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Synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones and their ring-transformation into 5,6-dihydrobenzo[*h*]chromones, 5,6,7,8-tetrahydrochromones and pyran-4-ones

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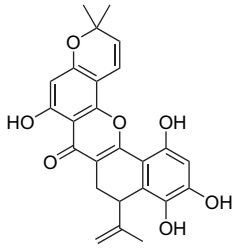
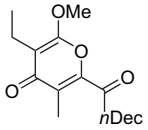
Abstract—Acid-mediated ring-transformations of 5-alkylidene-2,5-dihydropyrrol-2-ones, available by cyclization of 1,3-diketone dianions with bis(imidoyl) dichlorides of oxalic acid, resulted in formation of functionalized pyran-4-ones, such as 5,6-dihydrobenzo[*h*]chromones and 5,6,7,8-tetrahydrochromones.

1. Introduction

Pyran-4-ones (γ-pyrones) and chromones are of pharmacological relevance and occur in a number of natural products.[1] 5,6-Dihydrobenzo[*h*]chromones and 5,6,7,8-tetrahydrochromones are present, for example, in artobiloxanthone,[2] artonol C or in the artonins A, N and T.[3] Monocyclic pyran-4-ones are also present in nature, e.g., in 8-methyl-1′-oxopodopyrone (Scheme 1).[4]



artobiloxanthone



8-methyl-1'-oxopodopyrone

Scheme 1. Pyran-4-one natural products.

Pyran-4-ones have been prepared, for example, by acid-mediated cyclization of 1,3,5-tricarbonyl compounds and the biosynthesis also follows this pathway.[5] Recently, we have reported a convenient approach to functionalized pyran-4-ones, such as 5,6-dihydrobenzo[*h*]chromones and 5,6,7,8-tetrahydrochromones, based on a new ring-trans formation of 5-alkylidene-2,5-dihydropyrrol-2-ones.[6] The starting materials are available by cyclization of 1,3-dicarbonyl dianions with bis(imidoyl) dichlorides of oxalic acid, a reaction recently developed by us.[7,8] Herein, we wish to report full details of this methodology and studies related to the preparative scope. In this context, the synthesis of a variety of new 5-alkylidene-2,5-dihydropyrrol-2-ones and pyran-4-ones is reported.

2. Results and discussion

The cyclization of the dianion of 2-acetyltetralone (**1a**) with oxalic acid–bis(imidoyl) dichlorides **2a–e** afforded the *E*-configured 5-alkylidene-3-arylamino-2,5-dihydropyrrol-2-ones **3a–e**. The formation of **3a–e** proceeds, as previously reported for related reactions of β-ketoester dianions,[7] by *C*,*O*-cyclization (intermediate **A**) and subsequent Dimroth-rearrangement (Schemes 2 and 3, Table 1). Treatment of a THF solution of **3a–e** with an aqueous solution of HCl afforded the unexpected 5,6-dihydrobenzo[*h*]chromones **5a–e** (Scheme 2). In case of **5d**, the 5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-one **4a** was isolated as a side-product. The formation of **5a–e** can be explained by hydrolysis of the enamine group, protonation (intermediate **B**), attack of water (intermediate **C**), cleavage of the pyrrolidinone ring (intermediate **D**) and, finally, acid-mediated recyclization with extrusion of water (Scheme 2).

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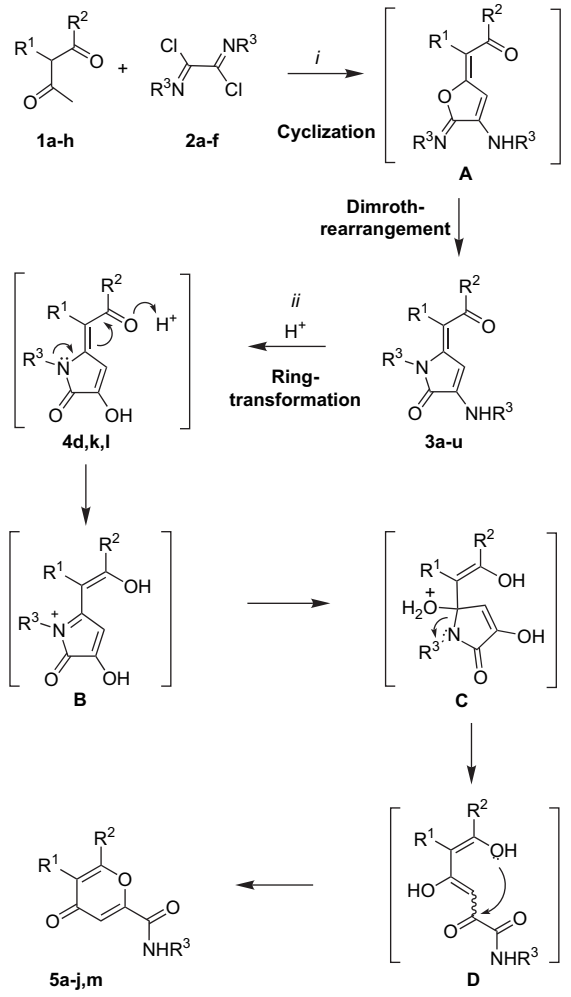
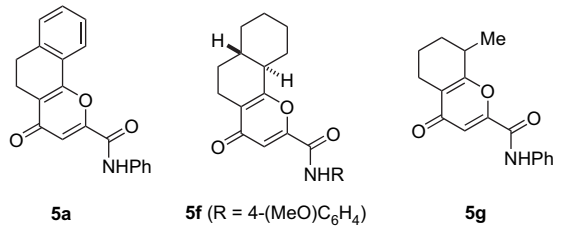


Scheme 2. Synthesis of 5-alkylidene-2,5-dihydropyrrol-2-ones **3a–u** and **4d,k,l** and of pyran-4-ones **5a–j,m**, *i*: (1) 2.2 equiv LDA, (2) **2a–f**, THF, −78→20 °C; *ii*: HCl (1 M), THF, 1 h, 40 °C.



Scheme 3. Structures of **5a**, **5f**, and **5g**.

The cyclization of the dianion of 2-acetyl-1-decalone (**1b**) with **2d** afforded the 5-alkylidene-2,5-dihydropyrrol-2-one **3f**, which was transformed into **5f** (Scheme 2, Table 1). 2-Acetyl-6-methylcyclohexan-1-one (**1c**) was prepared by reaction of 1-trimethylsilyloxy-6-methylcyclohex-1-ene with acetyl chloride. The reaction of dilithiated **1c** with oxalic acid–bis(imidoyl) dichlorides **2a–d** gave the 5-alkylidene-2,5-dihydropyrrol-2-ones **3g–j**, which were transformed into the 5,6,7,8-tetrahydrochromones **5g–j**.

The cyclization of the dianions of 2-acetylcyclopentan-1-one (**1d**) and 2-acetylindan-1-one (**1e**) with **2a** afforded **3k** and **3l**, respectively. Treatment of **3k** and **3l** with hydrochloric acid resulted only in hydrolysis of the enamine moiety and formation of the 5-alkylidene-2,5-dihydropyrrol-2-ones **4k** and **4l**, respectively. The cyclization of the dianion of benzoylacetone (**1f**) with **2a** gave the 5-alkylidene-2,5-dihydropyrrol-2-one **3m**. Treatment of **3m** with hydrochloric acid afforded the carbamoylpyran-4-one **5m**. The cyclization of the dianions of benzoylacetone (**1f**), acetylacetone (**1g**) and 3-methylacetylacetone (**1h**) with various oxalic acid–bis(imidoyl) dichlorides afforded the 5-alkylidene-2,5-dihydropyrrol-2-ones **3n–u**. The reaction of the latter with an aqueous solution of hydrochloric acid resulted in decomposition or no conversion, depending on the concentration of the acid.

Table 1. Products, yields, and UV–vis absorptions

1	2	3–5	R^1	R^2	R^3	% [a]			UV–vis [b]	
						(3)	(4)	(5)	(3)	(5)
a	**a**	**a**		$-(CH_2)_2(C_6H_4)-$	Ph	45	0	75[c]	431 (4.5), 255 (4.3)	310 (4.0), 281 (4.1), 220 (4.1)
a	**b**	**b**		$-(CH_2)_2(C_6H_4)-$	2-MeC_6H_4	51	0	95	427 (4.4), 353 (4.1), 255 (4.2)	313 (4.1), 219 (4.3), 213 (4.4)
a	**c**	**c**		$-(CH_2)_2(C_6H_4)-$	2-(MeO)C_6H_4	85	0	85	433 (4.4), 272 (4.2), 249 (4.2)	312 (4.2), 219 (4.4), 213 (4.4)
a	**d**	**d**		$-(CH_2)_2(C_6H_4)-$	4-(MeO)C_6H_4	55	23	63	447 (4.5), 260 (4.4)	311 (4.2), 290 (4.2), 219 (4.3)
a	**e**	**e**		$-(CH_2)_2(C_6H_4)-$	1-Naph	84	0	92	436 (4.4), 314 (4.1), 219 (5.0)	313 (4.2), 291 (4.2), 221 (4.8)
b	**d**	**f**		$-C_6H_{10}(CH_2)_2-$	4-(MeO)C_6H_4	42	0	77[c]	405 (4.4), 256 (4.3)	284 (4.0), 250 (3.8)
c	**a**	**g**		$-(CH_2)_3CH(Me)-$	Ph	80	0	79[c]	399.8 (4.2), 257 (4.1)	275 (4.1), 221 (4.3)
c	**b**	**h**		$-(CH_2)_3CH(Me)-$	2-MeC_6H_4	58	0	89	396 (4.2), 257 (4.1)	269 (4.0), 221 (4.3)
c	**c**	**i**		$-(CH_2)_3CH(Me)-$	2-(MeO)C_6H_4	61	0	75	400 (4.3), 304 (3.9), 265 (4.2)	280 (4.0), 221 (4.3)
c	**d**	**j**		$-(CH_2)_3CH(Me)-$	4-(MeO)C_6H_4	42	0	61	403 (4.3), 299 (3.8), 255 (4.2)	280 (4.0), 222 (4.2)
d	**a**	**k**		$-CH_2CH_2CH_2-$	Ph	50	95	0	—	—
e	**a**	**l**		$-CH_2(C_6H_4)-$	Ph	37	99	0	—	—
f	**a**	**m**	H	Ph	Ph	54	0	30	419 (4.4), 250 (4.3)	278 (3.5)
f	**b**	**n**	H	Ph	2-MeC_6H_4	54	0	0	—	—
f	**f**	**o**	H	Ph	4-MeC_6H_4	56	0	0	—	—
f	**d**	**p**	H	Ph	4-(MeO)C_6H_4	56	0	0	—	—
g	**a**	**q**	H	Me	Ph	46	0	0	—	—
g	**b**	**r**	H	Me	2-MeC_6H_4	40	0	0	—	—
g	**f**	**s**	H	Me	4-MeC_6H_4	43	0	0	—	—
g	**d**	**t**	H	Me	4-(MeO)C_6H_4	58	0	0	—	—
h	**a**	**u**	Me	Me	Ph	58	0	0	—	—

[a] Isolated yields; for the configuration of the exocyclic double bond of **3** and **4**, see Section 3; no conversion was observed for **3n–u**.
[b] UV–vis (CH_3CN, nm): λ_{max} (log ε).
[c] Structure see below (Scheme 3).

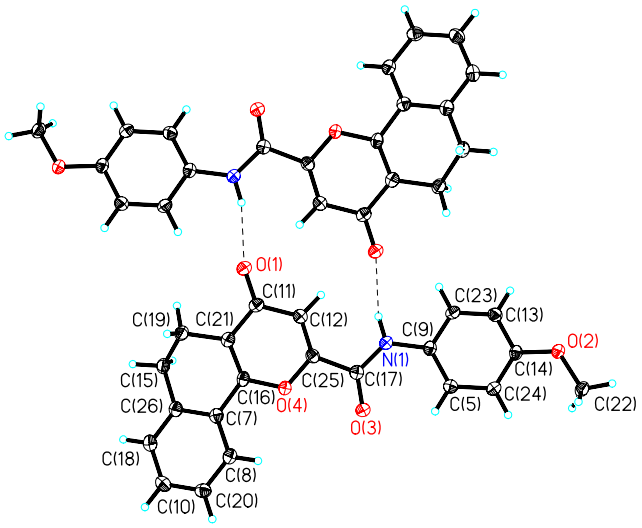


Figure 1. Ortep plot of **5d**.

The structure and the configuration of compounds **3** were elucidated by spectroscopic methods (NOESY measurements). The structure of all products was studied by spectroscopic methods; the structure of **5d** was independently confirmed by crystal structure analysis (Fig. 1). In the crystal lattice of **5d**, dimers are formed by hydrogen bonding (N1–H1 0.885 Å, H1···O1 2.113 Å, N1–H1···O1 166.06°, N1···O1 2.980 Å).[10]

Notably, all products **5a**–**j** and **5m** exhibit strong UV absorptions (Table 1). A hypsochromic effect is generally observed for the colourless pyran-4-ones **5a**–**j**,**m** with respect to the yellow coloured 5-alkylidene-2,5-dihydropyrrol-2-ones **3a**–**j**,**m**.

In conclusion, we reported the synthesis of functionalized pyran-4-ones, such as 5,6-dihydrobenzo[*h*]chromones and 5,6,7,8-tetrahydrochromones, based on acid-mediated ring-transformations of novel 5-alkylidene-2,5-dihydropyrrol-2-ones, which are available by cyclization of 1,3-dicarbonyl dianions with oxalic acid–bis(imidoyl) dichlorides. The best yields were obtained for reactions of 5-alkylidene-2,5-dihydropyrrol-2-ones derived from cyclic 1,3-diketones. For β-ketoester derived 5-alkylidene-2,5-dihydropyrrol-2-ones, the reactions stopped with the simple hydrolysis of the enamine moiety and a ring-transformation was not observed. This can be explained by the lower reactivity of the exocyclic double bond of these substrates in conjugate addition reactions.

3. Experimental section

3.1. 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), Varian Inova 500 (500 MHz). For ^{1}H NMR, the solvents $CDCl_3$ (δ=7.26), [D_8]THF (δ=1.73, 3.58), [D_6]acetone (2.04), [D_6]-dimethylsulfoxide (2.50), and [D_4]methanol (3.30) were used. Tetramethylsilane (TMS) was used as 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), Varian Inova 500 (125.7 MHz). As solvents were used: $CDCl_3$ (δ=77.0), [D_6]acetone (δ=29.8), [D_6]DMSO (39.5), [D_4]methanol (49.0), [D_8]THF (25.5, 67.7). The multiplicity of the carbon atoms was determined by the DEPT 135 (DEPT=Distortionless Enhancement by Polarisation Transfer) and APT technique (APT=Attached Proton Test) and quoted as CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms. IR: Perkin Elmer 2000 FT-IR, FT-IR Bruker Vector 22, Bruker IFS 66, Nicolett 205 FT-IR. UV spectroscopy: Perkin Elmer UV/Vis/IR-Spectrometer Lambda 19; as solvent, CH_3CN was used. Mass spectroscopy: Finnigan MAT 95 spectrometer (electronic ionization: EI, 70 eV), Finnigan LC-Q (electrospray ionization, ESI). Chemical ionization with water: CI, H_2O. For preparative scale chromatography silica gel (60–200 mesh) was used (solvents: petroleum ether (PE, bp 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). Diffraction data for compound **5d** was collected at −173 °C on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. Cu Kα radiation (λ=1.54178 Å) was used. The structure was solved by direct methods using SHELXS[9] and refined against F_o^2 using SHELXL.[11] All non-hydrogen atoms were refined anisotropically, the hydrogen atom bond to nitrogen was refined isotropically with a distance restraint, while the riding model was used for the remaining hydrogen atoms.

3.2. 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 (3.05 ml, 4.4 mmol, 1.5 M solution in hexane) to a THF solution (40 ml) of diisopropylamine (0.45 g, 0.62 ml, *d*=0.722, 4.4 mmol) at 0 °C. To the LDA solution, 2.00 mmol of the dicarbonyl compound was added at 0 °C. The yellow coloured solution was stirred at 0 °C for 60 min and was subsequently cooled to −78 °C and transferred into a THF solution (40 ml) of 2.00 mmol of oxalic acid–bis(arylimidoyl) dichloride at −78 °C. The solution was warmed up to 20 °C overnight. To the solution, 100 ml of an aqueous solution of ammonium chloride (1 M) was added. The organic layer was separated and the aqueous layer was extracted with ether (4×150 ml). The combined organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, pentane/ether=10:1→1:1) to give the 3-arylamino-2,5-dihydropyrrol-2-ones **3** as yellow to red solids.

3.2.1. (5*E*)-5-(3,4-Dihydro-1-oxonaphthalen-2(1*H*)-ylidene)-1-phenyl-3-(phenylamino)-1*H*-pyrrol-2(5*H*)-one (3a). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 2-acetyltetralone (3.0 mmol, 0.57 g) and a THF solution (40 ml) of oxalic acid–bis(phenylimidoyl)

chloride (3.0 mmol, 0.83 g), **3a** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.53 g, 45%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.98 (t, 2H, CH_2), 3.06 (t, 2H, CH_2), 7.08 (d, 1H, CH, Ar), 7.1 (d, 1H, CH–Ar), 7.13 (d, 1H, CH, Ar), 7.21 (m, 1H, CH, Ar), 7.24 (m, 1H, CH, Ar), 7.28 (m, CH, Ar), 7.36 (m, CH, Ar), 7.38 (m, 1H, CH, Ar), 7.41 (m, CH, Ar), 7.43–7.46 (m, 3H, 2CH, Ar+NH), 7.5 (CH, Ar), 7.53 (CH, Ar), 7.68 (s, 1H, CH, C4), 8.07 (d, 1H, CH, Ar), 8.09 (d, 1H, CH–Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=24.8, 28.6 (CH_2), 99.9 (CH), 109.6 (C), 118.1 (2CH, Ar), 123.2 (2CH, Ar), 124.8, 126.0, 126.9, 127.3, 128.1 (CH), 129.0 (2CH, Ar), 129.3 (2CH, Ar), 129.7 (CH), 132.6, 134.9, 139.6, 139.6, 142.9, 143.7, 151.3 (C), 161.3 (CO), 187.6 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3438(br s), 3378 (s), 3362 (s), 1689 (s), 1654 (s), 1622 (s), 1597 (s), 1558 (s), 1493 (m), 1348 (m), 1289 (m), 1239 (s), 1156 (m), 1091 (m), 931 (s), 744 (m), 691 (m), 619 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=255.2 (4.32), 431.2 (4.45). MS (EI, 70 eV): *m*/*z* (%)=393 ([M+1]$^+$, 25.9), 392 (M$^+$, 100), 375 (8), 289 (5), 272 (31), 186 (7), 141 (25), 114 (27), 90 (17), 77 (46), 51 (9). HRMS (EI, 70 eV): calcd for $C_{26}H_{20}O_2N_2$: 392.1525; found: 392.1525±2 ppm ([M]$^+$).

3.2.2. (5*E*)-3-(2-Tolylamino)-5-(3,4-dihydro-1-oxonaphthalen-2(1*H*)-ylidene)-1-(2-tolyl)-1*H*-pyrrol-2(5*H*)-one (3b). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 2-acetyltetralone (3.0 mmol, 0.57 g) and a THF solution (40 ml) of oxalic acid–bis(2-tolylimidoyl) chloride (3.0 mmol, 0.91 g), **3b** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.640 g, 51%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.32 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.89 (t, 2H, CH_2), 2.94 (t, 2H, CH_2), 6.95–6.99 (m, Ar), 7.05–7.1 (m, Ar), 7.16 (s, 1H, C4), 7.21–7.44 (m, Ar, NH), 7.86 (d, 1H, Ar), 7.89 (d, 1H, Ar), 7.90–8.04 (m, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=17.6, 18.6 (CH_3), 99.8, 109.19, 109.4, 117.9, 122.8, 123.6, 125.9, 126.6, 127.1, 128.3, 130.9, 131.4, 132.1, 135.2, 138.1 (CH), 140.0, 141.0, 143.2, 151.1, 161.7, 177.2 (C), 187.8, 194.0 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3374(m), 3289 (w), 2950 (w), 1699 (m), 1661 (m), 1633 (s), 1599 (s), 1563 (s), 1545 (s), 1459 (m), 1348 (m), 1292 (m), 1242 (s), 1157 (m), 1081 (m), 928 (m), 738 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=255.5 (3.18), 299.8 (3.96), 352.8 (4.11), 426.7 (4.35). MS (EI, 70 eV): *m*/*z* (%)=423 (M$^+$+1, 25), 422 (M$^+$, 94), 392 (17), 315 (20), 286 (69), 275 (20), 247 (19), 141 (34), 114 (42), 105 (66), 91 (100), 66 (34), 28 (40). HRMS (EI, 70 eV): calcd for $C_{28}H_{24}O_2N_2$: 420.1838; found: 420.1838±2 ppm ([M]$^+$). Anal. Calcd for $C_{28}H_{24}O_2N_2$: C, 79.98; H, 5.80. Found: C, 79.99; H, 6.01.

3.2.3. (5*E*)-3-(2-Methoxyphenylamino)-5-(3,4-dihydro-1-oxonaphthalen-2-(1*H*)-ylidene)-1-(2-methoxyphenyl)-1*H*-pyrrol-2(5*H*)-one (3c). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 2-acetyltetralone (3.0 mmol, 0.57 g) and a THF solution (40 ml) of oxalic acid–bis(2-methoxyphenyl)imidoyl chloride (3.0 mmol, 1.01 g), **3c** was isolated after chromatography (*n*-hexane/EtOAc=25:1→20:1) as a yellow solid (1.15 g, 85%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.89 (m, 2H, CH_2), 2.96 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 3.94 (s, 3H, CH_3), 6.91–6.94 (m, 1H, Ar), 6.99–7.05 (m, 2H, Ar), 7.17–7.26 (m, 2H, Ar), 7.32–7.51 (m, 4H, Ar), 7.69 (s, 1H, C4), 7.87 (s, NH), 8.06–8.09 (dd, 1H, CH, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=24.8, 28.8 (CH_2), 55.9, 56.2 (CH_3), 100.3 (CH), 109.0 (C), 110.6, 112.3, 116.6, 121.0, 121.5, 122.9, 123.9, 126.5, 127.1, 127.5, 128.2 (CH), 129.6 (C),132.7 (CH), 134.2, 135.3, 139.4, 143.2, 148.9, 152.4, 152.7 (C), 161.7, 187.8 (CO). MS (EI, 70 eV): *m*/*z* (%)=454 (M$^+$+2, 4), 453 (M$^+$+1, 27), 452 (M$^+$, 100), 423 (46), 330 (16), 302 (74), 274 (5), 141 (32), 114 (36), 77 (25). IR (KBr, cm^{-1}): $\tilde{\nu}$=3369(m), 3346 (m), 1701 (s), 1631 (s), 1596 (s), 1558 (s), 1536 (s), 1491 (s), 1461 (s), 1346 (s), 1297 (s), 1243 (s), 1210 (m), 1122 (s), 1027 (s), 928 (s), 738 (s). UV–vis (CH_3CN, nm): λ_{max} (log ε)=248.9 (4.17), 271.6 (4.21), 433.2 (4.39). Anal. Calcd for $C_{28}H_{24}O_4N_2$: C, 74.30; 5.35. Found: C, 73.99; H, 5.02. HRMS (EI, 70 eV): calcd for $C_{28}H_{24}O_4N_2$: 452.1736; found: 452.1736±2 ppm ([M]$^+$).

3.2.4. (*E*)-1-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)-5-(1-oxo-1,2,3,4-tetrahydro-2-naphthylidene)-2,5-dihydropyrrol-2-one (3d). Starting with 2-acetyltetralone (0.56 g, 3.0 mmol) and oxalic acid–bis[(4-methoxyphenyl)-imidoyl]chloride (1.01 g, 3.0 mmol), **3d** was isolated as a yellow solid (745 mg, 55%, *E*/*Z*>98:2). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.97 (m, 4H, CH_2), 3.78, 3.81 (2×s, 2×3H, OCH_3), 6.92 (t, *J*=9 Hz, 4H, Ar), 7.04 (s, 1H, NH), 7.12–7.25 (m, 5H, Ar+C-4), 7.54 (m, 3H, Ar), 8.07 (d, *J*=12 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=24.6, 28.5 (CH_2), 55.4, 55.5 (OCH_3), 98.0 (CH, C-4), 107.7 (C), 114.1, 114.8, 119.9, 126.8, 127.1, 127.1, 128.0, 132.8 (CH, Ar), 132.3, 135.1, 136.6, 140.8, 142.8, 149.5, 155.7, 157.9, 162.1, 187.2 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3360(w), 2952 (w), 2936 (w), 2905 (w), 2837 (w), 1683 (m), 1653 (s), 1622 (s), 1599 (s), 1559 (s), 1532 (s), 1507 (s), 1459 (m), 1350 (s), 1299 (m), 1278 (m), 1245 (s), 1238 (s), 1170 (s), 1031 (m), 928 (s), 834 (m), 815 (m), 743 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=446.9 (4.48), 259.9 (4.36). MS (EI, 70 eV): *m*/*z* (%)=452 ([M]$^+$, 100), 121 (69). HRMS (EI, 70 eV): calcd for $C_{28}H_{24}N_2O_4$: 452.1736; found: 452.1736±2 ppm ([M]$^+$). Anal. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35. Found: C, 74.49; H, 5.49.

3.2.5. (5*E*)-5-(3,4-Dihydro-1-oxonaphth-2(1*H*)-ylidene)-1-(naphth-1-yl)-3-(naphth-1-ylamino)-1*H*-pyrrol-2(5*H*)-one (3e). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 2-acetyltetralone (3.0 mmol, 0.57 g) and a THF solution (40 ml) of oxalic acid–bis(naphth-1-yl-imidoyl) chloride (3.0 mmol, 1.13 g), **3e** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (1.20 g, 84%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.94 (t, 2H, CH_2), 3.02 (t, 2H, CH_2), 7.25 (s, 1H, CH, C4), 7.31–7.34 (m, Ar), 7.42 (m, Ar), 7.51–7.6 (m, Ar), 7.69–7.72 (m, Ar), 7.76–7.81 (m, Ar), 7.88–7.95 (m, Ar), 8.0–8.13 (m, Ar), 8.24–8.26 (m, Ar), 8.45–8.48 (m, Ar). ^{13}C NMR ($CDCl_3$, 250 MHz): δ=24.9, 28.8 (CH_2), 100.9, 109.9, 115.8, 119.0, 120.4, 122.1, 124.0, 126.2, 126.4, 126.5, 126.5, 127.5, 128.3, 129.2, 131.1, 135.0, 135.1 (CH), 140.3, 140.9, 143.2, 152.4 (C), 161.4, 187.7 (CO). MS (EI, 70 eV): *m*/*z* (%)=492 (M$^+$, 9), 491 (36), 322 (26), 204 (7), 167 (10), 148 (23), 143 (36), 114 (18), 90 (7), 32 (17), 28 (100). IR (KBr, cm^{-1}): $\tilde{\nu}$=3436(br s), 3392 (s), 1679 (m), 1654 (m), 1616 (s), 1599 (s), 1497 (m), 1400 (m), 1345 (m), 1243 (s), 1156 (m), 925 (m), 704 (m), 679 (m), 616

(w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=219.1 (4.96), 277.7 (4.11), 314.0 (4.13), 435.6 (4.44). HRMS (EI, 70 eV): calcd for $C_{34}H_{24}O_2N_2$: 492.1838; found: 492.1838±2 ppm ($[M]^+$).

3.2.6. (*E*)-1-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)-5-(1-oxo-1,2,3,4,4a,5,6,7,8,8a-decahydro-2-naphthylidene)-2,5-dihydropyrrol-2-one (3f). Starting with 2-acetyldecalone (0.58 g, 3.0 mmol) and oxalic acid–bis[(4-methoxyphenyl)imidoyl]chloride (1.01 g, 3.0 mmol), **3f** was isolated as a yellow solid (578 mg, 42%, *E*/*Z*>98:2). ^1H NMR ($CDCl_3$, 250 MHz): δ=1.05–1.55 (m, 11H, CH, CH_2), 2.31, 2.81, 3.02 (3×m, 3×1H, CH, CH_2), 3.82, 3.85 (2×s, 2×3H, OCH_3), 6.89 (m, 4H, Ar), 7.19 (m, 3H, Ar), 7.24 (s, 1H, C-4), 7.54 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=24.8, 25.8, 26.2, 26.5, 30.4, 34.3 (CH_2), 39.4, 54.4 (CH), 55.3, 55.4 (OCH_3), 97.9 (CH, C-4), 108.0 (C), 114.0, 114.7, 119.6, 127.2 (CH, Ar), 132.9, 136.7, 140.0, 149.6, 155.4, 157.8, 161.1, 201.31 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3352(w), 3293 (w), 3041 (w), 2923 (s), 2851 (m), 1684 (s), 1658 (m), 1621 (s), 1555 (s), 1535 (s), 1507 (s), 1463 (m), 1443 (m), 1349 (m), 1295 (m), 1247 (s), 1170 (m), 1076 (m), 1035 (m), 924 (w), 836 (m), 820 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=404.8 (4.40), 256.0 (4.28). MS (EI, 70 eV): *m*/*z* (%)=458 ($[M]^+$, 100). HRMS (EI, 70 eV): calcd for $C_{28}H_{30}N_2O_4$: 458.2205; found: 458.2205±2 ppm ($[M]^+$). Anal. Calcd for $C_{28}H_{30}N_2O_4$: C, 73.34; H, 6.59. Found: C, 73.16; H, 6.72.

3.2.7. (5*E*)-5-(3-Methyl-2-oxocyclohexylidene)-1-phenyl-3-(phenylamino)-1*H*-pyrrol-2(5*H*)-one (3g). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 2-acetyl 6-methylcyclohexanone (3.0 mmol, 0.433 g) and a THF solution (40 ml) of oxalic acid–bis(phenylimidoyl) chloride (3.0 mmol, 0.83 g), **3g** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.743 g, 80%). ^1H NMR ($CDCl_3$, 250 MHz): δ=1.19 (d, 3H, CH_3), 1.21–1.32 (m, 2H, CH_2), 1.53–1.62 (m, 2H, CH_2), 1.85–1.89 (m, 2H, CH_2), 2.37–2.42 (m, 1H, C*H*CH_3), 7.05–7.10 (m, 2H, Ar), 7.19–7.2 (m, Ar), 7.12 (s, 1H, C4), 7.12–7.22 (m, Ar), 7.35–7.50 (m, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=16.8 (CH_3), 22.1 (CH_2), 26.3 (CH_2), 31.7 (CH_2), 44.5 (CH), 100.2 (CH), 110.2 (C), 118.2 (CH, Ph), 123.2 (CH), 125.2 (CH, Ph), 126.2 (CH), 129.2, 129.8 (CH, Ph), 139.2, 139.9, 144.0, 151.7 (C), 160.5 (CO), 203.6 (CO). MS (EI, 70 eV): *m*/*z* (%)=359 (M^++1, 26), 358 (M^+, 100), 315 (18), 238 (35), 210 (14), 154 (7), 77 (31), 55 (6), 29 (6). IR (KBr, cm^{-1}): $\tilde{\nu}$=3360(w), 2973 (m), 2932 (m), 2862 (m), 2361 (w), 1688 (s), 1623 (s), 1596 (s), 1561 (s), 1495 (m), 1447 (m), 1349 (m), 1288 (m), 1228 (m), 1154 (m), 1116 (m), 1091 (m), 927 (m), 750 (m), 690 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=257.2 (4.09), 399.84 (4.17). HRMS (EI, 70 eV): calcd for $C_{24}H_{22}O_2N_2$: 367.1208; found: 367.1208±2 ppm ($[M]^+$).

3.2.8. (5*E*)-5-(3-Methyl-2-oxocyclohexylidene)-1-phenyl-3-(phenylamino)-1*H*-pyrrol-2(5*H*)-one (3h). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 2-acetyl-6-methylcyclohexanone (3.0 mmol, 0.433 g) and a THF solution (40 ml) of oxalic acid–bis(2-tolylimidoyl) chloride (3.0 mmol, 0.91 g), **3h** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.676 g, 58%). ^1H NMR ($CDCl_3$, 250 MHz): δ=1.19 (d, 3H, CH_3), 1.39–1.42 (m, 2H, CH_2), 1.51–1.62 (m, 2H, CH_2), 1.81–1.87 (m, 2H, CH_2), 2.13 (s, 6H, 2CH_3), 2.30–2.47 (m, 1H, C*H*CH_3), 6.99 (s, 1H, CH, C4), 7.01–7.03 (m, Ar), 7.09–7.14 (m, Ar), 7.14–7.29 (m, Ar, NH), 7.40–7.47 (m, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=16.8, 17.6, 18.6 (CH_3), 22.1, 26.2, 31.7, 35.6 (CH_2), 44.5, 99.8 (CH), 110.2 (C), 117.6, 122.8, 123.4, 125.8, 126.5 (CH), 127.1, 127.7 (C), 130.7, 131.1 (CH), 133.5, 138.2, 142.6, 151.2 (C), 160.6, 203.6 (CO). MS (EI, 70 eV): *m*/*z* (%)=388.5 (M^++2, 4), 387.5 (M^++1, 28), 386 (M^+, 100), 343 (12), 280 (18), 252 (55), 224 (10), 158 (5), 130 (14), 118 (14), 91 (30), 66 (10). IR (KBr, cm^{-1}): $\tilde{\nu}$=3365(w), 2931 (s), 2846 (m), 1685 (s), 1625 (s), 1597 (s), 1574 (s), 1536 (s), 1495 (s), 1350 (m), 1292 (m), 1229 (m), 1187 (m), 1156 (w), 1082 (m), 964 (m), 928 (m), 760 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=257.2 (4.09), 395.55 (4.22). HRMS (EI, 70 eV): calcd for $C_{25}H_{26}O_2N_2$: 386.1994; found: 386.1994±2 ppm ($[M]^+$).

3.2.9. (5*E*)-3-(2-Methoxyphenylamino)-1-(2-methoxyphenyl)-5-(3-methyl-2-oxocyclohexylidene)-1*H*-pyrrol-2(5*H*)-one (3i). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 2-acetyl-6-methylcyclohexanone (3.0 mmol, 0.433 g) and a THF solution (40 ml) of oxalic acid–bis(2-methoxyphenyl)imidoyl chloride (3.0 mmol, 1.01 g), **3i** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.768 g, 61%). ^1H NMR: δ=1.18 (d, 3H, CH_3), 1.61–1.70 (m, 1H, CH_2), 1.81–1.89 (m, 1H, CH_2), 1.98–2.05 (m, 2H, CH_2), 2.35–2.42 (m, 1H, CH_2), 2.51–2.61 (m, 1H, CH_2), 2.78–2.85 (m, 1H, C*H*CH_3), 3.89 (s, 3H, OCH_3), 3.92 (s, 3H, CH_3), 6.96 (s, 1H, C4), 6.99–7.02 (m, Ar), 7.14 (d, 1H, Ar), 7.16 (d, 1H, Ar), 7.19 (d, 1H, Ar), 7.33 (s, 1H, NH) 4.35 (d, 1H, Ar), 7.39–7.43 (m, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=16.8 (CH_3), 22.1, 26.0, 31.7 (CH_2), 44.4 (CH), 55.9, 56.2 (CH_3), 100.3 (CH), 109.8 (C), 110.5, 112.2, 116.4, 120.9, 121.4, 122.7, 123.9, 126.4 (CH), 129.7, 134.2, 138.7, 148.8, 152.6, 152.7 (C), 160.6, 203.6 (CO). MS (EI, 70 eV): *m*/*z* (%)=422.6 (M^++2, 4), 421 (M^++1, 29), 420 (100), 387 (51), 375 (13), 296 (9), 268 (38), 134 (9), 77 (11), 66 (5). IR (KBr, cm^{-1}): $\tilde{\nu}$=3376(s), 2932 (m), 1702 (s), 1630 (s), 1557 (s), 1532 (s), 1462 (s), 1348 (m), 1294 (m), 1247 (s), 1182 (m), 1129 (m), 1026 (m), 924 (m), 751 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=264.8 (4.18), 303.9 (3.91), 400.2 (4.32). HRMS (EI, 70 eV): calcd for $C_{25}H_{26}O_4N_2$: 418.1893; found: 418.1893±2 ppm ($[M]^+$). Anal. Calcd for $C_{25}H_{26}O_4N_2$: C, 71.70; H, 6.26. Found: C, 70.70; H, 6.47.

3.2.10. (*E*)-1-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)-5-(6-methyl-2-oxo-cyclohex-1-ylidene)-2,5-dihydropyrrol-2-one (3j). Starting with 2-acetyl-6-methylcyclohexanone (463 mg, 3.0 mmol) and oxalic acid–bis[(4-methoxyphenyl)imidoyl]chloride (1.01 g, 3.0 mmol), **3j** was isolated as a yellow solid (527 mg, 42%). ^1H NMR ($CDCl_3$, 250 MHz): δ=1.19 (d, ^3J=6.8 Hz, 3H, CHC*H*$_3$), 1.42–1.60 (m, 1H, CH_2), 1.62–1.80 (m, 1H, CH_2), 1.82–2.00 (m, 2H, CH_2), 2.30–2.50 (m, 1H, CH_2), 2.58–2.78 (m, 1H, CH_2), 2.83–3.05 (m, 1H, C*H*CH_3), 3.81 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.89–6.97 (m, 5H, Ar+NH), 7.17 (d, *J*=7.9 Hz, 2H, Ar), 7.25 (s, 1H, CH, C-4), 7.53 (d, *J*=8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=16.70 (CH_3), 21.88, 25.99, 31.41 (CH_2), 44.06 (CH), 55.42, 55.55 (OCH_3),

98.05 (CH, C-4), 108.54 (C), 114.14, 114.79, 119.91, 126.95 (CH, PMP), 132.97, 136.70, 140.40, 149.90, 155.64, 157.86 (C), 161.11 (NCO), 203.25 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3372(m), 3296 (m), 2932 (m), 2837 (w), 1682 (s), 1658 (s), 1619 (s), 1529 (s), 1508 (s), 1460 (m), 1443 (m), 1350 (m), 1323 (w), 1296 (s), 1247 (s), 1176 (s), 1113 (w), 1081 (m), 1033 (s), 963 (w), 924 (m), 836 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=402.6 (4.33), 299.2 (3.85), 255.2 (4.21). MS (EI, 70 eV): *m*/*z* (%)=418 ($[M]^+$, 100), 375 (8), 296 (6), 268 (10), 134 (8). HRMS (EI, 70 eV): calcd for $C_{25}H_{26}N_2O_4$: 418.1893; found: 418.1893±2 ppm ($[M]^+$).

3.2.11. (*E*)-5-(2-Oxocyclopent-1-ylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3k). Starting with 2-acetylcyclopentanone (0.47 ml, 4.0 mmol) and oxalic acid–bis(phenylimidoyl) chloride (1.11 g, 4.0 mmol), **3k** was isolated as a yellow solid (660 mg, 50%, *E*/*Z*>98:2). ^1H NMR ($CDCl_3$, 250 MHz): δ=1.49 (quint, *J*=8 Hz, 2H, CH_2), 2.14, 2.60 (2×t, *J*=8 Hz, 2×2H, CH_2), 6.89 (m, 2H, Ph), 6.95–7.14 (m, 5H, Ph, C-4), 7.35 (t, *J*=7 Hz, 2H, Ph), 7.65 (d, *J*=7 Hz, 2H, Ph), 7.72 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=18.40, 25.42, 38.44 (CH_2), 95.42 (CH, C-4), 107.43 (C), 117.33, 118.83, 122.65, 127.09, 127.28, 127.68 (CH, Ar), 138.17, 138.64, 142.35, 149.97, 156.73, 204.70 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3332(m), 3059 (w), 2967 (w), 2950 (w), 1701 (s), 1679 (s), 1631 (s), 1595 (s), 1579 (s), 1536 (s), 1488 (m), 1444 (m), 1325 (m), 1292 (m), 1281 (m), 1222 (m), 1212 (m), 1195 (m), 1089 (m), 974 (m), 776 (m), 752 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=406.0 (4.26), 382.0 (4.20), 256.5 (4.20). MS (EI, 70 eV): *m*/*z* (%)=330 ($[M]^+$, 100), 240 (51). HRMS (EI, 70 eV): calcd for $C_{21}H_{18}N_2O_2$: 330.1368; found: 330.1368±2 ppm ($[M]^+$).

3.2.12. (*E*)-5-(1-Oxo-indan-2-ylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3l). Starting with 2-acetylindan-1-one (0.35 g, 2.0 mmol) and oxalic acid–bis(phenylimidoyl) chloride (554 mg, 2.0 mmol), **3l** was isolated as a yellow solid (280 mg, 37%, *E*/*Z*>98:2). ^1H NMR ($CDCl_3$, 250 MHz): δ=3.84 (s, 2H, CH_2), 7.08 (t, 1H, Ar), 7.22 (m, 4H, Ar), 7.30–7.60 (m, 10H, CH, Ar, NH), 7.80 (d, *J*=9 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=30.1 (CH_2), 97.8 (CH, C-4), 109.4 (C), 118.1, 123.2, 123.3, 125.1, 125.9, 126.3, 127.2, 129.0, 129.7, 133.5 (CH, Ar), 138.9, 139.3, 140.5, 143.4, 147.7, 151.2, 160.0, 193.3 (C). MS (EI, 70 eV): *m*/*z* (%)=378 ($[M]^+$, 100), 349 (10), 258 (40). HRMS (EI, 70 eV): calcd for $C_{25}H_{18}N_2O_3$: 378.1368; found: 378.1368±2 ppm ($[M]^+$). Anal. Calcd for $C_{25}H_{18}N_2O_2$: C, 79.35; H, 4.79. Found: C, 78.91; H, 5.04.

3.2.13. (*E*)-5-(2-Oxo-2-phenylethylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3m). Starting with benzoylacetone (486 mg, 3.0 mmol) and oxalic acid–bis(phenylimidoyl) chloride (831 mg, 3.0 mmol), **3m** was isolated as a yellow solid (592 mg, 54%, *E*/*Z*=10:1). ^1H NMR ($CDCl_3$, 250 MHz): δ=6.65 (s, 1H, CH–CO), 7.11 (t, *J*=9 Hz, 1H, Ar), 7.20–7.55 (m, 14H, Ar, C-4, NH), 7.97 (d, *J*=9 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=96.21 (*C*H–CO), 98.47 (CH, C-4), 118.46, 123.74, 124.81, 126.37, 127.76, 128.55, 129.05, 129.69, 132.32 (CH, Ph), 139.08, 139.42, 141.10, 142.85, 151.05, 167.61, 189.61 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3356(m), 3306 (m), 3060 (w), 2919 (s), 2851 (m), 1694 (s), 1651 (s), 1625 (s), 1595 (s), 1582 (s), 1559 (s), 1531 (s), 1494 (s), 1446 (s), 1402 (m), 1285 (m), 1249 (s), 1178 (m), 1086 (m), 1044 (m), 940 (m), 773 (m), 754 (m), 691 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=419.0 (4.44), 250.0 (4.29). MS (EI, 70 eV): *m*/*z* (%)=366 ($[M]^+$, 100), 261 (35), 105 (69). HRMS (EI, 70 eV): calcd for $C_{24}H_{18}N_2O_2$: 366.1368; found: 366.1368±2 ppm ($[M]^+$). Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95. Found: C, 77.81; H, 5.34.

3.2.14. (*E*)-5-(2-Oxo-2-phenylethylidene)-1-(2-tolyl)-3-(2-tolylamino)-2,5-dihydropyrrol-2-one (3n). Starting with benzoylacetone (162 mg, 1.00 mmol) and oxalic acid–bis-(2-tolylimidoyl) chloride (305 mg, 1.00 mmol), **3n** was isolated as a yellow solid (212 mg, 54%, *E*/*Z*=1:1). ^1H NMR ($CDCl_3$, 250 MHz) *E*-isomer: δ=2.38 (s, 3H, Me), 2.39 (s, 3H, Me), 6.66 (s, 1H, C*H*–CO), 7.08 (dd, *J*=7.9, 7.4 Hz, 1H, Ar), 7.24–7.36 (m, 6H, Ar, C-4, NH), 7.42–7.56 (m, 5H, Ar), 7.95 (d, *J*=7.3 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 50.3 MHz) *E*-isomer: δ=17.4 (Ar*C*H_3), 18.3 (Ar*C*H_3), 96.3 (*C*H–CO), 98.0 (CH, C-4), 118.2, 121.2, 122.4, 124.0, 125.9, 126.4, 127.0, 127.7 (CH), 128.4 (C), 128.5, 130.6, 131.0 (CH), 132.7, 134.3, 137.3, 139.4, 141.3, 142.3 (C), 167.72 (NCO), 189.76 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3366(m), 3287 (m), 3056 (w), 2923 (w), 2852 (w), 1692 (m), 1665 (s), 1629 (s), 1596 (s), 1580 (s), 1562 (s), 1537 (s), 1525 (s), 1485 (m), 1458 (m), 1264 (m), 1252 (m), 1114 (w), 1042 (m), 938 (w), 737 (s), 703 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=412.5 (4.19), 245.5 (4.21). MS (EI, 70 eV): *m*/*z* (%)=394 ($[M]^+$, 100), 289 (60), 275 (60), 261 (8), 105 (20).

3.2.15. (*E*)-5-(2-Oxo-2-phenylethylidene)-1-(4-tolyl)-3-(4-tolylamino)-2,5-dihydropyrrol-2-one (3o). Starting with benzoylacetone (162 mg, 1.00 mmol) and oxalic acid–bis(4-tolylimidoyl) chloride (305 mg, 1.00 mmol), **3o** was isolated as a yellow solid (223 mg, 56%, *E*-isomer: 130 mg, 32%, *E*/*Z*=10:1; *Z*-isomer: 93 mg, 24%, *E*/*Z*=1:10). ^1H NMR ($CDCl_3$, 300 MHz) *E*-isomer: δ=2.25 (s, 3H, Me), 2.28 (s, 3H, Me), 6.53 (s, 1H, C*H*–CO), 7.08 (s, 1H, C-4), 7.14–7.29 (m, 6H, Ar, NH), 7.35–7.46 (m, 6H, Ar), 7.87 (dd, *J*=7.6, 1.5 Hz, 2H, Ar); *Z*-isomer: δ=2.34 (s, 3H, Me), 2.44 (s, 3H, Me), 6.33 (s, 1H, C*H*–CO), 7.11 (s, 1H, C-4), 7.13–7.24 (m, 6H, Ar, NH), 7.32–7.51 (m, 6H, Ar), 7.79 (dd, *J*=8.3, 1.5 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 50.3 MHz) *E*-isomer: δ=20.79 (Ar*C*H_3), 21.12 (Ar*C*H_3), 95.62 (*C*H–CO), 97.62 (CH, C-4), 118.52, 124.79, 127.61, 128.43, 129.58, 130.12, 132.10 (CH), 133.44, 136.27, 136.53, 139.54, 140.78, 141.59, 150.46 (C), 167.88 (NCO), 189.66 (CO); *Z*-isomer: δ=20.83 (Ar*C*H_3), 21.27 (Ar*C*H_3), 95.53 (*C*H–CO), 100.35 (CH, C-4), 118.24, 127.74, 128.02, 128.46, 130.14, 130.29 (CH), 130.56 (C), 132.25 (CH), 133.08, 136.81, 138.38, 139.66, 154.89, 154.95 (C), 166.68 (NCO), 190.01 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3356(w), 3304 (w), 3056 (w), 2922 (m), 2855 (w), 1689 (m), 1650 (s), 1627 (s), 1614 (s), 1597 (s), 1579 (s), 1556 (s), 1530 (s), 1447 (m), 1404 (m), 1309 (m), 1285 (m), 1247 (s), 1168 (m), 1046 (m), 940 (m), 808 (m), 774 (m), 697 (m), 651 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=426.0 (4.27), 252.5 (4.24). MS (EI, 70 eV): *m*/*z* (%)=394 ($[M]^+$, 80), 289 (100), 261 (16), 172 (8), 105 (20). HRMS (EI, 70 eV): calcd for $C_{26}H_{22}N_2O_2$: 394.1681; found: 394.1681±2 ppm ($[M]^+$).

3.2.16. (*E*)-5-(2-Oxopropylidene)-1-aryl-3-arylamino-2,5-dihydropyrrol-2-one (3p). Starting with a THF solution

(40 ml) of LDA (6.9 mmol, 2.3 equiv), benzoylacetone (3.0 mmol, 0.49 g) and a THF solution (40 ml) of oxalic acid–bis(4-methoxyphenyl)imidoyl chloride (3.0 mmol, 1.01 g), **3p** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.72 g, 56%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=3.84 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 6.65 (s, 1H, CHCO), 6.94 (d, 2H, CH,Ar), 6.97 (d, 2H, 2CH, Ar), 7.17 (s, 1H, NH), 7.24–7.27 (m, CH, Ar), 7.38 (s, 1H, CH, C4), 7.54 (d, 2H, 2CH, Ar), 7.58 (d, 2H, 2CH, Ar), 7.97 (d, 2H, 2CH, Ar), 7.99 (d, 2H, 2CH, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=55.5 (CH_3O), 55.6 (CH_3O), 95.2 (CHCO), 96.7 (CH, C4), 114.3 (2CH, Ar), 114.9 (2CH, Ar), 120.5 (2CH, Ar), 126.9 (2CH, Ar), 132.1 (CH, Ar), 132.3 (C), 136.4 (C–NH), 139.7 (C–CO), 142.6 (C4-NH), 149.5 (C–OCH_3), 156.3 (C–OCH_3), 158.3 (=CN), 168.2 (CO), 189.8 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3432(br s), 1645 (s), 1625 (s), 1555 (s), 1509 (s), 1246 (s), 1170 (m), 1032 (m), 942 (m), 836 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=255.4 (5.31), 431.2 (5.41). MS (EI, 70 eV): *m*/*z* (%)=429 (M^++1, 26), 428 (M^+, 100), 349 (3), 321 (44), 276 (10), 265 (5), 171 (6), 122 (14). HRMS (EI, 70 eV): calcd for $C_{26}H_{22}O_4N_2$: 426.1580; found: 426.1580±2 ppm ($[M]^+$).

3.2.17. (*E*)-5-(2-Oxopropylidene)-1-phenyl-3-phenylamino-2,5-dihydropyrrol-2-one (3q). Starting with acetylacetone (600 mg, 0.62 ml, 6.0 mmol) and oxalic acid–bis(phenylimidoyl) chloride (1.66 g, 6.0 mmol), **3q** was isolated as a yellow solid (840 mg, 46%, *E*/*Z*>98:2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ=2.25 (s, 3H, $COCH_3$), 5.90 (s, 1H, $CHCOCH_3$), 7.00–7.60 (m, 11H, 4-H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ=31.75 ($COCH_3$), 98.06 (CH, $CHCOCH_3$), 99.54 (CH, C-4), 118.39, 123.65, 124.53, 126.20, 128.96, 129.67 (CH, Ph), 139.13, 140.59, 143.44 (C, C-3, Ph–C to N), 151.17 (C, C-5), 165.54 (C, NCO), 197.30 (C, $COCH_3$). IR (KBr, cm^{-1}): $\tilde{\nu}$=3367(s), 3093 (m), 2930 (m), 2873 (m), 1702 (m), 1635 (m), 1617 (m), 1585 (m), 1529 (s), 1481 (s), 1445 (m), 1401 (m), 1352 (s), 1204 (m), 1093 (m), 922 (w), 892 (m), 805 (s), 733 (s), 691 (m), 674 (m), 605 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=264.5 (4.17), 207.0 (4.29). MS-FAB: *m*/*z* (%)=305 ($[M+H]^+$). Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.77; H, 5.40; N, 9.15.

3.2.18. (*E*)-5-(2-Oxopropylidene)-1-(2-tolyl)-3-(2-tolylamino)-2,5-dihydropyrrol-2-one (3r). Starting with acetylacetone (600 mg, 0.62 ml, 6.0 mmol) and oxalic acid–bis(2-tolylimidoyl) chloride (1.83 g, 6.0 mmol), **3r** was isolated as a yellow solid (797 mg, 40%, *E*/*Z*=5:3). ^{1}H NMR ($CDCl_3$, 200 MHz): δ=2.24, 2.35, 2.37, 2.40 (s, 3H, $COCH_3$), 5.36 (s, 1H, $CHCOCH_3$, *Z*-isomer), 5.89 (s, 1H, $CHCOCH_3$, *E*-isomer), 6.14 (s, 1H, CH, *Z*-isomer), 7.03–7.15 (m, 2H, 4-H, Tol), 7.21–7.38 (m, 6H, Tol+NH), 7.44 (d, *J*=7.9 Hz, 1H, Tol), 7.50 (d, *J*=7.7 Hz, 1H, Tol). ^{13}C NMR ($CDCl_3$, 50.3 MHz) *E*-isomer: δ=17.34, 18.28 (ArCH_3), 31.73 ($COCH_3$), 97.64 (CH, $CHCOCH_3$), 99.55 (CH, C-4), 118.05, 122.35, 123.94, 125.84, 126.29 (CH, Tol), 127.42 (C), 127.46, 130.52, 131.01 (CH, Tol), 132.67, 137.36, 140.73, 142.22, 150.85 (C), 165.66 (C, NCO), 197.32 (C, $COCH_3$); *Z*-isomer: δ=17.34, 18.28 (ArCH_3), 30.69 ($COCH_3$), 98.41 (CH, $CHCOCH_3$), 102.88 (CH, C-4), 117.79, 122.29, 123.90, 126.15, 126.37, 127.29 (CH, Tol), 127.66 (C), 130.60, 131.21 (CH, Tol), 133.15, 137.55, 138.36, 141.95, 150.03 (C), 162.07 (C, NCO), 195.92 (C, $COCH_3$). MS (EI, 70 eV): *m*/*z* (%)=333 ($[M+H]^+$, 22), 332 ($[M]^+$, 100), 317 (16), 289 (44), 275 (16), 247 (12), 233 (8), 198 (12), 174 (8), 156 (8), 130 (10), 107 (12).

3.2.19. (*E*)-5-(2-Oxopropylidene)-1-(4-tolyl)-3-(4-tolylamino)-2,5-dihydropyrrol-2-one (3s). Starting with acetylacetone (600 mg, 0.62 ml, 6.0 mmol) and oxalic acid–bis(*p*-tolylimidoyl) chloride (1.83 g, 6.0 mmol), **3s** was isolated as a yellow solid (856 mg, 43%, *E*/*Z*>98:2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ=2.22, 2.30, 2.33 (s, 9H, $COCH_3$, Tol–CH_3), 5.87 (s, 1H, $CHCOCH_3$), 7.00–7.50 (m, 9H, 4-H, Tol). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ=20.79, 21.12 (Tol–CH_3), 31.64 ($COCH_3$), 97.17 (CH, $CHCOCH_3$), 98.90 (CH, C-4), 118.40, 124.71, 129.51, 130.06 (CH, Tol), 133.25, 136.51, 136.56 (C, C-3, Tol–C to CH_3), 140.73, 141.02 (C, Tol–C to N), 150.54 (C, C-5), 165.83 (C, NCO), 197.20 (C, $COCH_3$). IR (KBr, cm^{-1}): $\tilde{\nu}$=3225(w), 3028 (w), 1700 (m), 1664 (s), 1630 (s), 1560 (s), 1523 (s), 1415 (m), 1235 (m), 1078 (m), 960 (m). MS (CI, H_2O): *m*/*z* (%)=333 ($[M+H]^+$). Anal. Calcd for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.07; N, 8.42. Found: C, 75.68; H, 6.27; N, 8.58.

3.2.20. (5*E*)-3-(4-Methoxyphenylamino)-1-(4-methoxyphenyl)-5-(2-oxopropylidene)-1*H*-pyrrol-2(5*H*)-one (3t). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), acetylacetone (3.0 mmol, 0.30 g) and a THF solution (40 ml) of oxalic acid–bis(4-methoxyphenyl)imidoyl chloride (3.0 mmol, 1.01 g), **3t** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.637 g, 58%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.24 (s, 3H, CH_3CO), 3.833 (s, 3H, CH_3O), 3.85 (s, 3H, CH_3O), 5.89 (s, 1H, CHCO), 6.91 (d, 2H, 2CH, Ar), 6.94 (d, 2H, 2CH, Ar), 7.14 (s, 1H, NH), 7.19 (d, 2H, 2CH, Ar), 7.22 (d, 2H, 2CH, Ar), 7.49 (s, 1H, CH, C4), 7.52 (s, 1H, CHCO). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=35.5, 55.7, 55.8 (CH_3), 96.5, 98.8, 114.4 (CH), 114.5 (2CH, Ar), 115.2 (2CH, Ar), 115.9 116.8, 117.6, 118.6 (C), 120.7 (2CH, Ar), 127.0 (2CH, Ar), 158.4, 167.8 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3434(br s), 3322 (m), 3044 (w), 3000 (w), 1694 (m), 1661 (m), 1628 (s), 1597 (s), 1531 (s), 1507 (s), 1462 (m), 1358 (m), 1294 (m), 1247 (s), 1229 (m), 1175 (s), 1075 (s), 1033 (m), 955 (m), 833 (m), 567 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=255.3 (4.29), 297.4 (3.89), 394.0 (4.36). MS (EI, 70 eV): *m*/*z* (%)=365 (M^++1, 25), 364 (100), 349 (34), 321 (46), 307 (7), 214 (17), 188 (17), 172 (30), 122 (12.56), 77 (12), 43 (34), 28.0 (3). HRMS (EI, 70 eV): calcd for $C_{21}H_{20}O_2N_2$: 364.1423; found: 364.1423±2 ppm ($[M]^+$).

3.2.21. (5*E*)-5-(3-Oxobutan-2-ylidene)-1-phenyl-3-(phenylamino)-1*H*-pyrrol-2(5*H*)-one (3u). Starting with a THF solution (40 ml) of LDA (6.9 mmol, 2.3 equiv), 3-methyl 2,4-pentanedione (3.0 mmol, 0.343 g) and a THF solution (40 ml) of oxalic acid–bis(phenylimidoyl) chloride (3.0 mmol, 0.83 g), **3u** was isolated after chromatography (*n*-hexane/EtOAc=20:1) as a yellow solid (0.50 g, 58%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.16 (s, 3H, CH_3C), 2.34 (s, 3H, CH_3CO), 6.54 (s, 1H, C4), 7.08–7.13 (m, 3H, Ar), 7.19–7.26 (m, 3H, Ar), 7.35–7.49 (m, 4H, 3H, Ar, NH),

7.67–7.70 (dd, 2H, 2CH, Ar). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=13.8, 29.9 (CH_3), 100.0 (CH), 108.8 (C), 117.2, 118.5, 123.3, 124.1, 124.9, 125.8, 126.2, 129.0, 129.2, 129.5 (CH), 136.5, 139.9, 144.0, 151.6 (C), 161.2, 199.7 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3354(m), 3351 (m), 2925 (w), 2361 (w), 1687 (s), 1668 (s), 1568 (s), 1531 (s), 1493 (s), 1358 (s), 1321 (s), 1229 (s), 1068 (s), 974 (s), 941 (s), 752 (s), 688 (s), 584 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=256.5 (4.17), 392.27 (4.23). MS (EI, 70 eV): *m/z* (%)=319 (M^++1, 24), 318 (M^+, 100), 303 (24), 275 (46), 240 (18), 198 (21), 156 (33), 144 (22), 77 (30), 43 (18). HRMS (EI, 70 eV): calcd for $C_{26}H_{20}O_2N_2$: 364.1423; found: 364.1423±2 ppm ($[M]^+$).

3.3. General procedure for the synthesis of 5-alkylidene-3-hydroxy-2,5-dihydropyrrol-2-ones (4) and pyran-4-ones (5)

The 3-arylamino-2,5-dihydropyrrol-2-one **3** was dissolved in THF at room temperature. To this solution, an aqueous solution of hydrochloric acid (15 ml, 10%) was added under vigorous stirring. The temperature of the mixture rised to ca. 40 °C during the addition and the colour changed from yellow to orange. After stirring for 24 h at 25 °C, the pale yellow solution was poured into 150 ml of water. The organic and the aqueous layer were separated and the latter was extracted with 3×100 ml of diethyl ether. The combined organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, pentane/ether=10:1→1:1) to give **4** and/or **5** as yellow crystals.

3.3.1. 5,6-Dihydro-4-oxo-*N*-phenyl-4*H*-benzo[*h*]chromene-2-carboxamide (5a). To a THF solution (25 ml) of **3a** (40 mg) was added an aqueous solution of HCl (15 ml, 10%). The solution was stirred for 24 h at 20 °C. The mixture was purified by chromatography (silica gel, *n*-hexane/EtOAc=5:1→3:1) to give **5a** as a yellow solid (25 mg, 75%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.87 (t, 2H, CH_2), 2.94 (t, 2H, CH_2), 7.19–7.22 (m, 1H, Ar), 7.27 (s, 1H, CH–CO), 7.33–7.34 (d, 2H, Ar), 7.41–7.46 (m, 2H,), 7.68 (d, 2H, Ar), 7.74–7.66 (d, 2H, Ar), 8.31 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=19.0, 26.9 (CH_2), 116.1, 120.3, 123.1, 126.2, 127.5, 128.9, 129.6, 131.8 (CH), 136.6, 139.4, 154.2, 157.2 (C), 157.5, 178.4 (CO). MS (EI, 70 eV): *m/z* (%)=318.8 (M^++1, 1.4), 317.8 (M^+, 13), 317 (66), 316 (100), 287.8 (3), 197 (25), 172 (6), 141 (28), 127 (17), 114 (25), 93 (4), 77.3 (8). IR (KBr, cm^{-1}): $\tilde{\nu}$=3426(br m), 3304 (m), 3296 (m), 2855 (m), 1685 (m), 1643 (s), 1600 (s), 1542 (s), 1426 (s), 1324 (m), 1248 (m), 1155 (m), 764 (m), 697 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=220.3 (4.13), 280.8 (4.05), 288.8 (4.05), 310.4 (4.00). HRMS (EI, 70 eV): calcd for $C_{20}H_{15}O_3N$: 317.1052; found: 317.1052±2 ppm ($[M]^+$).

3.3.2. 5,6-Dihydro-4-oxo-*N*-(2-tolyl)-4*H*-benzo[*h*]chromene-2-carboxamide (5b). To a THF solution (40 ml) of **3b** (80 mg) was added an aqueous solution of HCl (30 ml, 10%). The solution was stirred for 24 h at 20 °C. The mixture was purified by chromatography (silica gel, *n*-hexane/EtOAc=5:1→3:1) to give **5b** as a yellow solid (60 mg, 95%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.45 (s, 3H, CH_3), 2.88 (m, 2H, CH_2), 2.99 (m, 2H, CH_2), 7.15–7.20 (m, Ar), 7.29–7.48 (m, Ar), 7.73 (d, 1H, Ar), 8.13 (d, 1H, CH), 8.36 (br, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=17.9 (CH_3), 18.9, 26.9 (CH_2), 116.2, 122.6, 122.7 (CH), 122.9 (C), 126.2, 127.4, 127.5, 127.6 (CH), 128.5 (C), 128.9, 130.9, 131.7 (CH), 134.7, 139.5, 154.2, 157.0, 157.0 (C), 157.3, 178.4 (CO). MS (EI, 70 eV): *m/z* (%)=332 (M^+, 8), 331 (67), 329 (100), 197 (20), 159 (13), 141 (56), 126.8 (32), 114.2 (77), 90.9 (64), 28 (75). IR (KBr, cm^{-1}): $\tilde{\nu}$=3438(br s), 3365 (s), 1698 (s), 1643 (s), 1594 (s), 1567 (s), 1500 (s), 1458 (s), 1424 (s), 1156 (m), 750 (s). UV–vis (CH_3CN, nm): λ_{max} (log ε)=213.3 (4.36), 218.8 (4.34), 278.1 (4.16), 288.9 (4.15), 312.54 (5.14). HRMS (EI, 70 eV): calcd for $C_{21}H_{17}O_3N$: 331.1208; found: 331.1208±2 ppm ($[M]^+$).

3.3.3. 5,6-Dihydro-*N*-(2-methoxyphenyl)-4-oxo-4*H*-benzo[*h*]chromene-2-carboxamide (5c). To a THF solution (50 ml) of **3c** (120 mg) was added an aqueous solution of HCl (40 ml, 10%). The solution was stirred for 24 h at 20 °C. The mixture was purified by chromatography (silica gel, *n*-hexane/EtOAc=5:1→3:1) to give **5c** as a colourless solid (68 mg, 85%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.87 (t, 2H, CH_2), 2.97 (t, 2H, CH_2), 4.03 (s, 3H, CH_3), 6.96–7.06 (m, 1H, Ar), 7.13–7.18 (m, 1H, Ar), 7.24 (s, 1H, CHCO), 7.31 (d, 1H, Ar), 7.41–7.46 (m, 1H, Ar), 7.44 (d, 2H, Ar), 7.85 (d, 1H, Ar), 8.51 (d, 1H, Ar), 9.37 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=18.9, 26.9 (CH_2), 56.3 (CH_3O), 110.3, 115.6, 119.9, 121.7 (CH), 122.5 (C), 122.9, 125.2 (CH), 126.6 (C), 127.3 (CH), 127.6 (C), 128.9, 131.7 (CH), 139.4, 148.3, 154.1, 156.4 (C), 157.2, 178.6 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3408(m), 2942 (w), 1765 (m), 1694 (s, 1651 (s), 1603 (s), 1536 (s), 1463 (s), 1417 (s), 1333 (m), 1253 (s), 1159 (m), 1122 (m), 1024 (m), 758 (m), 633 (m), 543 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=213.17 (4.40), 219.4 (4.40), 252.0 (4.14), 290.5 (4.18), 311.7 (4.24). MS (EI, 70 eV): *m/z* (%)=348.7 (M^++1, 2), 347 (M^+, 19), 347 (88), 346 (100), 197 (20), 171 (20), 141 (29), 114 (21), 92 (8), 28 (6). HRMS (EI, 70 eV): calcd for $C_{21}H_{17}O_4N$: 347.1158; found: 347.1158±2 ppm ($[M]^+$).

3.3.4. (*E*)-3-Hydroxy-1-(4-methoxyphenyl)-5-(1-oxo-1,2,3,4-tetrahydro-2-naphthylidene)-2,5-dihydropyrrol-2-one (4d). Starting with **3d** (60 mg, 0.13 mmol), **4d** was isolated as an orange solid (10 mg, 23%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=3.00+3.08 (2d, J=6.7 Hz, 4H, $2CH_2$), 3.82 (s, 3H, OMe), 6.67 (br s, 1H, OH), 6.93 (d, ^3J=8.8 Hz, 2H, AA′, PMP), 7.14 (d, ^3J=8.9 Hz, 2H, XX′, PMP), 7.27 (d, ^3J=6.4 Hz, 1H, Ar), 7.35 (t, ^3J=7.5 Hz, 1H, Ar), 7.48 (d, ^3J=7.5 Hz, 1H, Ar), 7.61 (s, 1H, C-4), 8.05 (d, ^3J=7.7 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ=25.31, 28.59 (CH_2), 55.65 (OCH_3), 102.62 (CH, C-4), 113.28 (C), 115.20, 120.13 (PMP), 127.03, 127.56, 128.26 (CH, Ar), 131.50, 132.20 (C), 133.06 (CH, Ar),134.64, 143.21, 156.60, 156.82 (C), 166.05 (NCO), 207.34 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3339(s), 3294 (w), 2957 (w), 2929 (w), 2854 (w), 1763 (s), 1658 (m), 1636 (s), 1599 (s), 1564 (s), 1541 (m), 1512 (s), 1456 (w), 1343 (m), 1279 (m), 1237 (s), 1177 (m), 1156 (m), 1087 (m), 1031 (m), 923 (m), 801 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=431.9 (4.13), 296.2 (3.92), 247.6 (3.86). MS (EI, 70 eV): *m/z* (%)=347 ($[M]^+$, 100), 300 (20), 186 (56), 123 (28). HRMS (EI, 70 eV): calcd for $C_{21}H_{17}NO_4$: 347.1158; found: 347.1158±2 ppm ($[M]^+$). Anal. Calcd for

$C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.45; H, 4.84; N, 3.89.

3.3.5. 2-[*N*-(Methoxyphenyl)carbamoyl]-5,6-dihydrobenzo[*h*]chromone (5d). Starting with **3d** (60 mg, 0.13 mmol), **5d** was isolated as a colourless solid (30 mg, 63%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.84 (d, J=6.1 Hz, 2H, CH_2, C-5), 2.91 (d, J=6.1 Hz, 2H, CH_2, C-6), 3.81 (s, 3H, OMe), 6.91 (d, J=8.3 Hz, 2H, C-3′, C-5′), 7.21 (s, 1H, C-3), 7.29 (d, J=7.2 Hz, 1H, C-9), 7.40 (t, J=5.9 Hz, 2H, C-7, C-8), 7.61 (d, J=8.7 Hz, 2H, C-2′, C-6′), 7.75 (d, J=6.2 Hz, 1H, C-10), 8.50 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ=18.83 (CH_2, C-5), 26.78 (CH_2, C-6), 55.55 (OMe), 114.54 (CH, C-3′, C-5′), 115.70 (CH, C-3), 122.36 (CH, C-2′, C-6′), 122.64 (C, C-4a), 122.94 (CH, C-10), 127.19 (CH, C-7), 127.38 (C, C-10a), 128.59 (CH, C-9), 129.55 (C, C-1′), 131.52 (CH, C-8), 139.15 (C, C-6a), 154.25 (C, C-2), 156.94 (C, C-4′), 157.26 (C, C-10b), 157.54 (NCO), 178.12 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3332(m), 3304 (m), 2957 (w), 1685 (m), 1638 (s), 1618 (s), 1549 (s), 1511 (s), 1437 (s), 1415 (m), 1249 (s), 1173 (m), 1131 (w), 1090 (m), 1033 (m), 944 (w), 831 (m), 807 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=311.3 (4.16), 289.9 (4.16), 249.9 (4.01), 218.9 (4.32). MS (EI, 70 eV): m/z (%)=347 ([M]$^+$, 100), 197 (20), 141 (36), 122 (60), 115 (40), 95 (24). HRMS (EI, 70 eV): calcd for $C_{21}H_{17}NO_4$: 347.1158; found: 347.1158±2 ppm ([M]$^+$).

Crystal data: $C_{21}H_{17}NO_4$: Mr=347.36, monoclinic, space group $P2_1/c$, a=14.564(3) Å, b=15.281(3) Å, c=7.217(1) Å, β=93.22(3)°, V=1603.6(5) Å^3, Z=4, ρ_{calcd}=1.439 g cm^{-1}, F(000)=728, μ(Cu Kα)=0.820 mm^{-1}, 3.04°<θ<59.83°, 5353 reflections were collected, of which 2312 were independent (R_{int}=0.0143) and used for the refinement; 241 parameters were refined. The R values were: $R1=\sum|F_o-F_c|/\sum F_o$=0.0261 for $I>2\sigma(I)$ and $wR1=[\sum w(F_o^2-F_c^2)^2/\sum F_c^4]^{1/2}$=0.0657 for all data; max/min residual electron density:0.143/−0.146 e Å^{-3}.

3.3.6. 5,6-Dihydro-*N*-(naphthalene-1-yl)-4-oxo-4*H*-benzo[*h*]chromene-2-carboxamide (5e). To a THF solution (25 ml) of **3e** (80 mg) was added an aqueous solution of HCl (30 ml, 10%). The solution was stirred for 24 h at 20 °C. The mixture was purified by chromatography (silica gel, *n*-hexane/EtOAc=5:1→3:1) to give **5e** as a yellow solid (55 mg, 92%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.91 (t, 2H, CH_2), 2.98 (t, 2H, CH_2), 7.35 (s, 1H, C4), 7.45–7.86 (m, 2H, Ar), 7.55–7.66 (m, 4H, Ar), 7.81–7.86 (m, 2H, Ar), 8.86 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=19.1, 27.0 (CH_2), 116.4, 120.1, 121.2, 122.9 (CH), 123.1 (C), 126.1, 126.6, 127.1, 127.2, 127.5 (CH), 127.6 (C), 128.9, 129.4 (CH), 130.9 (C), 131.8 (CH), 134.4, 139.5, 154.2, 157.5 (C), 157.5, 178.4 (CO). MS (EI, 70 eV): m/z (%)=368 (M$^+$+1, 27), 367 (M$^+$, 65), 348 (21), 320 (11), 222 (24), 195 (47), 167 (10), 141 (40), 114 (84), 70 (9). IR (KBr, cm^{-1}): $\tilde{\nu}$=3442(m), 1693 (s), 1652 (s), 1629 (s), 1599 (s), 1541 (s), 1498 (s), 1421 (s), 1344 (m), 1258 (m), 1157 (m), 984 (m), 881 (m), 772 (m), 757 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=220.6 (4.83), 290.5 (4.19), 312.6 (4.21). HRMS (EI, 70 eV): calcd for $C_{24}H_{17}O_3N$: 367.1208; found: 367.1208±2 ppm ([M]$^+$).

3.3.7. 2-[*N*-(Methoxyphenyl)carbamoyl]-5,6,6a,7,8,9,10,10a-octahydrobenzo[*h*]chromone (5f). Starting with **3f** (129 mg, 0.28 mmol), **5f** was isolated as a pale yellow solid (77 mg, 77%). ^{1}H NMR ([D_6]DMSO, 250 MHz): δ=1.15–1.38 (m, 6H, CH_2), 1.40–1.95 (m, 4H, CH_2), 2.00–2.45 (m, 4H, CH_2, CH), 3.33 (s, 3H, OMe), 5.74 (br s, 1H, NH), 6.84 (s, 1H, C-3), 6.94 (d, ^3J=9.0 Hz, 2H, AA′, PMP), 7.61 (d, ^3J=9.0 Hz, 2H, XX′, PMP). ^{13}C NMR ([D_6]DMSO, 50.3 MHz): δ=20.91, 25.39, 25.67, 27.13, 27.81, 32.57 (6CH_2), 39.08 (CH, overlapped by the DMSO-signal), 43.08 (CH), 55.16 (OCH_3), 113.26 (CH, C-3), 113.79, 122.66 (CH, PMP), 122.76, 130.41, 155.24, 156.27, 157.44 (C), 164.35 (NCO), 177.96 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3319(s), 3082 (w), 2927 (s), 2860 (m), 1687 (s), 1639 (s), 1613 (s), 1606 (s), 1582 (s), 1550 (s), 1511 (s), 1436 (s), 1413 (m), 1329 (m), 1259 (s), 1241 (s), 1180 (m), 1167 (m), 1029 (s), 1000 (m), 968 (m), 879 (m), 840 (s), 683 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=284.2 (3.99), 250.3 (3.83). MS (EI, 70 eV): m/z (%)=353 ([M]$^+$, 100), 298 (6), 176 (20), 122 (16). HRMS (EI, 70 eV): calcd for $C_{21}H_{23}NO_4$: 353.1627; found: 353.1627±2 ppm ([M]$^+$). Anal. Calcd for $C_{21}H_{23}NO_4$: C, 71.37; H, 6.56. Found: C, 71.11; H, 6.48.

3.3.8. 5,6,7,8-Tetrahydro-8-methyl-4-oxo-*N*-phenyl-4*H*-chromene-2-carboxamide (5g). To a THF solution (40 ml) of **3g** (100 mg) was added an aqueous solution of HCl (30 ml, 10%). The solution was stirred for 24 h at 20 °C. The mixture was purified by chromatography (silica gel, *n*-hexane/EtOAc=5:1→3:1) to give **5g** as a yellow solid (62 mg, 79%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=1.39 (d, 3H, CH_3), 1.60–1.70 (m, 1H, CH_2), 1.81–1.89 (m, 1H, CH_2), 1.95–2.06 (m, 1H, CH_2), 2.52 (m, 1H, CH_2), 2.89 (m, 1H, C*H*CH_3), 7.15 (s, 1H, C4), 7.38–7.40 (m, 2H, Ar), 7.63–7.66 (d, 2H, Ar), 8.21 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=19.0 (CH_3), 19.2, 27.2 (CH_2), 30.7 (CH), 32.5 (CH_3), 115.1 (CH), 120.6 (2CH), 124.6, 125.8 (CH), 129.5 (2CH), 136.3, 154.4, 157.2 (C), 165.8, 179.3 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3318(m), 3290 (m), 2936 (m), 1696 (s), 1643 (s), 1613 (s), 1587 (s), 1553 (s), 1434 (s), 1321 (s), 1167 (m), 957 (m), 759 (s), 694 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=221.4 (4.31), 274.9 (4.14). MS (EI, 70 eV): m/z (%)=284 (M$^+$+1, 16), 283 (M$^+$, 100), 268 (55), 213 (6), 163 (14), 146 (89), 91 (10), 77 (15), 70 (12). HRMS (EI, 70 eV): calcd for $C_{17}H_{17}O_3N$: 283.1208; found: 283.1208±2 ppm ([M]$^+$).

3.3.9. 5,6,7,8-Tetrahydro-8-methyl-4-oxo-*N*-(2-tolyl)-4*H*-chromene-2-carboxamide (5h). To a THF solution (50 ml) of **3h** (110 mg) was added an aqueous solution of HCl (30 ml, 10%). The solution was stirred for 24 h at 20 °C. The mixture was purified by chromatography (silica gel, *n*-hexane/EtOAc=5:1→3:1) to give **5h** as a yellow solid (75 mg, 89%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=1.42 (d, 3H, CH_3), 1.62–1.69 (m, 2H, CH_2), 1.81–1.87 (m, 1H, C*H*$_2$CH$_2$), 1.98–2.05 (m, 1H, C*H*$_2$CH$_2$), 2.19 (s, 3H, CH_3), 2.47–2.54 (m, 2H, CH_2), 2.89 (m, 1H, C*H*CH_3), 7.11 (d, 1H, Ar), 7.14 (s, 1H, C4), 7.17 (d, 1H, Ar), 7.23–7.30 (m, 1H, Ar), 8.09 (d, 1H, Ar), 8.26 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=17.7, 18.8 (CH_3), 19.4, 21.7, 30.8 (CH_2), 32.5, 114.9, 122.3 (CH), 124.6 (C), 126.0, 127.4 (CH), 128.3 (C), 130.8 (CH), 134.7, 154.5, 157.0 (C), 165.6, 179.3 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3428(br s), 2940

(m), 1689 (s), 1655 (s), 1609 (s), 1591 (s), 1529 (s), 1457 (s), 1417 (s), 1309 (m), 1255 (m), 1145 (s), 1034 (w), 773 (m), 590 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=220.5 (4.26), 268.9 (4.02). MS (EI, 70 eV): *m*/*z* (%)=298 (M^+, 18), 297 (94), 282 (35), 268 (7), 227 (9), 186 (14), 160 (100), 131 (10), 106 (20), 77 (13). HRMS (EI, 70 eV): calcd for $C_{18}H_{19}O_3N$: 297.1365; found: 297.1365±2 ppm ($[M]^+$). Anal. Calcd for $C_{18}H_{19}O_3N$: C, 72.69; H, 6.46. Found: C, 72.78; H, 6.72.

3.3.10. 5,6,7,8-Tetrahydro-*N*-(2-methoxyphenyl)-8-methyl-4-oxo-4*H*-chromene-2-carboxamide (5i). To a THF solution (50 ml) of **3i** (120 mg) was added an aqueous solution of HCl (15 ml, 10%). The solution was stirred for 24 h at 20 °C. The mixture was purified by chromatography (silica gel, *n*-hexane/EtOAc=5:1→3:1) to give **5i** as a slightly pink solid (67 mg, 75%). ^1H NMR ($CDCl_3$, 250 MHz): δ=1.43 (d, 3H, CH_3), 1.58 (m, 2H, CH_2), 1.85 (m, 1H, CH_2), 2.07 (m, 1H, CH_2), 2.45 (m, 1H, CH_2), 2.58 (m, 1H, CH_2), 2.95 (m, 1H, C*H*CH_3), 3.95 (s, 3H, CH_3O), 6.93–6.95 (d, 1H, Ar), 7.02–7.04 (m, 1H, Ar), 7.11–7.14 (m, 1H, Ar), 7.11 (s, 1H, C4), 8.48 (d, 1H, CH), 9.12 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=18.3 (CH_3), 19.8, 21.8 (CH_2), 31.0 (CH), 32.7 (CH_2), 56.2 (CH_3), 110.3, 114.6, 120.1, 121.6 (CH), 124.4 (C), 125.2 (CH), 126.6, 148.4, 154.6, 156.7 (C), 165.6, 179.4 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3438(br m), 3379 (s), 2941 (m), 1686 (s), 1654 (s), 1629 (s), 1603 (s), 1530 (s), 1486 (s), 1464 (s), 1629 (s), 1603 (s), 1530 (s), 1486 (s), 1464 (s), 1416 (s), 1336 (m), 1258 (s), 660 (m), 554 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=220.9 (4.33), 280.3 (4.03). MS (EI, 70 eV): *m*/*z* (%)=315 (M^++2, 2), 314 (M^++1, 20), 313 (M^+, 100), 298 (33), 284 (5), 202 (8), 176 (54), 135 (11), 123 (8), 92 (10), 70 (9), 53 (3). HRMS (EI, 70 eV): calcd for $C_{18}H_{19}NO_4$: 313.1314; found: 313.1314±2 ppm ($[M]^+$).

3.3.11. 2-[*N*-(Methoxyphenyl)carbamoyl]-8-methyl-5,6,7,8-tetrahydrochromone (5j). Starting with **3j** (21 mg, 0.05 mmol), **5j** was isolated as a colourless solid (10 mg, 61%). ^1H NMR ($CDCl_3$, 250 MHz): δ=1.38 (d, ^3J=7.0 Hz, 3H, CHC*H*$_3$), 1.45–2.10 (m, 6H, 3CH_2), 2.88 (m, 1H, C*H*CH_3), 3.81 (s, 3H, OMe), 6.91 (d, ^3J=8.9 Hz, 2H, AA′, PMP), 7.14 (s, 1H, C-3), 7.55 (d, ^3J=9.1 Hz, 2H, XX′, PMP), 8.19 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ=18.93, 21.50, 30.40 (CH_2), 30.93 (CH*C*H_3), 32.19 (*C*HCH_3), 55.49 (OCH_3), 114.34 (CH, PMP), 114.55 (CH, C-3), 122.11 (CH, PMP), 124.23, 129.29, 154.37, 156.74, 157.24 (C), 165.69 (NCO), 179.21 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3316(m), 2938 (w), 1688 (m), 1639 (s), 1615 (s), 1602 (s), 1584 (m), 1552 (m), 1528 (m), 1513 (s), 1434 (m), 1414 (w), 1245 (s), 1166 (m), 1030 (m), 840 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=279.7 (4.03), 222.0 (4.24). MS (EI, 70 eV): *m*/*z* (%)=313 ($[M]^+$, 100), 298 (16), 176 (24), 122 (28). HRMS (EI, 70 eV): calcd for $C_{18}H_{19}NO_4$: 313.1314; found: 313.1314±2 ppm ($[M]^+$).

3.3.12. (*E*)-3-Hydroxy-5-(2-oxocyclopent-1-ylidene)-1-phenyl-2,5-dihydropyrrol-2-one (4k). Starting with **3k** (53 mg, 0.16 mmol), **4k** was isolated as a yellow solid (39 mg, 95%). ^1H NMR ($CDCl_3$, 250 MHz): δ=2.01 (quint, ^3J=7.5 Hz, 2H, CO–CH_2C*H*$_2$), 2.43 (t, ^3J=7.8 Hz, 2H, CC*H*$_2$$CH_2$), 2.91 (t, ^3J=7.2 Hz, 2H, C*H*$_2$CO), 6.82 (br s, 1H, OH), 7.07–7.17 (m, 3H, Ar), 7.35–7.44 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ=20.03, 27.45, 40.34 (CH_2), 101.51 (CH, C-4), 114.61 (C), 117.90, 123.66, 129.73 (CH, Ph), 132.62, 138.92, 153.72 (C), 166.88 (NCO), 207.64 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3289(s), 3132 (m), 2956 (m), 2927 (m), 2854 (w), 1789 (s), 1734 (w), 1696 (s), 1641 (s), 1599 (s), 1575 (s), 1544 (s), 1501 (m), 1445 (s), 1324 (s), 1288 (m), 1272 (m), 1227 (m), 1201 (s), 1182 (m), 1086 (m), 1018 (m), 972 (s), 838 (m), 816 (m), 770 (m), 751 (s), 687 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=398.7 (4.33), 294.6 (3.69), 251.6 (4.02). MS (EI, 70 eV): *m*/*z* (%)=255 ($[M]^+$, 100), 240 (8), 213 (8), 154 (20), 77 (70). HRMS (EI, 70 eV): calcd for $C_{15}H_{13}NO_3$: 255.0895; found: 255.0895±2 ppm ($[M]^+$). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.59; H, 5.15; N, 5.28.

3.3.13. (*E*)-3-Hydroxy-5-(1-oxo-indan-2-ylidene)-1-phenyl-2,5-dihydropyrrol-2-one (4l). Starting with **3l** (90 mg, 0.24 mmol), **4l** was isolated as a yellow solid (71 mg, 99%; *E*-isomer: 36 mg, 50%, *E*/*Z*>98:2; *Z*-isomer: 35 mg, 49%, *E*/*Z*<2:98). ^1H NMR ($CDCl_3$, 600 MHz) *E*-isomer: δ=3.95 (s, 2H, CH_2), 6.83 (br s, 1H, OH), 7.12 (t, ^3J=7.7 Hz, 1H, Ph, C-4′), 7.21 (d, ^3J=7.8 Hz, 2H, Ph, C-2′, C-6′), 7.40 (t, ^3J=7.7 Hz, 2H, Ph, C-3′, C-5′), 7.42 (td, ^3J=7.7 Hz, ^4J=2.2 Hz, 1H, indane, C-6″), 7.52 (t, ^3J=8.3 Hz, 1H, indane, C-4″), 7.60 (td, ^3J=7.7 Hz, ^4J=1.5 Hz, 1H, indane, C-5″), 7.70 (s, 1H, CH, C-4), 7.82 (d, ^3J=7.7 Hz, 1H, indane, C-7″); *Z*-isomer: δ=5.29 (s, 2H, CH_2), 6.93 (br s, 1H, OH), 7.19–7.24 (m, 3H, Ph: C-4′, indane, C-4″, C-6″), 7.26–7.30 (m, 3H, Ph: C-2′, C-6′, indane, C-5″), 7.45 (t, ^3J=7.9 Hz, 2H, Ph, C-3′, C-5′), 7.54 (d, ^3J=7.9 Hz, 1H, indane, C-7″), 7.89 (s, 1H, C-4). ^{13}C NMR ($CDCl_3$, 150.8 MHz) *E*-isomer: δ=30.21 (CH_2), 101.79 (CH, C-4), 113.67 (C, C-5), 118.07 (CH, Ph, C-2′, C-6′), 123.62 (CH, indane, C-7″), 123.96 (CH, Ph, C-4′), 126.21 (CH, indane, C-4″), 127.57 (CH, indane, C-6″), 129.84 (CH, Ph, C-3′, C-5′), 132.97 (C, C-3, C–OH), 134.41 (CH, indane, C-5″), 138.80 (C, Ph, C-1′), 139.85 (C, indane, C-7a″), 148.04 (C, indane, C-3a″), 154.94 (C, indane, C-2″), 166.57 (NCO), 193.72 (CO); *Z*-isomer: δ=44.57 (CH_2), 101.49 (CH, C-4), 116.23 (C, C-5), 118.30 (CH, Ph, C-2′, C-6′), 123.28 (CH, indane, C-7″), 124.27 (CH, Ph, C-4′), 125.33 (CH, indane, C-4″), 128.16 (CH, indane, C-6″), 129.92 (CH, Ph, C-3′, C-5′), 133.38 (C, C-3, C–OH), 134.24 (CH, indane, C-5″), 138.70 (C, Ph, C-1′), 139.82 (C, indane, C-7a″), 147.93 (C, indane, C-3a″), 155.79 (C, indane, C-2″), 166.16 (NCO), 193.29 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3335(m), 3065 (w), 3017 (w), 2960 (w), 2918 (w), 2850 (w), 1793 (s), 1771 (s), 1683 (s), 1637 (s), 1610 (s), 1591 (s), 1577 (s), 1537 (s), 1445 (m), 1329 (m), 1265 (s), 1218 (m), 1137 (m), 1064 (m), 918 (s), 798 (w), 749 (m), 733 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=425.0 (3.98), 290.5 (3.65), 240.0 (3.73). MS (EI, 70 eV): *m*/*z* (%)=303 ($[M]^+$, 100), 259 (40), 228 (65), 144 (24). HRMS (EI, 70 eV): calcd for $C_{19}H_{13}NO_3$: 303.0895; found: 303.0895±2 ppm ($[M]^+$).

3.3.14. 6-Phenyl-2-(phenylcarbamoyl)-4*H*-pyran-4-one (5m). Starting with **3m** (420 mg, 1.15 mmol), **5m** was isolated as a yellow solid (100 mg, 30%). ^1H NMR ([D_6]DMSO, 250 MHz): δ=6.99 (d, J=2.1 Hz, 1H, C-5), 7.12 (d, J=2.1 Hz, 1H, C-3), 7.18 (t, ^3J=7.2 Hz, 1H, Ph), 7.40 (t, ^3J=7.8 Hz, 2H, Ph), 7.50–7.62 (m, 3H, Ph), 7.74 (d, ^3J=8.1 Hz, 2H, Ph), 8.08 (t, ^3J=7.8 Hz, 2H, Ph), 9.50

(br s, 1H, NH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ=112.07, 115.53 (CH, C-3, C-5), 121.11, 124.85, 126.51, 128.72, 128.98 (CH, Ph), 130.35 (C), 131.72 (CH, Ph), 137.54, 156.21, 157.81, 162.85 (NCO), 178.60 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3424(s), 3331 (s), 1693 (w), 1639 (s), 1602 (m), 1549 (w), 1498 (w), 1448 (w), 1409 (m), 1324 (w), 1049 (m), 1028 (s), 1003 (s), 826 (w), 767 (m), 689 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=278.1 (3.52). MS (EI, 70 eV): *m*/*z* (%)=291 ([M]$^+$, 50), 186 ([M−COPh]$^+$, 100), 172 (18), 105 (24), 77 (18), 69 (40). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}NO_3$: 291.0895; found: 291.0895±2 ppm ([M]$^+$).

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