Stereoselective Synthesis of 2-Alkylidene-3-iminoindoles by Reaction of 1,1-Dianions with Oxalic Acid Bis(imidoyl) Chlorides

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Treatment of dilithiated nitriles and sulfones with oxalic acid bis(imidoyl) chlorides resulted in a new cyclization reaction which provided a variety of (3-imino-2,3-dihydro-1*H*-indol-2-ylidene)-acetonitriles and -sulfones in good yields. The reactions proceeded by condensation of the dianions with the first imidoyl chloride group of the bis(imidoyl) chloride, subsequent intramolecular attack of the *ortho* carbon of the arylimino group onto the second imidoyl chloride group, and final aromatization. Excellent stereoselectivities were observed in most cases.

The 1,2-dione unit represents an important structural feature of compounds of pharmaceutical interest and of materials such as NIR dyes.[1,2] A formal 1,2-dione unit is contained in aurones which represent a small group of 2-benzylidenecoumaranone-based yellow pigments. Aurones are biogenetically formed by oxidation of chalcones and include a variety of natural products such as the pigment aureusidine **1a**. 2-Alkylidene-3-oxindoles **1b**, which can be regarded as azaanalogous aurones, have recently been recognized as powerful dienophiles[3,4] in Diels−Alder reactions of normal electron demand[5] for the construction of the spirocyclic *Aristotelia* alkaloid framework **1d**.[6] 2-Alkylidene-3-oxindoles have also been used as heterodienes in hetero-Diels−Alder reactions of inverse electron demand for the preparation of the potentially antitumor-active pyrano[3,2-*b*]indole **1e**[7] and of *δ*-carboline **1f**.[8] In addition, 2-alkylidene-3-oxindoles represent useful starting materials for the preparation of mycotoxin brevianamides.[9] Danishefsky recently reported the need for an enamino ester of type **1b** ($R^1 = CO_2R''$) in the synthesis of the anticancer drug camptothecin.[10] Stille also used an 2-alkylidene-3-oxindole as a building block in the synthesis of tashiromine.[11]

To date, previous syntheses of 2-alkylidene-3-oxindoles utilized the aldol reaction[4,8a] of 3-oxindoles or the Heck reaction of iodoanilines with alkynes in the presence of CO[12] as the key steps. Using the first approach, 3-oxindoles **1b** ($R^1 = CO_2R''$) were obtained with good stereoselectivities but low yields (12−44% yield).[4] The aldolization with benzaldehyde derivatives (R^1 = aryl) proceeded with low stereocontrol.[8a] Due to the problems associated with the synthesis of this type of compounds, we envisaged that 2-alkylidene-3-iminoindoles **1c**, containing a masked carbonyl group, could be equally useful as synthons for the synthesis of alkaloids. In addition, these compounds represent interesting starting materials for the generation of photochromic spiroindoles[13] and of novel NIR dyes.[14] In the course of our interest in the reaction of oxalic acid bis(imidoyl) chlorides $C_2Cl_2(NAr)_2$ **2**[15] with carbon nucleophiles,[16] we have recently developed a new cyclization reaction which allows a convenient and stereoselective synthesis of 3-iminoindoles **1c**.[17] Herein, we

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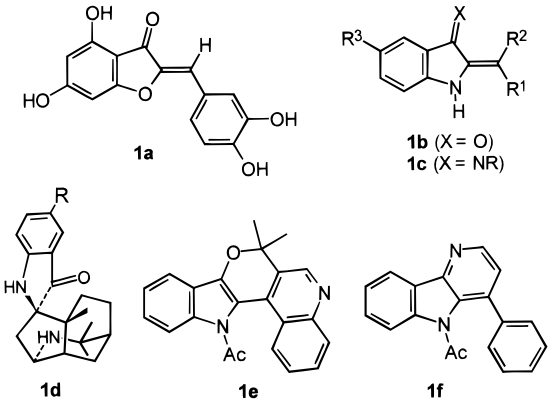
Chart 1

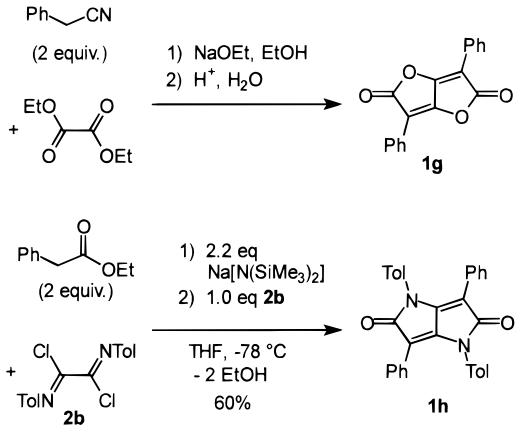


report full details and investigations related to the scope and the limitations of this new reaction.

Results and Discussion

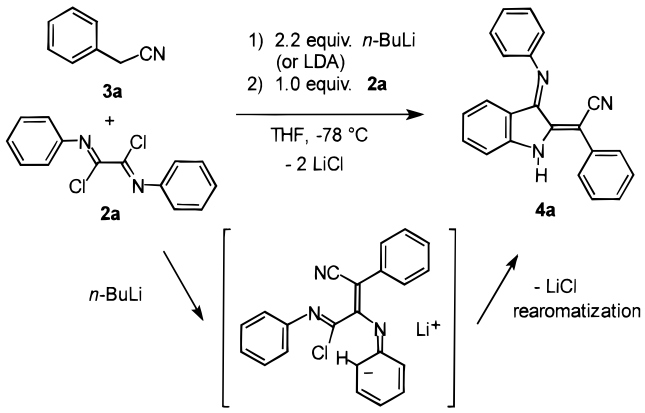
Reaction of oxalic acid bis(imidoyl) chlorides **2** with dianions can, in principle, result in a simple 2:1 condensation, cyclization, or polymerization. Condensation of diethyl oxalate with 2 equiv of the monoanion of phenylacetonitrile was reported to give an open-chain product which could be cyclized by treatment with acid to give the dilactone **1g** of pulvinic acid (Scheme 1).[2c] Very recently, we have developed an efficient synthesis of pyrrolo[3,2-*b*]pyrrole-2,5-diones by reaction of oxalic acid bis(imidoyl) chlorides **2** with ester monoanions.[16f] For example, reaction of the carbanion of ethyl phenylacetate with oxalic acid bis(*p*-tolylimidoyl) chloride **2b** afforded the pyrrolo[3,2-*b*]pyrrole-2,5-dione **1h**. On the basis of these results, we expected that reaction of lithiated phenylacetonitrile **3a** with bis(phenylimidoyl) chloride **2a** would result in formation of an open-chain product or of dilactam **1h**.

Scheme 1. Reaction of Phenyl Acetonitrile with Diethyl Oxalate and of Ethyl Phenylacetate with Oxalic Acid Bis(*p*-tolylimidoyl) Chloride



Much to our surprise, a completely different product was formed in this reaction: Addition of a THF solution of lithiated **3a** to a solution of bis(imidoyl) chloride **2a** at −78 °C afforded the (3-imino-2,3-dihydro-1*H*-indol-2-ylidene)acetonitrile **4a** in 43% yield (Scheme 2). The yield

Scheme 2. Reaction of Dilithiated Phenylacetonitrile with Bis(imidoyl) Chloride 2a



could be improved to 75% when the 1,1-dianion[18] of **3a** (generated by addition of 2 equiv of *n*-BuLi to phenylacetonitrile) was used.[19] It is important to note that the product was formed with excellent stereoselectivity (*E*:*Z* > 95:5). Similarly, reaction of dilithiated phenylacetonitrile with bis(imidoyl) chlorides **2b**,**c** provided the *E*-configured (3-imino-2,3-dihydro-1*H*-indol-2-ylidene)acetonitriles **4b**,**c** in 76 and 67% yields, respectively (Table 1). In all reactions reported herein, LDA rather than *n*-BuLi could be equally successfully used.

Formation of the 2-alkylidene-3-iminoindole **4a** can be rationalized by the following mechanism: Initial attack of the dianion[18] on the dielectrophile gives an ambident anionic intermediate. A 5-*exo*-*trig* cyclization subsequently occurs from the *ortho* carbon of the arylimino group, and rearomatization leads to the final product. The phenylimino group which does not participate in the cyclization exerts a stereochemical bias for the enamine formation (by interaction with the bulky phenyl group). Therefore, an excellent stereoselectivity in favor of the *E*-configured product was observed.

A brief discussion of the spectroscopic data of **4b** and of other 2-alkylidene-3-iminoindoles is appropriate. The signal of the NH group is located at 6.38 ppm. The singlet assigned to H4 (^{1}H NMR, $CDCl_3$, δ = 6.42) is shifted upfield by ca. 1 ppm relative to 3-oxindoles. This effect can be explained by the fact that the arylimino group attached to C3 is twisted out of plane and H4 is located within the anisotropic cone of the aryl group and thus resonates at higher field. In the ^{13}C NMR spectrum of **4b** and of other 3-iminoindoles, carbon C4 is shifted

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Scheme 3. Reaction of Nitrile- and Sulfone-Derived Carbanions with Bis(imidoyl) Chlorides

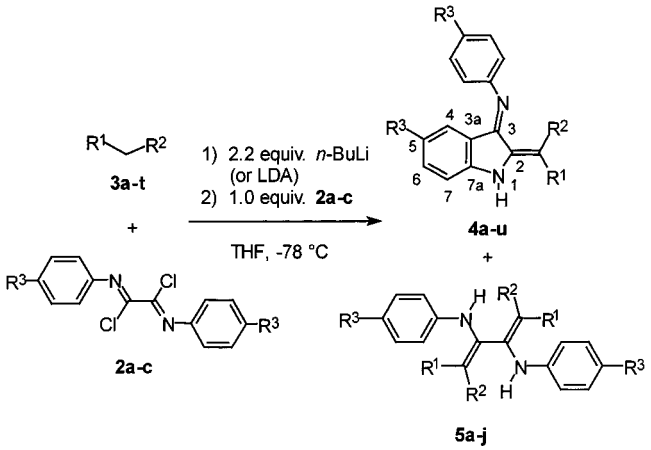

Table 1. Preparation of 2-Alkylidene-3-iminoindoles 4 and of Bis-Enamines 5

3	4	5	R^1	R^2	R^3	*E*:*Z*[a]	yield (**4**) [%][b]	yield (**5**) [%][c]
a	**a**	**a**	C_6H_5	CN	H	>95:5	75	7
a	**b**	–	C_6H_5	CN	CH_3	>95:5	76	0
a	**c**	–	C_6H_5	CN	OCH_3	>95:5	67	0
b	**d**	–	2-naphthyl	CN	CH_3	>95:5	68	0
b	**e**	–	2-naphthyl	CN	OCH_3	>95:5	51	0
c	**f**	–	4-$(CH_3)C_6H_4$	CN	H	>95:5	73	0
d	**g**	**b**	4-$(CH_3O)C_6H_4$	CN	H	>95:5	72	10
e	**h**	–	2-$(CH_3O)C_6H_4$	CN	H	>95:5	56	0
f	**i**	**c**	3,4-$(CH_3O)_2C_6H_3$	CN	CH_3	>95:5	67	9
g	**j**	**d**	2-pyridyl	CN	CH_3	>95:5	12	53
h	**k**	–	2-thienyl	CN	CH_3	>95:5	68	0
i	**l**	–	2-benzimidazolyl	CN	CH_3	>95:5	84	0
j	**m**	–	$SiMe_3$	CN	H	5:1	34	0
j	**n**	–	H	CN	H	5:1	34	0
k	**o**	–	N=C$(C_6H_5)_2$	CN	H	1:6	21	0
l	**p**	–	2-thienylsulfonyl	CN	CH_3	<5:95	62	0
m	–	**e**	COPh	CN	CH_3	–	0	14
n	–	**f**	CO_2Et	CN	H	–	0	48
n	–	**g**	CO_2Et	CN	CH_3	–	0	72
o	–	**h**	CO[N$(CH_2)_5$]	CN	CH_3	–	0	56
p	–	**i**	CO[N$(CH_2)_4$O]	CN	CH_3	–	0	36
q	–	**j**	2-pyridyl	H	CH_3	–	0	44
r	**q**	–	SO_2Ph	CN	H	<5:95	74	0
r	**r**	–	SO_2Ph	CN	CH_3	<5:95	77	0
s	**s**	–	SO_2Ph	H	CH_3	<5:95	21	0
t	**t**	–	SO_2Ph	Ph	CH_3	1:2	61	0
t	**u**	–	SO_2Ph	Ph	OCH_3	1:2	58	0

[a] Stereochemical assignment based on analogy to **4b**. [b] Isolated yields. For **4m**,**n**: combined yield of **4m** and **4n**. [c] Isolated yields. The yields of **5d**–**j** refer to experiments where 2 rather than only 1 equiv of the nucleophile was used.

upfield. As expected, this effect is not observed for carbon C7 which is located on the opposite side of the molecule. The presence of the nitrile-substituted exocyclic double bond and the presence of the imino group results in a downfield shift of the signal of carbon atom C2 by 23.2 ppm relative to carbon C2 of indole. In the ^{1}H NMR spectrum of **4b**, a significant difference (0.36 ppm) between the chemical shifts of the two methyl groups is observed. This difference is characteristic also for all other 2-alkylidene-3-iminoindoles **4** derived from bis(imidoyl) chlorides **2b**,**c** and can again be explained by location of the methyl or the methoxy group attached to carbon C5 within the anisotropic cone of the arylimino group which results in a shift of the respective signals to higher field relative to the methyl or methoxy group attached at the arylimino group.

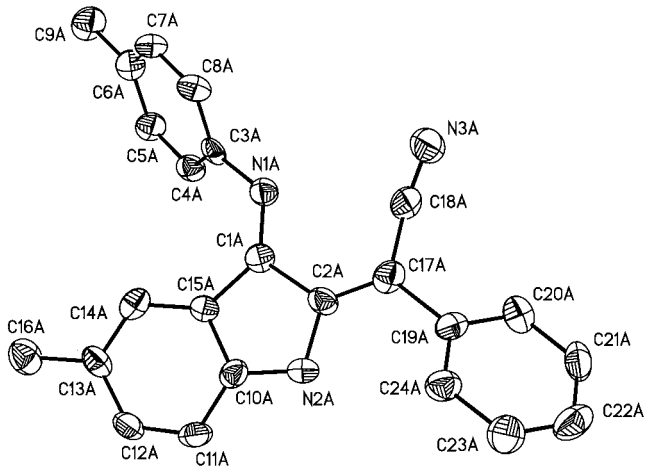

Figure 1. X-ray structure of **4b**: Selected bond lengths [Å]: N(1A)–C(1A) 1.281(9), C(1A)–C(2A) 1.501(10), C(10A)–C(11A) 1.411(11), C(2A)–C(17A) 1.398(11), C(10A)–C(15A) 1.389(10), C(12A)–C(13A) 1.398(11), N(2A)–C(2A) 1.382(9), C(1A)–C(15A) 1.475(10), C(11A)–C(12A) 1.359(11), C(13A)–C(14A) 1.375(10), C(14A)–C(15A) 1.404(10), N(2A)–C(10A) 1.377(9).

X-ray diffraction of single crystals of **4b** (which were grown from a DMSO solution) unambigiously proved the *E*-configuration of the exocyclic double bond (Figure 1). The alternation of the bond lengths within the indole unit indicates that the aromaticity of **4b** is disturbed. The *p*-tolyl group of the imino group is twisted out of the plane of the indole moiety. Thus, the crystal structure showed that the hydrogen atom H4 and the methyl group attached to C5 are indeed located within the anisotropic cone of the *p*-tolylimino group as suggested by the NMR data. The phenyl group attached to the exocyclic double bond is only slightly twisted out of plane. It is noteworthy that the geometry of the nitrile group is slightly distorted by 8° from the expected value of 180°. This can be explained by electrostatic repulsion of the nitrogen atoms of the nitrile and of the imine. The solvent DMSO was incorporated in the crystal lattice and a hydrogen bond N–H···O was observed between the nitrogen atom of the indole and the oxygen atom of DMSO (H···O distance: 1.920 Å).

To investigate the scope and the limitations of the new cyclization reaction, the substituents were systematically varied (Scheme 3, Table 1). Treatment of 2-naphthylacetonitrile **3b** with bis(imidoyl) chlorides **2b**,**c** afforded the *E*-configured 2-alkylidene-3-iminoindoles **4d**,**e** in good yields. Reaction of methyl- and methoxy-substituted aryl acetonitriles **3c**–**f** with **2a** or **2b** gave the indoles **4f**–**i** in good yields. In contrast, reaction of 2-pyridylacetonitrile **3g** with **2b** gave a complex reaction mixture from which the indole derivative **4j** could be isolated in only 12% yield. The major product of this reaction was the open-chain bis-enamine **5d**. In the reactions of all other aryl acetonitriles, open-chain products were isolated in only low yields or not at all. The reactions of 2-thienyl acetonitrile **3h** and 2-benzimidazolyl acetonitrile **3i** with bis(imidoyl) chloride **2b** stereoselectively afforded the deeply red and orange colored indoles **4k** and **4l** in 68 and 84% yields, respectively. The use of trimethylsilyl acetonitrile **3j** afforded a 1:5 mixture of the indoles **4m** and **4n** (34% yield by ^{1}H NMR). The latter was presumably formed by base-induced desilylation of the initially formed trimethylsilyl-substituted indole **4m**. Reaction of

$Ph_2C{=}NCH_2CN$ **3k** with bis(imidoyl) chloride **2a** gave the corresponding indole **4o**. Reaction of thienylsulfonyl acetonitrile **3l** with **2b** gave the 2-alkylidene-3-iminoindole **4p** in good yield.

Treatment of sodium diethyl malonate with oxalic acid bis(*m*-chlorophenylimidoyl) chloride was reported to give the corresponding open-chain bis-enamine in low yield.[20] Reaction of 2 equiv of benzoyl acetonitrile **3m** with **2b** gave the bis-enamine **5e** and treatment of 2 equiv of ethyl cyanoacetate **3n** with the bis(imidoyl) chlorides **2a** and **2b** afforded the bis-enamines **5f** and **5g** rather than the corresponding 2-alkylidene-3-iminoindoles.[16d] Likewise, reaction of *N*-(cyanoacetyl)piperidine and -morpholine **3o** and **3p** afforded the open-chain bis-enamines **5h** and **5i**. Reaction of 2 equiv of lithiated 2-picoline **3q** with **2a** afforded the open-chain product **5j**. The open-chain products **5e**−**j** were obtained as the major products also when only one rather than 2 equiv of the nucleophile and 2 equiv of LDA were employed. Again no 2-alkylidene-3-iminoindoles could be isolated in these reactions. According to the ^1H and ^{13}C spectra of all condensation products **5**, symmetrical structures are adopted in solution. The configuration of the double bonds of the dienes was proven by NMR: as indicated by the low field shifts (^1H NMR) of the respective N−H hydrogen atoms of **5e**−**i**, isomers containing intramolecular hydrogen bonds (N−H···O) are present in solution. Similarly, intramolecular hydrogen bonds (N−H···N) involving the pyridine functionality were present for the pyridine-subtituted dienes **5d** and **5j**. For dienes **5a**−**c**, symmetrical structures are also adopted. However, the configuration of the double bonds could not be unambigiously determined. It is noteworthy, that the resonance of the intramolecular hydrogen bond (N−H···O) of the amide **5h** is shifted upfield relative to the resonances of the esters **5f**,**g**. The N−H resonances of the esters are shifted upfield relative to the respective resonance of the ketone **5e**. It is noteworthy that 1,4-diazabutadienes and 2,3-diaminobutadienes have recently been used as efficient ligands in transition metal-catalyzed olefin polymerization reactions.[21,22]

The reaction of sulfone-dianions with bis(imidoyl) chlorides resulted in clean cyclization reactions to give the 2-alkylidene-3-iminoindoles **4q**−**u** in good yields (except for **4s**): Employment of phenylsulfonyl acetonitrile **3r** with **2a**,**b** afforded the indoles **4q**,**r** with very good stereocontrol. Treatment of bis(imidoyl) chloride **2b** with methyl phenyl sulfone **3s** gave the indole **4s** in low yield. Reaction of benzylphenyl sulfone **3t** with bis(imidoyl) chlorides **2b**,**c** resulted in formation of the indoles **4t** and **4u** in good yields. However, due to the similar steric demand of the phenylsulfonyl and the phenyl group attached to the exocyclic double bond, 2-alkylidene-3-iminoindoles **4t** and **4u** were obtained as a mixture of stereoisomers (*E*:*Z* = 1:2).

Scheme 4. Cyclization Reactions of Substituted Benzimidazoles with 2b

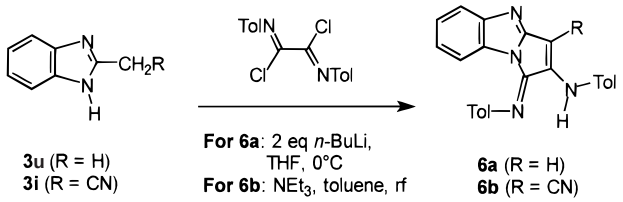

Table 2. UV-Vis Data of Selected Indoles 4

4	λ_{max} (lg ϵ) (acetonitrile/nm)
b	283 (4.26), 309 (4.14), 480 (3.98)
g	347 (4.15), 484 (3.75)
i	281 (4.33), 487 (4.05)
l	279 (4.40), 331 (3.97), 481 (3.82)
p	265 (4.38), 476 (3.91)
q	279 (4.50), 473 (4.02)
t	281 (4.32), 465 (3.87)

In the reaction of bis(imidoyl) chloride **2b** with 2-(cyanomethyl)benzimidazole (**3i**), the 2-alkylidene-3-iminoindole **4l** was formed in 84% yield (s. a.). In contrast, regioselective cyclization via the nitrogen atom of the benzimidazole moiety was observed when **2b** was treated with dilithiated 2-methylbenzimidazole **3u** to give the orange-colored 1-(arylimino)-1*H*-pyrrolo[1,2-*a*]benzimidazol-2-amine **6a** (Scheme 4).[16b] This type of cyclization could be induced also for 2-(cyanomethyl)benzimidazole **3i** when triethylamine rather than *n*-BuLi was used as the base to give the 1*H*-pyrrolo[1,2-*a*]benzimidazole **6b** in moderate yield.

The UV−vis spectra of 2-alkylidene-3-iminoindoles **4** exhibit strong $\pi \rightarrow p^*$ absorptions λ_2 and λ_3, and the colors of the indoles vary from orange (for **4m**) to deep red (for **4k**). The high absorption coefficients can be explained by the indigo-type electronic structure of the 3-iminoindoles **4** which can thus be regarded as heterocyclic merocyanines. It is interesting to compare cyano-substituted indoles (R^2 = CN) containing different substituents R^1 (Table 2): Relative to **4b** (R^1 = Ph), bathochromic shifts are observed for indoles containing electron-donating aryl groups (**4g**, **4i**). In contrast, hypsochromic effects are observed for sulfone-substituted indoles (**4p**, **4q**, and **4t**).

Conclusions. To explain the formation of 2-alkylidene-3-iminoindoles **4**, open-chain products **5** and pyrrolo[3,2-*b*]pyrrole-2,5-diones it is interesting to compare representative substrates (Chart 2).

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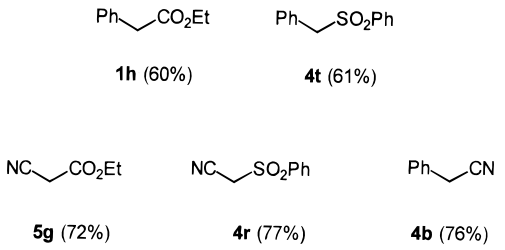
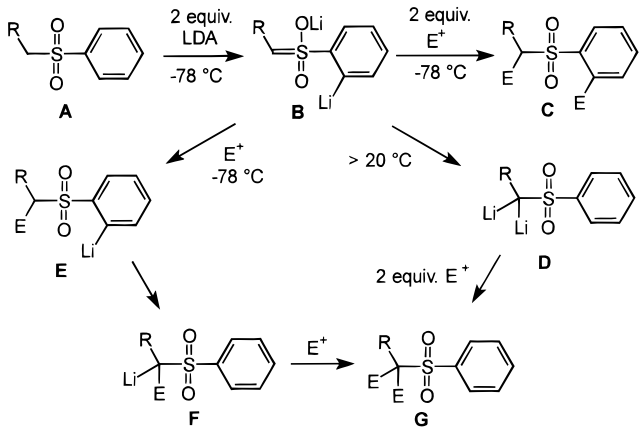
Chart 2. Reaction of Selected Substrates with Oxalic Acid bis(*p*-tolylimidoyl) Chloride 2b[a]

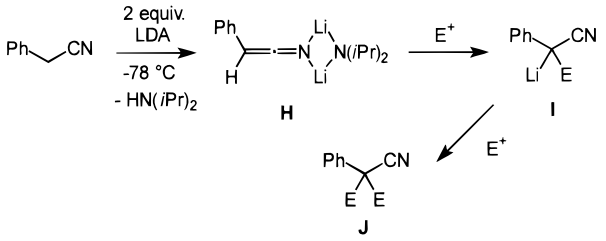


[a]Below the formulas the numbers and the yields of the main products are given.

Scheme 5. Formation and Reactions of Sulfone Dianions



Scheme 6. Formation and Reactions of Nitrile Dianions



2-Alkylidene-3-iminoindoles **4** could be prepared in good yields exclusively from starting materials which are known to form "1,1-dianions". The presence of an aryl group in the dianionic substrate is advantageous. However, cyclizations could also be induced employing methyl phenyl sulfone **3s**, cyanomethyl phenyl sulfone **3r** and (trimethylsilyl)acetonitrile **3j**.

Sulfones are known to form true dianions: the lithiation occurs at the CH_2 group and at the *ortho* position of the phenyl group (Scheme 5). At elevated temperature the α,*ortho*-dianion rearranges to a α,α-dianion. At low temperature, the first attack of the α,*ortho*-dianion onto the electrophile occurs at the α-carbon atom and subsequent rearrangement affords an α-monoanion which subsequently reacts with the second equivalent of the electrophile to give a α,α-difunctionalized sulfone. It is known that treatment of nitriles with 2 equiv of LDA results in formation of monoanions associated with 1 equiv of the base rather than in formation of a true dianion (Scheme 6). However, treatment of these reagents with 2 equiv of an electrophile gives rise to formation of α,α-difunctionalized products by deprotonation of the initially formed condensation product.

The use of diethyl malonate, ethyl cyanoacetate **3n**, or cyano-substituted amides **3o**,**p**, containing *two* electron-withdrawing groups, resulted in formation of the open-chain products **5e**−**i**, respectively. Interestingly, employment of (phenylsulfonyl)acetonitrile **3r**, a sulfone containing a cyano rather than an aryl substituent, resulted in clean cyclization reactions to give the 2-alkylidene-3-iminoindoles **4q**,**r**. The striking difference between substrates **3n**−**p** and **3r** can be explained by the fact that, in contrast to phenyl sulfones, substrates **3n**−**p** cannot be transformed into 1,1-dianions. In these reactions, indole formation requires deprotonation of the initially formed condensation product. However, this reaction appears to be slow compared to attack of a second equivalent of the nucleophile onto the imidoyl chloride group. Alternatively, it is possible that the deprotonation does take place, but does not lead to cyclization. This can be explained by the fact that for **3n**−**p** the negative charge is localized at the oxygen atom rather than delocalized within the aryl group from where the cyclization can occur. Reaction of ethyl phenylacetate with bis(imidoyl) chloride **2b** resulted in formation of the pyrrolo[3,2-*b*]-pyrrole-2,5-dione **1h**, due to nucleophilic attack of the nitrogen atoms onto the electrophilic ester groups.[16f]

In summary, reaction of lithiated nitriles and sulfones with oxalic acid bis(imidoyl) chlorides provided an efficient and stereoselective synthesis of a variety of 2-alkylidene-3-iminoindoles from simple starting materials. Variation of the bis(imidoyl) chloride and the dianion allowed the introduction of different substituents both at the indole moiety and at the exocyclic double bond, respectively. In contrast to known methods for the preparation of 2-alkylidene-3-oxindoles, protection of the indole nitrogen is not necessary, since the latter is formed during the cyclization. Our current work is directed toward application of the new cyclization reaction to the synthesis of alkaloids.

Experimental Section

General Comments. All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. The oxalic acid bis(imidoyl) dichlorides **2** were prepared according to literature procedures.[15] For the ^1H and ^{13}C NMR spectra (^1H NMR: 200, 300, and 400 MHz, ^{13}C NMR: 50, 75, and 100 MHz), the deuterated solvents indicated were used. The multiplicity of the ^{13}C NMR signals were determined with the DEPT 135 technique and quoted as CH_3, CH_2, CH, and C for primary, secondary, tertiary, and quaternary carbon atoms. Mass spectral data (MS) were obtained using the electron ionization (70 eV) or the chemical ionization technique (CI, H_2O). For the preparative scale chromatography, silica gel (60−200 mesh) was used. Melting points are uncorrected. Elemental analyses were performed at the microanalytical laboratories of the Universities of Göttingen and Jena.

X-ray Diffraction. The crystals were measured on a CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by direct methods (SHELXS) and refined by full-matrix least squares techniques against F^2 (SHELXL-93).

Crystal Data for (4b): $C_{24}H_{19}N_3 \cdot C_2H_6OS$, M_r = 855.10 gmol^{-1}, red quader, size 0.40 × 0.38 × 0.36 mm^3, monoclinic, space group *P*2(1) No. 4, a = 10.059(2), b = 45.792(9), c = 10.297(2) Å, β = 108.09(3)°, V = 4508(1) Å^3, Z = 8, ρ_{calcd} = 1.26 gcm^{-3}, μ (Mo Kα) = 1.66 cm^{-1}, F(000) = 1808, 9764 refelctions in ±h, −k, −l, measured in the range 19.1° ≤ Θ ≤ 22.1°, 9258 independent reflections, R_{int} = 0.068, 1137 param-

eters, $R = 0.063$, $wR^2 = 0.152$, GOOF = 1.18, largest difference peak: 0.50 eÅ^{-3}.

General Procedure for the Preparation of (3-Imino-2,3-dihydro-1*H*-indol-2-ylidene)acetonitriles and -sulfones (4). To a THF solution (20 mL) of the nitrile or sulfone (6 mmol; volume or weight is indicated in each following section) was added *n*-BuLi (9.8 mL, 2.2 molar equiv., 1.6 M solution in hexane) 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 color 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 water. The color of the organic layer changed to deep red. The aqueous layer was extracted five times with a mixture of THF and ethyl ether (1:4, 200 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. Addition of ethyl ether (15 mL) to the crude product resulted in precipitation of intensely red colored **4** which was washed with ethyl ether (50 mL) and dried in vacuo. In case of the products **4c**, **4e**−**k**, **4m**−**p**, and **4s**−**u**, purification by chromatography (silica gel, ethyl ether:petroleum ethyl ether = 1:10 → 3:1) was necessary. In all reactions LDA rather than *n*-BuLi can be used.

(2*E*,3*E*)-[1,3-Dihydro-3-(phenylimino)-2*H*-indol-2-ylidene]phenylacetonitrile (4a). Starting with 0.69 mL of phenyl acetonitrile, 1.46 g (76%) of **4a** was isolated as deep orange crystals, mp 153−156 °C. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 6.42 (d, J = 8 Hz, 1 H, H-4), 6.62 (t, J = 8 Hz, 1 H, H-5), 6.95−7.75 (m, 12 H, Ar), 10.38 (br, 1 H, NH). ^{13}C NMR (DMSO-d_6, 50 MHz): δ_c 84.36 (C, CCN), 112.20, 117.91 (CH, C-4, C-7), 117.19 (C, CN), 119.77 (C, C-3a), 120.56, 124.59, 125.83, 128.41, 129.02, 129.46, 129.82, 134.07 (CH, Ph, C-5, C-6), 133.84 (C, Ph-C to C), 146.90, 149.34, 150.84 (C, C-2, Tol-C to N, C-7a), 157.76 (C, C-3). IR (KBr, cm^{-1}): 3300 (w); 3060 (w), 2195 (m, CN), 1642 (m), 1618 (s), 1590 (s), 1464 (s), 1341 (m), 1218 (s), 1148 (m), 1100 (m), 750 (m). MS (FAB): 322 (100, M$^+$ + 1). Anal. Calcd for $C_{22}H_{15}N_3$: C 82.23, H 4.70, N 13.07. Found: C 80.94, H 5.26, N 12.20.

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-[(4-methylphenyl)imino]-2*H*-indol-2-ylidene]phenylacetonitrile (4b). Starting with 0.69 mL of phenyl acetonitrile, 1.57 g (75%) of **4b** was isolated as red crystals, mp 155−157 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.06, 2.42 (s, 6H, Tol-CH_3), 6.42 (s, 1H, H-4), 6.71 (d, J = 8 Hz, 1H, H-7), 6.90−7.70 (m, 10H, Ar). ^{13}C NMR (DMSO-d_6, 50 MHz): δ_c = 20.72, 20.78 (Tol-CH_3), 83.63 (C, *C*CN), 111.89, 118.09 (CH, C-4, C-7), 117.30 (C, CN), 119.93 (C), 120.55, 125.82, 128.95, 129.40, 130.09, 134.64 (CH, Ph, Tol, C-6), 129.16, 133.67, 134.01 (C, C-5, Ph-C, Tol-C to C), 147.32, 148.13 (C, C-2, Tol-C to N), 157.62 (C, C-7a), 158.64 (C, C-3). IR (KBr, cm^{-1}): 3300 (br), 3025 (w), 2922 (w), 2198 (m, CN), 1643 (m), 1620 (s), 1587 (s), 1502 (m), 1488 (s), 1332 (m), 1220 (s), 815 (m). MS (FAB): 350 (100, M$^+$ + 1). Anal.: Calcd. for $C_{24}H_{19}N_3$: C 82.50, H 5.48, N 12.02. Found C 81.92, H 5.88, N 11.60.

(2*E*,3*E*)-[1,3-Dihydro-5-methoxy-3-[(4-methoxyphenyl)imino]-2*H*-indol-2-ylidene]phenylacetonitrile (4c). Starting with 0.69 mL of phenyl acetonitrile, 1.53 g (67%) of **4c** was isolated as red crystals, mp 160−163 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.45, 3.80 (s, 6H, OCH_3), 6.48 (d, 1 H, H-4), 6.70 (m, 2 H, Ar), 7.00−8.00 (m, 10 H, Ar). ^{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-11), 117.10 (C, CN), 119.71 (C, C-3a), 120.52, 125.82, 128.95, 129.40, 130.09, 131.64, 132.01 (C, C-13, Ph-C, Tol-C to C), 141.20, 142.78, 147.32, 148.13, 157.62, 158.64. MS (FAB): 382 (100, M$^+$ + 1).

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-[(4-methylphenyl)imino]-2*H*-indol-2-ylidene](2-naphthyl)acetonitrile (4d). Starting with 1.00 g of 2-naphthylacetonitrile, 1.63 g (68%) of **4d** was isolated as a red solid, mp 167−170 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.08, 2.42 (s, 6 H, Tol-CH_3), 6.62 (s, 1 H, H-4), 6.72 (d, J = 8 Hz, 1 H, Ar), 6.90−8.00 (m, 16 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_c 20.91, 21.08 (Tol-CH_3), 85.44 (C, *C*CN), 110.78, 118.18 (CH, C-4, C-7), 118.19 (C, CN), 119.38 (C, C-3a), 125.72, 126.81, 126.90, 126.95, 127.80, 128.02, 128.13, 129.39, 129.80, 134.06 (CH, Ph, Naph, C-6), 130.52, 131.38, 132.81, 133.49, 135.21 (C, C-5, Naph-C, Tol-C to C), 145.62, 147.90 (C, C-2, Tol-C to N), 156.50 (C, C-7a), 156.54 (C, C-3). IR (KBr, cm^{-1}): 3300 (br), 3024 (w), 2920 (w), 2198 (m, CN), 1640 (m), 1618 (m), 1586 (s), 1500 (m), 1480 (s); 1328 (m), 1220 (m), 815 (m). MS-FAB: 401 (100, M$^+$ + 2), 400 (65.0, M$^+$ + 1), 399 (75.4, M$^+$), 398 (76.6, M$^+$ − 1), 309 (32.9), 295 (31.6). Anal. Calcd for $C_{28}H_{21}N_3$: C 84.19, H 5.30, N 10.51. Found: C 84.01, H 5.35, N 10.22.

(2*E*,3*E*)-[1,3-Dihydro-5-methoxy-3-[(4-methoxyphenyl)imino]-2*H*-indol-2-ylidene](2-naphthyl)acetonitrile (4e). Starting with 1.00 g of 2-naphthylacetonitrile, 1.31 g (51%) of **4e** was isolated as a red solid, mp 170−173 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.47, 3.85 (s, 6H, OCH_3), 6.45 (d, 1 H, H-4), 6.78 (m, 2 H, Ar), 6.98 (m, 4 H, Ar), 7.40−8.10 (7 H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ_c = 55.51, 55.60 (OCH_3), 85.29 (C, *C*CN), 110.68, 111.43 (CH, C-4, C-7), 114.50 (CH, Ar), 118.66 (C, CN), 119.53 (C, Ar), 120.21, 120.25, 125.68, 126.85, 126.88, 127.76, 127.96, 128.07, 129.31, 131.35, 132.75, 133.43, 141.82, 143.31, 148.21, 154.06, 156.55, 157.27. MS (FAB): 432 (100, M$^+$ + 1).

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-(phenylimino)-2*H*-indol-2-ylidene](4-methylphenyl)acetonitrile (4f). Starting with 0.53 g of (4-methylphenyl)acetonitrile, 0.98 g (73%) of **4f** was isolated as orange solid, mp 161−163 °C. ^{1}H NMR (DMSO-d_6, 200 MHz): δ = 2.39 (s, 3 H, Tol-CH_3), 6.39 (d, J = 8 Hz, 1 H, H-4), 6.60 (t, J = 8 Hz, 1 H, Ar), 6.90−7.00 (m, 3 H, Ar), 7.15−7.55 (m, 8 H, Ar). ^{13}C NMR (DMSO-d_6, 50 MHz): δ_c = 20.86 (Tol-CH_3), 84.31 (C, *C*CN), 111.96, 116.99, 117.71, 120.27, 124.36, 125.61, 128.70, 129.61, 129.82, 130.66, 133.84, 137.85, 146.39, 149.13, 150.69, 157.49. MS (70 eV): 335 (44, M$^+$), 334 (100, M$^+$ − 1). Anal. Calcd for $C_{23}H_{17}N_3$: C 82.37, H 5.11, N 12.52. Found: C 82.54, H 5.02, N 12.27.

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-(phenylimino)-2*H*-indol-2-ylidene]-(4-methoxyphenyl)acetonitrile (4g). Starting with 0.525 g of (4-methoxyphenyl)acetonitrile, 1.01 g (72%) of **4g** was isolated as orange solid, mp 157−159 °C. ^{1}H NMR (DMSO-d_6, 200 MHz): δ = 3.83 (s, 3 H, OCH_3), 6.40 (d, J = 8 Hz, 1 H, H-4), 6.60 (t, J = 8 Hz, 1 H, Ar), 7.00 (m, 3 H, Ar), 7.10 (d, J = 8 Hz, 2 H, Ar), 7.25 (m, 2 H, Ar), 7.50 (m, 2 H, Ar), 7.55 (d, J = 8 Hz, 2 H, Ar). ^{13}C NMR (DMSO-d_6, 50 MHz): δ_c = 55.37 (OCH_3), 84.33 (C, *C*CN), 111.93, 114.73, 117.04, 117.73, 119.63, 120.18, 124.31, 125.59, 129.61, 130.22, 133.80, 146.02, 149.14, 150.74, 157.44, 159.12. MS (CI, H_2O): 352 (100, M$^+$ − 1). Anal. Calcd for $C_{23}H_{17}N_3O$: C 78.62, H 4.88, N 11.95. Found: C 78.38, H 5.02, N 11.66.

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-(phenylimino)-2*H*-indol-2-ylidene](2-methoxyphenyl)acetonitrile (4h). Starting with 0.525 g of (2-methoxyphenyl)acetonitrile, 785 mg (56%) of **4h** was isolated as an orange solid, mp 149−152 °C. ^{1}H NMR (acetone-d_6, 200 MHz): δ = 3.92 (s, 3 H, OCH_3), 6.58 (m, 2 H, Ar), 6.83 (d, J = 8 Hz, 1 H, Ar), 7.00−7.50 (m, 10 H, Ar), 8.98 (br, 1 H, NH). ^{13}C NMR (acetone-d_6, 50 MHz): δ_c = 55.16 (OCH_3), 82.37 (C, *C*CN), 111.13, 111.95, 117.67, 117.84, 120.12, 121.02, 122.00, 124.17, 126.23, 129.50, 130.51, 131.16, 133.69, 147.32, 149.00, 151.35, 157.16, 157.20. MS (CI, H_2O): 352 (100, M$^+$ − 1). Anal. Calcd for $C_{23}H_{17}N_3O$: C 78.62, H 4.88, N 11.95. Found: C 78.44, H 5.10, N 11.78.

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-[(4-methylphenyl)imino]-2*H*-indol-2-ylidene](3,4-dimethoxyphenyl)acetonitrile (4i). Starting with 0.8 g of (3,4-dimethoxyphenyl)-acetonitrile, 1.24 g (67%) of **4i** was isolated as an orange solid, mp 155−157 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 2.04, 2.42 (2 × s, 2 × 3 H, Tol-CH_3), 3.83, 3.86 (2 × s, 2 × 3 H, OCH_3), 6.55 (s, 1 H, H-4), 6.71 (d, 1 H, Ar), 6.90−7.20 (m, 7 H, Ar), 7.27 (s, 1 H, NH). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ_c = 20.90, 21.02 (Tol-CH_3), 56.22, 56.34 (OCH_3), 85.77 (C, *C*CN), 110.81, 112.15, 112.26, 118.39, 118.69, 119.62, 120.06, 126.65, 127.11, 130.30, 130.69, 134.48, 134.65, 146.11, 147.56, 148.41, 149.78, 150.20, 157.12. IR (Nujol, cm^{-1}): 3324 (m), 3300 (m), 2195 (m, CN), 1730 (s), 1643 (s), 1618 (s), 1589 (s), 1515 (s), 1464 (s), 1377 (m), 1254 (s), 1207 (s). Anal. Calcd for $C_{26}H_{23}N_3O_2$: C 76.27, H 5.66, N 10.26. Found: C 76.48, H 5.40, N 10.54.

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-[(4-methylphenyl)imino]-2*H*-indol-2-ylidene](2-pyridyl)acetonitrile (4j). Starting with 708 mg of (2-pyridyl)acetonitrile, 252 mg (12%) of **4j** was isolated as a deep red solid. This compound was contaminated by ca. 15% of an inseparable impurity. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.08, 2.40 (2 × s, 2 × 3 H, Tol-CH_3), 6.90−7.80 (m, 11 H, Ar). IR (KBr, cm^{-1}): 3348 (m); 3028 (w), 2920 (w), 2208 (m, CN), 1604 (s), 1560 (s), 1508 (m), 1464 (w), 1332 (w), 1260 (w), 1176 (m). MS (210 °C): 350 (10, $M^+ + 1$), 349 (16, M^+), 337 (26.8), 261 (63.8), 234 (64.9).

(2*E*,3*E*)-[1,3-Dihydro-5-methyl-3-[(4-methylphenyl)imino]-2*H*-indol-2-ylidene](2-thienyl)acetonitrile (4k). Starting with 492 mg of (2-pyridyl)acetonitrile, 252 mg (68%) of **4k** was isolated as a red solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.06, 2.36 (2 × s, 2 × 3 H, Tol-CH_3), 6.60−7.60 (m, 10 H, Ar). IR (KBr, cm^{-1}): 3346 (m); 3032 (w), 2918 (w), 2209 (m, CN), 1600 (s), 1564 (s), 1512 (m), 1332 (w), 1180 (m). MS (CI, H_2O): 356 (100, $M^+ + 1$). Anal. Calcd for $C_{22}H_{17}N_3S$: C 74.34, H 4.82, N 11.82. Found: C 74.45, H 4.60, N 12.04.

Preparation of (2*E*,3*E*)-{1,3-Dihydro-5-methyl-3-[(4-tolyl)imino]-2*H*-indol-2-ylidene}benzimidazole-2-acetonitrile (4l). To a THF solution (30 mL) of 1.57 g of 2-(cyanomethyl)benzimidazole (10 mmol) was added at 0 °C a THF solution (50 mL) of 33 mmol of LDA which was prepared starting with 3.3 mL of diisopropylamine and with 21 mL of a 1.6 M solution of *n*-BuLi in *n*-hexane. After being stirred for 2 h, the solution was cooled to −20 °C and a THF solution (50 mL) of 3.05 g of **2b** (10 mmol) was added. The temperature was allowed to rise to 20 °C, and the mixture was stirred for 2 h. The solution was poured into 250 mL of a 5 M aqueous solution of NH_4Cl and was extracted three times with a THF/Et_2O mixture (1:1, 200 mL). The combined organic fractions were dried ($MgSO_4$) and filtered, and the solvent of the filtrate was removed in vacuo. To the residue was added ethyl ether (2 mL), and the precipitated deep red solid was recrystalized from toluene to give 1.64 g (84%) of red crystals, mp 324−327 °C. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 2.00 (s, 3 H, Indole-CH_3); 2.29 (s, 3 H, Tol-CH_3), 6.48 (s, 1 H, Hetar), 6.95 (d, 2 H, J = 8.1 Hz, Ar), 7.23−7.38 (m, 6 H, Ar), 7.54, 7.51 (2 × br, 2 × 1 H, Hetar), 11.89, 12.62 (2 × br, 2 × 1 H, NH). ^{13}C NMR (50 MHz, DMSO-d_6): δ 20.4, 20.5 (Tol-CH_3), 71.7, 111.7, 112.8, 116.7, 117.1, 117.9, 122.1, 122.9, 125.2, 125.7, 128.1, 128.8, 129.8, 130.5, 134.1, 134.5, 143.1, 145.8, 147.4, 148.8, 149.3, 157.3. IR (Nujol, cm^{-1}): ν 3319, 3298 (m, ν_{NH}), 2211 (s, $\nu_{C\equiv N}$), 1692 (s), 1637 (s), 1620 (s), 1606 (s), 1589 (s), 1563 (s), 1524 (s), 1504 (s), 1481 (s). MS [CI (H_2O), *m*/*z* (%)]: 378 ($M^+ + 1$, 100), 272, 195, 108. Anal. Calcd for $C_{24}H_{19}N_5$ (377.45): C 76.37%; H 5.07%; N 18.55%. Found: C 76.70%; H 5.09%; N 18.75%.

(2*E*,3*E*)-[1,3-Dihydro-3-(phenylimino)-2*H*-indol-2-ylidene](trimethylsilyl)acetonitrile (4m) and (2*E*,3*E*)-[1,3-Dihydro-3-(phenylimino)-2*H*-indol-2-ylidene]acetonitrile (4n). Starting with 0.9 g of (trimethylsilyl)acetonitrile, 0.69 g of an inseparable mixture (1:5) of **4m** and **4n** was obtained (34% by ^{1}H NMR). Each compound was formed as a *E*:*Z* = 5:1-mixture of stereoisomers. **4m**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.08 (s, 9 H, minor isomer, $SiMe_3$), 0.35 (s, 9 H, major isomer, $SiMe_3$), 7.00−7.60 (m, 9 H, Ar). **4n**: 5.35 (s, 1 H, minor isomer, =CH), 5.40 (s, 1 H, major isomer, =CH), 6.58 (m, 2 H, Ar), 6.90 (m, 2 H, Ar), 7.20 (m, 2 H, Ar), 7.45 (m, 2 H, Ar), 7.70 (d, 1 H, Ar), 8.05 (br, 1 H, NH). **4n** (major isomer): ^{13}C NMR ($CDCl_3$, 50 MHz): δ_c 66.17 (C, *C*CN), 110.94, 118.00, 118.10, 118.43, 119.91, 121.08, 124.84, 126.75, 129.27, 129.55, 134.02, 148.76, 150.38, 154.11, 155.81.

(2*E*,3*E*)-[1,3-Dihydro-3-(phenylimino)-2*H*-indol-2-ylidene](diphenyl-1-azaethylidene)acetonitrile (4o). Starting with 0.8 g of (diphenyl-1-azaethylidene)acetonitrile which was lithiated by LDA, 323 mg (21%) of **4o** was isolated as deep orange crystals, mp 154−157 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.60 (d, 1 H), 6.80−7.50 (m, 18 H, Ar), 8.02 (br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_c 84.02 (C, *C*CN), 110.05, 112.55, 114.83, 117.15, 119.96, 120.09, 121.42, 126.48, 127.31, 127.77, 127.85, 128.28, 129.35, 130.20, 133.78, 134.50, 139.51, 142.04, 142.17, 145.26, 147.04, 151.45. MS (70 °C): 424 ($M^+ + 1$, 40), 347 (100).

(2*Z*,3*E*)-*N*-[1,2-Dihydro-5-methyl-2-[cyano(2-thiazolylsulfonyl)methylene]-3*H*-indol-3-ylidene]-4-methylbenzenamine (4p). Starting with 0.9 g of cyanomethyl (2-thiazolyl) sulfone, 1.25 g (62%) of **4p** was isolated as a deep orange solid, mp 158−161 °C. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 2.00, 2.31 (2 × s, 2 × 3 H, Tol-CH_3), 6.47 (s, 1 H, H-4), 7.00 (d, 2 H, Ar), 7.10−7.40 (m, 5 H, Ar), 7.97 (d, 1 H, Hetar), 8.16 (d, 1 H, Hetar), 11.28 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6, 50 MHz): δ_c 20.45, 20.53 (Tol-CH_3), 84.02, 113.53, 116.34, 117.91, 125.35, 128.48, 128.55, 129.82, 132.06, 133.75, 134.70, 134.99, 135.83, 141.05, 145.42, 146.28, 151.17, 157.00. IR (Nujol, cm^{-1}): 3324 (m), 2194 (m, CN), 1643 (m), 1603 (m), 1584 (s), 1462 (s), 1377 (m), 1316 (m), 1131 (m). MS (CI, H_2O): 420 ($M^+ + 1$).

(2*Z*,3*E*)-*N*-[1,2-Dihydro-2-[cyano(phenylsulfonyl)methylene]-3*H*-indol-3-ylidene]benzenamine (4q). Starting with 1.09 g of (phenylsulfonyl)acetonitrile, 1.71 g (74%) of **4q** was isolated as a deep orange solid, mp 159−162 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 6.50 (d, J = 8 Hz, 1 H, H-4), 6.81 (t, J = 8 Hz, 1 H, H-5), 7.01 (d, J = 9 Hz, 2 H, Ar), 7.25−7.65 (m, 8 H, Ar), 7.78 (m, 2 H, Ar), 11.42 (br, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 84.12 (C, *C*CN), 112.65, 117.82 (CH, C-4, C-7), 114.72 (C, CN), 116.60 (C, C-3a), 120.75, 123.31, 125.72, 125.78, 127.19, 129.91, 130.18, 134.70 (CH, Ph, C-5, C-6), 140.28 (C, Ph-C to S), 147.92, 149.50 (C, C-2, Ph-C to N), 157.82 (C, C-7a), 158.92 (C, C-3). IR (KBr, cm^{-1}): 3332 (m), 3060 (m), 2196 (m, CN), 1636 (m), 1620 (m), 1580 (s), 1464 (s); 1344 (m), 1320 (m), 1140 (m), 1080 (m), 1008 (w). MS (190 °C): 386 (7.5, $M^+ + 1$), 385 (4.6, M^+), 320 (7.1), 244 (100). Anal. Calcd for $C_{22}H_{20}N_3O_2S$: C 68.56, H 3.92, N 10.90. Found: C 68.13, H 4.32, N 10.38.

(2*Z*,3*E*)-*N*-[1,2-Dihydro-5-methyl-2-[cyano(phenylsulfonyl)methylene]-3*H*-indol-3-ylidene]-4-methylbenzenamine (4r). Starting with 1.09 g of (phenylsulfonyl)-acetonitrile, 1.91 g (77%) of **4r** was isolated as a red solid, mp 157−159 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.00, 2.36 (s, 6 H, Tol-CH_3), 6.44 (d, J = 10 Hz, 2 H, Ar), 6.50 (s, 1 H, H-4), 7.10−7.40 (m, 4 H, Ar), 7.78 (m, 3 H, Ar), 8.10 (m, 2 H, Ar), 11.38 (br, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 19.02, 21.03 (Tol-CH_3), 83.20 (C, *C*CN), 113.89, 118.11 (CH, C-4, C-7), 114.80 (C, CN), 116.81 (C, C-3a), 120.62, 125.70, 127.11, 129.52, 130.10, 134.98 (CH, Ph, Tol, C-6), 132.31, 135.20 (C, C-5, Tol-C to C), 141.00 (C, Ph), 145.82, 146.73 (C, C-2, Tol-C to N), 157.30 (C, C-7a), 158.81 (C, C-3). IR (KBr, cm^{-1}): 3350 (br), 3320 (m), 3022 (s), 2920 (s), 2198 (m, CN), 1641 (m), 1589 (s), 1487 (s); 1340 (s), 1322 (m), 1150 (s), 1138 (s), 1081 (s), 1035 (m). MS (FAB): 414 (100, $M^+ + 1$). Anal. Calcd for $C_{24}H_{19}N_3O_2S$: C 69.72, H 4.63, N 10.16. Found: C 68.63, H 5.07, N 10.34.

(2*Z*,3*E*)-*N*-[1,2-Dihydro-5-methyl-2-[(phenylsulfonyl)-methylene]-3*H*-indol-3-ylidene]-4-methylbenzenamine (4s). Starting with 936 mg of methyl phenyl sulfone, 490 mg (21%) of **4s** was isolated as an orange solid, mp 148−151 °C. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 1.94, 2.33 (s, 6 H, Tol-CH_3), 6.07 (s, 1 H, 6.29 (s, 1 H, H-4), 6.82 (d, J = 8 Hz, 2 H, Ar), 7.20 (m, 3 H, Ar), 7.69 (m, 4 H, Ar), 8.03 (m, 2 H, Ar). ^{13}C NMR (DMSO-d_6, 50 MHz): δ_c 20.37, 20.47 (Tol-CH_3), 94.65 (CH, *C*HSO_2Ph), 112.20, 117.90 (CH, C-4, C-7), 116.36 (C, C-3a), 120.28, 125.47, 126.22, 129.46, 129.83 134.82 (CH, Ph, Tol, C-6), 129.31, 133.80, 135.07 (C, C-5, Ph-C and Tol-C to C), 147.47, 148.19 (C, C-2, Tol-C to N), 158.34 (C, C-7a), 158.38 (C, C-3). MS−FAB: 389 (68.2, $M^+ + 1$), 247 (100).

(2*Z*,3*E*)-*N*-[1,2-Dihydro-5-methyl-2-[phenyl(phenylsulfonyl)methylene]-3*H*-indol-3-ylidene]-4-methylbenzenamine (4t). Starting with 1.39 g of benzylphenyl sulfone, 1.69 g (61%) of **4t** was isolated as an orange solid as an unseparable mixture of isomers (*E*:*Z* = 1:2), mp 160−163 °C (refers to the mixture of isomers). Major isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.92, 2.24 (s, 6 H, Tol-CH_3), 6.16 (s, 1 H, H-4), 6.38 (d, J = 8 Hz, 2 H, Ar), 7.00−7.80 (m, 14 H, Ar), 10.77 (br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_c 19.91, 20.12 (Tol-CH_3), 61.05 (C, *C*SO_2PH), 112.80, 117.02 (CH, C-4, C-7), 117.76 (C, C-3a), 121.77, 125.69, 127.62, 128.31, 128.48, 128.70, 129.52, 132.40, 134.13 (CH, Ph, Tol, C-6), 133.88, 134.16, 134.76, (C, C-5, Ph-C and Tol-C to C), 142.02 (C, Ph-C to S), 146.70, 147.52 (C, C-2, Tol-C to N), 157.86 (C, C-7a), 158.08

(C, C-3). IR (KBr, cm^{-1}): 3300 (m); 3025 (w), 2920 (w), 1640 (s), 1618 (m), 1584 (s), 1502 (m), 1478 (m), 1326 (m), 1218 (m). MS (140 °C): 464 (3.19, M^+), 463 (7.5, $M^+ - 1$), 323 (100). Anal. Calcd for $C_{29}H_{24}N_2O_2S$: C 74.98, H 5.21, N 6.03. Found: C 74.01, H 5.55, N 6.40.

(2*Z*,3*E*)-*N*-[1,2-Dihydro-5-methyl-2-[4-methoxyphenyl-(phenylsulfonyl)methylene]-3*H*-indol-3-ylidene]-4-methoxybenzenamine (4u). Starting with 1.39 g of benzyl phenyl sulfone, 1.61 g (58%) of **4u** was isolated as an orange solid as an unseparable mixture of isomers (*E*:*Z* = 1:2), mp 160−162 °C (refers to the mixture of isomers). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.41, 3.73 (s, 6 H, OCH_3, major isomer), 3.62, 3.81 (s, 6 H, OCH_3, minor isomer), 6.22 (s, 1 H, H-4, major isomer), 6.19 (s, 1 H, H-4, minor isomer), 6.50 (m, 2 H, Ar), 6.70−7.90 (m, 13 H, Ar), 9.55 (br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_c 55.48, 55.52, 55.62, 110.67, 111.31, 112.36, 112.40, 114.10, 114.28, 114.39, 115.89, 117.51, 118.93, 120.14, 121.13, 121.27, 122.88, 123.78, 127.84, 128.01, 128.61, 128.75, 128.89, 129.17, 129.59, 129.79, 130.81, 131.32, 132.35, 133.09, 133.69, 133.72, 138.00, 140.38, 141.61, 142.56, 143.27, 143.50, 151.53, 153.47, 156.78, 157.94, 158.48, 159.17, 161.13, 163.37. MS (FAB): 497 (3.19, $M^+ + 1$), MS (140 °C): 464 (3.19, M^+).

Isolation of Bis-Enamines (5a−c). During the course of the isolation of the 2-alkylidene-3-iminoindoles **4,** open-chain products **5** could be frequently isolated in low yields. Whereas the indoles **4** were soluble in ethyl ether/THF, the 1:2-products **5** precipitated out and could be isolated by filtration and subsequent recrystallization from EtOH.

(*E*,*E*)-Bisphenyl-(*Z*,*Z*)-1,4-dicyano-2,3-bis(4-tolyl)aminobutadiene (5a): mp 336−339 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.28 (s, 6 H, Tol-CH_3), 7.00−7.20 (m, 18 H, Ar). IR (Nujol): ν = 3268 (w), 1618 (m), 1595 (m), 1512 (m), 1461 (s), 1377 (m), 1233 (m), 1101 (m) cm^{-1}. MS [CI (H_2O), *m*/*z* (%)]: 467 [$M^+ + 1$] (100).

(*E*,*E*)-Bis(4-methoxyphenyl)-(*Z*,*Z*)-1,4-dicyano-2,3-bis-(4-tolyl)aminobutadiene (5b): mp 244−246 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.29 (s, 6 H, Tol-CH_3), 3.73 (s, 6 H, OMe), 6.50−6.70 (m, 6 H, Ar), 6.80−7.10 (m, 10 H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C = 21.03 (Tol-CH_3), 55.24 (OCH_3), 113.42, 114.87, 118.42, 122.17, 126.93, 130.91, 132.43, 133.83, 137.04, 144.33, 158.94. IR (Nujol): ν = 3398 (m, ν_{NH}), 2194 (m), 1635 (m), 1622 (s), 1598 (m), 1579 (m), 1510 (s), 1488 (s), 1488 (s), 1464 (s), 1457 (s), 1249 (s), 1223 (m), 1034 (m) cm^{-1}. MS [70 °C, *m*/*z* (%)]: 526 ($M^+ + 1$).

(*E*,*E*)-Bis(3,4-dimethoxyphenyl)-(*Z*,*Z*)-1,4-dicyano-2,3-bis(4-tolyl)aminobutadiene (5c): mp 244−247 °C. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 2.32 (s, 6 H, Tol-CH_3), 3.39, 3.80 (2 × s, 2 × 6 H, OMe), 6.33 (s, 2 H, Ar), 6.70−6.85 (m, 4 H, Ar), 7.05 (m, 8 H, Ar), 7.82 (br, 2 H, NH). ^{13}C NMR (50 MHz, CD_2Cl_2): δ_C = 21.14 (Tol-CH_3), 55.66, 56.23 (OCH_3), 102.20, 111.55, 114.28, 122.51, 123.03, 127.45, 129.54, 133.29, 137.50, 144.50, 148.95, 149.14, 168.59. IR (Nujol): ν = 3467, 3298 (s, ν_{NH}), 1623 (m), 1595 (m), 1518 (s), 1459 (s), 1377 (m), 1225 (m), 1134 (m), 1021 (m) cm^{-1}. MS [CI (H_2O), *m*/*z* (%)]: 587 ($M^+ + 1$, 100).

Preparation of (*E*,*E*)-Bis(2-pyridyl)-(*Z*,*Z*)-1,4-dicyano-2,3-bis(4-tolyl)aminobutadiene (5d). To a THF solution (30 mL) of (2-pyridyl)acetonitrile (1.2 g, 10 mmol) was added a THF solution of LDA (5.5 mL, 2 M) at 0 °C. To this solution a THF solution (50 mL) of **2b** (1.53 g, 8 mmol) was added slowly at −78 °C. After stirring for 2 h at 20 °C, the solvent was removed in vacuo. To the residue was added CH_2Cl_2, the precipitated LiCl was removed by filtration (Celite), and the solvent of the filtrate was removed in vacuo. To the residue was added ethyl ether, and the precipitated product was washed with ethyl ether and recrystallized from toluene to give a yellow-colored solid (1.24 g, 53%), mp 244−247 °C. ^{1}H NMR (200 MHz, DMSO-d_6, 90 °C): δ = 2.32 (s, 6 H, Tolyl-CH_3), 6.37−8.60 (m, 16 H, Ar), 10.08 (s, 2 H, NH). IR (Nujol): ν = 3359, 3323 (s, ν_{NH}), 2216 (s, $\nu_{C\equiv N}$), 1632 (s), 1604 (s), 1588 (s), 1558 (s), 1532 (s), 1490 (s) cm^{-1}. MS [CI (H_2O), m/z (%)]: 469 ($M^+ + 1$, 13), 353 (9), 131 (15), 119 (100), 108 (46). Anal. Calcd for $C_{30}H_{24}N_6$ (468.56): C 76.90%, H 5.16%, N 17.94%. Found: C 76.29%, H 5.49%, N 17.67%.

General Procedure for the Preparation of Bis-Enamines (5e−i). To a THF solution (20 mL) of the respective cyanoacetic derivatives or benzoyl acetonitrile (10 mmol) was added a THF solution (25 mL) of 10 mL of $NaN(SiMe_3)_2$ (1M solution in THF) or of a THF solution (25 mL) of LDA (prepared by addition of 10 mmol of *n*-BuLi to a THF solution of 10 mmol of diisopropylamine). After stirring for 10 min at 0 °C, the suspension was transferred to a THF solution (25 mL) of the respective oxalic acid bis(imidoyl) dichloride (**2a**: 1.5 g, **2b**: 1.2 g, 5 mmol) at −20 °C. The cooling bath was removed, and the reaction mixture was stirred at 50 °C for 24 h. After being cooled to room temperature, the reaction mixture was poured into an aequous solution of 300 mL of NH_4Cl which was extracted with ethyl ether/THF (1:1). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo. To the residue was added 2 mL of methanol. The precipitated product was washed twice with methanol and was dried in vacuo. Open-chain products were obtained as the major products also when only 1 rather than 2 equiv of the nucleophile in the presence of 2 equiv of LDA were used.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(*p*-tolyl)aminobutadiene-1,4-bis(phenyl ketone) (5e). Starting with benzoylacetonitrile (0.5 g, 3.4 mmol) and **2b** (0.5 g, 1.7 mmol), 125 mg of **5e** (14%) was isolated, yellow crystals, mp 308−310 °C. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 2.38 (s, 6 H, Tol-CH_3), 6.98 (d, J = 8.4 Hz, 4 H, Ar), 7.20 (d, J = 8.3 Hz, 4 H, Ar), 7.56 (m, 6 H, Ar), 7.85 (d, J = 8.0 Hz, 4 H, Ar), 13.35 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ_C 21.2 (Tol-CH_3), 85.6 (C, *C*CN), 118.8 (C, CN), 123.5, 128.7, 130.6, 132.8, 133.9, 138.5, 139.1 (CH, C, Ar), 159.4 (C, *C*NHTol), 193.3 (CO). IR (Nujol): ν = 2199 (s) cm^{-1}, 1612 (s), 1591 (s), 1570 (s), 1514 (s), 1494 (m). MS (CI, H_2O); *m*/*z* (%): 523 (22) [$M^+ + 1$], 416 (26), 261 (4) [M^+/2]. Anal. Calcd for $C_{34}H_{26}N_4O_2$ (522.6): C 78.14, H 5.01, N 10.72. Found: C 77.71, H 5.03, N 10.52.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(phenyl)aminobutadiene-1,4-dicarboxylic Acid Diethyl Ester (5f). Starting with ethyl cyanoacetate (1.1 mL, 10 mmol) and **2a** (1.35 g, 5 mmol), 2.1 g of **5f** (48%) was isolated, yellow crystals, mp 206−209 °C. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.32 (t, J = 6.9 Hz, 6 H, CH_2CH_3), 4.27 (m, J = 6.9 Hz, 4 H, CH_2CH_3), 6.97 (m, 4 H, Ph), 7.32 (m, 6 H, Ph), 11.38 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ_C 14.2 (CH_2CH_3), 62.3 (CH_2CH_3), 77.8 (C, *C*CN), 115.8 (C, CN), 123.1, 127.9, 129.8 (CH, Ph), 136.2 (C, Ph), 157.4 (C, *C*NHPh), 167.5 (CO). IR (Nujol): ν = 3292 (w) cm^{-1}, 3183 (m), 2213 (s), 1670 (s), 1593 (s), 1580 (s), 1497 (m). MS (CI, H_2O); *m*/*z* (%): 431 (100) [$M^+ + 1$], 385 (10), 357 (16). Anal.: Calcd. for $C_{24}H_{22}N_4O_4$ (430.46): C 66.97, H 5.15, N 13.02. Found: C 67.17, H 5.08, N 13.07.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(*p*-tolyl)aminobutadiene-1,4-dicarboxylic Acid Diethyl Ester (5g). Starting with ethyl cyanoacetate (1.1 mL, 10 mmol) and **2b** (1.5 g, 5 mmol), 3.3 g of **5g** (72%) was isolated, yellow crystals, mp 196−199 °C. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.35 (t, J = 7.2 Hz, 6 H, CH_2CH_3), 2.34 (s, 6 H, Tol-CH_3), 4.27 (m, J = 7.2 Hz, 4 H, CH_2CH_3), 6.87, 7.13 (d, J = 8.5 Hz, 8 H, Tol), 11.29 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ_C 14.4 (CH_2CH_3), 21.1 (Tol-CH_3), 62.3 (CH_2CH_3), 77.4 (C, *C*CN), 116.0 (C, CN), 123.2, 130.4 (CH, Tol), 134.0 (C, Tol-C to C), 138.4 (C, Tol-C to N), 157.9 (C, *C*NHTol), 167.2 (CO). IR (Nujol): ν = 3322 (m) cm^{-1}, 2213 (s), 1670 (s), 1595 (s). MS (EI); *m*/*z* (%): 458 (19) [M^+], 385 (57), 339 (100), 229 [M^+/2]. Anal. Calcd for $C_{26}H_{26}N_4O_4$ (458.5): C 68.11, H 5.72, N 12.22. Found: C 68.52, H 5.79, N 11.97.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(p-tolyl)aminobutadiene-1,4-dicarboxylic Acid Piperidide (5h). Starting with (cyanoacetyl)piperidine (0.76 g, 5 mmol) and **2b** (0.76 g, 2.5 mmol), 1.5 g of **5h** (56%) was isolated, slight yellow solid, mp 285−287 °C. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.28 (m, 12 H, CH_2), 2.39 (s, 6 H, Tol-CH_3), 2.70, 3.31, 3.74 (m, 20 H, NCH_2), 7.24 (m, 8 H, Tol), 8.36 (s, 2 H, NH). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ_C 21.2 (Tol-CH_3), 24.6, 25.5, 26.5, 42.8, 48.2 (CH_2), 96.5 (C, *C*CN), 126.5, 129.7 (CH, Tol), 137.9 (C, Tol-C to C), 145.2 (C, Tol-C to N), 161.7 (C, *C*NHTol), 165.8 (CO). IR (Nujol): ν = 3297 (s) cm^{-1}, 1678 (m). MS (CI, H_2O); *m*/*z* (%): 537 (3) [$M^+ + 1$], 452 (8), 268 (3) [M^+/2], 147 (100). Anal. Calcd for $C_{32}H_{36}N_6O_2$ (536.68): C 71.62, H 6.76, N 15.66. Found: C 71.29, H 6.88, N 15.41.

(*Z*,*Z*)-1,4-Dicyano-2,3-di(*p*-tolyl)aminobutadiene-1,4-dicarboxylic Acid Morpholide (5i). Starting with (cyanoacetyl)morpholine (1.00 g, 6.48 mmol) and **2b** (0.99 g, 3.24 mmol), 1.26 g of **5i** (36%) was isolated, slight yellow solid, mp 307−308 °C. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 2.34 (s, 6 H, Tol-CH_3), 3.28, 3.32 (m, 16 H, CH_2), 7.24 (m, 8 H, Tol), 8.73 (s, 2 H, NH). IR (Nujol): ν = 3475 (m) cm^{-1}, 3445 (s), 3276 (s), 1676 (w), 1635 (s), 1590 (s), 1579 (s), 1515 (m). MS (CI, H_2O); *m*/*z* (%): 541 (12) [$M^+ + 1$], 454 (2), 88 (100). Anal. Calcd for $C_{30}H_{32}N_6O_4$ (540.62): C 66.65, H 5.97, N 15.55. Found: C 66.41, H 6.05, N 15.71.

Preparation of *trans*-(*E*,*E*)-1,4-Bis(2-pyridyl)-(*Z*,*Z*)-2,3-bis(4-tolyl)aminobutadiene (5j). To a THF solution (50 mL) of 0.62 mL of 2-picoline (6.25 mmol) was added 10 mL of *n*-BuLi (1.6 M solution in hexane). The reaction mixture was warmed to 20 °C. After being stirred for 2 h, the mixture was cooled to −78 °C and a THF solution (50 mL) of **2b** (0.95 g, 3.12 mmol) was added. The mixture was warmed to 20 °C and was stirred for 6 h. The solvent was removed in vacuo, and to the residue was added CH_2Cl_2. The suspension obtained was filtered (Celite), and the solvent of the filtrate was removed in vacuo. The crude product was precipitated by addition of methanol to the residue. The yellow solid obtained was filtered and dried in vacuo to give 0.56 g (44%) of **5j** as yellow crystals, mp 247−249 °C. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 2.23 (s, 6 H, Tolyl-CH_3), 5.80 (s, 2 H, =CH), 6.76, 6.89 (2 d, 8 H, Ar, J = 8.5 Hz), 6.96 (t, 2 H, Hetar, J = 5.3 Hz), 7.13 (d, 2 H, Hetar, J = 8.2 Hz), 7.58 (t, 2 H, Hetar, J = 7.6 Hz), 8.44 (d, 2 H, Hetar, J = 4.6 Hz), 11.28 (s, 2 H, NH). ^{13}C NMR (50 MHz, CD_2Cl_2): δ_C = 20.8 (Tol-CH_3), 101.4, 118.7, 120.3, 123.2, 129.2, 131.3, 136.2, 139.1, 145.6, 147.7, 159.2. IR (Nujol): ν = 1630 (s, $\nu_{C=C}$), 1609 (s), 1589 (s), 1548 (s), 1517 (s) cm^{-1}. MS [CI (H_2O), *m*/*z* (%)]: 419 ($M^+ + 1$, 100), 340 (16), 312 (10), 209 (M^+/2, 12). Anal. Calcd for $C_{28}H_{26}N_4$ (418.54): C 80.35%, H 6.26%, N 13.39%. Found: C 79.71%, H 6.23%, N 13.15%.

Preparation of 3-Cyano-*N*-(4-methylphenyl)-1-[(4-methylphenyl)imino]-1*H*-pyrrolo[1,2-*a*]benzimidazol-2-amine (6b). 2-(Cyanomethyl)benzimidazole (1.57 g, 10 mmol), NEt_3 (3.1 mL, 22 mmol), and **2b** (3.05 g, 10 mmol) were dissolved in toluene (100 mL). After being stirred for 24 h at 60 °C, the precipitated $HNEt_3Cl$ was removed by filtration and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (toluene/acetone = 10/1) to give 0.98 g of yellow crystals (25%), mp 224−226 °C (from methanol). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.42, 2.45 (2 × s, 2 × 3 H, Tol-CH_3), 5.09 (d, 1 H, J = 8.1 Hz, Hetar), 6.74 (t, 1 H, J = 8.4 Hz, Hetar), 6.94 (d, 2 H, J = 8.3 Hz, Ar), 7.03 (t, 1 H, J = 7.4 Hz, Hetar), 7.18−7.31 (m, 6 H, Ar), 7.43 (d, 1 H, J = 8.1 Hz, Hetar), 8.29 (s, 1 H, NH). ^{13}C NMR (50 MHz, CD_2Cl_2): δ_C 21.2, 21.3 (Tol-CH_3), 113.8, 120.1, 121.3, 124.0, 124.3, 124.6, 128.7, 129.2, 130.3, 130.4, 131.3, 133.3, 136.2, 138.3, 144.4, 151.3. IR (Nujol, cm^{-1}): ν 3313 (br, ν_{NH}), 2212 (m, $\nu_{C\equiv N}$), 1731 (m), 1693m), 1634 (m), 1621 (s), 1606 (s), 1564 (s), 1557 (s), 1525 (m), 1505 (m). MS [CI (H_2O), *m*/*z* (%)]: 390 ($M^+ + 1$, 100), 279, 253, 205, 198, 149, 93.

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Supporting Information Available: Details of the structure determination including atomic coordinates, H-atom coordinates, bond distances and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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