One-Pot Synthesis of Functionalized Indoles by Cyclization of Lithiated Amides and Nitriles with Oxaldiimidoyl Dichlorides

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The reaction of the dianion of phenylacetonitrile with substituted oxalic acid bis(imidoyl)chlorides resulted in the formation of 2-alkylidene-3-iminoindoles, containing substituents at different positions of the heterocyclic nucleus. The cyclization of lithiated amides with bis(imidoyl)chlorides afforded (3-imino-2,3-dihydro-1*H*-indol-2-ylidene)acetic amides. Excellent regio- and *E*-diastereoselectivities were observed in all reactions.

Introduction

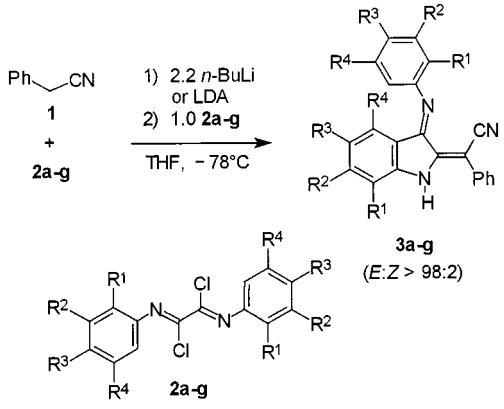
2-Alkylidene-3-oxindoles represent aza-analogous aurones and have been used as dienophiles[1,2] in cycloaddition reactions[3] for the construction of the spirocyclic *Aristotelia* alkaloid framework.[4] 2-Alkylidene-3-oxindoles have also been used as heterodienes in hetero-Diels−Alder reactions of inverse electron demand for the preparation of δ-carbolines[5] and potentially antitumour active pyrano[3,2-*b*]-indoles.[6]

We have recently reported a new cyclization of nitrile and sulfone dianions with oxalic acid-bis(imidoyl)chlorides.[7] This reaction results in the regio- and stereoselective formation of 2-alkylidene-3-iminoindoles which represent masked 2-alkylidene-3-oxindoles. In our initial studies, the dianion moiety was varied systematically. Herein, we wish to report two significant extensions. Firstly, variation of the bis(imidoyl)chloride which allows the synthesis of indoles containing substituents at different positions on the heterocyclic moiety. Secondly, the use of amides as starting materials which allows for the preparation of amide-substituted 2-alkylidene-3-iminoindoles. In addition to the preparative progress, the latter experiments showed for the first time that not only dianions, but also monoanions, can be successfully employed as substrates in our cyclization reaction.

Results and Discussion

Cyclizations of Substituted Oxalic Acid-Bis(imidoyl)chlorides

Reaction of the geminal dianion of phenylacetonitrile **1** with oxalic acid-bis(2-tolylimidoyl)chloride (**2a**) and bis(2-methoxyphenylimidoyl)chloride (**2b**) afforded the 2-alkylidene-3-iminoindoles **3a** and **3b**, containing a methyl and a methoxy group at carbon C7 of the indole moiety, respectively. The cyclization of **1** with bis(3-tolylimidoyl)chloride (**2c**) afforded indole **3c**, containing a methyl group at carbon C6, rather than C4, regioselectively. The cyclization of the dianion of **1** with oxalic acid-bis(4-methoxyphenylimidoyl)chloride gave indole **3d**, containing a methoxy group at carbon C5. The cyclization of phenylacetonitrile with oxalic acid-bis(3,5-dimethylphenylimidoyl)dichloride **2e**, oxalic acid-bis(2,4-dimethylphenylimidoyl)dichloride **2f** and bis(3,4-dimethylphenylimidoyl)dichloride **2g** afforded the



Scheme 1. Synthesis of substituted 2-alkylidene-3-iminoindoles **3a−g**

Table 1. Cyclization of dilithiated phenylacetonitrile with substituted oxalic acid-bis(imidoyl)chlorides **2a−f**

2	3	R^1	R^2	R^3	R^4	(%)[a]
a	**a**	Me	H	H	H	53
b	**b**	OMe	H	H	H	44
c	**c**	H	Me	H	H	33
d	**d**	H	H	OMe	H	67
e	**e**	H	Me	H	Me	58
f	**f**	Me	H	Me	H	27
g	**g**	H	Me	Me	H	53

[a] Isolated yield.

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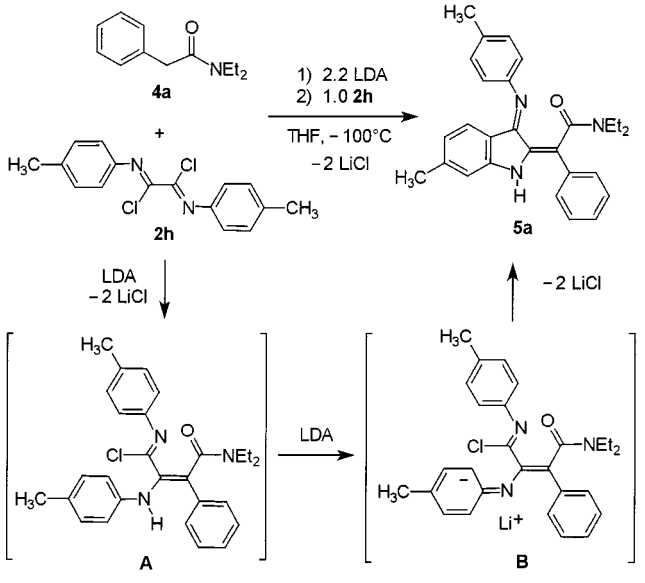
indoles **3e, 3f** and **3g**, respectively (Scheme 1 and Table 1), each containing two methyl groups at the indole moiety.

Cyclizations of Amide Carbanions

The addition of a THF solution of lithiated *N*,*N*-diethylphenylacetic amide (**4a**) (2 equiv.) to a solution of oxalic acid-bis(tolylimidoyl)chloride **2h** (1 equiv.) at −78 °C afforded the (3-imino-2,3-dihydro-1*H*-indol-2-ylidene)acetic amide **5a**, although in low yield. A thorough optimization of the reaction conditions proved important to obtain **5a** in good yield (Scheme 2, Table 2); the yield increased when only one equivalent of **4a** was used. The use of two equivalents of LDA was essential since employment of only one equivalent resulted in the formation of significant amounts of open-chain side products. Optimal yields were obtained when a THF solution of the carbanion was added to a solution of the bis(imidoyl)chloride at −100 °C. The yields decreased when an inverse addition protocol or higher temperatures were employed.

The formation of **5a** can be rationalized as follows: initial attack of monolithiated **4a** onto the dielectrophile **2g** affords intermediate **A**, which is subsequently deprotonated by LDA to give the ambident intermediate **B**. The *ortho* carbon of the arylimino group attacks the second imidoyl chloride group and re-aromatization leads to the final product. It is important to note that the product was formed with excellent stereoselectivity (*E*/*Z* > 98:2), which can be explained based on steric reasons. The structure of 3-iminoindole **5a** was confirmed independently by crystal structure analysis.[8]

To study the preparative scope of the cyclization reaction, the substituents of the amide and the bis(imidoyl)chloride were varied systematically (Scheme 3, Table 3). Variation of the dielectrophile offers the possibility to install substituents at different positions of the indole moiety: reaction of lithiated *N*,*N*-dimethyl-4-phenylacetic amide (**4a**) with bis-



Scheme 2. Cyclization of *N*,*N*-diethylphenylacetic amide with **2g**

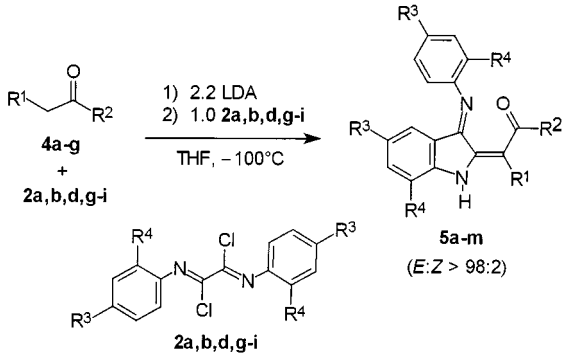
Table 2. Optimization of the synthesis of indole **5a**

No.	*T* [°C]	*t* [h][a]	**5a** (equiv.)	LDA (equiv.)	Yield (%)[b]
1	−78 → 20	12 + 2	2.0	2.2	11
2	−78 → 20	12 + 2	1.0	1.1	8
3	−78 → 20	12 + 48	1.0	2.2	32
4	−100 → 20	12 + 48	1.0	2.2	50
5	0 → 20	2 + 12	1.0	2.2	0
6	−100 → 20	2 + 48	1.0	2.2	24

[a] Reaction time at −78 → 20 °C + Reaction time at 20 °C. – [b] Isolated yield of **5a**.

(imidoyl)chlorides containing phenyl, 4-tolyl, 2-tolyl, 4-methoxyphenyl, and 2-methoxyphenyl groups afforded the 2-alkylidene-3-iminoindoles **5a**−**f** in acceptable yields and with very good stereoselectivities.

Variation of the amide was studied next. Cyclization of oxalic acid-bis(2-tolylimidoyl)chloride (**2a**) with the carbanions of *N*,*N*-diethyl-3-tolylacetic amide and *N*,*N*-dimethyl-4-tolylacetic amide afforded the 2-alkylidene-3-iminoindoles **5g** and **5h**, respectively, in good yields and with very good *E*-selectivities. Reaction of oxalic acid-bis(2-tolylimidoyl)chloride with the carbanion of *N*,*N*-diethyl-3-methoxyphenylacetic amide gave the indole **5i**. Cyclization of lithiated *N*,*N*-diethyl-4-methoxyphenylacetic amide with different oxalic acid bis(imidoyl)chlorides afforded the in-



Scheme 3. Cyclization of lithiated amides **4** with bis(imidoyl)chlorides **2**

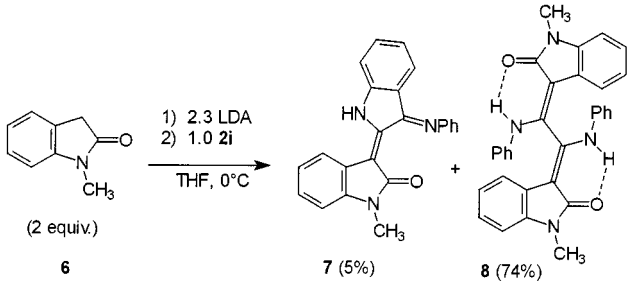
Table 3. Synthesis of 2-alkylidene-3-iminoindoles **5a**−**m**

2	**5**	R^1	R^2	R^3	R^4	(%)[a]
h	**a**	C_6H_5	NEt_2	CH_3	H	50
i	**b**	C_6H_5	NEt_2	H	H	25
a	**c**	C_6H_5	NEt_2	H	CH_3	44
a	**d**	C_6H_5	NMe_2	H	CH_3	31
d	**e**	C_6H_5	NEt_2	OCH_3	H	17
b	**f**	C_6H_5	NMe_2	H	OCH_3	30
a	**g**	3-$(H_3C)C_6H_4$	NEt_2	H	CH_3	33
a	**h**	4-$(H_3C)C_6H_4$	NMe_2	H	CH_3	10
a	**i**	3-$(H_3CO)C_6H_4$	NEt_2	H	CH_3	48
i	**j**	4-$(H_3CO)C_6H_4$	NEt_2	H	H	48
a	**k**	4-$(H_3CO)C_6H_4$	NEt_2	H	CH_3	45
d	**l**	4-$(H_3CO)C_6H_4$	NEt_2	OCH_3	H	25
a	**m**	C_6H_5	$N(CH_2)_4$	H	CH_3	13

[a] Isolated yield.

doles **5j**−**l** in acceptable yields and with very good stereoselectivities. It is noteworthy that the best results were obtained when amides containing a *N*,*N*-dimethyl- or a *N*,*N*-diethylamino-group were used. Surprisingly, significantly lower yields were obtained for pyrrolidine, piperidine and morpholine derivatives (see, for example, the formation of indole **5m**).

The treatment of one equivalent of lithiated *N*-methyl-2-oxindole **6** with one equivalent of oxalic acid-bis(phenylimidoyl)chloride resulted in formation of the yellow-coloured, open-chain product **8** in 32% yield. The deeply red coloured bis-indole **7** was obtained in only 7% yield. Employment of two equivalents of the amide afforded the products **8** and **7** in 74 and 5% yields, respectively (Scheme 4). The striking difference between the reactions of amides **4a** and **6** can be explained by the assumption that, in case of **6**, the second deprotonation step is slow relative to condensation with a second carbanion. The use of aliphatic amides resulted in the formation of open-chain 2:1 products.



Scheme 4. Reaction of *N*-methyl-2-oxindole **6** with **2i**

In summary, the reaction of amide carbanions with oxalic acid-bis(imidoyl) chlorides allows an efficient preparation of (3-imino-2,3-dihydro-1*H*-indol-2-ylidene)acetic amides from simple starting materials. These products are of pharmacological relevance and represent useful building blocks for the synthesis of natural products. Variation of the dielectrophile and the amide offer the possibility to install different substituents at the indole moiety and at the exocyclic double bond, respectively. No chromatographic purification or tedious separation of *E*/*Z* isomers is necessary. In addition, protection of the indole nitrogen is not required, since the latter is formed in the course of the cyclization.

Experimental Section

General Comments: See ref.[17]

Procedure for the Preparation of 2-Alkylidene-3-iminoindoles (3): *n*BuLi (9.8 mL, 2.2 molar equiv., 1.6 M solution in hexane) was added to a THF solution (20 mL) of phenylacetonitrile (6 mmol) at 0 °C. A clear yellow solution was formed. After stirring for 60 min at 0 °C the solution was transferred within 10 min to a stirred THF solution (80 mL) of the bis(imidoyl)chloride **2** at −78 °C. The colour of the solution changed to green. The temperature was allowed to rise to 20 °C within 30 min to give a deep green to black solution. After stirring for 2 h at 20 °C the reaction mixture was poured into 100 mL of a 1 M solution of NH_4Cl in water. The colour of the organic layer changed to deep red. The aqueous layer was extracted five times with ethyl ether (200 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The product was purified by chromatography (silica gel, diethyl ether/petroleum ether = 1:10 → 3:1).

(*E*)-2-(1-Cyano-1-phenylmethylidene)-7-methyl-3-(2-tolyl)imino-2,3-dihydro-1*H*-indole (3a): Starting with phenylacetonitrile (0.469 g, 4.00 mmol, 1 equiv.) and oxalic acid-bis(2-tolylimidoyl)chloride (1.220 g, 4.00 mmol, 1 equiv.), **3a** was isolated by chromatography (silica gel, petroleum ether/diethyl ether = 10:1→1:1→1:10) as a red solid (0.742 g, 2.12 mmol, 53%, *E*/*Z* > 98:2), m.p. 208−210 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.18, 2.25 (2 × s, 2 × 3 H, CH_3), 6.50−6.63 (m, 2 H, Ar), 6.88 (dd, *J* = 7.7, *J* = 1.1 Hz, 1 H, Ar), 7.07−7.14 (m, 3 H, Ar, NH), 7.20 (dd, *J* = 7.6, *J* = 1.4 Hz, 1 H, Ar), 7.24−7.27 (m, 1 H, Ar), 7.30−7.44 (m, 1 H, Ar), 7.54 (ddd, *J* = 7.9, *J* = 7.8, *J* = 1.5 Hz, 2 H, Ar), 7.70 (dd, *J* = 7.8, *J* = 1.4 Hz, 2 H, Ar). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.70, 17.97 (CH_3), 86.41 (*C*-CN), 116.96 (CH), 118.16, 119.05, 119.53 (C), 121.41, 123.95, 124.50, 126.52 (CH), 126.91 (C), 128.41, 128.58, 129.65, 130.74 (CH), 133.90 (C), 134.22 (CH), 146.01, 146.99, 149.17, 156.31 (C). − IR (KBr): $\tilde{\nu}$ = 3058 (w, Ar-H), 3012 (w), 2977(w), 2945 (w), 2923 (w, C−H), 2860 (w), 2197 (m, C≡N), 1652 (m), 1618 (m), 1595 (s), 1492 (m), 1456 (m), 1340 (s), 1220 (s), 1183 (m), 1110 (w), 1034 (w), 762 (m), 749 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 349 (44) [M$^+$], 348 (100) [M − 1]$^+$, 323 (4), 256 (3). − $C_{24}H_{19}N_3$ (349.4): C 82.49, H 5.48, N 12.03; found C 82.22, H 5.61, N 12.13.

(*E*)-2-(1-Cyano-1-phenylmethylidene)-7-methoxy-3-(2-methoxyphenyl)imino-2,3-dihydro-1*H*-indole (3b): Starting with phenylacetonitrile (0.469 g, 4.00 mmol, 1 equiv.) and oxalic acid-bis(2-methoxyphenylimidoyl)chloride (1.348 g, 4.00 mmol, 1 equiv.), **3b** was isolated by chromatography (silica gel, petroleum ether/diethyl ether = 10:1→1:1→1:10) as a red solid (0.676 g, 1.77 mmol, 44%, *E*/*Z* > 98:2), m.p. 212−214 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.78, 3.82 (2 × s, 2 × 3 H, OCH_3), 6.37 (d, *J* = 7.9 Hz,1 H, Ar), 6.62 (t, *J* = 7.9 Hz, 1 H, Ar), 6.80 (d, *J* = 8.0 Hz, 1 H, Ar), 6.97−7.02 (m, 3 H, Ar, NH), 7.13−7.20 (m, 1 H, Ar), 7.27−7.42 (m, 2 H, Ar), 7.52 (ddd, *J* = 7.8, *J* = 7.2, *J* = 1.3 Hz, 2 H, Ar), 7.68 (dd, *J* = 7.1, *J* = 1.4 Hz, 2 H, Ar). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 55.55, 56.12 (OCH_3), 86.74 (*C*-CN), 112.45, 114.04, 118.06 (CH), 119.12, 119.71 (C), 119.76, 121.28, 121.56, 125.41, 128.42, 128.48, 129.48 (CH), 133.91, 137.06, 139.57, 144.39, 146.79, 148.56, 157.68 (C). − IR (KBr): $\tilde{\nu}$ = 3040 (w, Ar-H), 2926 (m, C−H), 2853 (w), 2195 (m, C≡N), 1652 (s), 1635 (s), 1581 (s), 1488 (s), 1447 (s), 1379 (m), 1246 (s), 1223 (m), 1179 (m), 1114 (w), 1028 (w), 742 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 381 (60) [M$^+$], 380 (100) [M − 1]$^+$, 365 (12), 274 (11). − $C_{24}H_{19}N_3O_2$ (381.4): C 75.57, H 5.02, N 11.02; found C 75.67, H 5.24, N 10.89.

(*E*)-2-(1-Cyano-1-phenylmethylidene)-6-methyl-3-(3-tolyl)imino-2,3-dihydro-1*H*-indole (3c): Starting with phenylacetonitrile (0.359 g, 3.06 mmol, 1 equiv.) and oxalic acid-bis(3-tolylimidoyl)chloride (0.934 g, 3.06 mmol, 1 equiv.), **3c** was isolated by chromatography (silica gel, petroleum ether/diethyl ether = 10:1→1:1→1:10) as a red solid (0.353 g, 1.01 mmol, 33%, *E*/*Z* > 98:2), m.p. 205−208 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.27, 2.37 (2 × s, 2 × 3 H, CH_3), 6.47 (d, *J* = 7.7 Hz, 1 H, Ar), 6.60 (s, d, *J* = 7.6 Hz, 2 H, Ar), 6.80−6.86 (m, 2 H, Ar, NH), 7.00 (d, *J* = 7.5 Hz, 1 H, Ar), 7.21 (s, 1 H, Ar), 7.28−7.41 (m, 2 H, Ar), 7.51 (ddd, *J* = 7.8, *J* = 7.2, *J* = 1.9 Hz, 2 H, Ar), 7.63 (dd, *J* = 7.1, *J* = 1.9, 2 H, Ar). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.25, 21.82 (CH_3), 85.85 (*C*-CN), 111.14, 114.98 (CH), 115.61 (C), 118.72 (CH), 119.44 (C),

121.92, 124.93, 126.34, 128.21, 128.59, 129.00, 129.19 (CH), 133.79, 139.09, 144.55, 147.92, 148.20, 150.55, 156.56 (C). − IR (KBr): $\tilde{\nu}$ = 2918 (w, C−H), 2197 (m, C≡N), 1627 (s), 1583 (s), 1570 (s), 1450 (m), 1344 (s), 1262 (m), 1221 (m), 1153 (m), 1116 (w), 759 (m), 711 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 349 (40) [M^+], 348 (100) [M − 1]$^+$, 332 (2). − $C_{24}H_{19}N_3$ (349.4): C 82.49, H 5.48, N 12.03; found C 82.23, H 5.42, N 12.01.

(*E*)-2-(1-Cyano-1-phenylmethylidene)-6-methoxy-3-(4-methoxyphenyl)imino-2,3-dihydro-1*H*-indole (3d): Starting with phenylacetonitrile (0.469 g, 4.00 mmol), 1.53 g (67%, *E*/*Z* > 98:2) of **3d** was isolated as red crystals, m.p. 160−163 °C. The synthesis of this compound has been reported previously.[7] − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.45, 3.80 (s, 6 H, OCH_3), 6.48 (d, 1 H, 4-H), 6.70 (m, 2 H, Ar), 7.00−8.00 (m, 10 H, Ar, NH). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ_c = 55.47, 55.72 (OCH_3), 86.29 (C, *C*CN), 112.10, 118.02 (CH, C-4, C-7), 117.10 (C, CN), 119.71 (C, C-3a), 120.52, 125.82, 128.95, 129.40, 130.09, 131.64, 132.01 (CH), 141.20, 142.78, 147.32, 148.13, 157.62, 158.64 (C). − MS (FAB): *m*/*z* (%) = 382 (100) [M^+ + 1].

Procedure for the Synthesis of Indoles 3e−g: *n*BuLi (1.06 mL, 2.36 M solution in hexane, 2.50 mmol) was added to a THF solution (20 mL) of diisopropylamine (233 mg, 2.30 mmol) at 0 °C. After stirring for 30 min phenylacetonitrile (0.117 g, 1.00 mmol) was added at 0 °C. The solution was stirred for 60 min and subsequently cooled to −78 °C, then a THF solution (40 mL) of oxal-bis(3,5-dimethylphenylimidoyl) dichloride (0.367 g, 1.10 mmol) was added. The solution was warmed to 20 °C within 60 min and then stirred for 30 min at 20 °C. An aqueous solution of NH_4Cl (250 mL, 1 M) was added and the mixture was extracted with ether (3 × 100 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, petroleum ether/diethyl ether = 5:1) to give **3e** as a red solid (0.219 g, 0.580 mmol, 58%, *E*/*Z* > 98:2).

(*E*)-2-(1-Cyano-1-phenylmethylidene)-4,6-dimethyl-3-(3,5-dimethylphenyl)imino-2,3-dihydro-1*H*-indole (3e): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, ArCH_3), 2.28 (s, 9 H, 3 × ArCH_3), 6.45 (s, 1 H, Ar), 6.46 (s, 1 H, Ar), 6.57 (s, 2 H, Ar), 6.71 (s, 1 H, Ar), 7.33 (m, 2 H, Ph), 7.47 (dd, *J* = 7.8, *J* = 7.2 Hz, 2 H, Ph), 7.60 (m, 1 H, Ph). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.95 (Ar*C*H_3), 21.29 (Ar*C*H_3), 21.65 (Ar*C*H_3), 22.36 (Ar*C*H_3), 84.97 (*C*-CN), 108.69 (CH), 116.06 (C), 117.00 (CH), 119.41 (C), 125.53, 126.02, 128.16, 128.47, 129.42 (CH), 134.03, 137.99, 138.23, 138.24, 144.23, 149.51, 150.69, 154.40 (C). − IR (KBr): $\tilde{\nu}$ = 3056 (w, Ar-H), 3027 (w), 2918 (m, C−H), 2857 (w), 2194 (m, C≡N), 1717 (m), 1624 (s), 1596 (s), 1570 (s), 1494 (m), 1452 (m), 1341 (m), 1290 (m), 1154 (m), 1028 (m), 966 (w), 838 (m), 759 (m), 698 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 377 (64) [M^+], 376 (100) [M − 1]$^+$, 362 (12), 270 (10). − $C_{26}H_{23}N_3$ (377.5): C 82.73, H 6.14, N 11.13; found C 82.58, H 5.93, N 10.97.

(*E*)-2-(1-Cyano-1-phenylmethylidene)-5,7-dimethyl-3-(2,4-dimethylphenyl)imino-2,3-dihydro-1*H*-indole (3f): Starting with phenylacetonitrile (0.117 g, 1.00 mmol) and oxal-bis(2,4-dimethylphenylimidoyl) dichloride (0.367 g, 1.10 mmol), **3f** was isolated as a red solid (0.105 g, 0.277 mmol, 27%, *E*/*Z* > 98:2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.05 (s, 3 H, ArCH_3), 2.14 (s, 3 H, ArCH_3), 2.24 (s, 3 H, ArCH_3), 2.37 (s, 3 H, ArCH_3), 6.47 (s, 1 H, Ar), 6.79 (d, *J* = 7.9 Hz, 1 H, Ar), 6.91 (s, 1 H, Ar), 7.02 (m, 2 H, Ar, NH), 7.11 (s, 1 H, Ar), 7.40 (d, *J* = 7.3 Hz, 1 H, Ar), 7.51 (t, *J* = 7.5 Hz, 2 H, Ar), 7.69 (dd, *J* = 7.3, *J* = 1.3 Hz, 2 H, Ar). − ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 16.23 (Ar*C*H_3), 17.46 (Ar*C*H_3), 20.47 (Ar*C*H_3), 20.55 (Ar*C*H_3), 84.59 (*C*-CN), 116.72 (CH), 117.69, 119.91, 121.46 (C), 122.61 (CH), 126.00 (C), 127.10, 127.96, 128.78, 129.08 (CH), 129.54 (C), 131.23 (CH), 133.35, 133.97 (C), 135.73 (CH), 145.79, 146.52, 147.90, 157.41 (C). − IR (KBr): $\tilde{\nu}$ = 3052 (w, Ar-H), 3014 (w), 2970 (w), 2919 (m, C−H), 2855 (w), 2199 (m, C≡N), 1685 (w), 1652 (m), 1616 (m), 1586 (s), 1510 (m), 1484 (s), 1447 (m), 1330 (m), 1224 (m), 1201 (s), 1155 (w), 1119 (w), 1030 (w), 760 (m), 696 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 377 (42) [M^+], 376 (100) [M − 1]$^+$, 310 (40), 257 (20), 196 (80). − $C_{26}H_{23}N_3$ (377.5): C 82.73, H 6.14, N 11.13; found C 82.55, H 6.03, N 11.02.

(*E*)-2-(1-Cyano-1-phenylmethylidene)-5,6-dimethyl-3-(3,4-dimethylphenyl)imino-2,3-dihydro-1*H*-indole (3g): Starting with phenylacetonitrile (0.117 g, 1.00 mmol) and oxal-bis(3,4-dimethylphenylimidoyl) dichloride (0.367 g, 1.10 mmol), **3g** was isolated as a red solid (0.199 g, 0.527 mmol, 53%, *E*/*Z* > 98:2), m.p. 220−222 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 1.84 (s, 3 H, ArCH_3), 2.12 (s, 3 H, ArCH_3), 2.25 (s, 3 H, ArCH_3), 2.27 (s, 3 H, ArCH_3), 6.34 (br, 1 H, NH), 6.72 (d, 1 H, Ar), 6.79 (s, 2 H, Ar), 7.20 (d, 1 H, Ar), 7.36−7.63 (2 m, 5 H, Ph). − ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 18.71 (Ar*C*H_3), 19.09 (Ar*C*H_3), 19.23 (Ar*C*H_3), 20.25 (Ar*C*H_3), 83.21 (*C*-CN), 112.48 (CH), 114.97 (C), 115.14, 119.24 (CH), 119.49 (C), 125.89, 127.78 (CH), 127.84 (C), 128.56, 129.01, 130.03 (CH), 131.92, 133.77, 137.13, 142.99, 147.31, 147.54, 148.12, 156.96 (C). − IR (KBr): $\tilde{\nu}$ = 3056 (w, Ar-H), 3021 (w), 2967 (w), 2919 (w, C−H), 2858 (w), 2189 (m, C≡N), 1732 (m), 1624 (s), 1595 (s), 1581 (s), 1495 (s), 1446 (s), 1332 (s), 1220 (m), 1206 (m), 1112 (m), 1021 (w), 762 (m), 715 (m), 699 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 377 (42) [M^+], 376 (100) [M − 1]$^+$, 350 (4), 270 (2). − $C_{26}H_{23}N_3$ (377.5): C 82.73, H 6.14, N 11.13; found C 82.61, H 6.15, N 11.09.

General Procedure for the Synthesis of 2-Alkylidene-3-iminoindoles (5): A THF solution (20 mL) of LDA (2.2 equiv.) was prepared by addition of *n*BuLi (1.6 M solution in hexane) to a THF solution of diisopropylamine at 0 °C. To this solution was added a THF solution (10 mL) of *N*,*N*-diethyl phenylacetic amide (**4a**) (0.5 mL, 2.62 mmol) at 0 °C. A clear orange solution was formed. After stirring for 60 min at 0 °C the solution was transferred within 10 min to a stirred THF solution (80 mL) of oxalic acid bis(*p*-tolylimidoyl)chloride (**2a**; 2.62 mmol) at −100 °C. The colour of the solution changed to deep green. The temperature was allowed to rise to 20 °C within 12 h. After stirring for an additional 24 h the reaction mixture was poured into 100 mL of water. The colour of the solution changed to red. The aqueous layer was extracted twice with ether. The combined organic layers were dried ($MgSO_4$), filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, ether/petroleum ether = 1:1) to give **5a** as an orange solid.

(*E*)-2-(*N*,*N*-Diethyl-1-carbamoyl-1-phenylmethylidene)-5-methyl-3-(*p*-tolylimino)-1*H*-indole (5a): Starting with *N*,*N*-diethylphenylacetic amide (**4a**; 0.50 mL, 2.62 mmol) and oxalic acid-bis(*p*-tolylimidoyl)chloride (**2g**; 2.62 mmol), indole **5a** was isolated as an orange solid (0.56 g, 50%, *E*/*Z* > 98:2), m.p. 217−219 °C. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.91, 1.04 (2 × t, *J* = 7.1 Hz, 2 × 3 H, CH_2CH_3), 2.01, 2.39 (2 × s, 2 × 3 H, Tol-CH_3), 3.14−3.60 (m, 4 H, CH_2CH_3), 6.47 (s, 1 H, Hetar), 6.68−7.66 (m, 11 H, Ar, Hetar). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 12.2, 13.9 (CH_2CH_3), 21.0, 30.1 (Tol-CH_3), 39.0, 42.5 (CH_2CH_3), 110.8, 115.3, 118.6, 126.9, 128.0, 128.1, 128.6, 128.8, 129.6, 130.2, 133.5, 134.1, 136.4, 136.6, 148.7, 149.6, 158.0, 163.8. − IR (Nujol): $\tilde{\nu}$ = 3479 (br), 3143 (br, ν_{NH}), 1639 (m), 1619 (m), 1602 (s), 1574 (m), 1564 (m), 1518 (w), 1488 (s) cm^{-1}. − MS (CI, H_2O): *m*/*z* (%) = 424 [M^+ + 1]

(10), 351 (22), 192 (27). − $C_{28}H_{29}N_3O$ (423.6): C 79.40, H 6.90, N 9.92; found C 78.70, H 7.09, N 9.75.

(*E*)-2-(*N,N*-Diethyl-1-carbamoyl-1-phenylmethylidene)-3-phenylimino-1*H*-indole (5b): Starting with *N,N*-diethylphenylacetic amide (0.501 g, 2.62 mmol) and oxalic acid-bis(phenylimidoyl)chloride (**2h**; 0.726 g, 2.62 mmol), indole **5b** was isolated as an orange solid (0.262 g, 25%, *E*/*Z* > 98:2), m.p. 212−215 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (t, 3 H, CH_2CH_3), 1.09 (t, 3 H, CH_2CH_3), 3.06−3.80 (4 × m, 4 H, 2 × CH_2CH_3), 6.40−7.70 (m, 14 H, Ar). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.80 (CH_2CH_3), 13.39 (CH_2CH_3), 38.71 (CH_2CH_3), 42.06 (CH_2CH_3), 110.80 (CH), 115.04 (C), 118.15, 118.73, 119.02, 123.23 (CH), 126.32 (C), 127.53, 127.99, 129.02, 129.11, 132.65 (CH), 135.44, 135.55, 150.13, 151.55, 157.41 (C), 168.49 (C=O). − IR (KBr): $\tilde{\nu}$ = 3055 (w, Ar-H), 2973 (m, C−H), 2930 (m, C−H), 1645 (s), 1607 (s), 1587 (s), 1464 (s), 1330 (m), 1206 (m), 1137 (m), 772 (m), 747 (m), 708 (m), 696 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 395 (44) [M^+], 394 (100) [M − 1]$^+$, 323 (16), 295 (23), 222 (18), 194 (18). − $C_{26}H_{25}N_3O$ (395.50): C 78.96, H 6.37, N 10.62; found C 79.10, H 6.69, N 10.70.

(*E*)-2-(*N,N*-Diethyl-1-carbamoyl-1-phenylmethylidene)-7-methyl-3-(2-tolyl)imino-1*H*-indole (5c): Starting with *N,N*-diethylphenylacetic amide (0.586 g, 3.06 mmol) and oxalic acid-bis(2-tolylimidoyl)chloride (**2a**; 0.935 g, 3.06 mmol), indole **5c** was isolated as an orange solid (574 mg, 44%, *E*/*Z* > 98:2), m.p. 220−224 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82 (br. s, 3 H, CH_2CH_3), 1.04 (t, 3 H, CH_2CH_3), 2.12 (s, 6 H, 2 × CH_3), 3.05−3.40 (m, 2 H, CH_2CH_3), 3.40−3.78 (m, 2 H, CH_2CH_3), 6.30−7.78 (m, 12 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.78 (CH_2CH_3), 13.49 (CH_2CH_3), 15.87 (CH_3), 17.81 (CH_3), 38.80 (CH_2CH_3), 42.29 (CH_2CH_3), 115.83, 118.99, 119.47, 119.48 (C), 119.67, 123.29, 123.55, 126.44, 127.73, 128.22, 128.62, 129.24, 130.44, 133.29 (CH), 135.53, 135.77, 148.64, 150.36, 159.20 (C), 168.33 (C=O). − IR (KBr): $\tilde{\nu}$ = 3060 (w, Ar-H), 2975 (w, C−H), 2932 (w, C−H), 1616 (s), 1573 (m), 1493 (w), 1457 (m), 1430 (m), 1378 (w), 1326 (w), 1227 (m), 1178 (m), 1157 (m), 768 (w), 749 (m), 693 (w) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 423 (44) [M^+], 422 (100) [M − 1]$^+$, 350 (12), 324 (16). − $C_{28}H_{29}N_3O$ (423.56): C 79.40, H 6.90; found C 77.93, H 6.87.

(*E*)-2-(*N,N*-Dimethyl-1-carbamoyl-1-phenylmethylidene)-7-methyl-3-(2-tolyl)imino-1*H*-indole (5d): Starting with *N,N*-dimethylphenylacetic amide (0.500 g, 3.06 mmol) and oxalic acid-bis(2-tolylimidoyl)chloride (**2a**; 0.935 g, 3.06 mmol), indole **5d** was isolated as an orange solid (370 mg, 31%, *E*/*Z* > 98:2), m.p. 205−207 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.16 (s, 6 H, 2 × NCH_3), 2.94 (s, 3 H, CH_3), 3.02 (s, 3 H, CH_3), 6.35−7.75 (m, 12 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.89 (CH_3), 18.01 (CH_3), 34.67 (NCH_3), 37.14 (NCH_3), 115.12, 118.78, 119.48, 119.49 (C), 119.64, 123.53, 123.65, 126.44, 127.85, 127.99, 129.29, 129.30, 130.51, 133.38 (CH), 135.21, 135.62, 148.66, 150.58, 157.80 (C), 169.66 (C=O). − IR (KBr): $\tilde{\nu}$ = 3060 (w, Ar-H), 3008 (w, Ar-H), 2921 (m, C−H), 1618 (s), 1596 (s), 1575 (m), 1493 (m), 1458 (m), 1396 (m), 1325 (w), 1229 (m), 1162 (m), 1111 (w), 759 (m), 746 (m), 694 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 395 (44) [M^+], 394 (100) [M − 1]$^+$, 323 (16), 307 (12). − $C_{26}H_{25}N_3O$ (395.50): C 78.96, H 6.37; found C 78.90, H 6.42.

(*E*)-2-(*N,N*-Diethyl-1-carbamoyl-1-phenylmethylidene)-5-methoxy-3-(4-methoxyphenyl)imino-1*H*-indole (5e): Starting with *N,N*-diethylphenylacetic amide (0.501 g, 2.62 mmol) and oxalic acid-bis(4-methoxyphenylimidoyl)chloride (**2d**; 0.988 g, 2.62 mmol), indole **5e** was isolated as an orange solid (200 mg, 17%, *E*/*Z* > 98:2) m.p. 195−198 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, CH_2CH_3), 1.09 (t, 3 H, CH_2CH_3), 3.15 (m, 1 H, CH_2CH_3), 3.27 (m, 1 H, CH_2CH_3), 3.44 (s, 3 H, OCH_3), 3.48 (m, 1 H, CH_2CH_3), 3.75 (m, 1 H, CH_2CH_3), 3.82 (s, 3 H, OCH_3), 6.26−7.70 (m, 12 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.95 (CH_2CH_3), 13.38 (CH_2CH_3), 38.72 (CH_2CH_3), 42.12 (CH_2CH_3), 55.35 (OCH_3), 55.49 (OCH_3), 109.93, 111.62, 114.31 (CH), 114.79, 119.17 (C), 119.76, 120.27, 127.33, 128.01, 128.97 (CH), 135.72, 136.66, 144.62, 144.83, 152.56, 156.12, 157.93 (C), 168.76 (C=O). − IR (KBr): $\tilde{\nu}$ = 2992 (m), 2973 (m, C−H), 2933 (m, C−H), 2831 (w), 1637 (s), 1609 (s), 1574 (s), 1564 (s), 1486 (s), 1436 (s), 1311 (m), 1272 (m), 1233 (s), 1127 (m), 1036 (m), 850 (m), 756 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 456 (50) [M + 1$^+$], 455 (58) [M^+], 454 (100) [M − 1]$^+$, 382 (39), 356 (18), 339 (10). − $C_{28}H_{29}N_3O_3$ (455.55): C 73.82, H 6.42; found C 73.58, H 6.65.

(*E*)-2-(*N,N*-Dimethyl-1-carbamoyl-1-phenylmethylidene)-7-methoxy-3-(2-methoxyphenyl)imino-1*H*-indole (5f): Starting with *N,N*-dimethylphenylacetic amide (0.500 g, 3.06 mmol) and oxalic acid-bis(2-methoxyphenylimidoyl)chloride (**2b**; 1.156 g, 3.06 mmol), indole **5f** was isolated as an orange solid (392 mg, 30%, *E*/*Z* > 98:2), m.p. 220−223 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.95 (s, 3 H, NCH_3), 3.11 (s, 3 H, NCH_3), 3.77 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 6.24−7.76 (m, 12 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 34.70 (NCH_3), 36.95 (NCH_3), 55.40 (OCH_3), 55.68 (OCH_3), 111.91, 113.00 (CH), 114.90 (C), 117.98, 119.46, 119.68 (CH), 120.06 (C), 121.09, 124.35, 127.75, 128.12, 129.19 (CH), 135.35, 135.50, 139.96, 140.82, 144.73, 149.07, 158.33 (C), 169.82 (C=O). − IR (KBr): $\tilde{\nu}$ = 3040 (w, Ar-H), 2960 (w, C−H), 2924 (m, C−H), 2853 (w), 1626 (s), 1587 (m), 1488 (s), 1445 (m), 1373 (w), 1322 (w), 1248 (m), 1179 (m), 1155 (m), 749 (m), 739 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 427 (62) [M^+], 426 (100) [M − 1]$^+$, 351 (22), 224 (12). − $C_{26}H_{25}N_3O_3$ (427.50): C 73.05, H 5.89; found C 71.44, H 6.98.

(*E*)-2-[*N,N*-Diethyl-1-carbamoyl-1-(3-tolyl)methylidene]-7-methyl-3-(2-tolyl)imino-1*H*-indole (5g): Starting with *N,N*-diethyl-3-tolylacetic amide (0.628 g, 3.06 mmol) and oxalic acid-bis(2-tolylimidoyl)chloride (**2a**; 0.934 g, 3.06 mmol), indole **5g** was isolated as an orange solid (446 mg, 33%), m.p. 217−219 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (br. s, 3 H, CH_2CH_3), 1.05 (t, 3 H, CH_2CH_3), 2.14 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 3.10−3.40 (m, 2 H, CH_2CH_3), 3.41−3.80 (m, 2 H, CH_2CH_3), 6.29−7.57 (m, 11 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.73 (CH_2CH_3), 13.50 (CH_2CH_3), 15.80 (CH_3), 17.77 (CH_3), 21.50 (CH_3), 38.74 (CH_2CH_3), 42.24 (CH_2CH_3), 115.89 (C), 116.91 (CH), 118.89, 119.32 (C), 119.49, 123.17, 123.45, 124.95, 126.32, 128.48, 128.49, 128.97, 130.34, 133.18 (CH), 135.37, 135.58, 138.89, 138.90, 148.54, 150.31, 157.40 (CH), 168.26 (C=O). − IR (KBr): $\tilde{\nu}$ = 2973 (m, C−H), 2930 (m, C−H), 1630 (s), 1596 (s), 1480 (m), 1458 (m), 1430 (m), 1377 (w), 1322 (m), 1229 (m), 1149 (m), 1110 (w), 1038 (w), 748 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 437 (46) [M^+], 436 (100) [M − 1]$^+$, 364 (13), 338 (20). − $C_{29}H_{31}N_3O$ (437.58): C 79.60, H 7.14; found C 79.40, H 7.18.

(*E*)-2-[*N,N*-Dimethyl-1-carbamoyl-1-(4-tolyl)methylidene]-7-methyl-3-(2-tolyl)imino-1*H*-indole (5h): Starting with *N,N*-dimethyl-4-tolylacetic amide (0.542 g, 3.06 mmol) and oxalic acid-bis(2-tolylimidoyl)chloride (**2a**; 0.935 g, 3.06 mmol), indole **5h** was isolated as an orange solid (121 mg, 10%). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.16 (s, 6 H, $ArCH_3$), 2.40 (s, 3 H, $ArCH_3$), 2.94 (s, 3 H, NCH_3), 3.01 (s, 3 H, NCH_3), 6.36−7.64 (m, 11 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.89 ($ArCH_3$), 18.03 ($ArCH_3$), 21.32 ($ArCH_3$), 34.67 (NCH_3), 37.14 (NCH_3), 115.29, 118.85, 119.48, 119.49 (C), 119.55, 123.48, 123.65, 126.46, 127.89, 130.01, 130.02, 130.50 (CH), 132.22 (C), 133.30 (CH), 135.32, 137.87, 148.71,

150.66, 159.20 (C), 169.85 (C=O). − IR (KBr): ṽ = 2923 (s, C−H), 2854 (m, C−H), 1616 (s), 1457 (m), 1394 (w), 1328 (w), 1228 (w), 1158 (w), 752 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 409 (44) $[M^+]$, 408 (100) $[M - 1]^+$, 394 (13), 365 (12), 337 (13).

(*E*)-2-[*N,N*-Diethyl-1-carbamoyl-1-(3-methoxyphenyl)methylidene]-7-methyl-3-(2-tolyl)imino-1*H*-indole (5i): Starting with *N,N*-diethyl-3-methoxyphenylacetic amide (0.677 g, 3.06 mmol) and oxalic acid-bis(2-tolylimidoyl)chloride (**2a**; 0.934 g, 3.06 mmol), indole **5i** was isolated as an orange solid (661 mg, 48%, *E*/*Z* > 98:2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (t, 3 H, CH_2CH_3), 1.05 (t, 3 H, CH_2CH_3), 2.15 (s, 6 H, 2 × CH_3), 3.10−3.40 (m, 2 H, CH_2CH_3), 3.43−3.80 (m, 2 H, CH_2CH_3), 3.84 (s, 3 H, OCH_3), 6.30−7.41 (m, 11 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.80 (CH_2CH_3), 13.56 (CH_2CH_3), 15.85 (CH_3), 17.80 (CH_3), 38.87 (CH_2CH_3), 42.37 (CH_2CH_3), 55.23 (OCH_3), 112.73, 113.91 (CH), 115.55, 118.87, 119.40, 119.41 (C), 119.60, 120.24, 123.25, 123.49, 126.36, 130.11, 130.12, 130.38, 133.25 (CH), 135.56, 137.05, 148.54, 150.28, 150.29, 160.13 (C), 168.18 (C=O). − IR (KBr): ṽ = 2924 (m, C−H), 2853 (w), 1643 (m), 1594 (s), 1464 (s), 1377 (w), 1318 (m), 1230 (s), 1174 (w), 1030 (m), 749 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 453 (44) $[M^+]$, 452 (100) $[M - 1]^+$, 380 (8), 354 (30). − $C_{29}H_{31}N_3O_2$ (453.58): C 76.79, H 6.89; found C 76.69, H 7.73.

(*E*)-2-[*N,N*-Diethyl-1-carbamoyl-1-(4-methoxyphenyl)methylidene]-3-phenylimino-1*H*-indole (5j): Starting with *N,N*-diethyl-4-methoxyphenylacetic amide (0.580 g, 2.62 mmol) and oxalic acid-bis(phenylimidoyl)chloride (**2h**; 0.726 g, 2.62 mmol), indole **5j** was isolated as an orange solid (531 mg, 48%, *E*/*Z* > 98:2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 1.06 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 3.10−3.74 (3 × m, 4 H, 2 × CH_2CH_3), 3.78 (s, 3 H, OCH_3), 6.42−7.57 (m, 13 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.81 (CH_2-CH_3), 13.33 (CH_2CH_3), 38.70 (CH_2CH_3), 42.05 (CH_2CH_3), 55.12 (OCH_3), 111.14, 114.28 (CH), 115.13 (C), 118.24, 118.87 (CH), 118.94 (C), 123.06, 126.27 (CH), 127.63 (C), 129.07, 129.34, 132.49 (CH), 134.72, 150.52, 151.72, 157.44, 158.71 (C), 168.98 (C=O). − IR (KBr): ṽ = 3060 (w, Ar-H), 2972 (m, C−H), 2931 (m, C−H), 2835 (w), 1640 (w), 1605 (s), 1587 (s), 1509 (s), 1464 (s), 1328 (m), 1248 (s), 1138 (m), 751 (m), 697 (w) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 425 (40) $[M^+]$, 424 (100) $[M - 1]^+$, 352 (24), 325 (15), 281 (10).

(*E*)-2-[*N,N*-Diethyl-1-carbamoyl-1-(4-methoxyphenyl)methylidene]-7-methyl-3-(2-tolyl)imino-1*H*-indole (5k): Starting with *N,N*-diethyl-4-methoxyphenylacetic amide (0.677 g, 3.06 mmol) and oxalic acid-bis(2-tolylimidoyl)chloride (**2a**; 0.934 g, 3.06 mmol), indole **5k** was isolated as an orange solid (626 mg, 45%, *E*/*Z* > 98:2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82 (br. s, 3 H, CH_2CH_3), 1.04 (t, 3 H, CH_2CH_3), 2.08 (s, 6 H, 2 × CH_3), 3.05−3.80 (2 × m, 4 H, 2 × CH_2CH_3), 3.84 (s, 3 H, OCH_3), 6.30−7.78 (m, 11 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.77 (CH_2CH_3), 13.46 (CH_2CH_3), 15.88 (CH_3), 17.78 (CH_3), 38.74 (CH_2CH_3), 42.25 (CH_2CH_3), 55.24 (OCH_3), 114.57 (CH), 115.91, 119.19 (C), 119.53 (CH), 119.59 (C), 123.14, 126.37, 126.63 (CH), 127.91 (C), 129.35, 129.60, 130.36, 133.12 (CH), 134.82, 148.79, 150.47, 150.48, 157.44, 158.98 (C), 168.61 (C=O). − IR (KBr): ṽ = 3064 (w, Ar-H), 2960 (m, C−H), 2925 (s, C−H), 2853 (m), 1620 (s), 1596 (s), 1509 (s), 1461 (m), 1377 (w), 1323 (m), 1249 (s), 1227 (s), 1179 (s), 1039 (m), 754 (s), 724 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 453 (42) $[M^+]$, 452 (100) $[M - 1]^+$, 380 (14), 353 (12). − $C_{29}H_{31}N_3O_2$ (453.58): C 76.79, H 6.89, N 9.26; found C 75.61, H 6.91, N 9.18.

(*E*)-2-[*N,N*-Diethyl-1-carbamoyl-1-(4-methoxyphenyl)methylidene]-5-methoxy-3-(4-methoxyphenyl)imino-1*H*-indole (5l): Starting with *N,N*-diethyl-4-methoxyphenylacetic amide (0.580 g, 2.62 mmol) and oxalic acid-bis(4-methoxyphenylimidoyl)chloride (**2d**; 0.988 g, 2.62 mmol), indole **5l** was isolated as an orange solid (312 mg, 25%, *E*/*Z* > 98:2), m.p. 214−216 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, 3 H, CH_2CH_3), 1.09 (t, 3 H, CH_2CH_3), 3.10−3.30 (m, 2 H, CH_2CH_3), 3.44 (s, 3 H, OCH_3), 3.46−3.78 (m, 2 H, CH_2CH_3), 3.82 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 6.18−7.64 (m, 11 H, Ar). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.99 (CH_2CH_3), 13.45 (CH_2CH_3), 38.74 (CH_2CH_3), 42.14 (CH_2CH_3), 55.25 (OCH_3), 55.41 (OCH_3), 55.54 (OCH_3), 109.98, 111.63, 114.36, 114.42 (CH), 115.09, 119.52 (C), 119.79, 120.30 (CH), 128.00 (C), 129.43 (CH), 135.95, 144.84, 144.90, 152.65, 156.10, 157.83, 158.84 (C), 168.92 (C=O). − IR (KBr): ṽ = 3010 (w, Ar-H), 2960 (w, C−H), 2929 (m, C−H), 2845 (w, O−CH_3), 2835 (w), 1652 (m), 1602 (s), 1575 (m), 1559 (m), 1484 (s), 1436 (m), 1375 (w), 1271 (m), 1235 (s), 1131 (m), 1034 (s), 847 (w), 818 (w), 789 (w), 756 (w) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 485 (44) $[M^+]$, 484 (100) $[M - 1]^+$, 412 (41), 385 (16), 358 (16), 300 (100).

(*E*)-2-(Pyrrolidinyl-1-carbamoyl-1-phenylmethylidene)-7-methyl-3-(2-tolyl)imino-1*H*-indole (5m): Starting with phenylacetic pyrrolide (0.579 g, 3.06 mmol) and oxalic acid-bis(2-tolylimidoyl)chloride (**2a**; 0.934 g, 3.06 mmol), indole **5m** was isolated as an orange solid (108 mg, 13%, *E*/*Z* > 98:2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.82 (m, 4 H, 2 × CH_2), 2.16 (s, 6 H, 2 × CH_3), 3.20−3.70 (3 × m, 4 H, 2 × NCH_2), 6.31−7.77 (m, 12 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.85 (CH_3), 17.88 (CH_3), 24.50 (CH_2CH_2), 25.68 (CH_2CH_2), 45.27 (NCH_2CH_2), 46.71 (NCH_2CH_2), 116.14, 116.15, 118.75, 119.48, 119.49, 119.59, 123.37, 123.53, 126.44, 127.73, 128.08, 129.17, 130.42, 133.33, 134.95, 135.14, 148.58, 150.58, 157.59, 167.80. − IR (KBr): ṽ = 3058 (w, Ar-H), 2923 (m, C−H), 2868 (m), 1623 (s), 1595 (s), 1493 (m), 1481 (m), 1436 (m), 1322 (w), 1230 (m), 1169 (m), 1039 (w), 750 (m) cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 421 (50) $[M^+]$, 420 (100) $[M - 1^+]$, 350 (12), 323 (23), 307 (10). − $C_{28}H_{27}N_3O$ (421.5): C 79.78, H 6.46, N 9.97; found C 79.85, H 6.75, N 9.87.

Reaction of *N*-methyl-2-oxindole with Oxalic Acid-bis(phenylimidoyl)chloride: Starting with *N*-methyl-2-oxindole **6** (0.5 g, 3.4 mmol) and **2h** (1.7 mmol), **8** (0.63 g, 74%, *E*/*Z* < 2:98) and the red product **7** (30 mg, 5%) were isolated. Starting with *N*-methyl-2-oxindole (0.25 g, 1.7 mmol) and **2h** (1.7 mmol), products **8** and **7** were isolated in 32 and 7% yields, respectively.

8: M.p. 290−292 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.40 (s, 3 H, NCH_3), 6.80−7.30 (d, 9 H, Ar), 11.97 (s, 1 H, NH). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ_c = 25.10 (NCH_3), 98.02 (C), 120.10, 120.15 (CH), 122.00 (C), 125.02, 125.20, 129.10, 137.92 (CH), 138.84, 144.82, 169.12 (C). − MS (70 °C): 498 (98) $[M^+]$, 249 (100).

7: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.38 (s, 3 H, N−CH_3), 6.60 (m, 2 H, Ar), 6.90 (d, 1 H, Ar), 6.95 (d, 1 H, Ar), 7.05 (m, 3 H, Ar), 7.25 (m, 3 H, Ar), 7.45 (m, 3 H, Ar), 8.86 (s, 1 H, NH). − MS (EI, 70 eV): *m*/*z* (%) = 351 (100) $[M^+]$, 322 (39), 77 (64).

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