21.48 [Tol-CH_3, C(NPh)*C*H_3], 97.02, 98.90 [CH, C-3, *C*HC(NPh)CH_3], 118.90, 120.29, 123.24, 129.24, 129.33, 130.02, 130.38 (CH, Ar), 132.27, 132.78 (C, Tol-C to CH_3), 136.79, 138.54, 139.45 (C, Ph and Tol to N), 147.83 (C-4), 153.18 (C, C-2), 164.46 [C, *C*(NPh)CH_3], 166.37 (C, C-5) ppm. MS (CI, H_2O): *m*/*z* (%) = 408 $[M + 1]^+$. $C_{27}H_{25}N_3O$ (407.50): calcd. C 79.58, H 6.18, N 10.31; found C 79.22, H 6.49, N 10.78.

(*E*)-*N*-(4-Methylphenyl)-2-(4-methylphenyl)imino-5-(2-oxo-2-phenylethylidene)-1-phenyl-2,5-dihydro-1*H*-pyrrol-3-amine (12a): Starting from benzoylacetone anile **11** (1.42 g), **12a** was isolated as a yellow solid (985 mg, 35%). ^1H NMR ([D$_8$]THF, 200 MHz): δ = 2.09, 2.34 (s, 6 H, Tol-CH_3), 5.92 (s, 1 H, H-3), 6.43 (d, *J* = 8 Hz, 2 H, Ar), 6.64 (d, *J* = 8 Hz, 2 H, Ar), 7.00−7.80 (m, 15 H, C*H*COPh, Ar), 8.20 (br., 1 H, NH) ppm. ^{13}C NMR ([D$_8$]THF, 50 MHz): δ = 20.65, 20.79 (Tol-CH_3), 95.82 (CH, C-3), 95.44 (CH, *C*HCOPh), 119.51, 121.49, 127.95, 128.11, 128.80, 128.92, 129.36, 130.05, 130.54, 131.81 (CH, Ar), 132.18, 132.83, 137.32 (C, Ar to C), 139.04, 141.60, 142.93, 145.14 (C, C-4, Ar to N), 147.75 (C, C-2), 160.32 (C, C-5), 188.10 (C, *C*OPh) ppm. IR (KBr): $\tilde{\nu}$ = 3325 (w), 3030 (w), 2923 (w), 1630 (s), 1613 (s), 1580 (s), 1555 (s), 1527 (s), 1425 (m), 1350 (m), 1240 (m), 1228 (m), 1180 (m), 1130 (m), 1005 (m) cm^{-1}. MS (CI, H_2O): 470 $[M + 1]^+$. $C_{32}H_{27}N_3O$ (469.57): calcd. C 81.85, H 5.80, N 8.94; found C 81.72, H 5.90, N 9.02.

(*E*)-*N*,1-Diphenyl-2-phenylimino-5-(2-oxo-2-phenylethylidene)-2,5-dihydro-1*H*-pyrrol-3-amine (12b): Starting from **11** (1.42 g), **12b** was obtained as a yellow solid (847 mg, 32%). ^1H NMR ($CDCl_3$, 200 MHz): δ = 5.95 (s, 1 H, H-3), 6.50−7.80 (m, 21 H, C*H*COPh, Ph), 9.35 (br., 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 96.19 (CH, C-3), 95.72 (CH, *C*HCOPh), 118.22, 119.82, 120.85, 122.82, 122.89, 127.54, 127.94, 128.31, 128.80, 129.03, 129.61, 131.62 (CH, Ph), 135.70 (C, Ph to C), 139.79, 140.36, 141.04, 146.04 (C, C-4, Ph to N), 146.84 (C, C-2), 159.67 (C, C-5), 189.51 (C, *C*OPh) ppm. IR (KBr): $\tilde{\nu}$ = 3324 (w), 3030 (w), 2924 (w), 1631 (s), 1613 (s), 1580 (s), 1556 (s), 1527 (s), 1428 (m), 1352 (m), 1240 (m), 1179 (m), 1130 (m) cm^{-1}. MS (FAB): 442 $[M + 1]^+$. $C_{30}H_{23}N_3O$ (441.51): calcd. C 81.61, H 5.25, N 9.51; found C 81.32, H 5.69, N 9.98.

(*E*)-5-(Ethoxycarbonylmethylidene)-1-(4-tolylsulfonyl)-3-(4-tolylsulfonylamino)-2,5-dihydropyrrol-2-one (14): $TiCl_4$ (0.24 mL, 2.20 mmol) was added at −78 °C to a CH_2Cl_2 solution (18 mL) of **13** (300 mg, 1.10 mmol) and **2d** (477 mg, 1.10 mmol). The solution was stirred at −78 °C for 1 h, warmed to 20 °C during 2 h, and then stirred at 20 °C for 1 h before a 1:1 mixture of 10% aqueous hydrochloric acid and brine was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic fractions were dried ($MgSO_4$) and filtered, and then the filtrate was concentrated in vacuo. The residue was purified by chromatography (SiO_2; diethyl ether/PE, 1:10 → 1:1) to give **14** as a yellow solid (81 mg, 15%). ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.35 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 2.45 (s, 6 H, Tol-CH_3), 4.25 (q, *J* = 7 Hz, 2 H, OCH_2), 5.82 (s, 1 H, C*H*CO_2Et), 7.30−7.35 (m, 5 H, Ar, NH), 7.52 (s, 1 H, 4-H), 7.75−7.90 (2 × d, 2 × 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 490 (22) $[M^+]$, 335 (20), 155 (84), 91 (100).

Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius CAD4 diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[36] The structures were solved by direct methods (SHELXS)[37] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[38] The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[38] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 3a:[39] $C_{22}H_{22}N_2O_3$, M_r = 362.42 g·mol^{-1}, colourless prism, size 0.40 × 0.36 × 0.20 mm^3, monoclinic, space group *Cc*, *a* = 13.511(3), *b* = 16.441(3), *c* = 17.418(4) Å, β = 90.27(3)°, *V* = 3869.1(13) Å^3, *T* = −90 °C, *Z* = 8, $\rho_{calcd.}$ = 1.244 g·cm^{-3}, μ(Mo-K_α) = 0.83 cm^{-1}, *F*(000) = 1536, 4455 reflections in *h*(−17/0), *k*(0/21), *l*(−22/21), measured in the range 2.34° ≤ Θ ≤ 27.42°, completeness $\Theta_{max.}$ = 91.4%, 4199 independent reflections, R_{int} = 0.031, 3164 reflections with $F_o > 4\sigma(F_o)$, 487 parameters, 2 restraints, $R1_{obsd.}$ = 0.048, $wR^2_{obsd.}$ = 0.123, $R1_{all}$ = 0.083, wR^2_{all} = 0.148, GOOF = 1.129, Flack-parameter 1.2(16), largest difference peak and hole: 0.254/−0.282 e·Å^{-3}.

Crystal Data for 10:[39] $C_{27}H_{26}N_3O$, M_r = 408.51 g·mol^{-1}, red prism, size 0.40 × 0.38 × 0.36 mm^3, monoclinic, space group $P2_1/c$, *a* = 9.766(2), *b* = 20.643(4), *c* = 12.467(3) Å, β = 112.52(3)°, *V* = 2321.7(8) Å^3, *T* = 20 °C, *Z* = 4, $\rho_{calcd.}$ = 1.169 g·cm^{-3}, μ(Mo-K_α) = 0.72 cm^{-1}, *F*(000) = 868, 4680 reflections in *h*(−11/0), *k*(−25/0), *l*(−14/15), measured in the range 2.26° ≤ Θ ≤ 25.73°, completeness $\Theta_{max.}$ = 99.8%, 4416 independent reflections, R_{int} = 0.065, 1757 reflections with $F_o > 4\sigma(F_o)$, 280 parameters, 0 restraints, $R1_{obsd.}$ = 0.079, $wR^2_{obsd.}$ = 0.186, $R1_{all}$ = 0.229, wR^2_{all} = 0.246, GOOF = 1.204, largest difference peak and hole: 0.225/−0.400 e·Å^{-3}.

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