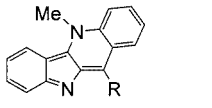
Domino Cyclization/Electrocyclization/Elimination Reactions of Arylacetonitriles with *N*,*N*′-Bis(1-naphthyl)oxaldiimidoyl Dichlorides: Efficient Synthesis of Fluorescent 15*H*-Benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines

Joachim T. Anders[a] and Peter Langer*[a]

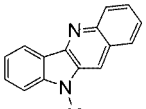
Keywords: Domino reactions / Electrocyclic reactions / Nitrogen heterocycles / Synthetic methods

15*H*-Benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines were prepared by domino cyclization/electrocyclization/elimination reactions of nitriles with *N*,*N*′-bis(1-naphthyl)oxaldiimidoyl dichlorides. The products can be regarded as hexacyclic δ-carbolines and are novel fluorescent dyes.

δ-Carbolines are of considerable pharmacological relevance and occur in a variety of natural products.[1−3] Benzo-annulated δ-carbolines (6*H*-indolino[3,2-*b*]quinolines) can be regarded as isomers of the antitumor agent ellipticin[4] and are pharmacologically relevant systems due to their potential cancerostatic activity. We have recently shown that δ-carbolines selectively bind to triplex or duplex DNA (intercalation).[5] The 6*H*-indolino[3,2-*b*]quinoline core structure occurs, for example, in the natural products cryptolepine, cryptoquindoline, biscryptolepine and neocryptolepine.[6,7] Cryptolepine and cryptoquindoline were first isolated from the West African plant *Cryptolepis sanguinolenta* and have been used for the treatment of Malaria. Extensive pharmacological studies have shown that cryptolepine possesses a variety of interesting features, including antimicrobial and antifungal activity.[8] The antifungal activity is of interest for the treatment of infections by the fungus *Cryptococcus neoformans*.[9] These infections are dangerous for AIDS patients, due to their weak immune systems. Cryptolepine has been recently studied[10] as a substitute for the commonly used drug amphotericin B, which has a number of side effects.

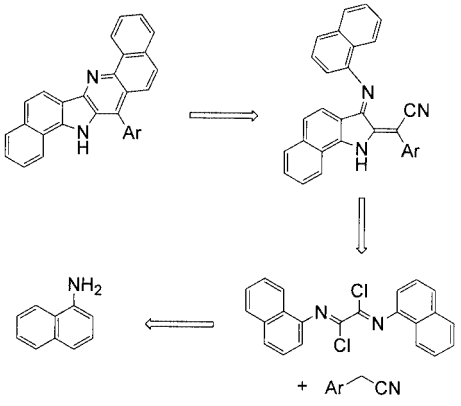


Cryptolepine (R = H)
Hdroxycryptolepine (R = OH)



Cryptoquindoline

We have recently reported[5] a new and efficient approach to 6*H*-indolino[3,2-*b*]quinolines by electrocyclization reactions of 2-alkylidene-3-iminoindoles, which are readily available from the reaction of nitriles with oxaldiimidoyl dichlorides.[11,12] Herein we wish to report the direct and efficient synthesis of 15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines by domino cyclization/electrocyclization/elimination reactions of arylacetonitriles with *N*,*N*′-bis(1-naphthyl)oxaldiimidoyl dichlorides (Scheme 1).[13] The products, hexacyclic δ-carboline derivatives, are of pharmacological relevance and are new fluorescent markers.



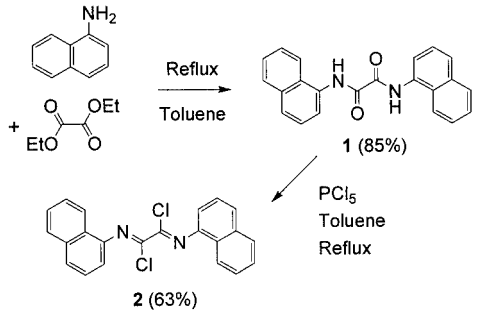
Scheme 1. Retrosynthetic analysis

Our starting point was the synthesis of *N*,*N*′-bis(1-naphthyl)oxaldiimidoyl dichloride (**2**). The synthesis was carried out analogously to the preparation of *N*,*N*′-diphenyloxaldiimidoyl dichloride.[14] The reaction of 1-aminonaphthalene with diethyl oxalate gave the bis(amide) **1**, which was transformed into **2** by chlorination with phosphorus(v) pentachloride (Scheme 2).

The reaction of **2** with dilithiated phenylacetonitrile (**3a**) afforded the 2-alkylidene-3-iminobenzindole **4a**, as a violet solid in 91% yield. It is assumed that **4a** possesses an (*E*)-configured double bond based on the structure established

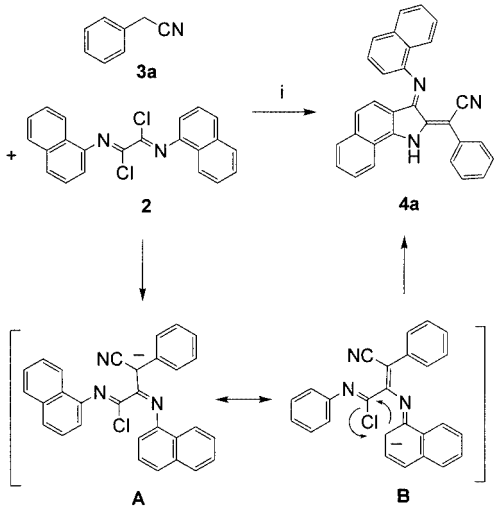
[a] Institut für Chemie und Biochemie der Ernst-Moritz-Arndt-Universität Greifswald,
Soldmannstr. 16, 17487 Greifswald, Germany

  DOI: 10.1002/ejoc.200400405



Scheme 2. Synthesis of *N*,*N*′-bis(1-naphthyl)oxaldiimidoyl dichloride

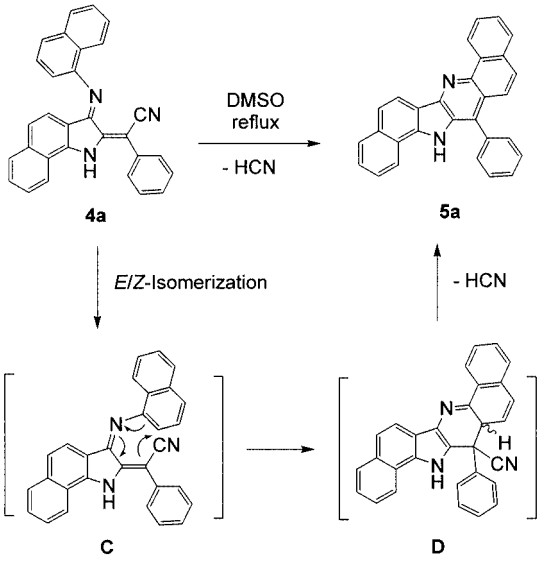
earlier for related 2-alkylidene-3-iminoindoles.[11] The formation of **4a** can be explained, in analogy to our recently published method for the synthesis of 2-alkylidene-3-iminoindoles,[11] by attack of **3a** on **2** to give intermediate **A**, followed by cyclization via the canonical form **B** and subsequent aromatization (Scheme 3).



Scheme 3. Synthesis of 2-alkylidene-3-iminobenzindole **4a**; *i*: 1) 2.5 equiv. LDA, THF, 0 °C, 2) **2**, −78 → 20 °C

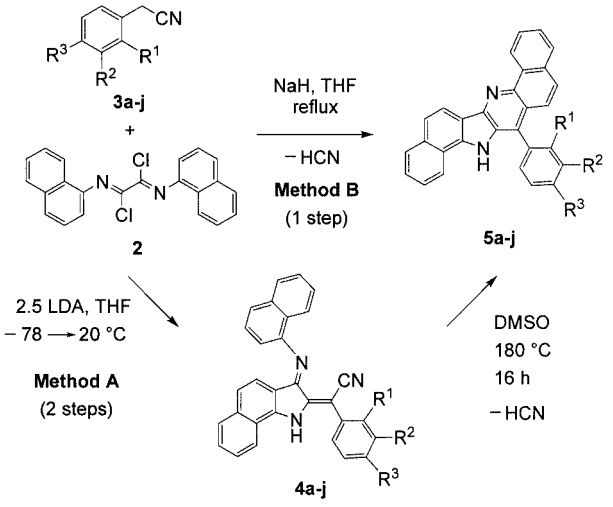
Reflux of a DMSO solution of **4a** resulted in formation of the 15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline **5a** in 65% yield (Scheme 4). The formation of **5a** can be explained by (*E*)/(*Z*) isomerization (intermediate **C**), electrocyclization (intermediate **D**), and subsequent extrusion of hydrogen cyanide. The structure of the S-shaped hexacyclic δ-carboline **5a** was established by spectroscopic methods. To the best of our knowledge, the synthesis of 15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines has not been reported to date.

The two-step synthesis of 15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline **5a** from **2** was accomplished in 59% overall yield (method A). We have also developed an alternative approach (Scheme 5): reflux of a THF solution of **3a** and **2** in the presence of sodium hydride directly afforded **5a** by a domino cylization/electrocyclization/elimination reaction (method B). The yield was significantly higher for the domino reaction (method B, 83%) than for the two-step synthesis (method A, 59%). The methyl-substi-



Scheme 4. Synthesis of **5a** by electrocyclization of **4a**

tuted δ-carbolines **5b**−**d** were prepared from **3b**−**d** (see Table 1). The methoxy-substituted product **5e** was prepared from **3e**, and the cyclization of (2-naphthyl)methyl cyanide (**3f**) with **2** afforded **5f**. The nitro-, cyano-, and bromo-substituted 15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines **5g**−**j** were prepared from the corresponding arylmethyl cyanides **3g**−**j** (Table 1). Significantly higher yields were generally obtained for method B than for method A. All products were formed in good to excellent yields. The use of LDA allowed the preparation of 2-alkylidene-3-iminobenzindoles **4**.



Scheme 5. Synthesis of 15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines **5**

The 15*H*-Benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines **5** show a strong fluorescence. Emission in the region 442−453 nm is observed for alkyl- and bromo-substituted derivatives. No shift of the emission wavelength was observed for meth-

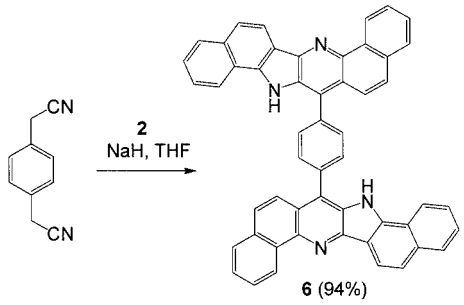
Table 1. Products and yields

5	Method	R^1	R^2	R^3	Yield (%)[a]	λ_{max} [nm][b]
a	B	H	H	H	83	447
a	A	H	H	H	59	447
b	B	Me	H	H	98	442
c	B	H	Me	H	92	446
d	B	H	H	Me	71	445
d	A	H	H	Me	27	445
e	B	H	H	OMe	90	442
e	A	H	H	OMe	48	442
f	B	H	$-C_4H_4-$		89	452
f	A	H	$-C_4H_4-$		48	452
g	B	H	H	NO_2	62	–
h	B	CN	H	H	96	472
i	B	H	Br	H	95	453
j	B	H	H	Br	96	452

[a] Yields of isolated products; yield over two steps for method A. [b] Fluorescence (CH_3CN).

oxy-substituted **5e**. A bathochromic shift was observed for cyano-substituted **5h**.

The reaction of 1,4-bis(cyanomethyl)benzene with **2** (2 equiv.) in the presence of sodium hydride (6 equiv.) resulted in the formation of bis(carboline) **6**, which is formed as a result of a double domino cyclization/electrocyclization/elimination reaction (Scheme 6).



Scheme 6. Cyclization of 1,4-bis(cyanomethyl)benzene with **2**

In summary, the domino cyclization/electrocyclization/elimination reaction of nitriles with *N*,*N*′-bis(1-naphthyl)oxaldiimidoyl dichlorides allows a convenient synthesis of 15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolines, which can be regarded as hexacyclic δ-carbolines and are novel fluorescent dyes.

Experimental Section

General: NMR measurements: Bruker AM 250 (250 MHz), Varian Unity 200 (200 MHz), Varian Mercury 200 (200 MHz), Varian Unity 300 (300 MHz), Varian Mercury 300 (300 MHz), Bruker AMX 300 (300 MHz). Mass spectrometry: EI (electron ionization, 70 eV); DCI (direct chemical ionization, 200 eV, NH_3) and HRMS: Finnigan MAT 95, ESI (electrospray-ionization): Finnigan LCQ. ESI-HRMS (high-resolution ESI): APEX IV (Bruker Deltonik) FT-ICR-MS. Infrared spectroscopy: FT-IR Bruker Vector 22, Bruker IFS 66, Nicolett 205 FT-IR. Fluorescence spectroscopy: Perkin−Elmer Luminescence Spectrometer LS 50B. UV/Vis spectroscopy: Perkin−Elmer Lambda 2 and Perkin−Elmer Lambda 19 UV/Vis/NR Spectrometer. The elemental analyses were carried out at the microanalytical laboratory of the University of Göttingen (Leco CHN 2000, Heraeus apparatus Mikro U/D). Chromatography: Merck silica gel 60 (0.063−0.200 mm, 70−230 mesh ASTM) or Merck silica gel 60 (0.040−0.063 mm, 230−400 mesh ASTM). All solvents were distilled prior to use. TLC: Merck silica gel 60 F_{254} and Macherey−Nagel Alugram® Sil G/UV_{254}.

***N*,*N*′-Bis(1-naphthyl)oxalamide (1):** A toluene solution (20 mL) of diethyl oxalate (1.46 g, 10.0 mmol) and 1-aminonaphthalene (2.86 g, 20.0 mmol) was refluxed for 8 h. The precipitate formed was filtered off and washed with EtOH to give **1** (2.90 g, 85%) as a colourless solid. M.p. 246.5 °C. IR (KBr): $\tilde{\nu}$ = 770 (m), 807 (s), 1493 (s), 1516 (s), 1672 (s), 1686 (s), 3328 (s) cm^{-1}. ^1H NMR (200 MHz, [D_6]DMSO): δ = 7.54−8.02 (m, 14 H, Ar), 10.91 (s, 2 H, NH) ppm. ^{13}C NMR (50 Hz, [D_6]DMSO): δ = 122.81, 122.83, 125.44, 126.12, 126.15, 126.60, 128.03 (CH), 128.27, 132.42, 133.63, 159.56 (C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 340 (79) $[M]^+$, 143 (100), 127 (37), 114 (64). $C_{22}H_{16}N_2O_2$ (340.22): calcd. C 77.66, H 4.70, N 8.22; found C 77.47, H 4.57, N 7.94.

***N*,*N*′-Bis(1-naphthyl)oxaldiimidoyl dichloride (2):** A toluene solution (20 mL) of **1** (3.40 g, 10.0 mmol) and PCl_5 (4.16 g, 20.0 mmol) was refluxed for 4 h. The mixture was concentrated in vacuo and was cooled to 20 °C to give a precipitate. The latter was filtered off and recrystallized from *n*-heptane to give **2** as yellow needles (2.40 g, 63%). M.p. 187 °C. IR (KBr): $\tilde{\nu}$ = 765 (m), 1490 (w), 1672 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.30−7.33 (d, 7 Hz, 2 H, Ar), 7.51−7.56 (m, 6 H, Ar), 7.78−7.80 (d, 7 Hz, 2 H, Ar), 7.78−7.89 (m, 2 H, Ar), 8.40 (s, 2 H, Ar) ppm. ^{13}C NMR (50 Hz, $CDCl_3$): δ = 110.55, 123.52, 125.50, 126.72, 126.80, 126.92, 127.38, 128.20, 130.40, 130.90, 140.20 ppm. MS (EI, 70 eV): *m*/*z* (%) = 377 (39) $[M]^+$, 188 (100), 153 (29), 127 (63). $C_{22}H_{14}N_2Cl_2$ (377.12): calcd. C 70.06, H 3.71, N 7.42; found C 69.34, H 4.60, N 8.12.

General Procedure for the One-Pot Synthesis of Benzo[*g*]indolino[3,2-*b*]benzo[*h*]quinolines (Method B): Sodium hydride (0.04 g, 1.5 mmol) and *N*,*N*′-bis(1-naphthyl)oxaldiimidoyl dichloride (**2**) (0.19 g, 0.5 mmol) were added to a THF solution (50 mL) of arylacetonitrile **3** (0.5 mmol) and the solution was refluxed for about 12 h (TLC control). An aqueous solution of NH_4Cl (250 mL, 1 M) was then added to the mixture. The organic and aqueous layers were separated and the latter was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel; *n*-pentane/diethyl ether, 10:1) to give **5a**−**j** as yellow solids.

General Procedure for the Two-Step Synthesis of Benzo[*g*]indolino[3,2-*b*]benzo[*h*]quinolines (Method A). Step 1: Synthesis of 3-(Arylimino)-2-(1-aryl-1-cyanomethylidene)indoles 4: A THF solution of lithium diisopropylamide (LDA) was prepared as follows: *n*-butyllithium (1.06 mL, 2.36 M solution in *n*-hexane, 2.50 mmol) was added at 0 °C to a THF solution (30 mL) of diisopropylamine (0.23 g, 2.30 mmol). The solution was stirred at 0 °C for 30 min. Compound **3** (1.00 mmol) was added dropwise at 0 °C to this LDA solution and the solution was stirred at 0 °C for 60 min. The solution was then cooled to −78 °C and was added by cannula to a THF solution (40 mL) of **2** (1.00 mmol) at −78 °C. The solution was warmed within 1.5 h to 20 °C. The progress of the reaction was monitored by TLC. An aqueous solution of NH_4Cl (250 mL, 1 M) was then added to the mixture. The organic and aqueous layers were separated and the latter was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried (Na_2SO_4) and

the solvent was removed in vacuo. The residue was purified by chromatography (silica gel; petroleum ether/diethyl ether, 10:1→1:1→1:10) to give compounds **4** as orange to violet solids. **Step 2: Transformation of 2-Alkylidene-3-iminoindoles 4 into Benzo[*g*]indolino-[3,2-*b*]benzo[*h*]quinolines 5:** A DMSO solution (25 mL) of **4** (0.25 mmol) was stirred at 150 °C for 4 h. The progress of the reaction was monitored by TLC. The solvent was then removed in vacuo and the residue was purified by chromatography (silica gel; *n*-pentane/diethyl ether, 10:1) to give compounds **5** as yellow solids.

(*E*)-2-(1-Cyano-1-phenylmethylidene)-3-(1-naphthylimino)-2,3-dihydro-1*H*-benzo[*g*]indole (4a): Starting with phenylacetonitrile (**3a**; 0.12 g, 1.00 mmol) and **2** (0.38 g, 1.00 mmol), **4a** was isolated as a violet solid (0.38 g, 91%, *E*/*Z* > 98:2). ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 6.65 (d, ^3J = 8.7 Hz, 1 H, Ar), 6.95 (d, ^3J = 8.7 Hz, 1 H, Ar), 7.15 (d, ^3J = 7.3 Hz, 1 H, Ar), 7.40−7.93 (m, 15 H, Ar, NH), 8.21 (d, ^3J = 7.9 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 88.59 (*C*−CN), 112.49 (CH), 113.27, 118.99, 119.40 (C), 120.98, 121.90, 124.14, 124.78, 125.64, 125.85 (CH), 126.17 (C), 126.33, 126.48, 127.67, 128.66, 128.76, 128.81, 128.85, 128.88, 129.72 (CH), 133.65, 134.29, 135.80, 146.39, 146.66, 147.62, 156.74 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3056 (m), 2929 (w), 2198 (m), 1685 (m), 1673 (m), 1635 (s), 1586 (s), 1572 (s), 1525 (s), 1492 (m), 1465 (s), 1447 (s), 1418 (m), 1391 (s), 1346 (m), 1321 (m), 1261 (m), 1203 (s), 1087 (m), 810 (m), 792 (m), 773 (s), 753 (s) cm^{-1}. UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 492.1 nm (3.89), 350.8 (4.11), 336.5 (4.13), 281.4 (4.41), 233.6 (4.62) ppm. MS (ESI): *m*/*z* (%) = 865 (100) [2 M + Na]$^+$, 863 (5) [2 M − 2 H + Na]$^-$, 722 (14), 539 (8), 422 (12) [M + H]$^+$, 421 (35) [M]$^-$, 420 (100) [M − H]$^-$, 395 (8) [M − CN]$^+$.

(*E*)-2-[1-Cyano-1-(4-tolyl)methylidene]-3-(1-naphthylimino)-2,3-dihydro-1*H*-benzo[*g*]indole (4d): Starting with 4-tolylacetonitrile (**3d**; 0.07 g, 0.50 mmol) and **2** (0.19 g, 0.50 mmol), **4d** was isolated as a violet solid (0.10 g, 44%, *E*/*Z* > 98:2). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.45 (s, 3 H, ArC*H*$_3$), 6.64 (d, ^3J = 8.8 Hz, 1 H, Ar), 6.95 (d, ^3J = 8.6 Hz, 1 H, Ar), 7.14 (d, ^3J = 7.2 Hz, 1 H, Ar), 7.37−7.80 (m, 11 H, Ar, NH), 7.90 (t, ^3J = 7.7 Hz, 2 H, Ar), 7.99 (d, ^3J = 8.0 Hz, 1 H, Ar), 8.21 (d, ^3J = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 21.35 (Ar*C*H$_3$), 88.89 (*C*−CN), 112.53 (CH), 113.38 (C), 119.21 (CH), 119.44 (C), 120.11, 120.95, 122.00, 124.20, 124.70, 125.65, 125.85 (CH), 126.18 (C), 126.50, 126.80, 127.68, 128.53, 128.78, 130.39 (CH), 130.72, 134.01, 134.33, 135.81, 139.08, 146.42, 146.80, 147.29, 158.15 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3430 (s), 3054 (w), 2956 (w), 2201 (m), 1673 (s), 1636 (s), 1635 (s), 1589 (m), 1573 (s), 1522 (s), 1490 (m), 1464 (m), 1447 (m), 1392 (m), 1344 (m), 1321 (m), 1265 (m), 1203 (s), 1086 (m), 806 (s), 772 (s), 754 (m) (cm^{-1}). UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 493.0 nm (3.75), 351.5 (3.94), 282.7 (4.30), 220.9 (4.81). MS (ESI): *m*/*z* (%) = 893 (100) [2 M + Na]$^+$, 870 (10) [2 M − 2 H]$^{2-}$, 797 (8), 458 (12) [M + Na]$^+$, 436 (10) [M + H]$^+$, 435 (35) [M]$^-$, 434 (100) [M − H]$^-$. The exact molecular mass [M + H]$^+$ for $C_{31}H_{21}N_3$ was confirmed by ESI-HRMS: calcd. 436.18082; found 436.18076.

(*E*)-2-[1-Cyano-1-(4-methoxyphenyl)methylidene]-3-(1-naphthylimino)-2,3-dihydro-1*H*-benzo[*g*]indole (4e): Starting with (4-methoxyphenyl)acetonitrile (**3e**; 0.15 g, 1.00 mmol) and **2** (0.38 g, 1.00 mmol), **4e** was isolated as a violet solid (0.33 g, 74%, *E*/*Z* > 98:2). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.89 (s, 3 H, OCH$_3$), 6.63 (d, ^3J = 8.7 Hz, 1 H, Ar), 6.95 (d, ^3J = 8.7 Hz, 1 H, Ar), 7.10 (d, ^3J = 8.8 Hz, 2 H, Ar), 7.15 (d, ^3J = 7.4 Hz, 1 H, Ar), 7.41−7.80 (m, 11 H, Ar, NH), 7.88 (t, ^3J = 8.2 Hz, 1 H, Ar), 8.21 (d, ^3J = 7.1 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 55.46 (OCH$_3$), 88.82 (*C*−CN), 112.54 (CH), 113.48 (C), 115.15 (CH), 119.05, 119.49 (C), 120.86, 120.97, 122.01, 124.20, 124.65, 125.67 (CH), 125.72 (C), 125.82 (CH), 126.23 (C), 126.29, 126.38, 126.46, 127.67, 128.76, 130.05 (CH), 134.34, 135.79, 146.44, 146.85, 146.98, 156.74, 159.94 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3328 (s), 3053 (w), 2967 (w), 2199 (m), 1673 (s), 1649 (m), 1640 (m), 1598 (m), 1573 (m), 1516 (s), 1489 (s), 1465 (m), 1438 (m), 1393 (m), 1347 (m), 1322 (m), 1251 (m), 1204 (m), 1181 (m), 1154 (m), 807 (s), 771 (s), 651 (m), 574 (m) cm^{-1}. UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 494.3 nm (3.36), 293.1 (4.28), 222.0 (4.98). MS (EI, 70 eV): *m*/*z* (%) = 451 (4) [M]$^+$, 450 (10) [M − H]$^+$, 424 (42) [M − HCN]$^+$, 340 (48), 143 (100). The exact molecular mass (*m*/*z* = 451.1685 ± 2 mD [M$^+$]) for $C_{31}H_{21}N_3O$ was confirmed by HRMS (EI, 70 eV).

(*E*)-2-[1-Cyano-1-(2-naphthyl)methylidene]-3-(1-naphthylimino)-2,3-dihydro-1*H*-benzo[*g*]indole (4f): Starting with (2-naphthyl)acetonitrile (**3f**; 0.17 g, 1.00 mmol) and **2** (0.38 g, 1.00 mmol), **4f** was isolated as a violet solid (0.42 g, 89%, *E*/*Z* > 98:2). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 6.68 (d, ^3J = 8.7 Hz, 1 H, Ar), 6.97 (d, ^3J = 8.9 Hz, 1 H, Ar), 7.17 (d, ^3J = 7.2 Hz, 1 H, Ar), 7.40−7.60 (m, 7 H, Ar, NH), 7.67−7.79 (m, 3 H, Ar), 7.87−7.96 (m, 5 H, Ar), 8.04 (d, ^3J = 8.6 Hz, 1 H, Ar), 8.23 (d, ^3J = 8.0 Hz, 1 H, Ar), 8.25 (s, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 88.87 (*C*−CN), 112.55 (CH), 113.41, 119.00, 119.48 (C), 121.01, 121.05, 121.97, 124.20, 124.83, 125.53, 125.65, 125.90 (CH), 126.25 (C), 126.35, 126.50, 127.09, 127.23, 127.69, 127.85, 128.25, 128.47, 128.79, 129.43, 129.63 (CH), 131.04, 133.02, 133.58, 134.35, 135.84, 146.43, 146.73, 147.85, 156.78 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3398 (w), 3053 (w), 2197 (m), 1677 (w), 1637 (s), 1572 (s), 1525 (s), 1464 (m), 1447 (m), 1417 (m), 1390 (s), 1320 (s), 1204 (s), 1087 (m), 803 (m), 772 (s), 753 (s) cm^{-1}. UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 497.9 nm (3.96), 353.6 (4.13), 276.8 (4.49), 221.9 (4.97). MS (ESI): *m*/*z* (%) = 965 (100) [2 M + Na]$^+$, 870 (10) [2 M − 2 H + Na]$^-$, 494 (15) [M + Na]$^+$, 471 (28) [M]$^-$, 470 (100) [M − H]$^-$. The exact molecular mass [M + H]$^+$ for $C_{31}H_{21}N_3$ was confirmed by ESI-HRMS: calcd. 472.18082; found 472.18108.

14-Phenyl-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5a): Method B: Starting with phenylacetonitrile (**3a**; 0.12 g, 1.00 mmol), **5a** was isolated as a yellow solid (0.33 g, 83%). Method A: Starting with **4a** (0.11 g, 0.26 mmol), **5a** was isolated as a yellow solid (0.07 g, 65%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.53−7.84 (m, 11 H, Ar), 7.88 (d, ^3J = 7.8 Hz, 1 H, Ar), 8.03−8.08 (m, 2 H, Ar), 8.54 (s, 1 H, NH), 8.66 (d, ^3J = 8.6 Hz, 1 H, Ar), 9.73 (d, ^3J = 8.2 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 118.09 (C), 119.76, 120.64 (CH), 120.80 (C), 121.01 (CH), 122.10 (C), 123.02, 124.74, 125.70, 126.10, 126.52, 126.69, 127.24, 127.51 (CH), 127.88 (C), 128.76, 129.13, 129.39 (CH), 129.94 (C), 130.23 (CH), 132.20, 132.30, 134.00, 134.61, 139.10, 142.72, 143.10 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3447 (m), 3052 (m), 1598 (m), 1564 (w), 1532 (m), 1518 (m), 1490 (m), 1466 (s), 1438 (m), 1420 (w), 1382 (s), 1361 (w), 1331 (m), 1285 (m), 1195 (s), 1183 (m), 826 (m), 800 (m), 757 (s), 738 (w), 699 (m), 671 (m) cm^{-1}. Fluorescence (CH$_3$CN): Ex ($F\lambda_{max}$) = 375 (447.49) nm. UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 381.7 nm (4.37), 363.2 (4.25), 306.5 (4.79), 260.7 (4.47), 243.5 (4.49). MS (EI, 70 eV): *m*/*z* (%) = 394 (100) [M]$^+$, 340 (4), 197 (20), 143 (5). The exact molecular mass (*m*/*z* = 394.1470 ± 2 mD [M$^+$]) for $C_{29}H_{18}N_2$ was confirmed by HRMS (EI, 70 eV). $C_{29}H_{18}N_2$ (394.47): calcd. C 88.30, H 4.60, N 7.10; found C 88.22, H 4.87, N 6.98.

14-(2-Tolyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5b): Starting with 2-tolylacetonitrile (**3b**; 0.07 g, 0.50 mmol), **5b** was isolated as a yellow solid (0.02 g, 98%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.04 (s, 3 H, ArC*H*$_3$), 7.40−7.57 (m, 7 H, Ar), 7.60−7.85 (m, 4 H, Ar), 7.90 (d, ^3J = 7.8 Hz, 1 H, Ar), 8.04 (d, ^3J = 7.9 Hz, 1 H, Ar), 8.10 (d, ^3J = 7.9 Hz, 1 H, Ar), 8.75 (d, ^3J = 8.6 Hz, 1 H, Ar),

8.81 (br. s, 1 H, NH), 9.81 (d, ^3J = 8.1 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.77 (Ar*C*H$_3$), 118.07 (C), 119.75, 120.82 (CH), 120.88 (C), 121.02 (CH), 122.55 (C), 123.09, 124.70, 125.67, 126.21, 126.46, 126.50, 126.69, 127.21, 127.55, 128.99, 129.07 (CH), 130.12 (C), 130.23, 130.76 (CH), 132.23, 132.40, 133.77, 134.01, 137.49, 139.24, 142.49, 143.29 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3431 (m), 3051 (m), 2955 (w), 2921 (w), 1631 (w), 1599 (w), 1566 (w), 1531 (m), 1512 (m), 1465 (m), 1451 (m), 1439 (m), 1422 (m), 1382 (s), 1330 (m), 1286 (m), 1243 (m), 1196 (m), 1179 (m), 829 (m), 802 (m), 761 (s) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 380 (442.49) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 381.1 nm (4.39), 362.4 (4.26), 322.9 (4.21), 305.8 (4.76), 266.3 (4.44), 260.4 (4.44), 241.5 (4.48), 216.0 (4.63). MS (EI, 70 eV): *m*/*z* (%) = 408 (100) [M]$^+$, 203 (14), 196 (8), 143 (4). The exact molecular mass (*m*/*z* = 408.1626 ± 2 mD [M$^+$]) for $C_{30}H_{20}N_2$ was confirmed by HRMS (EI, 70 eV).

14-(3-Tolyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5c): Starting with 3-tolylacetonitrile (**3c**; 0.07 g, 0.50 mmol), **5c** was isolated as a yellow solid (0.19 g, 92%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.56 (s, 3 H, ArC*H*$_3$), 7.47−7.81 (m, 11 H, Ar), 7.87 (d, ^3J = 8.6 Hz, 1 H, Ar), 8.03−8.06 (m, 2 H, Ar), 8.58 (br. s, 1 H, NH), 8.67 (d, ^3J = 8.6 Hz, 1 H, Ar), 9.74 (d, ^3J = 8.1 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.63 (Ar*C*H$_3$), 119.84, 120.72 (CH), 120.83 (C), 121.00 (CH), 122.20 (C), 123.16, 124.80, 125.68, 126.05, 126.51, 126.68, 127.23, 127.26, 127.52 (CH), 128.01, 128.14 (C), 129.13, 129.28, 129.54 (CH), 130.02 (C), 130.81 (CH), 132.36, 132.40, 133.77, 134.03, 134.53, 139.14, 139.20, 143.29 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3440 (s), 3050 (m), 2951 (w), 2921 (w), 1673 (m), 1630 (m), 1600 (m), 1531 (m), 1515 (m), 1487 (m), 1464 (m), 1449 (m), 1441 (m), 1382 (s), 1332 (m), 1285 (m), 1197 (m), 1166 (m), 827 (m), 802 (m), 766 (s) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 380 (445.92) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 381.6 nm (4.41), 363.2 (4.28), 306.5 (4.82), 267.7 (4.49), 260.7 (4.50), 242.6 (4.53), 216.1 (4.71). MS (EI, 70 eV): *m*/*z* (%) = 408 (100) [M]$^+$, 204 (10), 196 (15), 143 (52). The exact molecular mass (*m*/*z* = 408.1626 ± 2 mD [M$^+$]) for $C_{30}H_{20}N_2$ was confirmed by HRMS (EI, 70 eV).

14-(4-Tolyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5d): Method B: Starting with 4-tolylacetonitrile (**3d**; 0.13 g, 1.00 mmol), **5d** was isolated as a yellow solid (0.29 g, 71%). Method A: Starting with **4d** (0.10 g, 0.22 mmol), **5d** was isolated as a yellow solid (0.05 g, 60%). ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 2.49 (s, 3 H, ArC*H*$_3$), 7.46−7.81 (m, 11 H, Ar), 7.83 (d, ^3J = 7.8 Hz, 1 H, Ar), 8.04−8.10 (m, 1 H, Ar), 8.56 (d, ^3J = 8.6 Hz, 1 H, Ar), 8.89−8.94 (m, 1 H, Ar), 9.61 (d, ^3J = 7.7 Hz, 1 H, Ar), 11.77 (br. s, 1 H, NH) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 20.94 (Ar*C*H$_3$), 116.64 (C), 118.89, 120.39 (CH), 121.36, 121.94 (C), 123.12, 123.25, 124.08, 125.40, 126.11, 126.56, 127.15, 127.52, 128.03 (CH), 128.38 (C), 128.49, 129.50 (CH), 130.21 (C), 130.30 (CH), 131.09, 131.60, 131.76, 133.66, 137.66, 140.29, 141.25, 142.73 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3463 (s), 3049 (m), 1685 (w), 1674 (w), 1631 (w), 1599 (w), 1531 (m), 1511 (s), 1493 (m), 1466 (m), 1453 (m), 1438 (m), 1421 (m), 1381 (s), 1331 (m), 1284 (m), 1195 (m), 1184 (m), 826 (m), 798 (m), 786 (m), 765 (s), 567 (m) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 380 (444.97) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 381.6 nm (4.38), 363.1 (4.26), 306.7 (4.82), 268.0 (4.48), 260.5 (4.49), 243.6 (4.48). MS (EI, 70 eV): *m*/*z* (%) = 408 (100) [M]$^+$, 204 (10), 196 (15), 143 (52). The exact molecular mass (*m*/*z* = 408.1626 ± 2 mD [M$^+$]) for $C_{30}H_{20}N_2$ was confirmed by HRMS (EI, 70 eV).

14-(4-Methoxyphenyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5e): Method B: Starting with (4-methoxyphenyl)acetonitrile (**3e**; 0.15 g, 1.00 mmol), **5e** was isolated as a yellow solid (0.38 g, 90%). *Method A:* Starting with **4e** (0.07 g, 0.15 mmol), **5e** was isolated as a yellow solid (0.05 g, 65%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.91 (s, 3 H, OCH$_3$), 7.24 (d, ^3J = 8.7 Hz, 2 H, Ar), 7.57−7.83 (m, 9 H, Ar), 7.96 (d, ^3J = 7.6 Hz, 1 H, Ar), 8.07−8.11 (m, 1 H, Ar), 8.23 (br. s, 1 H, NH), 8.55 (d, ^3J = 8.6 Hz, 1 H, Ar), 8.90−8.94 (m, 1 H, Ar), 9.58 (d, ^3J = 7.8 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 55.19 (OCH$_3$), 114.42 (CH), 116.65 (C), 118.91, 120.36 (CH), 121.34, 122.10 (C), 123.16, 123.22, 124.07, 125.34, 125.41 (CH), 126.04 (C), 126.55, 127.14, 127.52 (CH), 128.25 (C), 128.50 (CH), 130.43, 131.60 (C), 131.68 (CH), 131.77, 133.64, 140.24, 141.28, 142.67, 159.37 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3460 (s), 3050 (m), 1630 (m), 1608 (s), 1568 (w), 1531 (m), 1509 (s), 1464 (m), 1440 (m), 1382 (s), 1332 (m), 1289 (m), 1247 (s), 1181 (s), 1028 (m), 830 (m), 798 (m), 766 (s), 736 (m), 573 (m) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 385 (441.98) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 381.4 nm (4.40), 363.2 (4.28), 307.7 (4.80), 261.4 (4.49), 228.6 (4.65), 218.4 (4.67). MS (EI, 70 eV): *m*/*z* (%) = 424 (100) [M]$^+$, 380 (10), 212 (10), 190 (14). The exact molecular mass (*m*/*z* = 424.1576 ± 2 mD [M$^+$]) for $C_{30}H_{20}N_2O$ was confirmed by HRMS (EI, 70 eV).

14-(2-Naphthyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5f): Method B: Starting with (2-naphthyl)acetonitrile (**3f**; 0.08 g, 0.50 mmol), **5f** was isolated as a yellow solid (0.20 g, 89%). Method A: Starting with **4f** (0.13 g, 0.28 mmol), **5f** was isolated as a yellow solid (0.07 g, 54%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.38−7.98 (m, 15 H, Ar), 8.06 (d, ^3J = 7.4 Hz, 1 H, Ar), 8.14 (s, 1 H, Ar), 8.47 (br. s, 1 H, NH), 8.57 (d, ^3J = 8.8 Hz, 1 H, Ar), 9.66 (d, ^3J = 8.1 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 118.06 (C), 119.75, 120.66 (CH), 120.79 (C), 121.02 (CH), 122.24 (C), 123.05, 124.74, 125.67, 126.12, 126.49, 126.68, 126.94, 126.96, 127.22, 127.56 (CH), 127.66 (C), 127.87, 128.01, 128.24, 129.07, 129.10, 129.39 (CH), 130.15, 132.11, 132.18, 132.32, 133.21, 133.62, 133.98, 135.72, 139.14, 142.66 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3462 (m), 3052 (m), 2961 (w), 2925 (w), 1630 (w), 1598 (m), 1564 (m), 1532 (m), 1506 (m), 1466 (m), 1437 (m), 1382 (s), 1324 (m), 1284 (m), 1262 (s), 1197 (s), 1173 (m), 1092 (m), 1017 (m), 824 (s), 797 (s), 764 (s), 747 (m) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 380 (452.47) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 382.2 nm (4.23), 364.1 (4.10), 307.2 (4.66), 260.9 (4.47), 243.0 (4.52), 236.6 (4.51), 224.1 (4.60). MS (EI, 70 eV): *m*/*z* (%) = 444 (100) [M]$^+$, 222 (24), 167 (6), 83 (16).

14-(4-Nitrophenyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5g): Starting with (4-nitrophenyl)acetonitrile (**3g**; 0.08 g, 0.50 mmol), **5g** was isolated as an orange solid (0.14 g, 62%). ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 7.57 (d, ^3J = 9.1 Hz, 1 H, Ar), 7.62−7.68 (m, 2 H, Ar), 7.74 (dd, ^3J = 7.7, ^4J = 1.4 Hz, 1 H, Ar), 7.83 (d, ^3J = 9.1 Hz, 3 H, Ar), 7.99 (d, ^3J = 9.0 Hz, 3 H, Ar), 8.09−8.14 (m, 1 H, Ar), 8.56 (dd, ^3J = 8.7, ^4J = 2.2 Hz, 3 H, Ar), 8.77−8.82 (m, 1 H, Ar), 9.59 (d, ^3J = 8.3 Hz, 1 H, Ar), 11.83 (br. s, 1 H, NH) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 116.43 (C), 118.86, 120.61 (CH), 121.13, 121.25 (C), 122.42, 122.96, 123.99, 124.02, 125.58 (CH), 125.94 (C), 126.12, 126.77, 126.82, 127.34, 127.65, 128.60 (CH), 129.82, 131.46, 131.72 (C), 132.17 (CH), 133.72, 140.55, 141.01, 141.39, 142.95, 147.66 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3428 (s), 3388 (s), 1652 (m), 1594 (w), 1505 (m), 1379 (m), 1342 (m), 1181 (m), 1147 (m), 1048 (s), 1026 (s), 1001 (s), 822 (w), 789 (m), 767 (s), 670 (m) cm^{-1}. UV/Vis (CH_3CN): λ_{max} (lg ε) = 383.1 nm (3.73), 365.0 (3.63), 302.6 (4.21), 265.4 (4.02), 242.5 (3.92). MS (EI, 70 eV): *m*/*z* (%) = 439 (100) [M]$^+$, 393 (30), 219 (4), 196 (10). MS (ESI): 441 (30) [M + 2 H]$^{2+}$, 440 (100) [M + H]$^+$, 439 (30) [M]$^-$, 438 (100) [M − H]$^{2-}$. The exact molecular mass [M + H]$^+$ for $C_{29}H_{17}N_3O_2$ was confirmed by ESI-HRMS: calcd. 440.13935; found 440.13960.

14-(2-Cyanophenyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5h): Starting with (2-cyanophenyl)acetonitrile (**3h**; 0.07 g, 0.50 mmol), **5h** was isolated as a yellow solid (0.20 g, 96%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.34 (d, ^3J = 9.1 Hz, 1 H, Ar), 7.38−7.98 (m, 13 H, Ar), 8.40 (br. s, 1 H, NH), 8.57 (d, ^3J = 8.5 Hz, 1 H, Ar), 9.62 (d, ^3J = 8.1 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 114.47, 117.08, 117.80 (C), 119.75, 120.66 (CH), 120.98 (C), 121.60, 122.03, 124.97, 125.81, 126.70, 127.01, 127.15, 127.48, 127.65, 129.27, 129.46 (CH), 129.87, 131.05 (C), 131.84 (CH), 132.37, 132.46 (C), 133.46, 133.99 (CH), 134.27, 134.36, 138.73, 139.59, 142.60, 143.44 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3326 (m), 3051 (w), 2229 (w), 1685 (m), 1673 (s), 1597 (m), 1532 (m), 1517 (m), 1491 (s), 1468 (m), 1438 (m), 1385 (s), 1332 (m), 1194 (m), 1180 (m), 825 (m), 799 (m), 765 (s), 743 (m) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 380 (471.64) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 383.9 nm (4.34), 365.3 (4.21), 306.1 (4.71), 262.0 (4.47), 241.9 (4.47), 231.4 (4.52). MS (EI, 70 eV): *m*/*z* (%) = 419 (100) $[M]^+$, 209 (16). The exact molecular mass (*m*/*z* = 419.1422 ± 2 mD $[M^+]$) for $C_{30}H_{17}N_3$ was confirmed by HRMS (EI, 70 eV).

14-(3-Bromophenyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5i): Starting with (3-bromophenyl)acetonitrile **3i** (0.10 g, 0.50 mmol), **5i** was isolated as a yellow solid (0.23 g, 95%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40−7.68 (m, 5 H, Ar), 7.71−7.87 (m, 6 H, Ar), 8.03−8.07 (m, 3 H, Ar), 8.46 (br. s, 1 H, NH), 8.63 (d, ^3J = 8.7 Hz, 1 H, Ar), 9.70 (d, ^3J = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 118.29 (C), 119.73, 120.65 (CH), 120.93 (C), 121.30 (CH), 121.92 (C), 122.49 (CH), 123.62 (C), 124.88, 125.80 (CH), 126.04 (C), 126.51, 126.61, 126.80, 127.34, 127.59, 128.96, 129.20 (CH), 129.79 (C), 130.92, 131.97 (CH), 132.30, 132.39 (C), 133.20 (CH), 134.22, 136.98, 139.27, 142.78, 143.51 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3439 (m), 3050 (m), 1631 (w), 1594 (m), 1560 (m), 1531 (m), 1517 (m), 1468 (s), 1451 (m), 1439 (m), 1418 (m), 1405 (m), 1383 (s), 1360 (m), 1330 (m), 1286 (m), 1191 (m), 1073 (w), 814 (m), 801 (m), 765 (s), 692 (m) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 385 (453.08) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 382.6 nm (4.41), 364.2 (4.29), 306.4 (4.82), 261.3 (4.53), 242.5 (4.57), 235.0 (4.57), 215.6 (4.71). MS (EI, 70 eV): *m*/*z* (%) = 474 (100) $[M]^+$, 472 (100) $[M]^+$, 393 (24), 196 (40). MS (ESI): *m*/*z* (%) = 969 (20) $[2\ M + Na]^+$, 944 (20) $[2\ M - 2\ H]^{2-}$, 475 (100) $[M\ (^{81}Br)]^+$, 473 (80) $[M\ (^{79}Br)]^-$, 471 (100) $[M - 2\ H]^{2-}$. The exact molecular mass $[M + H]^+$ for $C_{29}H_{17}BrN_2$ was confirmed by ESI-HRMS: calcd. 473.06479; found 473.06441.

14-(4-Bromophenyl)-15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinoline (5j): Starting with (4-bromophenyl)acetonitrile (**4j**; 0.10 g, 0.50 mmol), **5j** was isolated as a yellow solid (0.23 g, 96%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40−7.68 (m, 7 H, Ar), 7.71−7.87 (m, 5 H, Ar), 8.03−8.07 (m, 2 H, Ar), 8.46 (br. s, 1 H, NH), 8.63 (d, ^3J = 8.7 Hz, 1 H, Ar), 9.70 (d, ^3J = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 116.48 (C), 118.88, 120.52 (CH), 121.26, 121.57, 122.10 (C), 122.75, 123.07, 124.03, 125.53, 125.80, 126.71, 126.73 (CH), 126.98 (C), 127.28, 127.61, 128.57 (CH), 130.02, 131.48, 131.74 (C), 131.94, 132.65 (CH), 133.32, 133.68, 140.33, 141.10, 142.75 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3442 (s), 3051 (m), 1679 (m), 1631 (m), 1597 (m), 1567 (m), 1531 (m), 1487 (s), 1466 (m), 1438 (m), 1421 (m), 1383 (s), 1360 (m), 1331 (m), 1286 (m), 1243 (m), 1185 (s), 1070 (m), 1012 (m), 837 (m), 822 (s), 797 (s), 764 (s) cm^{-1}. Fluorescence (CH_3CN): Ex ($F\lambda_{max}$) = 385 (451.64) nm. UV/Vis (CH_3CN): λ_{max} (lg ε) = 382.2 nm (4.39), 364.0 (4.27), 307.9 (4.80), 261.4 (4.54), 242.8 (4.55), 217.1 (4.67). MS (EI, 70 eV): *m*/*z* (%) = 474 (100) $[M]^+$, 472 (100) $[M]^+$, 392 (28), 196 (44). MS (ESI): *m*/*z* (%) = 476 (30) $[M\ (^{81}Br) + H]^+$, 475 (100) $[M\ (^{81}Br)]^+$, 474 (30) $[M\ (^{79}Br) + H]^+$, 473 (100) $[M\ (^{79}Br)]^+$. The exact molecular mass $[M + H]^+$ for $C_{29}H_{17}BrN_2$ was confirmed by ESI-HRMS: calcd. 473.06479; found 473.06465.

1,4-Bis(15*H*-benzo[*h*]benzo[6,7]indolo[3,2-*b*]quinolinyl)benzene (6): The reaction was carried out according to the general procedure. Starting with 1,4-bis(cyanomethyl)benzene (0.08 g, 0.50 mmol), **2** (0.38 g, 1.00 mmol) and sodium hydride (0.07 g, 3.00 mmol), **6** was isolated, after chromatography, as a yellow solid (0.34 g, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56−7.64 (m, 8 H, Ar), 7.65−7.85 (m, 10 H, Ar), 7.88 (d, ^3J = 7.8 Hz, 4 H, Ar), 7.96−8.03 (m, 4 H, Ar), 8.66 (d, ^3J = 8.6 Hz, 1 H, Ar), 9.73 (d, ^3J = 8.2 Hz, 1 H, Ar), 10.90 (br. s, 2 H, NH) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$, 100 °C): δ = 118.55, 121.63, 121.93, 123.80, 124.93, 125.66, 125.71, 126.01, 126.17, 127.16, 127.66 (CH), 130.78, 131.92, 133.95 (C) ppm. Low signal/noise ratio, due to low solubility in many organic solvents. MS (ESI): *m*/*z* (%) = 1420 (35) $[2\ M + H]^+$, 711 (100) $[M + H]^+$, 434 (40). The exact molecular mass $[M + H]^+$ for $C_{52}H_{30}N_4$ was confirmed by ESI-HRMS: calcd. 711.25432; found 711.25440. $C_{52}H_{30}N_4$ (710.84): calcd. C 87.86, H 4.25, N 7.88; found C 87.57, H 4.43, N 7.66.

Acknowledgments

We thank Mrs Rita Schroeder for experimental contributions. Financial support from the Konrad-Adenauer-Stiftung (scholarship for J. T. A.) and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] δ-Carbolines: [1a] J.-Y. Mérour, A. Mérour, *Synthesis* **1994**, 767 and references cited therein; for β-carbolines, see: [1b] J. Kobayashi, J.-F. Cheng, T. Ohta, S. Nozoe, Y. Ohizumi, T. Sasaki, *J. Org. Chem.* **1990**, *55*, 3666. [1c] T. G. Hagen, K. F. Koehler, P. W. Codding, P. Skolnick, J. M. Cook, *J. Med. Chem.* **1990**, *33*, 2343. [1d] P. Rocca, F. Marsais, A. Godard, G. Queguiner, *Tetrahedron* **1993**, *46*, 3325.

[2] K. Cimanga, T. De Bruyne, L. Pieters, M. Claeys, A. Vlietinck, *Tetrahedron Lett.* **1996**, *37*, 1703.

[3] S. C. Benson, J. E. Li, J. K. Snyder, *J. Org. Chem.* **1992**, *57*, 5285.

[4] [4a] K. N. Kilminster, M. Sainsbury, *J. Chem. Soc., Perkin Trans. 1* **1972**, 2264. [4b] Y. Oikawa, O. Yonemitsu, *J. Chem. Soc., Perkin Trans. 1* **1976**, 1479.

[5] P. Langer, J. T. Anders, K. Weisz, J. Jähnchen, *Chem. Eur. J.* **2003**, *9*, 3951.

[6] [6a] A. N. Tackie, G. L. Boye, M. H. M. Sharaf, P. L. Schiff Jr., R. C. Crouch, T. D. Spitzer, R. L. Johnson, J. Dunn, D. Minick, *J. Nat. Prod.* **1993**, *56*, 653. [6b] J. L. Pousset, M.-T. Martin, A. Jossang, B. Bodo, *Phytochemistry* **1995**, *39*, 735. [6c] S. Y. Ablordeppey, P. Fan, A. M. Clark, A. Nimrod, *Bioorg. Med. Chem.* **1999**, *7*, 343. [6d] P. Fan, S. Y. Ablordeppey, *J. Heterocycl. Chem.* **1997**, *34*, 1789. [6e] T.-L. Ho, D.-G. Jou, *Helv. Chim. Acta* **2002**, *85*, 3823.

[7] [7a] M. M. Cooper, J. M. Lovell, J. A. Joule, *Tetrahedron Lett.* **1996**, *37*, 4283. [7b] K. Cimanga, T. D. Bruyne, L. Pieters, M. Claeys, A. J. Vlietinck, *Tetrahedron Lett.* **1996**, *37*, 1703. [7c] D. Dwuma-Badu, J. S. K. Ayim, N. I. Y. Fiagbe, J. E. Knapp, D. L. Schiff Jr., D. J. Slatkin, *J. Pharm. Sci.* **1978**, *67*, 433.

[8] [8a] A. O. Oyekan, S. Y. Ablordeppey, *Med. Chem. Res.* **1996**, *6*, 602. [8b] S. Y. Ablordeppey, P. Fan, *J. Heterocycl. Chem.* **1997**, *34*, 1789. [8c] K. Cimanga, T. D. Bruyne, A. Lasure, B. V. Poel, L. Pieters, M. Claeys, D.-V. Berghe, K. Kambu, L. Tona, A. J. Vlietinck, *Planta Med.* **1996**, *62*, 22. [8d] M. Singh, M. P. Singh, S. Y. Ablordeppey, *Drug. Dev. Ind. Pharm.* **1996**, *22*, 379. [8e] K. Boakye-Yiadom, S. M. Herman Ackah, *J. Pharm. Sci.* **1979**, *68*, 1510.

[9] [9a] A. Polak, *Prog. Drug. Res.* **1997**, *49*, 219. [9b] V. S. Georgiev, *Med. Chem. Res.* **1993**, *13*, 493.

[10] S. Y. Ablordeppey, P. Fan, A. M. Clark, A. Nimrod, *Bioorg. Med. Chem.* **1999**, *7*, 343.
[11] [11a] P. Langer, J. Wuckelt, M. Döring, H. Görls, *J. Org. Chem.* **2000**, *65*, 3603. [11b] P. Langer, J. T. Anders, *Eur. J. Org. Chem.* **2001**, 3953.
[12] For a review of oxaldiimidoyl dichlorides, see: P. Langer, M. Döring, *Eur. J. Org. Chem.* **2002**, 221.
[13] For reviews of domino and sequential reactions, see: [13a] L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131. [13b] L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115.
[14] D. Lindauer, R. Beckert, M. Döring, P. Fehling, H. Görls, *J. Prakt. Chem.* **1995**, *337*, 143.

Received June 8, 2004

