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TETRAHEDRON

Reactions of 2,3'-biindolyl: Synthesis of Indolo[3,2-*a*]carbazoles

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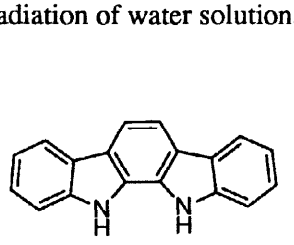
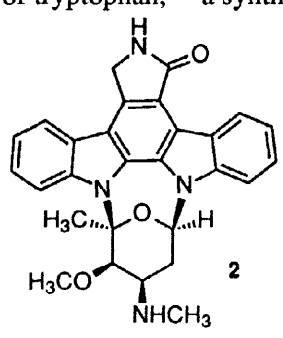
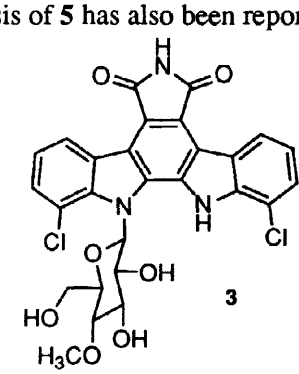
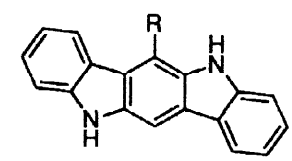
Abstract: 2,3'-biindolyl (**9**) has been transformed into indolo[3,2-*a*]carbazoles **16a-b** by means of formal [4 + 2] cycloadditions with co-formation of the Michael adducts **17a-b**. The parent indolo[3,2-*a*]carbazole (**6**) has been prepared in one step from **9** in excellent yield. Several 3-substituted 2,3'-biindolyls have also been prepared in good yields and underwent further transformations, demonstrating the versatility of 2,3'-biindolyl (**9**) as a building block for synthesis of indolo[3,2-*a*]carbazoles.

A great deal of effort has been devoted to studies of compounds containing the ring system of indolo[2,3-*a*]carbazole (**1**), including many natural products with diverse biological activities, such as staurosporine (**2**) and rebeccamycin (**3**).[1] Likewise, indolo[3,2-*b*]carbazoles have been intensely studied ever since it was discovered[2,3] that indolo[3,2-*b*]carbazole[4] (**4**) has an affinity to the aryl hydrogen (Ah) receptor approaching that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Indolo[3,2-*b*]carbazole (**4**) has also been identified[5,6] as an *in vivo* product after consumption of cruciferous vegetables. Recently, the extremely potent (4-8 times stronger than TCDD) 6-formylindolo[3,2-*b*]carbazole (**5**) has been identified as a minor product after irradiation of water solutions of tryptophan;[7,8] a synthesis of **5** has also been reported recently.[9]









In contrast to all studies aiming at indolo[2,3-*a*]carbazoles and indolo[3,2-*b*]carbazoles, the isomeric system indolo[3,2-*a*]carbazole[10,11] (**6**) has received only scant attention, which is surprising, considering the fact that the aza analogue **7** encompasses several derivatives demonstrated to be potent benzodiazepine receptor ligands.[12,13] In this work, we have focussed our interest on indolo[3,2-*a*]carbazole (**6**) and its derivatives. To our knowledge, no biological test results have yet been reported on these except for the parent

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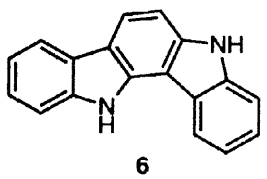
compound **6**.[14] The indolocarbazole **6** has previously been prepared in two different ways using quite laborious procedures.[10,11] Recently several fused pyrrole derivatives have been obtained in this laboratory from the reaction of indole with maleimides in acetic acid, e.g. compound **8** has been prepared according to this procedure.[15]



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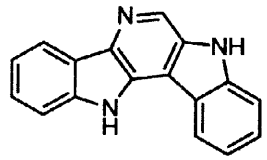

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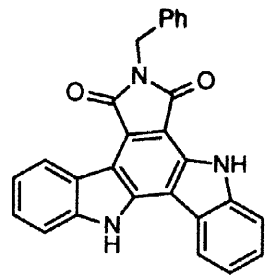

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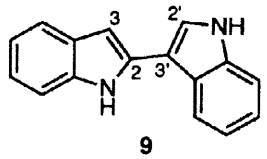
In our approach to the parent system **6**, we selected 2,3'-biindolyl[16-19] (**9**) as the precursor due to the highly useful reactivity of the 3-position, as well as the surprisingly high reactivity towards several dienophiles.



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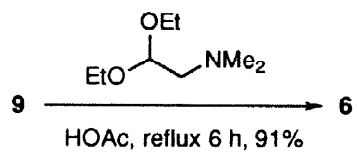
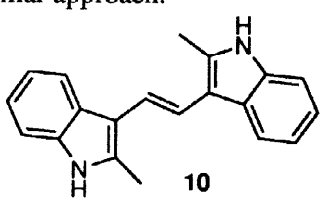
When the readily available[16-19] biindolyl **9** was reacted with dimethylaminoacetaldehyde diethyl acetal in refluxing acetic acid for 6 h, indolo[3,2-*a*]carbazole (**6**) was obtained in excellent yield. The same transformation could also be accomplished using methylaminoacetaldehyde dimethyl acetal under the same conditions, albeit in lower yield.



The indolocarbazole **6** displays UV-absorption data almost identical to those already reported (no IR or NMR data were available).[11] A reasonable mechanism involves initial attack at the protected aldehyde carbon; in the final step cyclisation takes place *via* elimination of dimethylamine. The bisindole **10** has previously been prepared from 2-methylindole using a similar approach.[20]



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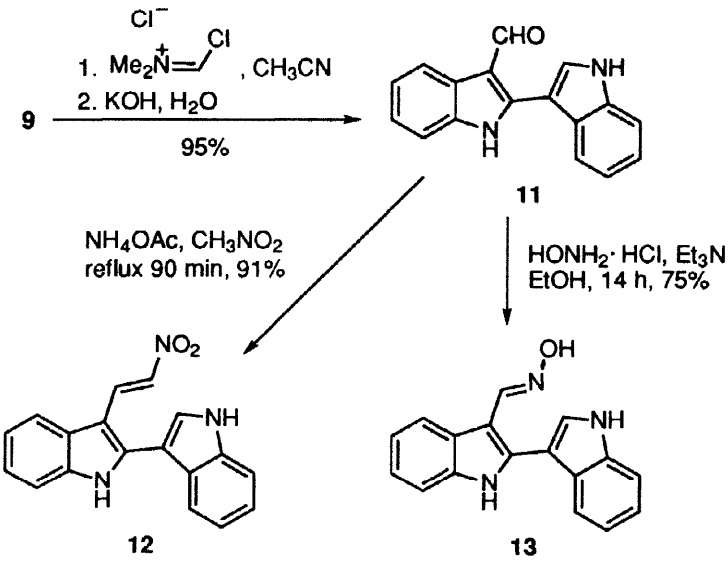
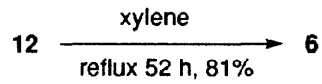
Furthermore, 2,3'-biindolyl (**9**) reacted readily with an excess of the Vilsmeier reagent in acetonitrile at room temperature to yield 2,3'-biindolyl-3-carboxaldehyde[21] (**11**), which was further transformed into the (*E*)-nitrovinyl compound **12** in excellent yield (91%) under Henry conditions. The oxime **13** was formed in the

reaction of the formyl compound **11** and hydroxylamine hydrochloride in ethanol in the presence of triethylamine (Scheme 1).

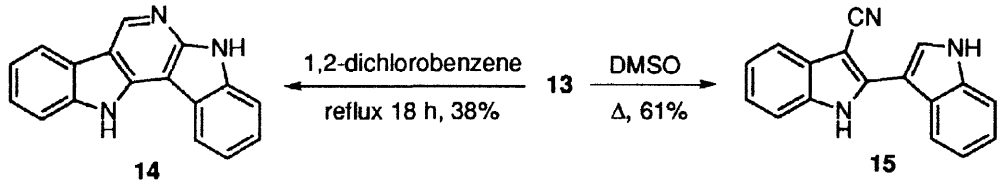


Scheme 1

Compound **12** underwent thermal cyclisation in refluxing xylene to give the indolocarbazole **6** in good yield (81%) after final elimination of the nitro group.

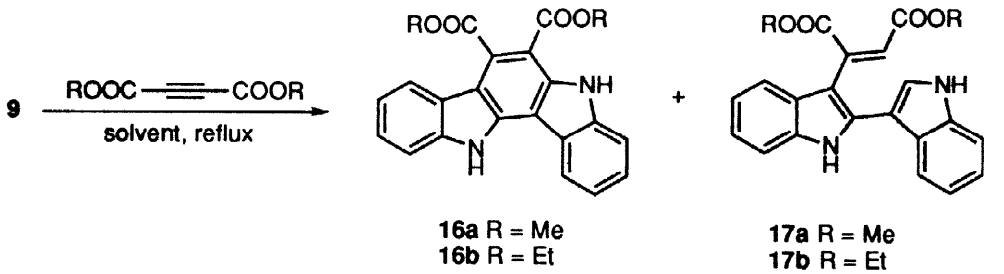


In a similar way, the oxime **13** was transformed into the novel pyridodiindole **14** on heating in 1,2-dichlorobenzene at reflux (Scheme 2). Similar reactions leading to indolo[2,3-*c*]carbazoles have previously been observed for 3,3'-biindolyl derivatives.[22] Heating **13** in DMSO at reflux for 1 h gave 3-cyano-2,3'-biindolyl (**15**) in 61% yield.



Scheme 2

An entry into substituted indolo[3,2-*a*]carbazoles *via* [4 + 2] cycloadditions was investigated by treatment of the biindolyl **9** with acetylenedicarboxylic acid derivatives in refluxing benzene, toluene or xylene. The indolocarbazoles **16a-b** and the substituted vinyl compounds **17a-b** were obtained by this procedure after separation on silica gel (Scheme 3 and Table 1).



16a R = Me
16b R = Et

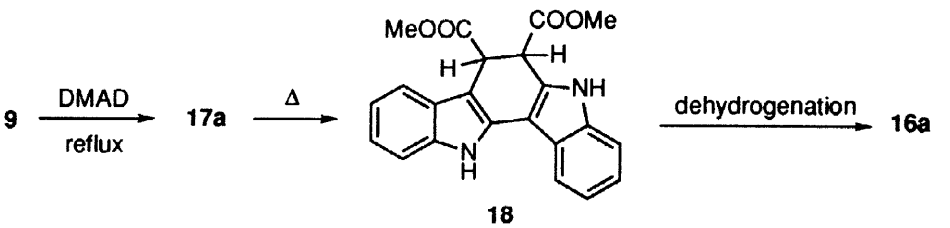
17a R = Me
17b R = Et

Scheme 3

R	Solvent	Reaction time (h)	Products & Yields
Me	benzene	20	**16a** 17%, **17a** 40%
Me	toluene	24	**16a** 21%, **17a** 40%
Me	xylene	18	**16a** 38%, **17a** 27%
Me	xylene	110	**16a** 51%, **17a** trace
Et	benzene	76	**16b** trace, **17b** 55%
Et	toluene	15	**16b** 16%, **17b** 46%
Et	xylene	48	**16b** 32%, **17b** 55%

Table 1

The cycloaddition approach towards indolocarbazoles has been investigated by several groups; indolo[2,3-*c*]carbazoles have been prepared from 3,3'-biindolyl[22], whereas the availability of 2,2'-biindolyl[23] has resulted in work aiming at indolo[2,3-*a*]carbazoles.[24-28] The formation of the indolocarbazoles **16a-b** seems to proceed *via* the Michael adducts **17a-b**, subsequent cyclization, and finally dehydrogenation as outlined in Scheme 4. This hypothesis is supported by the fact that small quantities (2.7% yield) of the expected intermediate **18** could be isolated by chromatography from the reaction of the biindolyl **9** with dimethyl acetylenedicarboxylate (DMAD) in xylene.



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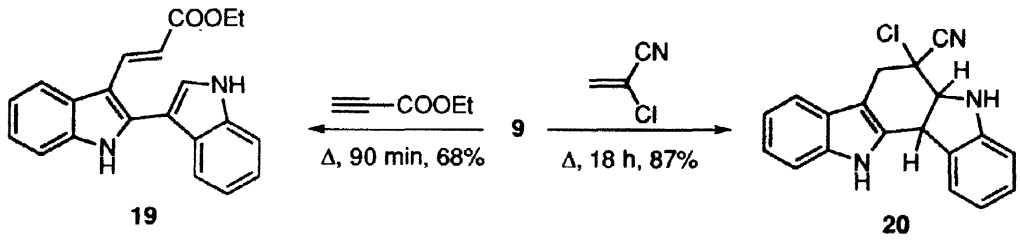
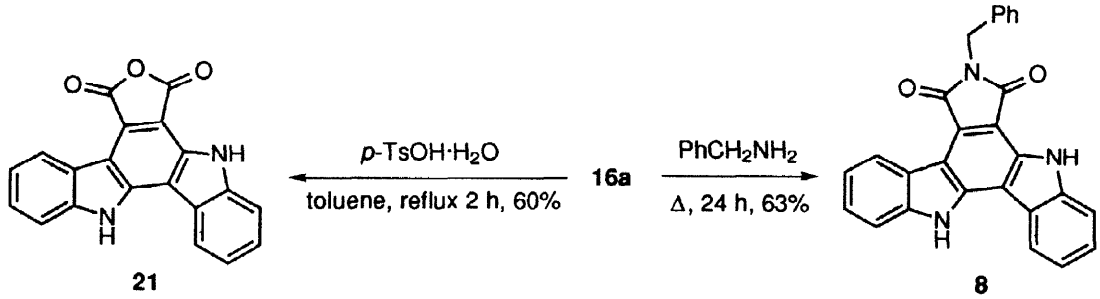
Scheme 4

A Michael addition was observed when **9** was heated in neat ethyl propiolate for 90 minutes leading to the (*E*)-vinyl compound **19** in 68% yield. 2,3'-Biindolyl (**9**) was also reacted with an excess of 2-chloro-acrylonitrile in xylene at 140°C in a sealed tube, giving the interesting compound **20**, which displays a quaternary carbon signal at 59.0 ppm as well as four aliphatic proton signals (Scheme 5). Attempted aromatization of **20** proved to be unsuccessful, most likely due to the preferred equatorial orientation of the chlorine atom, which prevents elimination of hydrogen chloride. Basic hydrolysis of **20** could not be accomplished, all attempts gave complex mixtures according to TLC.



Scheme 5

The indolocarbazole **16a** provided further routes to other derivatives, treatment of **16a** with *p*-toluenesulfonic acid monohydrate in refluxing toluene gave the anhydride **21** in 60% yield, while heating **16a** in neat benzylamine afforded the pyrrolo derivative **8**[15] (Scheme 6).



Scheme 6

In conclusion, we have prepared several indolo[3,2-*a*]carbazoles in respectable yields from the readily available 2,3'-biindolyl (**9**) and commercial starting materials *via* formal [4 + 2] cycloadditions. This convenient approach provides an easy access to the parent ring system **6** as well as a wide variety of derivatives, and gives us an opportunity to further investigate the properties and reactions of these interesting compounds.

EXPERIMENTAL

NMR spectra were recorded on a Bruker DPX 300 (300 MHz) spectrometer or, where indicated, on a Varian Unity Plus (400 MHz) instrument. IR spectra were recorded on a Perkin Elmer 1600 FT-IR instrument. Mass analyses were performed on a Micromass Platform II spectrometer. The UV spectrum was measured using a Pharmacia Biotech Ultrospec 3000 spectrophotometer. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Melting points were taken on a Büchi Melting Point B-545 apparatus and are uncorrected. All solvents were purified by distillation or were HPLC grade. Chromatography was performed on Merck Silica Gel 60, TLC analyses were run on Merck Silica Gel 60 F_{254} plates. The Vilsmeier salt was prepared from oxalyl chloride and DMF in dichloromethane.[29]

Indolo[3,2-*a*]carbazole (6). A mixture of 2,3'-biindolyl (**9**) (232 mg, 1.0 mmol) and dimethylaminoacetaldehyde diethyl acetal (0.2 ml, 1.1 mmol) in acetic acid (10 ml) was heated at reflux for 6 h. The mixture was allowed to cool and the solvent was evaporated. Column chromatography (40% ethyl acetate in hexane)

gave **6** as a white solid, yield 233 mg (91%). Mp. 295°C (lit.[10,11] 299-300, 298°C). IR (KBr): 3433, 3371, 1638, 1610, 1455, 1425, 1379, 1326, 1280, 1232, 779, 754, 746, 732 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.73 (s, 1H), 11.53 (s, 1H), 8.67 (d, *J*=7.7 Hz, 1H), 8.14-8.09 (m, 2H), 7.64 (d, *J*=7.9 Hz, 1H), 7.58 (d, *J*=8.0 Hz, 1H), 7.44-7.27 (m, 4H), 7.22 (t, *J*=7.5 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6) δ 139.3 (s), 139.2 (s), 138.7 (s), 133.8 (s), 124.1 (d), 123.6 (s), 123.3 (d), 121.3 (s), 121.2 (d), 118.9 (d), 118.8 (d), 118.6 (d), 118.3 (d), 114.4 (s), 111.0 (d), 110.7 (d), 106.5 (s), 103.5 (d) ppm. UV (EtOH) λ_{max} 291, 319, 339, 354 nm. MS (EI, 50 eV) *m/z* (%) 257 (M^++1, 19), 256 (M^+, 100), 255 (34), 128 (43).

2,3'-Biindolyl-3-carboxaldehyde (11). An excess (5 g) of freshly prepared Vilsmeier reagent was added in one portion to a solution of 2,3'-biindolyl (**9**) (2.0 g, 8.6 mmol) in acetonitrile (50 ml) at r.t. producing a cloudy yellow precipitate. The resulting mixture was stirred at r.t. for 90 min, aq. KOH (50 ml, 10%) was thereafter added cautiously and stirring was continued for 5 min. The sparingly soluble yellow product **11** was collected by filtration, washed with water and dried. Yield 2.12 g (95%). Mp. 202°C (lit.[21] 201-202°C). IR (KBr): 3406 (br), 3044 (w, br), 2814 (br), 1617, 1434, 1363, 1235, 1165, 925, 830, 756 cm^{-1}.

(*E*)-3-(2-Nitroethenyl)-2,3'-biindolyl (12). 2,3'-Biindolyl-3-carboxaldehyde (**11**) (780 mg, 3.0 mmol) was refluxed with ammonium acetate (510 mg, 6.6 mmol) in nitromethane (25 ml) for 90 min. Evaporation of the solvent and column chromatography (50% ethyl acetate in hexane) gave **12** as deep red crystals. Yield 835 mg (91%). Mp. 249°C. IR (KBr): 3408, 1600, 1573, 1435, 1298, 1273, 1258, 1222, 736 cm^{-1}; ^1H NMR (DMSO-d_6) δ 12.39 (s, 1H), 11.97 (s, 1H), 8.40 (d, *J*=13.2 Hz, 1H), 8.03 (d, *J*=13.2 Hz, 1H), 7.97-7.95 (m, 1H), 7.89 (s, 1H), 7.77 (d, *J*=7.8 Hz, 1H), 7.59 (d, *J*=8.0 Hz, 1H), 7.55-7.53 (m, 1H), 7.33-7.18 (m, 4H) ppm; ^{13}C NMR (DMSO-d_6) δ 144.6 (s), 137.6 (s), 136.5 (s), 134.9 (d), 129.9 (d), 128.2 (d), 125.4 (s), 125.4 (s), 123.4 (d), 122.6 (d), 122.1 (d), 120.6 (d), 120.5 (d), 119.3 (d), 112.3 (d), 112.3 (d), 105.0 (s), 104.8 (s) ppm. Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.28; H, 4.32; N, 13.85. Found: C, 70.99; H, 4.37; N, 13.78.

2,3'-Biindolyl-3-carboxaldehyde oxime (13). 2,3'-Biindolyl-3-carboxaldehyde (**11**) (1.30 g, 5.0 mmol) was suspended in ethanol (20 ml) containing triethylamine (1.0 ml). Hydroxylamine hydrochloride (386 mg, 5.55 mmol) was added in one portion producing a clear solution after approximately 5 min. The mixture was stirred for 14 h at r.t. and the solvent was thereafter evaporated. The residue was partitioned between ethyl acetate and aq. sat. $NaHCO_3$, the organic phase was washed with brine and dried over magnesium sulfate. Evaporation of the solvent gave a tan oil, which afforded a white precipitate on trituration with water containing a small amount of ethanol. The oxime **13** was collected by filtration, washed with water and dried. Yield 1.03 g (75%), white powder. Mp. 203°C. IR (KBr): 3534, 3379, 3291, 1631, 1584, 1574, 1430, 1318, 1243, 940, 896, 827, 753, 740 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.66 (s, 1H), 11.51 (s, 1H), 10.50 (s, 1H), 8.29 (s, 1H), 8.08 (d, *J*=7.5 Hz, 1H), 7.70 (m, 2H), 7.54 (d, *J*=7.9 Hz, 1H), 7.44 (d, *J*=7.7 Hz, 1H), 7.26-7.10 (m, 4H) ppm; ^{13}C NMR (DMSO-d_6) δ 145.1 (d), 136.6 (s), 136.3 (s), 135.8 (s), 126.1 (d), 125.8 (s), 125.7 (s), 122.0 (d), 121.9 (d), 121.3 (d), 120.1 (d), 119.9 (d), 119.4 (d), 112.1 (d), 111.2 (d), 106.1 (s), 105.1 (s) ppm.

Transformation of (*E*)-3-(2-nitroethenyl)-2,3'-biindolyl (12) into indolo[3,2-*a*]carbazole (6). Compound **12** (200 mg, 0.66 mmol) was heated at reflux in xylene (10 ml) for 52 h. Evaporation of the solvent gave a red-brown crude product, which was purified by column chromatography (40% ethyl acetate in hexane) to give indolo[3,2-*a*]carbazole (**6**) (137 mg, 81%). This material was identical in all respects to that prepared from 2,3'-biindolyl (**9**) and dimethylaminoacetaldehyde diethyl acetal in refluxing acetic acid.

***5H,8H*-Pyrido[2,3-*b*:4,5-*b*']diindole (14).** Compound **13** (250 mg, 0.91 mmol) was suspended in 1,2-dichlorobenzene (5 ml) and the mixture was heated at reflux for 18 h. A precipitate was formed after cooling. Filtration and subsequent washing with diethyl ether gave a grey solid, which afforded **14** (88 mg, 38%) as light grey needles after column chromatography (ethyl acetate). Mp.>400°C. IR (KBr): 3419, 3042 (w), 2974 (w), 2909 (w), 2828 (w), 2752 (w), 1649, 1615, 1468, 1375, 1252, 1229, 750, 732 cm^{-1}; ^1H NMR (DMSO-d_6) δ 12.19 (s, 1H), 11.91 (s, 1H), 9.21 (s, 1H), 8.60 (d, *J*=7.7 Hz, 1H), 8.23 (d, *J*=7.7 Hz, 1H), 7.66 (d, *J*=8.0 Hz, 1H), 7.57 (d, *J*=8.0 Hz, 1H), 7.47-7.41 (m, 2H), 7.35-7.25 (m, 2H) ppm; ^{13}C NMR (DMSO-d_6) δ 150.4 (s), 139.9 (d), 139.4 (s), 138.7 (s), 137.2 (s), 124.8 (d), 124.7 (d), 122.3 (s), 121.7 (d), 120.2 (d), 119.6 (s), 119.4 (d), 119.2 (d), 113.3 (s), 111.3 (d), 111.0 (d), 98.3 (s) ppm. Anal. Calcd for $C_{17}H_{11}N_3$: C, 79.36; H, 4.31; N, 16.33. Found: C, 79.26; H, 4.25; N, 16.28.

3-Cyano-2,3'-biindolyl (15). The oxime **13** (102 mg, 0.37 mmol) was heated in DMSO (3 ml) at reflux for 1 h. Water (20 ml) was added and a tan precipitate formed on standing overnight. The solid was collected, washed with water and dried. Yield 58 mg (61%). Mp. 245°C. IR (KBr): 3387, 3245 (br), 2209, 1573, 1457, 1438, 1318, 1243, 748 cm^{-1}; ^1H NMR (DMSO-d_6) δ 12.14 (s, 1H), 11.88 (s, 1H), 8.03-7.99 (m, 2H), 7.61-7.53 (m, 3H), 7.30-7.20 (m, 4H) ppm; ^{13}C NMR (DMSO-d_6) δ 142.4 (s), 136.4 (s), 135.5 (s), 128.2 (s), 126.8 (d), 124.3 (s), 122.8 (d), 122.4 (d), 121.6 (d), 120.3 (d), 119.8 (d), 117.7 (s), 117.6 (d), 112.3 (d), 112.3 (d), 105.1 (s), 80.0 (s) ppm. MS (EI, 70 eV) *m/z* (%) 258 (M^++1, 21), 257 (M^+, 100), 256 (29), 128 (23), 115 (16). Anal. Calcd for $C_{17}H_{11}N_3$: C, 79.36; H, 4.31; N, 16.33. Found: C, 79.19; H, 4.38; N, 16.41.

General procedure for synthesis of compounds 16a and 17a. A mixture of 2,3'-biindolyl (**9**) (232 mg, 1.0 mmol) and dimethyl acetylenedicarboxylate (0.13 ml, 1.06 mmol) in benzene, toluene or xylene (6 ml) was heated at reflux (for reaction times and yields: see Scheme 3). Evaporation of the solvent gave a product mixture which was subjected to chromatography (40% ethyl acetate in hexane) yielding compounds **16a** and **17a** (eluted in that order). Spectral data for compound **16a** (beige glass); IR (KBr): 3400 (br), 2948 (w), 1712 (br), 1692, 1613, 1479, 1456, 1327, 1293 (br), 1169, 731 cm^{-1}; ^1H NMR (DMSO-d_6) δ 12.27 (s, 1H), 11.59 (s, 1H), 8.67 (d, *J*=7.8 Hz, 1H), 7.87 (d, *J*=8.1 Hz, 1H), 7.80 (d, *J*=7.8 Hz, 1H), 7.75 (d, *J*=8.0 Hz, 1H), 7.55-7.45 (m, 2H), 7.39 (t, *J*=7.7 Hz, 1H), 7.28 (t, *J*=7.9 Hz, 1H), 4.10 (s, 3H), 4.04 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6) δ 169.5 (s), 166.0 (s), 140.5 (s), 139.5 (s), 137.3 (s), 136.8 (s), 128.2 (s), 125.4 (d), 125.4 (d), 121.4 (s), 121.3 (d), 120.4 (d), 120.2 (s), 119.8 (d), 119.7 (d), 112.1 (d), 111.8 (d), 111.7 (s), 107.0 (s), 101.7 (s), 52.7 (q), 52.2 (q) ppm. MS (EI, 50 eV) *m/z* (%) 373 (M^++1, 18), 372 (M^+, 68), 341 (15), 340 (24), 282 (34), 255 (33), 254 (100), 253 (46), 170 (31), 127 (49). Anal. Calcd for $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.33; N, 7.52. Found: C, 71.15;

H, 4.41; N, 7.49. Spectral data for compound **17a** (orange solid, mp. 136°C); IR (KBr): 3382 (br), 2949 (w), 1713, 1619, 1458, 1433, 1253, 745 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 11.55 (s, 1H), 11.46 (s, 1H), 7.67 (d, *J*=7.6 Hz, 1H), 7.46-7.42 (m, 2H), 7.38 (d, *J*=1.2 Hz, 1H), 7.19-7.17 (m, 1H), 7.15-7.07 (m, 3H), 7.03-7.00 (m, 1H), 6.70 (d, *J*=1.2 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 400 MHz) δ 168.0 (s), 165.5 (s), 138.9 (s), 136.2 (s), 136.1 (s), 134.7 (s), 127.6 (s), 125.7 (d), 125.5 (d), 125.2 (s), 121.9 (d), 120.8 (d), 119.7 (d), 119.5 (d), 119.5 (d), 118.1 (d), 111.8 (d), 111.4 (d), 107.3 (s), 105.7 (s), 52.2 (q), 51.3 (q) ppm. MS (EI, 50 eV) *m/z* (%) 374 (M^+, 28), 341 (8), 315 (20), 314 (33), 284 (23), 283 (100), 257 (18), 256 (86), 254 (29), 228 (20), 227 (16), 128 (14), 114 (15). Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.66; H, 4.87; N, 7.58.

General procedure for synthesis of compounds 16b and 17b. A mixture of 2,3'-biindolyl (**9**) (232 mg, 1.0 mmol) and diethyl acetylenedicarboxylate (0.19 ml, 1.19 mmol) in benzene, toluene or xylene (6 ml) was heated at reflux (for reaction times and yields: see Scheme 3). Evaporation of the solvent gave a product mixture which was subjected to chromatography (40% ethyl acetate in hexane) yielding compounds **16b** and **17b** (eluted in that order). Spectral data for compound **16b** (beige glass); IR (KBr): 3466, 3408, 2983 (w), 1706 (br), 1687, 1636, 1614, 1566, 1370, 1325, 1332 (br), 1240, 1176, 1024, 744, 729 cm^{-1}; ^1H NMR (DMSO-d_6) δ 12.23 (s, 1H), 11.56 (s, 1H), 8.72 (d, *J*=7.8 Hz, 1H), 7.86 (d, *J*=8.1 Hz, 1H), 7.80 (d, *J*=7.8 Hz, 1H), 7.71 (d, *J*=8.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.40 (t, *J*=7.3 Hz, 1H), 7.28 (t, *J*=7.3 Hz, 1H), 4.56 (q, *J*=7.1 Hz, 2H), 4.49 (q, *J*=7.1 Hz, 2H), 1.42 (t, *J*=7.1 Hz, 3H), 1.40 (t, *J*=7.1 Hz, 3H) ppm; ^{13}C NMR (DMSO-d_6) δ 168.8 (s), 165.6 (s), 140.5 (s), 139.5 (s), 137.6 (s), 136.7 (s), 128.0 (s), 125.3 (d), 125.3 (d), 121.5 (s), 121.2 (d), 120.3 (d), 120.1 (s), 119.7 (d), 119.7 (d), 112.2 (d), 111.7 (d), 111.6 (s), 106.9 (s), 101.8 (s), 61.5 (t), 60.9 (t), 14.3 (q), 13.9 (q) ppm. MS (EI, 50 eV) *m/z* (%) 401 (M^++1, 22), 400 (M^+, 77), 327 (26), 326 (92), 255 (44), 254 (100), 253 (41), 127 (16). Anal. Calcd for $C_{24}H_{20}N_2O_4$: C, 71.99; H, 5.03; N, 7.00. Found: C, 71.85; H, 5.05; N, 7.10. Spectral data for compound **17b** (orange crystals, mp. 202-204°C); IR (KBr): 3335 (br), 3057 (w), 2976 (w), 1710, 1692, 1619, 1585, 1461, 1257, 1200, 1028, 742 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.50 (s, 1H), 11.44 (d, *J*=1.5 Hz, 1H), 7.73 (d, *J*=7.8 Hz, 1H), 7.46-7.42 (m, 2H), 7.37 (d, *J*=2.6 Hz, 1H), 7.19-7.00 (m, 5H), 6.70 (s, 1H), 3.86 (q, *J*=7.1 Hz, 2H), 3.74 (q, *J*=7.1 Hz, 2H), 0.90 (t, *J*=7.1 Hz, 3H), 0.65 (t, *J*=7.1 Hz, 3H) ppm; ^{13}C NMR (DMSO-d_6) δ 167.3 (s), 165.2 (s), 139.1 (s), 136.2 (s), 136.1 (s), 134.5 (s), 127.7 (s), 125.9 (d), 125.5 (d), 125.2 (s), 121.8 (d), 120.7 (d), 119.8 (d), 119.4 (d), 119.2 (d), 118.3 (d), 111.7 (d), 111.3 (d), 107.6 (s), 105.7 (s), 60.8 (t), 59.9 (t), 13.6 (q), 13.1 (q) ppm. MS (EI, 50 eV) *m/z* (%) 403 (M^++1, 9), 402 (M^+, 33), 328 (29), 283 (71), 257 (33), 256 (100), 255 (28), 228 (20). Anal. Calcd for $C_{24}H_{22}N_2O_4$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.51; H, 5.68; N, 6.89.

Ethyl-(*E*)-3-(2,3'-biindol-3-yl)propenoate (19). 2,3'-Biindolyl (**9**) (114 mg, 0.49 mmol) was heated at reflux in neat ethyl propiolate (2 ml) for 90 min. After evaporation of the solvent and chromatography (40% ethyl acetate in hexane), **19** (110 mg, 68%) was obtained as a tan solid. Mp. 196°C (dec.). IR (KBr): 3380, 3272, 2979 (w), 1614, 1459, 1262, 1232, 1188, 741 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.85 (s, 1H), 11.76 (s, 1H), 7.97 (d, *J*=15.9 Hz, 1H), 7.89 (d, *J*=7.1 Hz, 1H), 7.70-7.67 (m, 2H), 7.57-7.47 (m, 2H), 7.24-7.13 (m, 4H),

6.38 (d, J=15.9 Hz, 1H), 4.12 (q, J=7.1 Hz, 2H), 1.20 (t, J=7.1 Hz, 3H) ppm; ^{13}C NMR (DMSO-d_6) δ 167.6 (s), 139.7 (s), 139.3 (d), 137.1 (s), 136.3 (s), 126.9 (d), 126.0 (s), 125.7 (s), 122.3 (d), 122.2 (d), 121.1 (d), 120.1 (d), 119.8 (d), 119.4 (d), 112.1 (d), 111.8 (d), 110.0 (d), 107.7 (s), 105.8 (s), 59.2 (t), 14.3 (q) ppm. MS (EI, 50 eV) *m/z* (%) 330 (M^+, 29), 285 (11), 258 (20), 257 (100), 256 (74), 255 (33), 128 (36). Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.46; H, 5.55; N, 8.51.

Compound 20. 2,3'-Biindolyl (**9**) (232 mg, 1.0 mmol) and an excess of 2-chloroacrylonitrile (0.2 ml) was heated at 140°C in xylene (4 ml) for 18 h in a sealed tube. After evaporation of the solvent, compound **20** was purified by column chromatography (40% ethyl acetate in hexane), yield 279 mg (87%) as a white solid. Mp. 222-223°C. IR (KBr): 3388, 2221 (w), 1603, 1480, 1461, 1321, 1235, 752 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.25 (s, 1H), 7.57 (d, J=7.2 Hz, 1H), 7.46 (d, J=7.6 Hz, 1H), 7.35 (d, J=8.0 Hz, 1H), 7.10-6.96 (m, 3H), 6.70-6.65 (m, 2H), 4.80 (d, J=8.5 Hz, 1H), 4.72-4.69 (distorted d, 1H), 3.72 (d, J=15.8 Hz, 1H), 3.50 (d, J=15.8 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6) δ 149.9 (s), 136.6 (s), 132.3 (s), 128.4 (s), 128.1 (d), 125.9 (s), 124.5 (d), 121.3 (d), 119.0 (s), 118.9 (d), 118.4 (d), 117.8 (d), 111.2 (d), 109.9 (d), 102.2 (s), 66.2 (d), 59.0 (s), 39.9 (d), 32.0 (t) ppm. Anal. Calcd for $C_{19}H_{14}N_3Cl$: C, 71.36; H, 4.41; N, 13.14. Found: C, 71.38; H, 4.49; N, 12.97.

Anhydride 21. The indolocarbazole **16a** (220 mg, 0.59 mmol) was heated at reflux with *p*-toluenesulfonic acid monohydrate (100 mg, 0.53 mmol) in toluene (10 ml) for 2 h. After evaporation of the solvent and column chromatography (50% ethyl acetate in hexane), compound **21** (115 mg, 60%) was obtained as an orange solid. Mp.>400°C. IR (KBr): 3391 (br), 1806, 1743, 1616, 1464, 1373, 1273, 1163, 886, 745, 724 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 12.54 (br s, 2H), 8.81 (d, J=7.9 Hz, 1H), 8.77 (d, J=7.8 Hz, 1H), 7.79-7.75 (m, 2H), 7.63-7.54 (m, 2H), 7.45 (t, J=7.2 Hz, 1H), 7.38 (t, J=7.3 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6) δ 170.4 (s), 164.8 (s), 163.7 (s), 141.3 (s), 141.2 (s), 139.1 (s), 132.9 (s), 127.1 (d), 127.1 (d), 123.1 (d), 122.3 (s), 122.2 (d), 121.0 (d), 120.7 (d), 119.9 (s), 112.7 (s), 112.5 (d), 112.0 (d), 111.9 (s), 105.7 (s) ppm. MS (EI, 70 eV) *m/z* (%) 327 (M^++1, 21), 326 (M^+, 91), 282 (16), 255 (22), 254 (100), 253 (34), 163 (17), 127 (64), 113 (18).

7-Benzyl-5*H*,13*H*-indolo[3,2-*a*]pyrrolo[3,4-*c*]carbazole-6,8-dione (8). The indolocarbazole **16a** (70 mg, 0.19 mmol) was heated in neat benzylamine (3 ml) at 170-210°C for 24 h. After cooling, the mixture was poured into aq. HCl (30 ml, 2 M) and was thereafter extracted with ethyl acetate (30 ml). The organic phase was washed with aq. HCl (2 M), followed by brine. Drying over magnesium sulfate, evaporation of the solvent and column chromatography (50% ethyl acetate in hexane) gave **8** (50 mg, 63%) as a yellow solid. Mp. 322°C. IR (KBr): 3367 (br), 1745, 1683, 1458, 1383, 1328, 1253, 749, 726 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 12.31 (s, 1H), 12.19 (s, 1H), 8.95 (d, J=7.8 Hz, 1H), 8.77 (d, J=7.8 Hz, 1H), 7.77-7.71 (m, 2H), 7.57-7.50 (m, 2H), 7.43-7.27 (m, 7H), 4.90 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6) δ 169.2 (s), 168.4 (s), 141.2 (s), 141.1 (s), 138.3 (s), 137.4 (s), 132.6 (s), 128.5 (d), 127.4 (d), 127.3 (d), 126.5 (d), 126.3 (d), 123.6 (d), 123.3 (s), 121.8 (d), 121.0 (s), 120.4 (d), 120.1 (d), 120.1 (s), 112.2 (s), 112.2 (d), 111.6 (d), 110.9 (s), 106.0 (s), 40.6 (t) ppm. MS (EI, 70 eV) *m/z* (%) 416 (M^++1, 31), 415 (M^+, 100), 388 (16), 369 (18), 282 (12), 255 (22), 254 (35), 253 (18), 229 (17), 147 (16), 121 (16), 101 (18), 91 (52).

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