# Pyrolytic Generation and Rearrangement of *N*-Substituted 1,2-Didehydrocarbazoles

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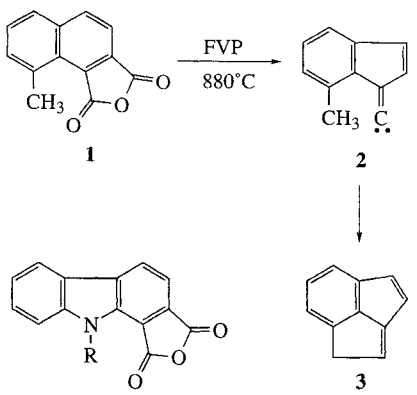
The flash vacuum pyrolysis (900–940°C) of a series of *N*-R-substituted carbazole-1,2-dicarboxylic anhydrides (R = methyl, phenyl, *o*-tolyl, benzyl, and ethyl) leads to 1,2-didehydrocarbazoles which undergo ring expansion, cyclisation, and other reactions but which appear not to undergo ring contraction to exocyclic carbenes. Thus the *N*-methyl compound **4** gives phenanthridine in 27% yield, the *N*-phenyl compound **5** undergoes C-2′–C-1 cyclisation to indolo[3,2,1-*jk*]carbazole **27**, and the *N*-*o*-tolyl compound **6** gives both C-6′–C-1 cyclisation and 2′-$CH_3$–C-1 cyclisation. The *N*-benzyl compound **7** mainly suffers loss of the benzyl group, but a minor product, benzo[*a*]carbazole **33**, is probably formed by an intramolecular cycloaddition. The *N*-ethyl compound **8** forms mainly carbazole and phenanthridine and in addition the minor C-2′–C-1 cyclisation products pyrrolo[3,2,1-*jk*]carbazole **44** and its 4,5-dihydro derivative **45**. The formation of phenanthridine from the *N*-methyl anhydride **4** has been investigated by labelling of **4** with $^{13}C$ at C-9a.

Flash vacuum pyrolysis (FVP) of 8-methylnaphthalene-1,2-dicarboxylic anhydride **1** leads to ring contraction of the intermediate aryne to a carbene **2** which by insertion into the methyl group forms cyclopent[*cd*]indene **3**[1]. Similar sequences have been observed in a number of cases[2]. It appeared possible that the *N*-methyl group in the carbazole **4** might also be an effective trap for an exocyclic carbene. We have now examined the behaviour of the five *N*-substituted carbazole anhydrides **4**–**8** on FVP at 900–940°C, and found strikingly different behaviour which appears not to involve exocyclic carbenes.




**4** R = $CH_3$
**5** R = $C_6H_5$
**6** R = *o*-$C_6H_4CH_3$
**7** R = $CH_2C_6H_5$
**8** R = $CH_2CH_3$

## Synthesis of *N*-Substituted Carbazole-1,2-dicarboxylic Anhydrides[*]

The anhydrides **4**–**8** were synthesised by standard methods[3] involving alkylation of indole-3-carboxaldehyde **9**[4] or Ullmann arylation[5] to give *N*-substituted aldehydes **9a**–**e**. Wittig reactions then afforded the vinylindoles **10a**–**e** which were immediately treated with dimethyl acetylenedicarboxylate **11**. In most cases the aromatic diesters **12a**–**e** rather than the expected dihydrocompounds were obtained directly after the reaction mixture had stood in air. Alkaline hydrolysis of the diesters **12a**–**e** generally gave the dicarboxylic acids, which were cyclised with acetic anhydride. However, the diester **12c** (R = *o*-tolyl) was very difficult to hydrolyse. The reaction stopped at the salt of monoacid **13**, but this monoacid lost methanol at 160–170°C to give the required anhydride **6**.

## Flash Vacuum Pyrolysis of *N*-Methyl Anhydride 4

The *N*-methyl anhydride **4** proved difficult to sublime and it was pyrolysed by dropping it from an internal spoon into the hot zone at 900°C/0.02 Torr; the later $^{13}C$-labelled sample **4a** sublimed satisfactorily. The brown pyrolysate (66% as $C_{13}H_9N$) was a complex mixture which contained phenanthridine **15** (27% yield by NMR) with small

[*] In this discussion anhydrides such as **4** are named as carbazoles in order to keep the same numbering as the precursor **12a** and the dehydro intermediate **14**. In the Experimental Section, however, **4** and related compounds are systematically named as furo[3,4-*a*]carbazole-1,3-diones, with consequent change of numbering.

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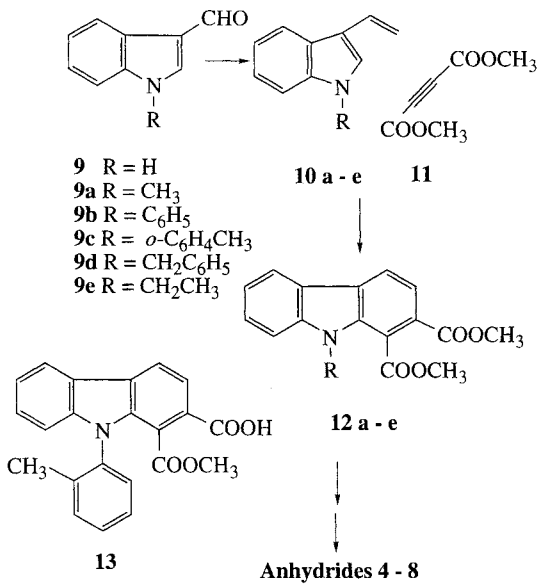
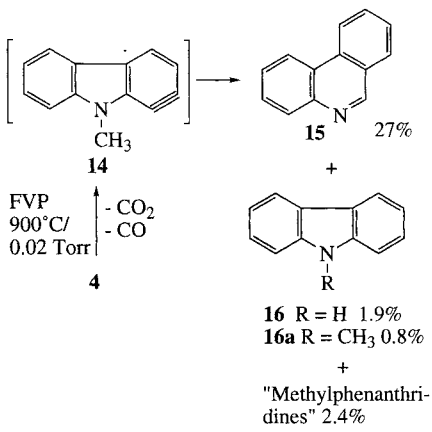
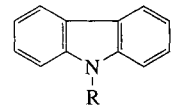



amounts of carbazole **16** and *N*-methylcarbazole **16a** and also of a fraction which we describe as "methylphenanthridines", of uncertain structure. None of these products was reminiscent of our standard aryne/exocyclic carbene/insertion sequence, and we have concentrated on the mechanism of phenanthridine formation, which clearly does not involve initial ring contraction of the aryne **14**.




The formation of phenanthridine from **14** requires transfer of 2H from the *N*-methyl group to the aryne ring, so that an N−$CH_2^{\bullet}$ or N−CH: intermediate could be involved. Two experiments bearing on this point are shown below. Pyrolysis of the *N*-benzoyloxymethylcarbazole **16b** at 600°C/0.02 Torr gave benzoic acid (95% by NMR), phenanthridine (7%), and carbazole (38%). If this is correctly regarded as α-elimination[6] of benzoic acid, then a carbene N−CH: is a possible intermediate in the pyrolysis of *N*-methyl anhydride **4**. The radical alternative was tested by pyrolysis of *N*-(4-chlorophenoxy)methylcarbazole **16c** at 710°C/0.02 Torr; the 4-chlorophenoxy radical has been established through the work of McNab[7] as an excellent pyrolytic leaving group for initiating ring expansion of five-membered heterocycles. Phenanthridine was obtained in 19% yield, accompanied by carbazole and 4-chlorophenol. This yield is poor compared to McNab's examples[7], but we still took this to mean that an N−$CH_2^{\bullet}$ centre could be involved in ring expansion of the aryne **14** to phenanthridine.



| | | % Yields | |
|---|---|---|---|
| | | Phenanthridine **15** | Carbazole **16** |
| **16b** R=$CH_2$−$O_2CC_6H_5$ | FVP 600°C | 7 | 38 |
| **16c** R=$CH_2$−O−C6H4−Cl | → | 19 | 22 |

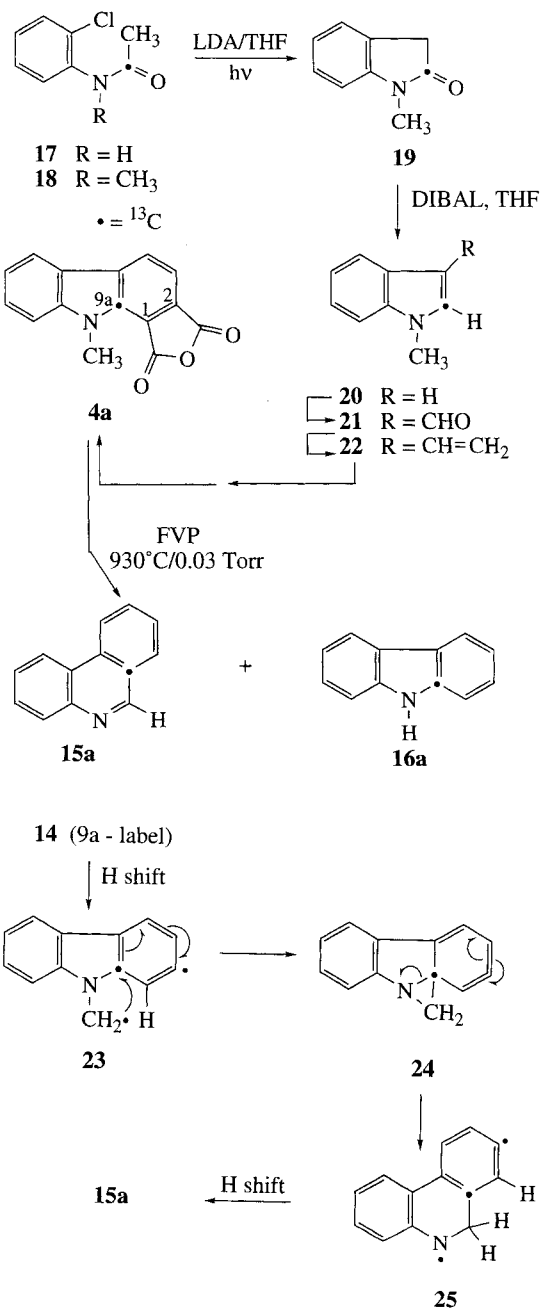
If a radical ring expansion is assumed, the direction of expansion is ambiguous. Does the methyl carbon of aryne **14** become bonded to the right-hand aryne ring as shown in **15**, to the left-hand arene ring, or randomly to either? To answer this question we made the *N*-methyl anhydride bearing $^{13}C$ at C-9a (carbazole numbering), **4a**. 2-Chloroaniline was acylated with [1-$^{13}$C]acetyl chloride and the *N*-acetyl compound **17** was *N*-methylated to give **18**. Photocyclisation of the carbanion formed from **18** with LDA/THF by the method of Goehring et al.[8] gave the 2-labelled indolinone **19** (50%), which was reduced with DIBAL to 2-labelled *N*-methylindole **20** and formylated with $POCl_3$/DMF to give the aldehyde **21** (80% crude yield over two steps). From this point the synthesis followed the unlabelled sequence, but unfortunately the Diels-Alder reaction of the crude 3-vinylindole **22** on this occasion gave the carbazole diester [9a-$^{13}$C]-**12** in only 6% yield. This sample was diluted with unlabelled diester **12** (R = $CH_3$) to give diester labelled with 20.9% $^{13}C$ at C-9a. Alkaline hydrolysis and cyclisation of the acidic product with acetic anhydride then gave the labelled anhydride **4a**.

FVP of **4a** at 930°C/0.03 Torr gave a pyrolysate from which phenanthridine and carbazole were separated. Examination of $^1H$ and $^{13}C$ spectra of these products showed that phenanthridine was labelled only at C-6a of **15a**, and the label in carbazole **16a** was retained at its original 9a position. These assignments were based mainly on coupling constants, of which the most significant were $^2J_{C\text{-}6a-6\text{-}H}$ = 9.6 Hz and $^1J_{C\text{-}6a-C\text{-}6}$ = 51.7 Hz for **15a**.

The original question has been answered: ring expansion occurs only towards the aryne ring of **14**.

We consider that this labelling result is best explained by hydrogen atom migration in the 1,2-didehydro species (9a-labelled **14**) leading to the diradical **23**. The preference for final attachment of the methylene carbon to the labelled C-9a can be rationalised through the cyclisation of **23** to give an allenic spiro-compound **24**, which can re-open in an alternative sense to give the phenanthridine skeleton as the diradical **25**. Hydrogen migration would then give the observed labelled phenanthridine **15a**.

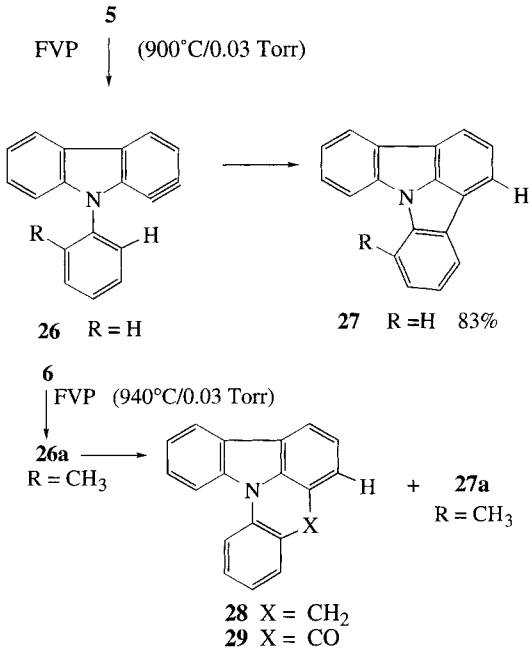
A Referee has proposed instead that the initial step in this sequence is a 1,5 shift of hydrogen to C-2, leading to the 1,4-diradical **i**. Cleavage of **i** would lead to the imine/diradical(aryne) **ii** which could then cyclise (arrows) to a



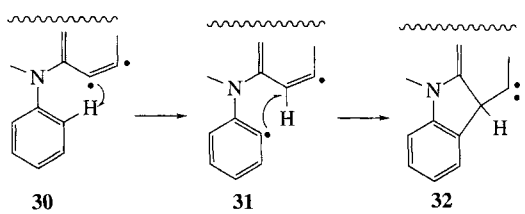

diradical, isomeric with **25**, with radical centres at $NCH_2$ and C-7. The authors are not convinced by the initial hydrogen shift.

i ii

We next examined the pyrolytic behaviour of the *N*-aryl anhydrides **5** and **6**. The *N*-phenyl anhydride **5** on FVP at 900°C/0.03 Torr gave a single product in 83% crude yield; this proved to be the highly symmetrical indolo[3,2,1-*jk*]carbazole **27** formed by overall addition of Ar–H across the formal triple bond of aryne **26**. The *N*-*o*-tolyl anhydride **6** on pyrolysis similarly added Ar–H or $ArCH_2$–H across the triple bond of **26a** to give the indolocarbazole **27a** and the indoloacridine **28** (45:55 by NMR). The indoloacridine **28** could not be isolated from the pyrolysate; radial chromatography gave only the product of autoxidation on the plate, 8*H*-indolo[3,2,1-*de*]acridin-8-one (**29**). Reduction of an authentic sample of **29**[9] with $AlCl_3/LiAlH_4$ afforded a crude sample of indoloacridine **28**, m.p. 88–90°C (ref.[10] m.p. 92.5–93.5°C), which showed the $CH_2$ signal at $\delta$ = 4.0 characteristic of the pyrolysate from **6**, but which still contained an estimated 8% of **29**.



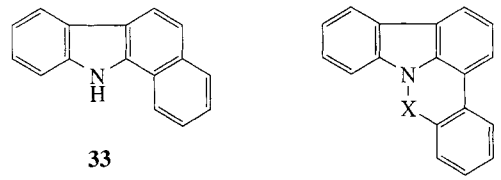

The mechanism of these cyclisations leading to systems such as **27** and **28** is uncertain. Electrophilic attack on an aryl group substantially out of the carbazole plane is possible, but would not account for attack on the methyl group in **26a**. We speculate that in such reactions the aryne behaves as a diradical **30**, and that a hydrogen atom is abstracted from the *N*-aryl ring to give a 1,6-diradical **31** which is not geometrically able to couple. Addition of the new aryl radical centre to C-1 of the 2-carbazolyl radical as in **31** would generate the carbene **32**, and the product **27** would then be formed by [1,2]H migration. In the *N*-*o*-tolyl case **26a** the ring size in the transition states for both abstraction of hydrogen from the methyl group and for addition of the resulting benzylic radical to C-1 would be larger, but the sequence still seems plausible.



**30** **31** **32**

The pyrolysis of the *N*-benzyl anhydride **7** at 910°C/0.04 Torr gave a complex mixture in which products derived from initial N···$CH_2$Ph cleavage predominated: bibenzyl, benzyl alcohol, benzaldehyde and carbazole were present in substantial amounts, although the mode of introduction of oxygen into the oxygenated products is uncertain. The minor products were more interesting and included benzo[*a*]carbazole **33** and 9*H*-indolo[3,2,1-*de*]phenanthridine (**34**). Unfortunately, the identification of the latter is tentative, and is dependent on comparison of features of the $^1$H-NMR spectrum of the pyrolysate and of its GLC-MS, with those of an impure sample of **34** made by $LiAlH_4/BF_3$ reduction of the known[11] 9*H*-indolo[3,2,1-*de*]phenanthridin-9-one (**35**).

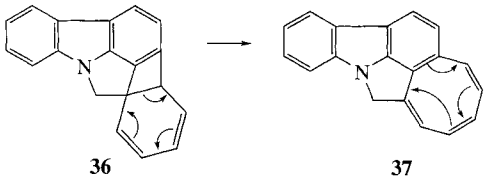
The formation of benzo[*a*]carbazole requires fusion of four carbon atoms of the benzyl group to the carbazole skeleton and loss of three carbon atoms. This can be rationalised through a sequence beginning with a [2 + 2] cycloaddition of the phenyl ring of the benzyl group to the 1,2-aryne centre of the carbazole system to give highly strained **36**. Electrocyclic ring opening to **37** and an alternative ring closure to **38** is followed by elimination of a propargyl chain, which is then lost from **39** in a radical process. This sequence (below) is highly speculative, but something like the proposed aryne/aromatic ring cycloaddition seems inescapable. The formation of the indolophenanthridine **34** seems to be analogous to the cyclizations in the *N*-aryl species derived from the anhydrides **5** and **6**.



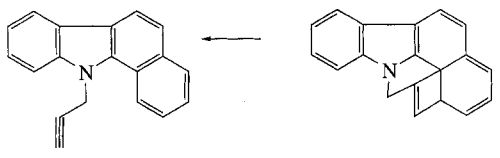
**33**



**34** X = $CH_2$
**35** X = C=O



**36** **37**



**39** **38**

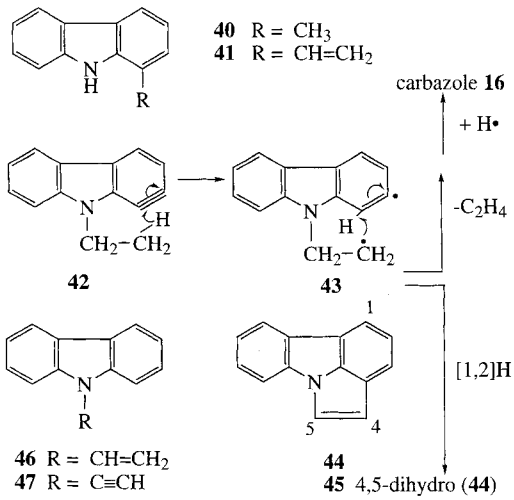
-$C_3H_3$• + H•

**33**

The pyrolysis of the *N*-ethylcarbazole anhydride **8** is considered separately from that of the *N*-methyl anhydride **4**, even through the major products of pyrolysis are similar. FVP of the *N*-ethyl anhydride at 920°C/0.04 Torr gave carbazole (40%), 1-methylcarbazole **40** (1.8%), phenanthridine **15** (7%), pyrrolo[3,2,1-*jk*]carbazole **44** (0.03%) and a trace of its 4,5-dihydro derivative **45**. The last compound was detected only by GLC-MS.

The formation of carbazole could involve direct elimination of ethene from the *N*-ethyl function, or it could also involve the aryne **42**, with elimination of ethene from the diradical **43**. Radical fission of the N−$CH_2$···$CH_3$ group could lead to phenanthridine, and migration of the $CH_3$ group to C-1 could ultimately form 1-methylcarbazole **40** with loss of the elements of $CH_2$. The minor pyrrolocarbazoles **44** and **45** may be formed by abstraction of a β-hydrogen atom from the *N*-ethyl group of **42** and cyclisation of the resulting diradical **43** leading to **45**; this is analogous to the cyclisation **31** to **32** proposed for the *N*-phenyl case. The dihydro compound **45** on FVP at 920°C/0.01 Torr gave starting material (23%), the pyrrolocarbazole **44** (10%) and 1-ethenylcarbazole **41** (24%). Dehydrogenation of **45** is thus possible on FVP, but the dominant process involves N···$CH_2$ fission. The *N*-ethenylcarbazole **46** was stable to FVP at 950°C, but at 1050°C/0.03 Torr it gave starting material, the pyrrolocarbazole **44**, and phenanthridine in the ratio 11.8:1.6:1 (by $^1$H NMR).

9-Ethynylcarbazole **47** on similar pyrolysis at 1050°C/0.04 Torr afforded the pyrrolocarbazole **44** (46%) and carbazole (33%).



**40** R = $CH_3$
**41** R = CH=$CH_2$

carbazole **16**

+ H•

-$C_2H_4$

**42** **43**

[1,2]H

**46** R = CH=$CH_2$
**47** R = C≡CH

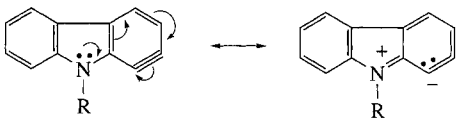
**44**
**45** 4,5-dihydro (**44**)

The study of the pyrolytic behaviour of the *N*-ethyl, *N*-ethenyl, and *N*-ethynyl species has confirmed but not significantly extended the scope of reactions involving the 1,2-didehydrocarbazole system.

## Conclusions

Considering all of the *N*-substituted didehydro systems examined, the transformations are dominated by ring expansion, dealkylation, ring closure by addition of Ar−H or $ArCH_2$−H across the formal triple bond, and, less promi-

nently, intramolecular cycloaddition reactions. Ring contraction of the aryne system to an exocyclic carbene appears to be completely suppressed in 1,2-didehydrocarbazoles, although it is the dominant process in carbocyclic arynes at high temperatures. We attribute this suppression to electron donation from nitrogen to the aryne ring, as in structures **48** and **49**, but it is difficult to be more specific about the cause of this change in reaction pathway.



**48** **49**

We thank the *Australian Research Council* for generous support of this work.

## Experimental Section

Melting points (uncorrected): Reichert hot stage m.p. apparatus. – UV: Hitachi 150–20 spectrophotometer. – IR: Perkin-Elmer 1640-FTIR spectrometer. – NMR: Bruker AC-200, AM-300, and DRX-400 spectrometers. – MS: VG Trio-1 spectrometer, coupled for GLC-MS to a Hewlett-Packard chromatograph via an S.G.E. open split interface of ratio 50:1. – GLC: Varian 3700 gas chromatograph with Hewlett-Packard 3396A integrator. – Microanalyses: National Analytical Laboratories, Blackburn, Victoria and Chemical and Micro Analytical Services, Essendon North, Victoria.

*Materials and Procedures:* Merck Kieselgel 60, Art. 9385, was used for flash chromatography. – Standard procedures, e.g. washing of extracts with dilute acid, with $NaHCO_3$ and with water, and drying with $Na_2SO_4$ are omitted from descriptions of synthetic experiments.

*Pyrolytic Apparatus:* This consisted of a horizontal silica tube (300 × 25 mm i.d.) heated with a Lindberg 55035 tube furnace. The temperature was measured with a thermocouple placed on the external wall of the tube, and pressure with a Dynavac TM 8 gauge mounted above the collecting cold finger (cooled with liquid nitrogen) at the exit end. Compounds were sublimed into the heated tube by warming with an air oven. Pyrolysis conditions are expressed in the form (tube temperature, pressure, sublimation temperature, time to complete sublimation).

*Dimethyl 9-Methylcarbazole-1,2-dicarboxylate* (**12a**): Treatment of 1-methylindole-3-carboxaldehyde[12] (1.0 g, 6.29 mmol) with an ether solution of the Wittig reagent from methyltriphenylphosphonium bromide (8.98 g, 25.2 mmol) and *n*-butyllithium (15 mmol) afforded 1-methyl-3-ethenylindole[13] (1.12 g, unpurified). Crude 1-methyl-3-ethenylindole (1.0 g) and dimethyl acetylenedicarboxylate (0.75 g, 6.36 mmol) were dissolved in ether (70 ml) and, after 2 h at room temp., the orange solution was concentrated and the residue chromatographed (silica gel, ethyl acetate/light petroleum ether, 1:4). The major fraction yielded yellow diester **12a** (0.60 g, 32%), m.p. 122.5–124°C, shrinkage, 127.5–128.5°C. – IR (mull): $\tilde{\nu}$ = 1741, 1716 $cm^{-1}$ (2 × COOMe). – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 1-COOMe), 3.95 (s, 2-COOMe), 4.08 (s, NMe), 7.28 (td, *J* = 7.4, 1.1 Hz, 6-H), 7.42 (d, *J* = 8.3 Hz, 5-H), 7.56 (td, *J* = 7.7, 1.1 Hz, 7-H), 7.90 (d, *J* = 8.3 Hz, 4-H), 8.11 (d, *J* = 8.2 Hz, 8-H), 8.15 (d, *J* = 8.3 Hz, 3-H). – $^{13}C$ NMR ($CDCl_3$/DMSO, 75.47 MHz): δ = 30.3 (NMe), 52.5, 52.8 (2 × OMe), 109.0, 118.7, 119.8, 120.3, 120.5, 120.9, 121.3, 124.4, 127.7, 128.0, 136.2, 142.8, 166.7 (CO), 169.6 (CO). – MS (70 eV); *m/z* (%): 297 (100) [$M^+$], 266 (34), 250 (48), 202 (12), 179 (82), 152 (17). – $C_{17}H_{15}NO_4$ (297.3): calcd. C 68.68, H 5.09, N 4.71; found C 68.4, H 5.0, N 4.5.

*10-Methyl-10H-furo[3,4-a]carbazole-1,3-dione* (Anhydride **4**): The dimethyl ester **12a** (0.52 g, 1.77 mmol) was heated with LiOH · $H_2O$ (0.24 g, 5.71 mmol) in water (10 ml) and DME (10 ml) for 16 h. After extraction of the cooled solution with ether, acidification to pH = 2 precipitated crude 9-methylcarbazole-1,2-dicarboxylic acid as a yellow powder (0.45 g), m.p. 190–200°C, resolidified, and 290–300°C (dec.) (anhydride). – IR (mull): $\tilde{\nu}$ = 3500–2400, 1689 $cm^{-1}$ (COOH). – This diacid (0.34 g, 1.27 mmol) was heated with acetic anhydride (10 ml) at 100°C for 4 h. The anhydride **4** was separated on cooling as yellow crystals (0.30 g, 94%), m.p. 290–300°C (dec.) (ref.[14] >290°C). – IR (mull): $\tilde{\nu}$ = 1839, 1804, 1759 $cm^{-1}$ (anhydride). – $^1H$ NMR (300 MHz, [$D_6$]DMSO): δ = 4.39 (s, NMe), 7.42 (t, *J* = 7.8 Hz, 7-H), 7.70 (t, *J* = 7.5 Hz, 8-H), 7.83 (d, *J* = 8.3 Hz, 6-H), 7.84 (d, *J* = 7.7 Hz, 5-H), 8.42 (d, *J* = 8.2 Hz, 9-H), 8.82 (d, *J* = 7.8 Hz, 4-H). – MS (70 eV); *m/z* (%): 251 (91) [$M^+$], 179 (100), 151 (17), 126 (7), 89 (14), 76 (15). – $C_{15}H_9NO_3$ (251.24): calcd. C 71.71, H 3.61, N 5.57; found C 71.4, H 3.8, N 5.5.

*Flash Vacuum Pyrolysis (FVP) of N-Methyl Anhydride* **4**: The anhydride **4** (108.5 mg, 0.432 mmol) was pyrolysed at 900°C/0.02 Torr by dropping it from an internal spoon into a vertically mounted silica tube which had the lowest third section packed with short pieces of silica tubing. A brown pyrolysate (51 mg) was collected; some anhydride **4** was lost by back-sublimation. The pyrolysate was examined by $^1H$-NMR spectroscopy and by GLC/MS (BP5, 30°C, 2 min; 30–100°C, 15°C/min; 100–220°C, 5°C/min) and the presence of the major products 9-methylcarbazole (**16a**), phenanthridine (**15**) and carbazole (**16**) was confirmed by spiking experiments with authentic samples, and from prominent features of the $^1H$-NMR spectrum [e.g. 6-H of phenanthridine at δ = 9.30 (s)]. A fourth fraction {MS: *m/z* (%): 193 (100) [$M^+$], 165 (21), 150 (2), 139 (5), 115 (2), 96 (5), 82 (7)} contained at least three isomers corresponding to methylphenanthridines; they are so described below, but there is no firm evidence as to their structure. Approximate yields were determined by GLC with a standard solution of phenanthridine (10.4 mg/25 ml of dichloromethane) for comparison: 9-methylcarbazole, $t_R$ = 12.4 min, 0.6 mg, 0.8%; phenanthridine, $t_R$ = 12.9 min, 21.3 mg, 27%; "methylphenanthridines", $t_R$ = 13.9 min, 2.0 mg, 2.4%; carbazole, $t_R$ = 16.1 min, 1.4 mg, 1.9%.

*FVP of (9-Carbazolyl)methyl Benzoate* (**16b**): The benzoate **16b**[15] (52.0 mg, 0.172 mmol) was pyrolysed through an unpacked silica tube (600°C, 0.02 Torr, 85–125°C, 3 h) to give a yellow solid (38.4 mg) which was examined by TLC, GLC (BP20, 150°C, 1 min, 150–200°C, 10°C/min), and by $^1H$ NMR. The major products (with approximate yields estimated from NMR) were benzoic acid (20 mg), phenanthridine (2 mg, 7%), and carbazole (11 mg, 38%) with traces of benzoate **16b** and unidentified products.

*9-(4-Chlorophenoxy)methylcarbazole* (**16c**): Carbazole (1.0 g, 6.0 mmol) in DMSO (10 ml) was alkylated by alternate addition of sodium hydride (80% in oil, 0.18 g, then 3 × 0.06 g, total 12.0 mmol) and 4-chloro(chloromethoxy)benzene [α,4-dichloroanisole (Aldrich), 4 × 0.38 g, 8.4 mmol] at 15-min intervals with stirring under nitrogen. After a further 2 h, water was added and the ether-soluble products isolated. Flash chromatography (silica gel, dichloromethane/light petroleum ether) and recrystallisation from ether gave colourless crystals of **16c** (0.82 g, 45%), m.p. 141–142.5°C. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 6.14 (s, $CH_2$), 6.91–6.85 (m, 2′-H, 6′-H), 7.22–7.17 (m, 3′-H, 5′-H), 7.32–7.22 (m, 3-H, 6-H), 7.45–7.43 (m, 1-H, 2-H, 7-H, 8-H), 8.06 (ddd, *J* =

7.8, 0.8, 0.8 Hz). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 72.4 ($CH_2$), 109.1 (C-1, C-8), 118.2 (C-2′, C-6′), 120.4 (C-2, C-3, C-6, C-7), 123.7 (C-4a, C-4b), 126.1 (C-4, C-5), 127.5 (C-4′), 129.5 (C-3′, C-5′), 139.9 (C-8a, C-9a), 155.5 (C-1′). – MS (70 eV); *m/z* (%): 307 (0.8) [$M^+$], 181 (14), 180 (100), 152 (19). – $C_{19}H_{14}{}^{35}ClNO$: calcd. 307.076; found 307.078 ± 0.003.

*FVP of 9-(4-Chlorophenoxy)methylcarbazole* (**16c**): Pyrolysis of **16c** (57.3 mg, 0.186 mmol) through an unpacked silica tube (710°C, 0.02 Torr, 110–130°C, 2.5 h) gave a yellow solid (26.4 mg) which was examined by TLC (silica gel, dichloromethane), GLC (BP20, 150°C, 1 min, 150–200°C, 10°C/min) and by $^1$H-NMR spectroscopy with cyclohexane (5 µl) as internal integration standard. The following components were identified by NMR and by GLC spiking experiment with authentic samples: 4-Chlorophenol ($t_R$ = 4.0 min, yield by NMR 4.8 mg, 20%); phenanthridine ($t_R$ = 8.8 min, 6.2 mg, 19%); carbazole ($t_R$ = 15.3 min, 7.0 mg, 22%). Extraction of a solution of the pyrolysate in dichloromethane with 4 M HCl, isolation of the basic fraction, and sublimation gave phenanthridine (5.7 mg, 17%), m.p. 104.5–106°C (ref.[16] 104°C).

*Synthesis of [10a-$^{13}$C]-10-Methyl-10H-furo[3,4-a]carbazole-1,3-dione* (**4a**): For the following sequence of reactions involving formation of labelled forms of known compounds only minimal spectroscopic data, sufficient to establish the site or extent of labelling, are given. Literature references are to unlabelled material.

*[1-$^{13}$C]-N-(2′-Chlorophenyl)acetamide* (**17**): Oxalyl chloride (9.17 g, 72.3 mmol) in ether (20 ml) was added dropwise to a stirred suspension of sodium [1-$^{13}$C]acetate (99 atom-%, Sigma-Aldrich; 5.0 g, 60.2 mmol) and DMF (0.1 ml) in ether (50 ml) at 0°C. The mixture was stirred for 6 h at room temp., then cooled to 0°C and 2-chloroaniline (15.36 g, 120.4 mmol) in pyridine (20 ml) and ether (40 ml) was added dropwise over 1 h. After 18 h, the mixture was poured into HCl (1 M) and the neutral fraction was isolated with dichloromethane. Concentration gave [1-$^{13}$C]-*N*-(2′-chlorophenyl)-acetamide (**17**) (9.76 g, 95%) as a yellow solid, m.p. 84–85.5°C (ref.[17] 86–88°C). – $^1$H NMR (200 MHz, $CDCl_3$): δ = 2.21 (d, $^2J_{CH}$ = 6.2 Hz, O=$^{13}$C-$CH_3$). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 24.7 (d, $^1J_{CC}$ = 49.4 Hz, O=[$^{13}$C]-$CH_3$), 134.6–121.9 (6 × Ar–C), 168.4 ($^{13}$C=O). – MS (70 eV); *m/z* (%): 170 (1.5) [$M^+$], 129 (30), 128 (17), 127 (100), 126 (36), 120 (19), 111 (11), 99 (24), 90 (27), 75 (14), 63 (11).

*[1-$^{13}$C]-N-(2′-Chlorophenyl)-N-methylacetamide* (**18**): The labelled acetamide **17** (9.76 g, 57.2 mmol) in DMSO (50 ml) was stirred under nitrogen with sodium hydride (80% in oil, 3.61 g, 120 mmol) for 16 h. Iodomethane (17.1 g) was added and stirring was continued for 10 h. Water (150 ml) was added and the crude product was extracted with dichloromethane. Kugelrohr distillation (75°C/0.2 Torr) gave the *n*-methylacetamide **18** (9.95 g, 94%) as a pale yellow oil (ref.[18], b.p. 126–132°C/6.0 Torr). – $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.80 (d, $^2J_{CH}$ = 6.1 Hz, O=$^{13}$C-$CH_3$), 3.19 (d, $^3J_{CH}$ = 2.7 Hz, N–$CH_3$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 21.8 (d, $^1J_{CC}$ = 53.3 Hz, O=[$^{13}$C]-$CH_3$), 35.4 (N–$CH_3$), 128.5–141.5 (6 × Ar–C), 169.8 ($^{13}$C=O). – MS (70 eV); *m/z* (%): 184 (1) [$M^+$], 150 (11), 149 (100), 143 (21), 142 (28), 141 (67), 140 (66), 77 (30), 75 (12).

*[2,$^{13}$C]-1-Methylindolin-2-one* (**19**): The *N*-methylacetamide **18** (2.0 g, 10.9 mmol) was photocyclised by the method of Goehring et al.[8] with LDA (32.4 mmol) in THF and irradiation at 366 nm. Flash chromatography of the crude product (silica gel, ethyl acetate/light petroleum ether, 1:19) gave the labelled indolinone **19** (0.80 g, 50%) as slightly orange crystals, m.p. 85.5–87°C (ref.[8] m.p. 86–88°C). – $^1$H NMR (200 MHz, $CDCl_3$): δ = 3.21 (d, $^3J_{CH}$ = 2.5 Hz, $NCH_3$), 3.51 (d, $^2J_{CH}$ = 5.8 Hz, 3-$CH_2$). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 26.1 ($NCH_3$), 35.7 (d, $^1J_{CC}$ = 49.2 Hz, C-3), 108.0 (d, $^3J_{CC}$ = 3.8 Hz, C-7), 122.3 (C-5), 124.2 (d, $^3J_{CC}$ = 4.9 Hz, C-4), 124.5 (C-3a), 127.9 (C-6), 145.2 (d, (d, $^2J_{CC}$ = 9.5 Hz, C-7a), 175.1 ($^{13}$[C]=O). – MS (70 eV); *m/z* (%): 148 (73) [$M^+$], 133 (10), 118 (100), 104 (11), 91 (24), 90 (12), 89 (12), 78 (21), 77 (21, 76 (11), 55 (13), 53 (16), 49 (15).

*[2-$^{13}$C]-1-Methylindole* (**20**): Diisobutylaluminium hydride (1.0 M in toluene, 31.4 ml, 31.4 mmol) was added dropwise over 30 min to a stirred solution of labelled indolinone **19** (3.10 g, 20.9 mmol) in THF (50 ml) at 0°C under nitrogen. After 3 h at room temp., ether (50 ml) was added, followed by dropwise addition of water (1.2 ml), 15% sodium hydroxide (1.2 ml), water (3.0 ml) and finally 1 M HCl (30 ml). The organic layer and a further ether extract (30 ml) were washed with water, dried, and concentrated below 30°C to give the crude 1-methylindole **20** as a brown oil. – $^1$H NMR (200 MHz, $CDCl_3$): δ = 3.78 (d, $^3J_{CH}$ = 3.3 Hz, 1-$CH_3$), 6.48 (ddd, $^2J_{CH}$ = 8.6 Hz, *J* = 3.1, 0.9 Hz, 3-H), 7.04 (dd, $^1J_{CH}$ = 181.2 Hz, *J* = 3.1 Hz, 2-H), 7.07–7.65 (m, 4 × Ar–H). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 56.0 (1-$CH_3$), 100.7 (d, $^1J_{CC}$ = 68.4 Hz, C-3), 109.0 (d, $^3J_{CC}$ = 2.7 Hz, C-7), 120.7 (d, $^4J_{CC}$ = 5.5 Hz, C-4), 128.6 ([$^{13}$C]-2), 136.3 (d, $^2J_{CC}$ = 8.2 Hz, C-7a); 119.1, 121.3, 128.4 (C-6, C-5, C-3a). MS (70 eV); *m/z* (%): 132 (100) [$M^+$], 131 (95), 117 (10), 103 (10), 90 (19), 89 (14), 78 (11), 77 (18).

*[2-$^{13}$C]-1-Methylindole-3-carboxyaldehyde* (**21**): Labelled 1-methylindole **20** (2.77 g, 20.9 mmol) was formylated with $POCl_3$/DMF according to James and Snyder[19]. The crude 3-aldehyde **21** (2.67 g, 80%) was obtained as a viscous red oil. – IR: $\tilde{\nu}$ = 1641 $cm^{-1}$ (C=O). – $^1$H NMR (200 MHz, $CDCl_3$): δ = 3.68 (d, $^3J_{CH}$ = 3.5 Hz, 1-$CH_3$), 7.50 (d, $^1J_{CH}$ = 183.2 Hz, H-2), 9.79 (d, $^3J_{CH}$ = 0.8 Hz, CHO); 7.18–7.35 (m, H-5, H-6, H-7), 8.20–8.27 (m, H-4). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 33.5 (1-$CH_3$), 110.0 (d, $^2J_{CC}$ = 2.7 Hz, C-7), 117.6 (d, $^1J_{CC}$ = 65.6 Hz, C-3), 121.8 (d, $^4J_{CC}$ = 3.7 Hz, C-6), 122.9, 123.9 (C-5, C-4), 125.2 (d, $^2J_{CC}$ = 9.4 Hz, C-3a), 137.8 (d, $^2J_{CC}$ = 6.1 Hz, C-7a), 140.0 ([$^{13}$C]-2), 184.8 (d, $^2J_{CC}$ = 9.7 Hz, CHO).

*Dimethyl [9a-$^{13}$C]-9-Methylcarbazole-1,2-dicarboxylate* ([9a-$^{13}$C]-**12a**): Crude [2-$^{13}$C]-1-methylindole-3-aldehyde **21** (2.67 g, 16.6 mmol) was treated with $Ph_3P{=}CH_2$ in ether, as described above for the unlabelled diester **12a**. The crude 3-ethenylindole thus formed (2.6 g, 16.7 mmol) and dimethyl acetylenedicarboxylate (3.56 g, 25.1 mmol) were dissolved in THF (10 ml) and left at room temp. under nitrogen for 48 h. Flash chromatography (silica gel, ethyl acetate/light petroleum ether, 1:9) of the oily product gave a fraction containing the diester **4a**; all other fractions were heated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.90 g, 8.35 mmol) in benzene (40 ml) for 18 h. A second flash chromatography of the dehydrogenated material then yielded a further quantity of diester. Recrystallisation of the combined products from ether gave the orange-yellow diester (0.31 g, 6%), m.p. 122–122.5°C (cf. **12a**, m.p. 122.5–124°C, shrinkage, then 127.5–128.5°C). – IR (mull): $\tilde{\nu}$ = 1742, 1716 $cm^{-1}$ (esters). – $^1$H NMR (200 MHz, $CDCl_3$; $^{13}$C-coupled signals only): δ = 3.82 (d, $^3J_{CH}$ = 2.8 Hz, 1-$CH_3$), 7.88 (dd, *J* = 8.3 Hz, $^4J_{CH}$ = 0.9 Hz, 3-H), 8.12 (t, *J* = 8.1 Hz, $^3J_{CH}$ = 8.1 Hz, 4-H). – $^{13}$C NMR (50 MHz, $CDCl_3$; $^{13}$C-coupled and labelled signals only): δ = 109.0 (d, $^3J_{CC}$ = 3.0 Hz, C-8), 120.9 (d, $^3J_{CC}$ = 4.1 Hz, C-5), 121.3 (d, $^2J_{CC}$ = 4.1 Hz, C-2), 124.4 (d, $^2J_{CC}$ = 1.5 Hz, C-4b), 127.9 (d, $^1J_{CC}$ = 39.6 Hz, C-4a), 136.2, [$^{13}$C]-9a, 142.8 (d, $^2J_{CC}$ = 7.1 Hz, C-8a), 166.9 (d, $^2J_{CC}$ = 5.5 Hz, 1-CO). – MS (70 eV); *m/z* (%): 298 (53) [$M^+$], 267 (30), 252 (25), 251 (37), 181 (24), 180 (100), 179 (38), 153 (34), 152 (21), 151 (12).

*[10a-$^{13}$C]-10-Methyl-10H-furo[3,4-a]carbazole-1,3-dione* (Labelled Anhydride **4a**): [9a-$^{13}$C]-Diester **12a** (0.31 g) was mixed with

unlabelled diester **12a** (1.22 g) to give diester (1.53 g, 5.12 mmol) containing 20.9% $^{13}C$ at C-10a. Hydrolysis with potassium hydroxide (0.86 g, 15.4 mmol) in ethanol (10 ml) and water (8.6 ml) at reflux for 20 h afforded the labelled dicarboxylic acid (1.19 g, 87%) as a light orange powder, m.p. 175–190°C, resolidified, and 290–300°C (dec.). This acid (1.18 g, 4.38 mmol) was heated with acetic anhydride (7.5 ml) for 20 h and the labelled anhydride **4a** which formed on cooling was washed with ether to give a bright yellow powder, m.p. 270–280°C, with sublimation. – IR (mull): $\tilde{\nu}$ = 1839, 1803, 1759 $cm^{-1}$. – MS (70 eV); *m/z* (%): 252 (32) [$^{13}C_1{}^{12}C_{14}H_9NO_3^+$], 251 (80) [$^{12}C_{15}H_9NO_3^+$], 180 (32), 179 (100), 178 (29), 152 (18), 151 (23), 150 (12), 126 (17), 89 (18), 76 (29).

*FVP of [10a-$^{13}C$]-10-Methyl-10H-furo[3,4-a]carbazole-1,3-dione* (**4a**): Labelled anhydride **4a** (266.7 mg, 1.06 mmol) was pyrolysed through an unpacked silica tube (930°C, 0.03 Torr, 160–240°C, 3.5 h). Radial chromatography (2 mm silica gel plate, ethyl acetate/light petroleum ether, 1:19) of the pyrolysate gave three minor components (not examined) and then carbazole and phenanthridine. The fractions containing phenanthridine were recrystallised from ether (charcoal) and sublimed at 95°C/0.05 Torr to give [6a-$^{13}C$]phenanthridine **15a** (73.3 mg, 39%) as colourless crystals, m.p. 104–105°C (ref.[16], m.p. 104°C). – $^1H$ NMR (200 MHz, $CDCl_3$, [6a-$^{13}C$]species only): δ = 7.59–7.83 (m, 2-H, 3-H, 8-H, 9-H), 7.95–8.00 (m, 7-H), 8.11–8.24 (m, 4-H), 8.48–8.54 (m, 1-H, 10-H), 9.25 (d, $^2J_{CH}$ = 9.6 Hz, 6-H). – $^{13}C$ NMR (75 MHz, $CDCl_3$, [6a-$^{13}C$]species only): 121.8 (d, $^2J_{CC}$ = 4.7 Hz, C-10), 122.2 (d, $^3J_{CC}$ = 3.1 Hz, C-1), 124.1 (d, $^2J_{CC}$ = 4.4 Hz, C-4b), 126.4 (s, $^{13}C$-6a), 127.1 (d, $^4J_{CC}$ = 8.5 Hz, C-2), 127.5 (d, $^2J_{CC}$ = 1.8 Hz, C-8), 128.7 (s, C-3), 128.8 (d, $^1J_{CC}$ = 57.7 Hz, C-7), 130.1 (d, $^4J_{CC}$ = 8.2 Hz, C-4), 131.0 (d, $^3J_{CC}$ = 8.5 Hz, C-9), 132.6 (d, $^1J_{CC}$ = 54.0 Hz, C-10a), 144.4 (d, $^3J_{CC}$ = 9.9 Hz, C-4a), 153.5 (d, $^1J_{CC}$ = 51.7 Hz, C-10). – MS (70 eV); *m/z* (%): 180 (35) [$^{13}C_1{}^{12}C_{12}H_9N^+$], 179 (100) [$^{12}C_{13}H_9N^+$], 178 (42), 177 (13, 153 (24), 152 (42), 151 (53), 150 (31). – Recrystallisation of the carbazole fractions from light petroleum ether gave [8a-$^{13}C$]carbazole **16a** (16.9 mg, 10%) as slightly green crystals, m.p. 240–242°C (ref.[20] 245°C). The $^1H$-NMR spectrum was similar to that of unlabelled carbazole. – $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 110.8 (s, C-1), 110.8 (d, $^1J_{CC}$ = 64.7 Hz, C-8), 118.7 (s, C-3, C-6), 120.0 (s, C-2, C-7), 122.9 (d, $^1J_{CC}$ = 64.7 Hz, C-4b), 122.9 (s, C-4a), 125.4 (s, C-4, C-5), 139.9 (s, C-8a, C-9a). – MS (70 eV); *m/z* (%): 168 (48) [$^{13}C_1{}^{12}C_{11}H_9N^+$], 167 (100) [$^{12}C_{12}H_9N^+$], 166 (35), 153 (21), 152 (26), 151 (21), 150 (12).

*3-Ethenyl-1-phenylindole* (**10b**): 1-Phenylindole-3-carboxaldehyde[5] (0.44 g, 2.0 mmol) in THF (10 ml) was treated with a solution of the Wittig reagent from methyltriphenylphosphonium bromide (1.4 g, 4.0 mmol) and *n*-butyl lithium (2.8 mmol) in ether (15 ml) at room temp. for 19 h. The ether-soluble products were absorbed on silica gel and separated by flash chromatography on silica gel (ethyl acetate/light petroleum ether, 1:5) to give 3-ethenyl-1-phenylindole **10b** (0.37 g, 85%) as a yellow oil. – IR (film): $\tilde{\nu}$ = 3053, 1630 (C=C), 1599, 1535, 1500 $cm^{-1}$. – $^1H$ NMR (200 MHz, $CDCl_3$): δ = 5.18 (dd, *J* = 11.3, 1.4 Hz, 2′-$H_A$), 5.72 (dd, *J* = 17.8, 1.4 Hz, 2′-$H_B$), 6.85 (dd, *J* = 17.8, 11.3 Hz, 1′-H), 7.09–7.83 (3 × m, 10 Ar–H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 110.7 (C-7), 111.3 (C-2′), 116.4 (C-3), 120.2 (C-4), 120.8 (C-5), 122.8 (C-6), 126.9 (C-2), 127.0 (C-3a), 128.9 (C-1′), 136.7 (C-7a); (phenyl) 124.3 (C-2″, C-6″), 126.6 (C-4″), 129.5 (C-3″, C-5″), 139.3 (C-1″). – MS (70 eV); *m/z* (%): 219 (100) [$M^+$], 218 (73), 217 (42), 216 (12), 115 (38), 108 (10). – $C_{16}H_{13}N$: calcd. C 219.105; found 219.105 ± 0.002.

*Dimethyl 9-Phenylcarbazole-1,2-dicarboxylate* (**12b**): Dimethyl acetylenedicarboxylate (1.6 g, 11 mmol) and 3-ethenyl-1-phenyl indole **10b** (1.1 g, 5.0 mmol) were dissolved in ether (10 ml) and the solution was stirred without exclusion of air for 4.5 d. A yellow solid separated and was recrystallised from ethanol to give the diester **12b** (0.78 g, 43%) as colourless crystals, m.p. 189–190°C. – IR (mull): $\tilde{\nu}$ = 1732 (1-C=O), 1715 (2-C=O) $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 3.26 (s, 1-COOMe), 3.89 (s, 2-COOMe), 7.03 (d, *J* = 8.1 Hz, 8-H), 7.28–7.60 (m, 6-H, 7-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 7.93 (d, *J* = 8.2 Hz, 4-H), 8.15 (d, *J* = 7.6 Hz, 5-H), 8.21 (d, *J* = 8.2 Hz, 3-H). – $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 52.0, 52.4 (2 × OMe); 110.4, 120.6, 120.7, 121.1, 127.8, 128.9, 129.4, 129.5 (11 × CH); 119.4, 121.4, 125.2, 128.2, 136.5, 136.8, 144.1 (7 × $C_q$); 166.8, 167.4 (2 × C=O). – MS (70 eV); *m/z* (%): 359 (100) [$M^+$], 297 (16), 296 (76), 268 (16), 241 (38), 240 (42), 239 (18). $C_{22}H_{17}NO_4$ (359.39): calcd. C 73.53, H 4.77, N 3.90; found C 73.36, H 4.77, N 3.53.

*10-Phenyl-10H-furo[3.4-a]carbazole-1,3-dione* (Anhydride **5**): Hydrolysis of the diester **12b** (0.34 g, 0.95 mmol) with potassium hydroxide (0.40 g, 7.1 mmol) in ethanediol (6 ml) under reflux for 48 h gave on work-up crude 9-phenylcarbazole-1,2-dicarboxylic acid (0.29 g, 94%) as a pale tan powder, m.p. 202°C. This acid (70 mg, 0.21 mmol) was heated with acetic anhydride (4 ml) for 24 h. Evaporation of excess acetic anhydride left a yellow solid which was recrystallised from ethyl acetate/light petroleum ether and then sublimed (160°C/1 Torr) to give the anhydride **5** (55 mg, 83%) as bright yellow crystals, m.p. 202–203°C. – IR (mull): $\tilde{\nu}$ = 1834, 1769 $cm^{-1}$ (anhydride). – $^1H$ NMR (200 MHz, $CDCl_3$): δ = 7.24 (ddd, *J* = 8.2, 1.8, 0.9 Hz, 9-H), 7.38–7.64 (m, 7-H, 8-H, and $C_6H_5$), 7.87 (d, *J* = 7.8 Hz, 5-H), 8.22 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 6-H), 8.58 (d, *J* = 7.8 Hz, 4-H). – $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 111.3, 116.1, 121.0, 122.0, 127.5, 128.5, 129.2, 129.5 (11 × CH); 121.46, 121.5, 131.5, 136.5, 137.5, 144.3 (7 × $C_q$); 160.6, 164.1 (2 × C=O). – MS (70 eV); *m/z* (%): 313 (93) [$M^+$], 269 (12), 242 (16), 241 (100), 240 (33), 239 (20), 238 (10). – $C_{20}H_{11}NO_3$ (313.32): calcd. C 76.67, H 3.54, N 4.47; found C 76.65, H 3.46, N 4.47.

*Flash Vacuum Pyrolysis of N-Phenyl Anhydride* **5**: The anhydride **5** (46 mg, 0.15 mmol) was pyrolysed through an unpacked silica tube (900°C, 0.03 Torr, 140–170°C, 2.3 h) to give a pale green pyrolysate (30 mg, 83% crude as $C_{18}H_{11}N$) which showed a single spot, plus a trace of baseline material, on TLC. Flash chromatography (silica gel, light petroleum ether) gave a pale yellow solid which was sublimed (110°C, 0.5 Torr) and recrystallised from light petroleum ether to give indolo[3,2,1-*j,k*]carbazole **27** as colourless crystals, m.p. 133.5–135.0°C (ref.[21] 136.5–138.5°C). – UV (ethanol): $\lambda_{max}$ (lg ε) = 236 nm (4.72), 266 (4.49), 270 (4.46), 283 (4.44), 290 (3.94), 307 (3.84), 318 (3.88), 361 (3.94). – $^1H$ NMR (200 MHz, $CDCl_3$): δ = 7.37 (dt, *J* = 7.6, 1.0 Hz, 3-H, 9-H), 7.57 (dt, *J* = 8.0, 1.2 Hz, 2-H, 10-H), 7.60 (t, *J* = 7.4 Hz, 6-H), 7.90–7.94 (m, 1-H, 11-H), 8.06 (d, *J* = 7.4 Hz, 5-H, 7-H), 8.13–8.18 (m, 4-H, 8-H). – $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 112.1, 119.4, 121.7, 122.8, 123.1 (11 × CH); 118.5, 130.0, 138.7, 143.8 (7 × $C_q$). – MS (70 eV); *m/z* (%): 241 (100) [$M^+$], 239 (12), 120 (23). – $C_{18}H_{11}N$: calcd. 241.089; found 241.089 ± 0.002. – Pyrolysis of anhydride **5** at 800°C/0.03 Torr gave indolo[3,2,1-*j,k*]carbazole **27** (51%) and anhydride **5** (30%) as estimated by $^1H$ NMR:

*1-(2-Methylphenyl)indole-3-carboxaldehyde* (**9c**): 2-Iodotoluene (2.5 g, 11.5 mmol), indole-3-carboxaldehyde (2.8 g, 19.3 mmol) and activated copper bronze (1 g) were heated under reflux in *N,N*-dimethylacetamide (10 ml) with vigorous stirring for 72 h, with further additions of 2-iodotoluene (2.5 g) and copper bronze (1 g) after 24 and 48 h. After filtration (Celite) and workup with aqueous ammonia, extraction with dichloromethane yielded a dark oil, which was subjected to flash chromatography (silica gel, ethyl ace-

tate/light petroleum ether, 1:4). The major fraction was distilled form bulb to bulb (220°C, 1 Torr). Recrystallisation of the major distillate from hexane gave the aldehyde **9c** (2.59 g, 57%) as pale yellow crystals, m.p. 75–76°C. – IR (mull): $\tilde{\nu}$ = 1679 $cm^{-1}$ (C=O). – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.1 (s, $CH_3$), 7.03 (br. d, *J* = 7.7 Hz, 7-H), 7.22–7.50 (m, 5-H, 6-H, 2′-H, 3′-H, 4′-H, 5′-H), 7.78 (s, 2-H), 8.39 (br. d, *J* = 6.5 Hz, 8-H), 10.1 (s, CHO). – $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.4 ($CH_3$), 111.1, 122.0, 123.2, 124.5, 127.2, 127.7, 129.5, 131.5, 138.9 (9 × CH); 119.2, 124.7, 136.5, 136.6, 138.3 (5 × $C_q$). – MS (70 eV); *m/z* (%): 235 (92) [$M^+$], 234 (100), 218 (20), 207 (11), 206 (63), 205 (28), 204 (83), 178 (23), 117 (23), 103 (44). – $C_{16}H_{13}NO$ (235.29): calcd. C 81.68, H 5.57, N 5.95; found C 81.5, H 5.7, N 6.1.

*Dimethyl 9-(2-Methylphenyl)carbazole-1,2-dicarboxylate* (**10c**): Treatment of the aldehyde **9c** (0.66 g, 2.8 mmol) with the Wittig reagent from methyltriphenylphosphonium bromide (2.0 g, 5.7 mmol) and *n*-butyllithium (4.0 mmol) in ether/THF for 19 h gave after flash chromatography a pale yellow oil, crude 3-ethenyl-9-*o*-tolylindole (0.60 g), which was used immediately. The crude 3-ethenyl compound (0.60 g, ca. 2.6 mmol) and dimethyl acetylenedicarboxylate (0.58 g, 4.1 mmol) were dissolved in ether (2 ml) and stirred for 40 h; a solid slowly separated. After filtration, flash chromatography (ethyl acetate/light petroleum ether, 1:5) of the filtrate gave further solid. Both solids were recrystallised from ethanol to give the title diester **12c** (0.48 g, 50%) as colourless needles, m.p. 142–143°C. – IR (mull): $\tilde{\nu}$ = 1735 (1-COOMe), 1714 (2-COOMe). – $^1H$ NMR (200 MHz, $CDCl_3$): δ = 1.94 (s, 2′-$CH_3$), 3.24 (s, 1-$COOCH_3$), 3.89 (s, 2-$COOCH_3$), 6.85–6.89 (m, 8-H), 7.27–7.48 (m, 6-H, 7-H, 3′-H, 4′-H, 5′-H, 6′-H), 7.96 (d, *J* = 8.2 Hz, 4-H), 8.17 (d, *J* = 7.7 Hz, 5-H), 8.23 (d, *J* = 8.3 Hz, 3-H). – $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.3 ($CH_3$); 110.3, 120.7, 120.8, 121.0, 126.8, 127.9, 129.5, 130.4, 131.00 (10 × CH); 119.6, 121.4, 124.7, 128.0, 135.2, 136.1, 138.9, 143.3 (8 × $C_q$), 166.7, 167.4 (2 × [C=O). – MS (70 eV); *m/z* 373 (86) [$M^+$], 342 (14), 310 (26), 299 (14), 298 (68), 282 (100), 255 (23), 254 (82), 253 (48), 252 (30), 141 (60). – $C_{23}H_{19}NO_4$ (373.13): calcd. C 73.98, H 5.13, N 3.75; found C 73.92, H 5.08, N 3.71.

*1-Methoxycarbonyl-9-(2-methylphenyl)carbazole-2-carboxylic Acid* (**13**) *and 10-(2-Methylphenyl)furo[3,4-a]carbazole-1,3-dione* (Anhydride **6**): The 1,2-diester **12c** (140 mg, 0.375 mmol) and potassium hydroxide (93 mg, 1.66 mmol) in methanol (20 ml) were heated under reflux for 48 h. Addition of water (20 ml) and acidification to pH = 1 then precipitated the 1-ester 2-acid **13** as an off-white powder (126 mg, 93% crude) which became yellow at 180°C and had m.p. 190–194°C. – IR (mull): $\tilde{\nu}$ = 3200–2500 (CO*OH*), 1746 (COOMe), 1687 (COOH) $cm^{-1}$. – $^1H$ NMR (200 MHz, [$D_6$]DMSO): δ = 1.82 (s, $CH_3$), 3.08 (s, 1-$COOCH_3$), 6.80 (d, *J* = 8.1 Hz, 8-H), 7.25–7.52 (m, 6-H, 7-H, 3′-H, 4′-H, 5′-H, 6′-H), 7.87 (d, *J* = 8.2 Hz, 4-H), 8.37 (d, *J* = 7.5 Hz, 5-H), 8.46 (d, *J* = 8.3 Hz, 3-H), 13.20 (br. s, 2-COOH). – MS (70 eV); *m/z* (%): 359 (2) [$M^+$], 327 (61) [M – MeOH], 282 (78), 254 (100). – $C_{22}H_{17}NO_4$: calcd. 359.116; found 359.117 × 0.004. – The 1-ester 2-acid **13** (120 mg, 0.334 mmol) was heated at 160–170°C for 75 min. Recrystallisation from ethyl acetate/light petroleum ether gave the anhydride **6** (96 mg, 88%) as yellow crystals, m.p. 184–185°C. – IR (mull): $\tilde{\nu}$ = 1832, 1767 $cm^{-1}$ (anhydride). – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.89 (s, $CH_3$), 7.02 (d, *J* = 8.3 Hz, 9-H), 7.24 (d, *J* = 7.3 Hz, 2′-H), 7.32–7.53 (m, 3′-H, 4′-H, 5′-H, 7-H, 8-H), 7.81 (d, *J* = 7.8 Hz, 6-H), 8.17 (d, *J* = 7.8 Hz, 5-H), 8.53 (d, *J* = 7.9 Hz, 4-H). – $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.3 ($CH_3$), 112.3 (C-9), 112.6 (C-6′); 115.9, 121.1, 121.5, 122.0, 127.0, 127.6, 129.0; 129.2 (C-6), 130.0 (C-5), 131.1 (C-4); 129.6, 131.4, 136.35, 136.4; 137.4 (C-10b), 143.8 (C-3a), 160.6 (1-C=O), 164.2 (3-C=O). – MS (70 eV); *m/z* (%): 327 (76) [$M^+$], 299 (19), 298 (17), 283 (23), 282 (81), 255 (22), 254 (100), 252 (33), 141 (25), 127 (34), 126 (43), 114 (18). – $C_{21}H_{13}NO_3$ (327.34): calcd. C 77.06, H 4.00, N 4.28, O 14.66; found C 77.16, H 4.01, N 4.27, O 14.56.

*FVP of Anhydride* **6** *and of Monomethyl Ester* **13**: (i) The *N-o*-tolyl anhydride **6** (27 mg, 0.08 mmol) was pyrolysed through an unpacked silica tube (940°C, 0.02 Torr, 140°C, 1 h) to give a green/yellow pyrolysate which showed two major spots on TLC. The $^1H$-NMR spectrum, assigned later, showed aromatic signals and two major signals at δ = 2.96 (s, $CH_3$) and at 4.40 (s, $CH_2$) attributed to two components in molar ratio 45:55, and some minor signals. Separation by radial chromatography (silica gel, light petroleum ether followed by ethyl acetate/light petroleum ether, 1:4) afforded two fractions. Fraction 1 (15 mg) was recrystallised from hexane to give colourless 1′-methylindolo[3,2,1-*jk*]carbazole (**27**), m.p. 127–129°C. – UV (ethanol): $\lambda_{max}$ (lg ε) = 236 nm (4.69), 259 (4.44), 264 (4.46), 273 (4.34), 285 (4.33), s302 (3.90), 316 (3.86), 345 (3.80), 358 (3.95). – $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, $CH_3$), 7.35 (m, 3H), 7.53 (m, 2H), 7.91 (m, 3H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.17 (d, *J* = 7.4 Hz, 1H). – MS (70 eV); *m/z* (%): 255 (100) [$M^+$], 254 (87), 252 (18), 241 (6), 127 (23), 126 (12). – $C_{19}H_{13}N$: calcd. 255.1048; found 255.1043. – Fraction 2 (3 mg) proved to be 8*H*-indolo[3,2,1-*de*]acridin-8-one (**29**)[9], an autoxidation product of the component showing δ = 4.40, which formed yellow crystals, m.p. 177–179°C (ref.[9] 178–180°C). – IR (mull): $\tilde{\nu}$ = 1649 $cm^{-1}$ (C=O). – $^1H$ NMR (200 MHz, $CDCl_3$): δ = 7.47 (t, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.88 (td, *J* = 7.8, 1.6 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 7.5 Hz, 1H), 8.46 (d, *J* = 8.6 Hz, 2H), 8.69 (dd, *J* = 8.0, 1.6 Hz, 1H). – MS (70 eV); *m/z* (%): 269 (100) [$M^+$], 241 (26), 240 (27), 239 (23), 135 (16), 121 (40), 120 (27). – These spectra were indistinguishable from those of a synthetic sample[9] of **29**, m.p. 177–179°C. Reduction of synthetic **29** (60 mg, 0.22 mmol) with $AlCl_3/LiAlH_4$ in ether/THF[10] afforded crude [8-*H*]-indolo[3,2,1-*de*]acridine (**28**) (35 mg, 61%), m.p. 88–90°C (ref.[10] 92.5–93.5°C). Spectra of this sample reproduced major features of the pyrolysate spectra, but ca. 8% of 8-one **29** was present (δ = 8.69, dd; *m/z*: 269 [$M^+$]. – $^1H$ NMR (200 MHz, $CDCl_3$): δ = 4.40 (s, $CH_2$), 7.2–8.1 (ca. 11 ArH). – MS (70 eV); *m/z* (%): 255 (62) [$M^+$], 254 (100), 252 (22), 1287 (31), 126 (30).

(ii) Pyrolysis of the 1-ester 2-acid **13** (32 mg) (930°C, 0.06 Torr, 130°C, 1 h) gave a pyrolysate similar to that from **6** in (i). By integration of the $^1H$-NMR spectrum with 1,1,2,2-tetrachloroethane (5 µl) as standard, the yield of indoloacridine **28** was estimated as 19%, and that of the methylindolocarbazole **27a** as 11%. Concentration of the solution gave a residue (14 mg, 61% as $C_{19}H_{13}N$).

*FVP of 10-(Phenylmethyl)-10H-furo[3,4-a]carbazole-1,3-dione* (**7**): The anhydride **7**[22] (28.7 mg, 0.009 mmol) was pyrolysed (910°C, 0.04 Torr, 160°C, 2 h) to give a brown solid (12.8 mg) which darkened in air. Examination by GLC-MS (BP5, 50°C, 2 min; 50–300°C, 10°C/min) showed a complex mixture: $t_R$ = 4.72 min, *m/z*: 106 [$M^+$], benzaldehyde; $t_R$ = 6.03 min, *m/z*: 108, benzyl alcohol; $t_R$ = 13.2 min, *m/z*: 182, bibenzyl; $t_R$ = 17.0 min, *m/z*: 167, carbazole; $t_R$ = 23.1 min, *m/z*: 217, 11*H*-benzo[*a*]carbazole (**33**); $t_R$ = 23.3 min, *m/z*: 229; $t_R$ = 26.4 min, *m/z*: 255. The identity of these components was confirmed by further GLC spiking experiments with authentic samples, including all three benzocarbazoles. This composition failed to account for the $^1H$-NMR spectrum of the total pyrolysate, which in addition to signals from bibenzyl, benzaldehyde, and heteroaromatic compounds showed a series of singlet signals at δ = 3.82, 4.09, 4.70, 4.94, 4.98, 5.01, 5.60. Yields of products have not been measured, but GLC peak areas were in the ratio benzaldehyde (1.0), benzyl alcohol (0.47), bibenzyl (0.77),

carbazole (0.21), benzo[*a*]carbazole (0.13), *m/z*: 229 (0.02), *m/z*: 255 (0.06). 9-Benzylcarbazole[23] (M = 257) and 6-phenylphenanthridine[24] (*M* = 255) were not detected. The minor product of $t_R$ = 26.4 min showed GLC-MS (70 eV); *m/z* (%): 255 (100) [$M^+$], 254 (75), 253 (21), 127 (55), 126 (16), 113 (13) and was possibly associated with the $^1$H-NMR signal at δ = 5.60 (s, $NCH_2Ar$), but this product was not isolated and its identity with 9*H*-indolo[3,2,1-*de*]-phenanthridine (**34**) below is uncertain.

*9H-Indolo[3,2,1-de]phenanthridine* (**34**): 9*H*-Indolo[3,2,1-*de*]-phenanthridine-9-one[11] (100 mg, 0.3 mmol) was reduced with lithium aluminium hydride (100 mg, 2.6 mmol) and boron trifluoride-ether (1.7 ml) in tetrahydrofuran (27 ml) at 0°C for 2 h and at reflux for 20 h. The reaction was quenched with 0.7 M hydrochloric acid and the product was extracted with dichloromethane. Concentration under nitrogen yielded substantially pure 9*H*-indolo[3,2,1-*de*]phenanthridine (**34**) (70 mg, 78%) as a light tan powder, m.p. 178–182°C, which rapidly darkened on exposure to air. – $^1$H NMR (200 MHz, $CDCl_3$): δ = 5.60 (s, $NCH_2Ar$), 7.20 (t, *J* = 7.6 Hz, 1H), 7.25–7.51 (m, 6 × ArH), 7.79 (d, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 6.9 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H). MS (70 eV); *m/z* (%): 255 (50) [$M^+$], 254 (100), 127 (50), 126 (50), 113 (10). – $C_{19}H_{13}N$: calcd. C 255.105; found 255.103 ± 0.003.

*Dimethyl 9-Ethylcarbazole-1,2-dicarboxylate* (**12**): Treatment of 1-ethylindole-3-carboxaldehyde[25] (4.0 g, 23.1 mmol) with an ether solution of the Wittig reagent from methyltriphenylphosphonium bromide (24.8 g, 69.3 mmol) and *n*-butyllithium (48.5 mmol) after 20 h afforded on workup crude 3-ethenyl-1-ethylindole as a red liquid. Dimethyl acetylenedicarboxylate (4.93 g, 34.7 mmol) in ether (20 ml) was added and the mixture was stirred under nitrogen for 24 h. Concentration and flash chromatography of the residue (silica gel, ethyl acetate/light petroleum ether, 1:9) gave the diester **12e** (1.07 g, 15%) as pale yellow needles. Sublimation (130°C/0.1 Torr) and recrystallisation from ethanol/water gave **12e** as fluorescent yellow needles, m.p. 138.5–139°C. – IR (mull): ṽ = 1716 $cm^{-1}$ (2 × COOMe). – $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.39 (t, *J* = 7.1 Hz, $CH_3$), 3.95, 4.07 (2 × s, 2 × $OCH_3$), 4.33 (q, *J* = 7.1 Hz, $CH_2$), 7.28 (ddd, *J* = 7.6, 7.0, 1.0 Hz, 6-H), 7.42 (br. d, *J* = 8.2 Hz, 8-H), 7.55 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 7-H), 7.90 (d, *J* = 8.2 Hz, 4-H), 8.11 (br. d, *J* = 7.6 Hz, 5-H), 8.14 (d, *J* = 8.2 Hz, 3-H). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 14.2 ($CH_3$), 38.8 ($CH_2$), 52.5, 52.9 (2 × $OCH_3$), 109.2 (C-8), 118.7 (C-1), 120.0 (C-6), 120.3 (C-3), 120.6 (C-4), 121.0 (C-5), 121.6 (C-2), 124.5 (C-4b), 127.7 (C-7), 128.3 (C-4a), 135.1 (C-9a), 142.0 (C-8a), 167.0 (1-CO), 169.9 (2-CO). – MS (70 eV); *m/z* (%): 311 (100) [$M^+$], 296 (51), 280 (21), 264 (51), 193 (59), 178 (30), 165 (45). – $C_{18}H_{17}NO_4$ (311.34): calcd. C 69.44, H 5.50, N 4.50; found C 69.38, H 5.39, N 4.34.

*10-Ethyl-10H-furo[3,4-a]carbazole-1,3-dione* (Anhydride **8**): Dimethyl 9-ethylcarbazole-1,2-dicarboxylate (**12e**) (0.92 g, 3.0 mmol) was heated with potassium hydroxide (0.50 g, 8.9 mmol) in water (5 ml) and ethanol (5 ml) for 20 h. Acidification gave an acidic fraction (0.36 g) which contained both dicarboxylic acid and monoester monoacid (NMR), but which on heating with acetic anhydride (15 ml) under reflux for 6 h gave the title anhydride. Evaporation of acetic anhydride and recrystallization of the residue from ethyl acetate gave anhydride **8** (0.29 g, 37%) as yellow crystals, m.p. (190°C subl.) 196–196.5°C. – IR (mull): ṽ = 1834, 1797, 1752 $cm^{-1}$ (anhydride). – $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.49 and 4.96 (t and q, *J* = 7.1 Hz, $CH_3CH_2$), 7.40 (ddd, *J* = 7.8, 6.8, 1.2 Hz, 7-H), 7.58 (br. d, *J* = 8.1 Hz, 9-H), 7.67 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 8-H), 7.78 (d, *J* = 7.8 Hz, 4-H), 8.20 (br. d, *J* = 7.8 Hz, 6-H), 8.54 (d, *J* = 7.8 Hz, H-5). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 13.7 ($CH_3$), 39.6 ($CH_2$), 108.7 (C-9), 110.1 (C-10b), 113.7 (C-4), 119.9 (C-7), 120.0 (C-5), 120.6 (C-3a), 126.4 (C-6), 127.5 (C-5b), 127.6 (C-8), 129.6 (C-5a), 134.2 (C-10a), 140.4 (C-9a), 161.2 (O=C-1), 162.5 (O=C-3). – MS (70 eV); *m/z* (%): 265 (100) [$M^+$], 251 (12), 250 (76), 193 (68), 192 (29), 191 (21), 178 (54), 165 (43), 164 (28). – $C_{16}H_{11}NO_3$ (265.271): calcd. C 72.45, H 4.18, N 5.28; found C 72.74, H 4.38, N 5.23.

*FVP of N-Ethyl Anhydride* **8**: The *N*-ethyl anhydride **8** (31.6 mg, 0.119 mmol) was pyrolysed through an unpacked silica tube (920°C, 0.04 Torr, 160°C, 15 min) to give an off-white film at the exit. This pyrolysate was collected ($CH_2Cl_2$) as a green solid (10.9 mg, 47% based on loss of $CO_2$ and CO only) and this was analysed by GLC/MS (BP5, 50°C, 2 min, 50–300°C, 10°C/min). The following were detected: phenanthridine ($t_R$ = 15.7 min), *m/z*: 179 [$M^+$]; carbazole ($t_R$ = 15.8 min), *m/z*: 167 [$M^+$]; pyrrolo[3,2,1-*jk*]carbazole (**44**)[26] ($t_R$ = 16.6 min), *m/z*: 191 [$M^+$]; 1-methylcarbazole (**40**)[27] ($t_R$ = 17.0 min), *m/z*: 181 [$M^+$]; 1,2-dihydropyrrolo[3,2,1-*jk*]carbazole (**45**)[26] ($t_R$ = 17.5 min), *m/z*: 193 [$M^+$]. Compounds were identified by GLC spiking experiments with authentic samples (BP1, 130–280°C, 5°C/min) and a second pyrolysate from **40** (12.5 mg; 920°C/0.04 Torr) but the trace of dihydro compound **45** was not detected in this second pyrolysate. Dihydro compound **45** could not be detected by $^1$H NMR in either pyrolysate. 1-Methylcarbazole (**40**) was initially identified by its characteristic $^1$H methyl shift, δ = 2.50 (ref.[27] 2.45). Yields of major products were estimated by quantitative $^1$H NMR with cyclohexane (2.0 µl, 0.031 µmol) as integration standard: carbazole (40%), phenanthridine (7%), 1-methylcarbazole (1.8%) and pyrrolo[3,2,1-*jk*]carbazole (0.03%).

*FVP of 4,5-Dihydropyrrolo[3,1,2-jk]carbazole* (**45**): Dihydro compound **45** (40.3 mg, 0.209 mmol) was pyrolysed through an unpacked silica tube (920°C, 0.01 Torr, 40°C, 45 min) to give an green solid (28.4 mg, 70.5% as $C_{14}H_{11}N$). Separation by radical chromatography (silica gel, diethyl ether/light petroleum ether, 1:9) gave pyrrolo[3,2,1-*jk*]carbazole (**44**) (4.1 mg, 10%), m.p. 84–85°C (ref.[26] 84–88°C); dihydro compound **45** (9.1 mg, 23%), m.p. 92–95°C (ref.[26] 94.5–95.5°C); 1-ethnyl carbazole[28] (**41**) (9.5 mg, 24%), m.p. 176–180°C (no m.p. in patent[28]). – IR (KBr): ṽ = 3420 $cm^{-1}$ (NH). – $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.48 (dd, *J* = 11.2, 0.8 Hz, 2′-$H_{cis}$), 5.86 (dd, *J* = 17.7, 0.8 Hz, 2′-$H_{trans}$), 7.04 (dd, *J* = 17.7, 11.2 Hz, 1′-H), 7.22 (t, *J* = 7.7 Hz, 3-H), 7.23–7.26 (m, 6-H), 7.39–7.47 (m, 2-H, 7-H, 8-H), 7.99 (d, *J* = 7.7 Hz, 4-H), 8.06 (d, *J* = 7.7 Hz, 5-H), 8.22 (br. s, NH). – $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 110.8 (C-8), 115.5 (C-2′), 119.7 (C-3), 119.8 (C-6), 119.9 (C-4), 120.4 (C-5), 121.2 (C-1), 123.5 (C-4a), 123.9 (C-2), 124.0 (C-4b), 126.0 (C-7), 133.3 (C-1′), 137.3 (C-9a), 139.6 (C-8a). – MS (70 eV); *m/z* (%): 193 (100) [$M^+$], 192 (46), 191 (22), 180 (17), 167 (19), 166 (15). – $C_{14}H_{11}N$; calcd. 193.089; found 193.089 ± 0.002.

*FVP of 9-Ethynylcarbazole* (**47**): Pyrolysis of 9-ethynylcarbazole[29] (42.0 mg, 0.22 mmol) through an unpacked silica tube (1050°C, 0.04 Torr, 30–40°C, 45 min) yielded a green solid (31.7 mg, 75% as $C_{14}H_9N$). Flash chromatography (silica gel, diethyl ether/light petroleum ether, 1:9) gave pyrrolo[3,2,1-*jk*]carbazole (**44**) (19.2 mg, 46%), m.p. 85–86.5°C (ref.[26] m.p. 84–88°C) and carbazole (12.1 mg, 33%), m.p. 241–244°C (ref.[20] m.p. 245°C), both further identified by comparison of their $^1$H-NMR spectra with those of authentic samples.

*FVP of 9-Ethenylcarbazole* (**46**): (i) 9-Ethenylcarbazole (19.5 mg) was recovered (18 mg) after attempted pyrolysis at 950°C/0.06 Torr. – (ii) 9-Ethenylcarbazole (20.2 mg, 0.105 mmol) was pyrolysed through an unpacked silica tube (1050°C/0.03 Torr, 50°C, 45 min)

to give a white solid (17.6 mg). Examination of the $^1$H-NMR spectrum indicated that the pyrolysate contained 9-ethenylcarbazole (**46**), pyrrolo[3,2,1-*jk*]carbazole (**44**), and phenanthridine in the approximate ratio 82:11:7.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