PERKIN 1

A versatile and convenient method for the synthesis of substituted benzo[*a*]carbazoles and pyrido[2,3-*a*]carbazoles

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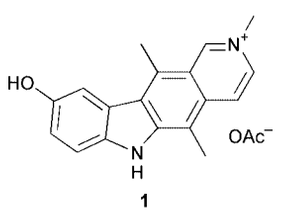
Received (in Cambridge, UK) 1st March 2000, Accepted 10th April 2000
Published on the Web 12th May 2000

Treatment of 2-(*o*-tolyl)- or 2-(3-methyl-2-pyridyl)-substituted indole-3-carbaldehydes with potassium *tert*-butoxide in DMF at 70–80 °C with simultaneous irradiation from a 400 W high-pressure mercury lamp afforded benzo[*a*]carbazoles and pyrido[2,3-*a*]carbazoles respectively in good yields.

Introduction

The indole nucleus is often found embedded in compounds exhibiting a wide range of biological activities.[1] Important members of this class include the benzo- and pyrido-fused carbazoles,[2,3] either as naturally occurring products or as compounds derived by synthesis. For example, the pyrido-fused compounds elliptinium (2-methyl-9-hydroxyellipticinium acetate) **1**[2] and ditercalinium **2**[2] have been used clinically for



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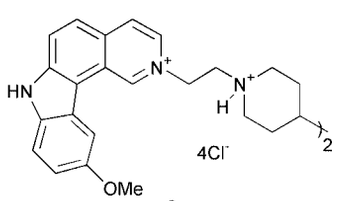

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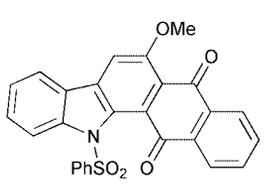

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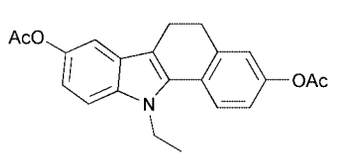

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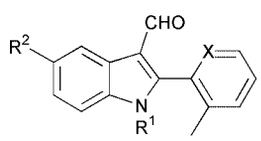
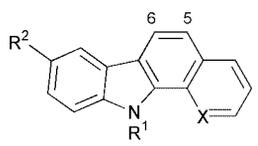
the treatment of cancers, while the naphtho[2,3-*a*]carbazole **3** is responsible for significant cell growth inhibition of a range of tumour cell lines.[3] A series of simple benzo[*a*]carbazoles such as **4** have been shown to bind to estrogen receptors and inhibit the growth of mammary tumours of rats,[4] while other benzo[*a*]carbazoles have been suggested as potential anti-tumour agents.[5] Benzo[*a*]carbazole derivatives have also found extensive application as photographic materials.[6]

In this paper we outline novel methodology for the synthesis of benzo[*a*]carbazoles and pyrido[2,3-*a*]carbazoles. This work is an extension of previous work done towards the synthesis of naphthalenes and phenanthrenes,[7,8] and part of the present work has been described previously in a communication.[9] The key step involves a novel light-assisted base-induced ring closure of precursors **5** to form the carbon–carbon bond between C-5 and C-6 of the benzocarbazole **6** (X = CH) or pyridocarbazole **6** (X = N) skeleton. It is believed that this novel cyclisation reaction proceeds through photo-enol intermediates as described in a previous publication.[8] Examination of the literature reveals a number of methods for the



5 X = CH or N



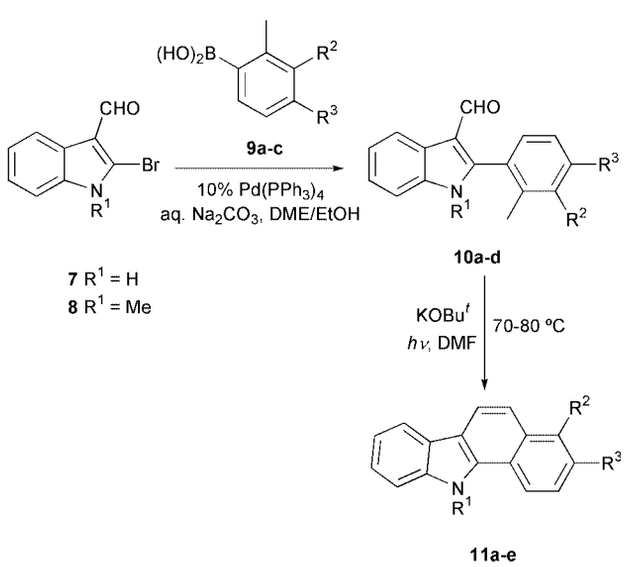
6 X = CH or N

synthesis of 11*H*-benzo[*a*]carbazoles[10] and 11*H*-pyrido[2,3-*a*]-carbazoles,[10c,11] but none in which the last step involves the formation of the C-5–C-6 bond.

Results and discussion

Synthesis of benzo[*a*]carbazoles

Exposure of oxindole (indolin-2-one) to a mixture of DMF and phosphorus oxybromide followed by hydrolysis gave 2-bromo-indole-3-carbaldehyde **7**.[12] Treatment of **7** with potassium bis-(trimethylsilyl)amide (KHMDS) and then methyl iodide afforded the *N*-methyl precursor **8** in good yield. This precursor was used in subsequent steps for the synthesis of benzo[*a*]carbazoles. The desired precursors **10a–c** were synthesised in high yields utilising the Suzuki reaction.[13] As shown in Scheme 1, this was achieved by treatment of **8** with the requisite boronic acid **9a–c** in the presence of a catalytic quantity of tetrakis-



Scheme 1

Table 1

Indole	Boronic acid **9**	Biaryl **10**; yield (%)	Benzo[*a*]carbazole **11**; yield (%)
8	**a**: $R^2 = R^3 = H$	**a**: R^1 = Me, $R^2 = R^3 = H$; 85	**a**: R^1 = Me, $R^2 = R^3 = H$; 77
8	**b**: R^2 = Me, $R^3 = H$	**b**: R^1 = Me, R^2 = Me, $R^3 = H$; 93	**b**: R^1 = Me, R^2 = Me; $R^3 = H$; 78[b]
8	**c**: $R^2 = H$, R^3 = OMe	**c**: R^1 = Me, $R^2 = H$, R^3 = OMe; 94	**c**: R^1 = Me, $R^2 = H$, R^3 = OMe; 52
7	**a**: $R^2 = R^3 = H$	**d**: R^1 = Bn, $R^2 = R^3 = H$; 84[a]	**d**: R^1 = Bn, $R^2 = R^3 = H$; 37

[a] Isolated after *N*-benzylation of the product from coupling **7** to **9a**. [b] After 5 min. **11e** (R^1 = Me, R^2 = CHO, $R^3 = H$) could also be isolated as minor product (9%) after 10 min (see Experimental section).

(triphenylphosphine)palladium(0) in 1,2-dimethoxyethane (DME) and ethanol together with aqueous sodium carbonate to afford high yields of the desired products **10a**–**c** (Table 1). To our knowledge this provides the first example of a Suzuki coupling reaction between substituted aromatic boronic acids and indoles possessing a carbonyl function at C-3. In the literature only three related Suzuki coupling reactions involving 2-substituted-indoles and aromatic boronic acids have been described.[14]

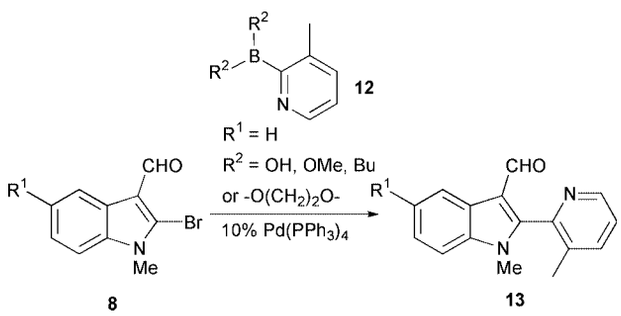
We found that it was necessary to protect the indole nitrogen for the next step of the synthesis. However since an *N*-methyl group is not easily removed, we chose to prepare the *N*-benzyl analogue **10d** as well. Treatment of the unprotected indole **7** with **9a** under the same conditions to those described above for the formation of **10a**–**c** followed by protection of the indole nitrogen with benzyl bromide afforded a high yield of the benzyl-protected 2-arylindole **10d** (Table 1). This strategy shows that unprotected indoles can successfully participate in Suzuki coupling reactions.

Evidence for the formation of **10a**–**d** was obtained from both the ^{1}H and ^{13}C NMR spectra. The aldehyde signal was evident at about δ 9.6 and the aromatic methyl signals were found between δ 2.04–2.37, while the *N*-methyl signal for **10a**–**c** appeared at approximately δ 3.5 in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum showed the carbon signals of the same groups at about δ 185, 20 and 30 respectively. The benzyl substituent of **10d** was observed in the ^{1}H NMR spectrum as a doublet at δ 5.12 with the remaining aromatic protons appearing between δ 7.18–7.42.

The stage was now set to attempt our novel light-assisted base-induced cyclisation reaction on indole precursors (Scheme 1). Treatment of the 2-arylindole-3-carbaldehydes **10a**–**d** with 4 mole equivalents of potassium *tert*-butoxide in DMF with simultaneous irradiation from a 400 W high-pressure mercury lamp for 10 min afforded the desired carbazoles **11a**–**d** in generally good yields (shown in Table 1). For the conversion of **10b**→**11b** over-oxidation afforded aldehyde **11e** as a side-product (**11e**, 9%, **11b**, 55%). However on stopping this reaction after 5 min, only **11b** was formed in 78% yield. Unfortunately, the *N*-benzyl protected precursor **10d** afforded **11d** in mediocre yield. Again, spectroscopic analysis confirmed the identity of the products. It was clear from both the ^{1}H NMR spectra and the ^{13}C NMR spectra that the aldehyde and aromatic methyl signals were no longer evident. A characteristic feature of the carbazole products was a substantial downfield shift of the *N*-methyl signal (*e.g.* **10c**→**11c**; δ 3.51→δ 4.12).

Synthesis of pyrido[2,3-*a*]carbazoles

We envisaged extending the synthesis of benzo[*a*]carbazoles to pyrido[2,3-*a*]carbazoles such as **6** (X = N) in order to gain access to "angular" analogues of elliptinium and related compounds. We wished to do this as it has been demonstrated that angular compounds of this type show significant biological activity.[15] However, we found that Suzuki coupling of **8** with pyridine-2-boronic acids, esters and related compounds **12**, in an analogous manner to that described for preparing benzo[*a*]carbazole precursors **10**, failed to yield the coupled products **13** despite numerous attempts (Scheme 2). This necessitated a change of strategy, and we investigated a "reversed" Suzuki synthesis in which the indole precursor was made to bear the boronic acid substituent.



Scheme 2

The synthesis of indole-2-boronic acid **14a** has been described in the literature,[16] and Suzuki coupling of **14a** with 3-bromopyridine has also been reported.[17] As a result we believed that this methodology could be used to afford the desired coupled products **13**. As outlined in Scheme 3, treatment of indole or 5-methoxyindole with di-*tert*-butyl dicarbonate in the presence of 4-dimethylaminopyridine (DMAP) gave the desired protected indoles **15a**–**b** in excellent yields. Exposure of each of these compounds to lithium 2,2,6,6-tetramethylpiperidide (LiTMP) followed by quenching with triisopropyl borate and hydrolysis with hydrochloric acid provided the desired boronic acids **14a**–**b**. These intermediates were not characterised, but used without further purification in the next reaction.

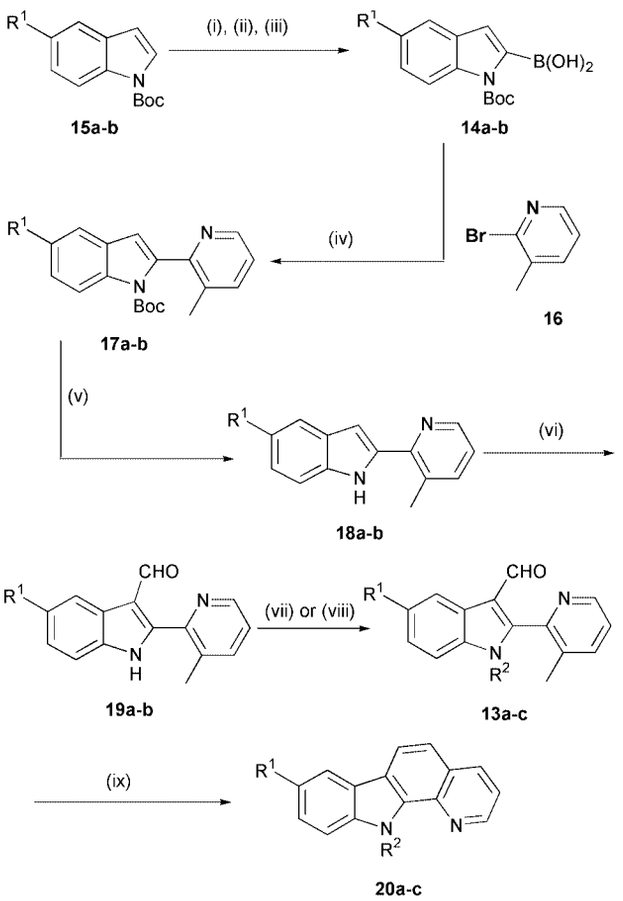
The next step entailed the cross-coupling of the indole-2-boronic acids **14a**–**b** with a suitably substituted pyridine partner. In a similar manner to that described by Johnson *et al.*,[17] treatment of **14a** and **14b** with 2-bromo-3-methylpyridine **16** in the presence of a catalytic quantity of tetrakis(triphenylphosphine)palladium(0) in 1,2-dimethoxyethane (DME) together with aqueous sodium carbonate afforded high yields of the desired products **17a**–**b**. It was clear from ^{1}H NMR spectroscopy that **17a** and **17b** had been formed as diagnostic singlets at about δ 2.2 assigned to the methyl on the pyridine ring were present in addition to the expected aromatic signals.

The position of coupling was confirmed by NOE spectroscopy of the coupled product **17b**. Irradiation of H-3 on the indole nucleus of **17b** showed enhancement of H-4, thus confirming arylation at C-2. Formation of the carbon–carbon bond between C-2 of the indole nucleus and a pyridine subunit has previously proved to be problematic for the synthesis of carbazoles as well as carbolines.[18] Therefore this method provides an excellent alternative for the construction of this bond.

As the formation of the 2-(2-pyridyl)indoles **17** had been completed, an aldehyde functional group had to be introduced at C-3 of the indole nucleus (Scheme 3). The Boc protecting group had to be removed to facilitate this reaction. This was accomplished in high yield (Table 2) by heating **17a** and **17b** adsorbed onto silica gel in a conventional microwave oven for 3 min to give **18a** and **18b**.[19] Both of these compounds were treated under conditions used for the Vilsmeier–Haack

Table 2

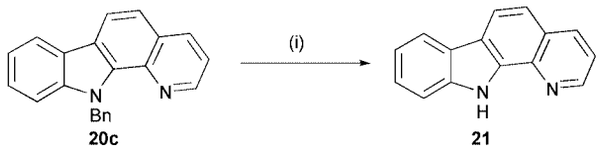
17; yield (%)	**18**; yield (%)	**19**; yield (%)	**13**; yield (%)	**20**; yield (%)
a: R^1 = H; 87 **b**: R^1 = OMe; 77	**a**: R^1 = H; 100 **b**: R^1 = OMe; 100	**a**: R^1 = H; 91 **b**: R^1 = OMe; 90	**a**: R^1 = H, R^2 = Me; 93 **b**: R^1 = OMe, R^2 = Me; 84 **c**: R^1 = H, R^2 = Bn; 77	**a**: R^1 = H, R^2 = Me; 78 **b**: R^1 = OMe, R^2 = Me; 77 **c**: R^1 = H, R^2 = Bn; 75



Scheme 3 *Reagents and conditions*: (i) LiTMP, −78 °C, THF, (ii) $B(OPr^i)_3$, (iii) H^+, **14a** and **14b**, 100% crude (over 3 steps); (iv) 10% $Pd(PPh_3)_4$, aq. Na_2CO_3, DME; (v) SiO_2, microwave oven, 3 min; (vi) $POCl_3$, DMF; (vii) KHMDS, MeI, THF, for **13a** and **13b** (viii) BnBr, KHMDS, THF, for **13c**; (ix) $KOBu^t$, DMF, *hv*, 70–80 °C (For yields see Table 2).

formylation reaction[20] to afford the desired products **19a** and **19b**. It was clear from ^{1}H NMR spectroscopy that aldehydes **19a** and **19b** had been formed, as singlets were present at δ 9.83 and δ 9.81 respectively. ^{13}C NMR spectroscopy showed *inter alia* peaks at δ 185.5 and 185.8. Finally, the indole nitrogen was protected. Indole **19a** was converted into both the methyl-protected compound **13a** as well as the benzyl protected compound **13c**, while indole **19b** was converted only into the methyl-protected compound **13b** as shown in Scheme 3.

We were now able to attempt our novel cyclisation reaction on these precursors. Treatment of **13a–c** in DMF with 4 mole equivalents of potassium *tert*-butoxide and simultaneous irradiation from a 400 W high-pressure mercury lamp provided the desired pyrido[2,3-*a*]carbazoles **20a–c** in good yields. Evidence for the formation of the desired products was obtained from the NMR spectra. For example, the ^{1}H NMR spectrum of **20c** showed that both the aldehyde and methyl signal of the starting material had been replaced by two doublets at δ 7.40 and δ 8.07 (J = 8.4 Hz) assigned to H-6 and H-5 respectively. The benzyl-protected compound **19c** was treated with aluminium trichloride in benzene[21] to afford **21** (Scheme 4), illustrating the value of a selectively removable protecting group.



Scheme 4 *Reagents and conditions*: (i) $AlCl_3$, 0 °C, benzene, 80%.

In summary, a new method for the preparation of benzo[*a*]carbazoles and pyrido[2,3-*a*]carbazoles is described. The synthesis of benzo[*a*]carbazoles proceeds in good yield in only three steps from oxindole (49% for **11a**, 54% for **11b**, 37% for **11c** and 23% for **11d**). The synthesis of **20a–c** also proceeds in good overall yield (57% for **20a**, 45% for **20b**, 46% for **20c**) in only six steps from indole or 5-methoxyindole. Work is in progress towards the synthesis of pyrido[2,3-*c*]carbazoles and these results will be reported in due course.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded either on a Bruker AC-200 or Bruker DRX 400 spectrometer at the frequency indicated. DEPT, CH-correlated and HMBC spectra were run on some samples to enable complete assignments of all the signals. NMR spectroscopic assignments with the same superscript may be interchanged. *J*-values are given in Hz. Infra-red spectra were recorded on either a Bruker IFS 25 Fourier Transform spectrometer, or on a Bruker Vector 22 Fourier Transform spectrometer. Mass spectra were recorded on a Kratos MS 9/50, VG 70E MS or a VG 70 SEQ mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyser. Macherey-Nagel Kieselgel 60 (particle size 0.063–0.200 mm) was used for conventional silica gel chromatography and Macherey-Nagel Kieselgel 60 (particle size 0.040–0.063 mm) was used for preparative flash chromatography. All solvents used for reactions and chromatography were distilled prior to use.

2-Bromo-1-methyl-1*H*-indole-3-carbaldehyde 8[22]

DMF (1.0 cm^3, 13.23 mmol) was added to phosphorus oxybromide (3.16 g, 11.02 mmol) at 0 °C under an atmosphere of nitrogen. Oxindole (596 mg, 4.41 mmol) in chloroform (15 cm^3) was added to the resulting salt and the reaction mixture was stirred at room temperature for 18 h. After this time the reaction was quenched with a saturated aqueous sodium chloride solution (30 cm^3) and made basic with 2 M aqueous sodium hydroxide. The mixture was extracted with dichloromethane (3 × 50 cm^3) and ethyl acetate (3 × 50 cm^3) and the combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude 2-bromo-1*H*-indole-3-carbaldehyde **7** was dissolved in THF (20 cm^3) and cooled to −78 °C. Potassium hexamethyldisilazide (KHMDS, 0.5 M solution in toluene, 10.4 cm^3, 5.22 mmol) was added dropwise and the reaction mixture stirred at −78 °C for 45 min. Methyl iodide (0.5 cm^3, 8.69 mmol) was added and the reaction mixture stirred for a further 45 min at −78 °C. After this time the mixture was warmed to room temperature and stirred for 30 min. The mixture was then quenched with water (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The organic fractions were combined and dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude residue was purified by chromatography (50% ethyl acetate–hexane) to afford the *product* **8** (791 mg,

75% over two steps) isolated as a white solid; mp 111–112 °C (ethanol) (lit.,[22a] 110–111.5 °C) (Found: M^+ 236.9799. $C_{10}H_8ONBr$ requires *M*, 236.9789); $\nu_{max}(CHCl_3)/cm^{-1}$ 3015 (ArC–H), 1653 (C=O) and 1501 (ArC=C); δ_H (200 MHz; $CDCl_3$; Me_4Si) 3.76 (3H, s, NCH_3), 7.29–7.32 (3H, m, 3 × ArH), 8.28–8.32 (1H, m, 7-H) and 10.01 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 31.4 (NCH_3), 109.5 (7-C), 114.8 (3-C), 120.6 (6-C)[a], 123.0 (5-C)[a], 123.8 (4-C)[a], 124.7 (2-C)[b], 126.3 (4a-C)[b], 137.0 (7a-C)[b] and 185.0 (CHO); *m/z* 236 (M^+, 82%), 235 (100), 157 (7), 129 (30), 89 (22) and 63 (18).

General procedure for the coupling of arylboronic acids to indoles

Typically, a solution of 2-bromo-1-methyl-1*H*-indole-3-carbaldehyde **8** or 2-bromo-1*H*-indole-3-carbaldehyde **7** (0.78 mmol) in DME (4 cm^3) was deoxygenated by passing nitrogen through the mixture for 5 min. The deoxygenated mixture was added to $Pd(PPh_3)_4$ (10%, 0.08 mmol) and stirred under an atmosphere of nitrogen at room temperature for 10 min. A solution of 2-methylphenylboronic acid **9a**,[23] 2,3-dimethylphenylboronic acid **9b**[24] or 4-methoxy-2-methylphenylboronic acid **9c**[25] (1.16 mmol) in ethanol (1.5 cm^3) was deoxygenated and added to the mixture. The mixture was stirred for a further 10 min. A 2 M aqueous sodium carbonate solution (6.60 mmol) was also deoxygenated and added to the reaction mixture. The mixture was stirred for 5 min at room temperature before being heated at reflux for 18 h. The mixture was cooled to room temperature and quenched with water (20 cm^3). The organic material was extracted into dichloromethane (3 × 30 cm^3), the combined organic extracts were dried with magnesium sulfate and the solvent was evaporated under reduced pressure. The crude product was subjected to chromatography (10–30% ethyl acetate–hexane). The following compounds were prepared by this method.

1-Methyl-2-(2-methylphenyl)-1*H*-indole-3-carbaldehyde 10a. The *product* **10a** (164 mg, 85%) was isolated as an off-white solid from 2-bromo-1-methyl-1*H*-indole-3-carbaldehyde **8** and 2-methylphenylboronic acid **9a**; mp 165–166.5 °C (ethyl acetate–methanol) (Found: M^+ 249.1146. $C_{17}H_{15}NO$ requires *M*, 249.1154); $\nu_{max}(CHCl_3)/cm^{-1}$ 3016 (ArC–H), 1647 (C=O), 1614, 1571 and 1528 (ArC=C) and 818 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.15 (3H, s, $ArCH_3$), 3.52 (3H, s, NCH_3), 7.31–7.46 (7H, m, 7 × ArH), 8.40–8.44 (1H, m, 7-H) and 9.57 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 19.8 ($ArCH_3$), 30.3 (NCH_3), 109.7 (7-C), 115.7 (3-C), 122.0 (3′-C)[a], 123.2 (4′-C)[a], 123.8 (5′-C)[a], 125.1 (3a-C)[b], 125.8 (6′-C)[a], 128.4 (2-C)[b], 130.1 (5-C)[c], 131.1 (4-C)[c], 137.3 (2′-C)[d], 138.2 (1′-C)[d], 151.3 (7a-C) and 186.0 (CHO); *m/z* 249 (M^+, 100%), 248 (34), 235 (10), 234 (52) and 232 (96).

1-Methyl-2-(2,3-dimethylphenyl)-1*H*-indole-3-carbaldehyde 10b. The *product* **10b** (115 mg, 99%) was isolated as an off-white solid from 2-bromo-1-methyl-1*H*-indole-3-carbaldehyde **8** and 2,3-dimethylphenylboronic acid **9b**; mp 157–159 °C (ethyl acetate) (Found: M^+ 263.1327. $C_{18}H_{17}NO$ requires *M*, 263.1310); $\nu_{max}(CHCl_3)/cm^{-1}$ 3105 (ArC–H), 1647 (C=O), 1613, 1581 and 1535 (ArC=C) and 817 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.04 and 2.37 (each 3H, s, $ArCH_3$), 3.51 (3H, s, NCH_3), 7.15 (1H, dd, *J* 1.7 and 7.5, 5′-H), 7.24 (1H, dd, *J* 7.5 and 9.2, 4′-H), 7.32–7.42 (4H, m, 4 × ArH), 8.39–8.44 (1H, m, 7-H) and 9.57 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 16.8 and 20.2 (each $ArCH_3$), 30.3 (NCH_3), 109.7 (7-C), 115.8 (3-C), 122.0 (4′-C)[a], 123.1 (5′-C)[a], 123.7 (6-C)[a], 125.0 (3a-C)[b], 125.5 (6′-C)[a], 128.3 (2-C)[b], 128.9 (5-C)[c], 131.5 (4-C)[c], 136.7 (3′-C)[d], 137.1 (2′-C)[d], 137.7 (1′-C)[d], 152.2 (7a-C) and 186.2 (CHO); *m/z* 263 (M^+, 100%), 262 (19), 249 (15), 248 (82) and 218 (26).

2-(4-Methoxy-2-methylphenyl)-1-methyl-1*H*-indole-3-carbaldehyde 10c. The *product* **10c** (117 mg, 94%) was isolated as a pale yellow solid from 2-bromo-1-methyl-1*H*-indole-3-carbaldehyde **8** and 4-methoxy-2-methylphenylboronic acid **9c**; mp 203–206 °C (toluene) (Found: M^+ 279.1248. $C_{18}H_{17}NO_2$ requires *M*, 279.1259); $\nu_{max}(CHCl_3)/cm^{-1}$ 3017 (ArC–H), 2839 (OCH_3), 1647 (C=O), 1610, 1580 and 1539 (ArC=C), 1243 (C–O) and 820 (ArH oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.12 (3H, s, $ArCH_3$), 3.51 (3H, s, NCH_3), 3.87 (3H, s, OCH_3), 6.86 (1H, dd, *J* 2.4 and 8.4, 5′-H), 6.91 (1H, d, *J* 2.4, 3′-H), 7.22 (1H, d, *J* 8.4, 6′-H), 7.34–7.39 (3H, m, 3 × ArH), 8.38–8.43 (1H, m, 7-H) and 9.58 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 20.1 ($ArCH_3$), 30.2 (NCH_3), 55.3 (OCH_3), 109.6 (7-C), 111.3 (3′-C)[a], 115.8 (5′-C)[a], 115.9 (3-C), 120.3 (3a-C)[b], 121.9 (6′-C)[a], 123.0 (6-C)[c], 123.6 (5-C)[c], 125.1 (2-C)[b], 132.3 (4-C)[c], 137.2 (2′-C)[d], 139.8 (1′-C)[d], 151.5 (7a-C), 160.8 (4′-C) and 186.2 (CHO); *m/z* 279 (M^+, 83%), 278 (21), 264 (41), 262 (100), 250 (12) and 249 (15).

1-Benzyl-2-(2-methylphenyl)-1*H*-indole-3-carbaldehyde 10d. 2-Bromo-1*H*-indole-3-carbaldehyde **7** (431 mg, 1.93 mmol) was treated with 2-methylphenylboronic acid **9a** as described in the general procedure to afford 2-(2-methylphenyl)-1*H*-indole-3-carbaldehyde (428 mg, 95%) as an off-white solid. This product was treated as an intermediate. A portion of the product (136 mg, 0.58 mmol) was dissolved in THF (5 cm^3) and cooled to −78 °C. Potassium hexamethyldisilazide (KHMDS, 0.5 M solution in toluene, 1.7 cm^3, 0.87 mmol) was added dropwise and the reaction mixture stirred at −78 °C for 30 min. Benzyl bromide (0.2 cm^3, 1.45 mmol) was added and the reaction mixture stirred for a further 30 min at −78 °C. After this time the mixture was warmed to room temperature and stirred for 30 min. The mixture was then quenched with water (50 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). The organic fractions were combined and dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude residue was purified by chromatography (5–20% ethyl acetate–hexane) to afford the *product* **10d** (159 mg, 84%) as a clear oil (Found: M^+ 325.1472. $C_{23}H_{19}NO$ requires *M*, 325.1467); ν_{max}(film)/cm^{-1} 3032 (ArC–H), 1653 (C=O), 1611, 1580 and 1538 (ArC=C), 1454 (C–N) and 750 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.04 (3H, s, $ArCH_3$), 5.12 (2H, d, *J* 7.6, NCH_2Ph), 6.86–6.90 (2H, m, 2 × ArH), 7.18–7.42 (10H, m, 10 × ArH), 8.41–8.45 (1H, m, ArH) and 9.60 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 19.9 ($ArCH_3$), 47.5 (NCH_2Ph), 110.7 (7-C), 116.1 (3-C), 122.2 (4-C)[a], 123.2 (6-C)[a], 123.9 (5-C)[a], 125.3 (2-C), 125.8 (ArCH)[a], 126.5 (2 × ArCH), 127.7 (5′-C)[a], 128.2 (ArC), 128.7 (2 × ArCH), 130.2 (6′-C)[b], 130.4 (4′-C)[b], 131.0 (3′-C)[b], 135.9 (3a-C)[c], 136.8 (2′-C)[c], 138.4 (1′-C)[c], 151.2 (7a-C) and 186.3 (CHO); *m/z* 325 (M^+, 56%), 324 (9), 310 (15), 308 (27), 204 (11) and 91 (100).

General procedure for cyclisation of 2-arylindole-3-carbaldehydes to benzo[*a*]carbazoles

Typically, the 2-aryl-3-acylindole (0.43 mmol) was dissolved in dry DMF (15 cm^3) and heated to 80 °C under nitrogen. Potassium *tert*-butoxide (1.72 mmol) was added and the reaction mixture was irradiated with a high-pressure mercury lamp through a quartz filter for 10 min. The reaction mixture was diluted with water and the organic material was extracted into diethyl ether. The organic fractions were combined, dried with magnesium sulfate and filtered. The diethyl ether was then evaporated under reduced pressure and the resulting residue was subjected to chromatography (5–20% ethyl acetate–hexane) to afford the desired benzo[*a*]carbazoles. The following compounds were prepared by this method.

11-Methyl-11*H*-benzo[*a*]carbazole 11a. The *product* **11a** (107 mg, 77%) was isolated as a pale yellow solid; mp 171–172.5 °C (ethyl acetate–methanol) (Found: M^+ 231.1043. $C_{17}H_{13}N$ requires *M*, 231.1048); $\nu_{max}(CHCl_3)/cm^{-1}$ 3058 (ArC–H), 1577, 1560 and 1528 (ArC=C) and 809 (ArH oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 4.19 (3H, s, NCH_3), 7.26 (1H, ddd, *J* 1.8, 6.0 and

6.8, 8-H), 7.39–7.51 (4H, m, 2-H, 3-H, 9-H and 10-H), 7.57 (1H, d, *J* 8.5, 6-H)[a], 7.95 (1H, dd, *J* 1.8 and 7.6, 4-H), 8.07 (1H, d, *J* 8.5, 5-H)[a], 8.08 (1H, dd, *J* 1.3 and 6.8, 7-H) and 8.57 (1H, dd, *J* 1.0 and 8.0, 1-H); δ_C (50.32 MHz; $CDCl_3$) 33.7 (NCH_3), 108.9 (10-C), 118.7 (4a-C)[a], 119.0 (7-C), 119.4 (8-C), 119.6 (5-C), 120.3 (6-C), 122.0 (1-C), 122.6 (7a-C)[a], 122.9 (6a-C)[a], 124.5 (3-C)[b], 124.6 (9-C)[b], 125.0 (2-C)[b], 129.3 (4-C), 133.5 (10a-C)[c], 135.3 (1a-C)[c] and 140.6 (11a-C)[c]; *m*/*z* 231 (M^+, 100%), 230 (22), 216 (27), 202 (7) and 116 (9).

4,11-Dimethyl-11*H*-benzo[*a*]carbazole 11b and 11-methyl-11*H*-benzo[*a*]carbazole-4-carbaldehyde 11e. 4,11-Dimethyl-11*H*-benzo[*a*]carbazole **11b** (139 mg, 78%) was isolated as a white solid (reaction time 5 min); mp 192–193.5 °C (ethyl acetate) (Found: M^+ 245.1208. $C_{18}H_{15}N$ requires *M*, 245.1205); $\nu_{max}(CHCl_3)/cm^{-1}$ 3019 (ArC–H), 1595 and 1535 (ArC=C) and 913 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.77 (3H, s, $ArCH_3$), 4.29 (3H, s, NCH_3), 7.25–7.34 (1H, m, 10-H), 7.37–7.46 (2H, m, 2-H and 3-H), 7.46–7.49 (2H, m, 8-H and 9-H), 7.77 (1H, dd, *J* 0.9 and 8.8, 5-H), 8.13 (1H, dd, *J* 1.4 and 7.8, 7-H), 8.15 (1H, d, *J* 8.8, 6-H) and 8.53 (1H, d, *J* 8.3, 1-H); δ_C (50.32 MHz; $CDCl_3$) 20.9 ($ArCH_3$), 34.1 (NCH_3), 109.0 (10-C), 116.2 (7-C)[a], 118.8 (8-C)[a], 119.4 (5-C)[a], 119.6 (6-C)[a], 120.4 (1-C)[a], 122.6 (6a-C)[b], 122.9 (7a-C)[b], 124.6 (3-C)[c], 124.7 (9-C)[c], 125.8 (2-C)[c], 132.4 (4a-C)[b], 135.4 (4-C and 10a-C)[b], 136.1 (1a-C)[d] and 140.9 (11a-C)[d]; *m*/*z* 245 (M^+, 100%), 244 (16), 230 (23), 202 (5), 150 (8) and 122 (8).

A second product, 11-methyl-11*H*-benzo[*a*]carbazole-4-carbaldehyde **11e** was isolated when the reaction mixture was irradiated for 10 min, as described in the general procedure. Chromatography (5% ethyl acetate–hexane) afforded firstly 4,11-dimethyl-11*H*-benzo[*a*]carbazole **11b** (46 mg, 55%) identical in all respects with that described above, followed by the *aldehyde* **11e** (8 mg, 9%) isolated as a yellow solid; mp 155–157 °C (ethanol) (Found: M^+ 259.0995. $C_{18}H_{13}NO$ requires *M*, 259.0997); $\nu_{max}(CHCl_3)/cm^{-1}$ 3017 (ArC–H), 1690 (C=O), 1653, 1591 and 1559 (ArC=C) and 826 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 4.41 (3H, s, NCH_3), 7.32–7.40 (1H, m, 10-H), 7.51–7.61 (2H, m, 8-H and 9-H), 7.74 (1H, dd, *J* 7.1 and 8.6, 2-H), 8.05 (1H, dd, *J* 1.2 and 7.1, 3-H), 8.21 (1H, dd, *J* 1.0 and 7.8, 7-H), 8.39 (1H, d, *J* 8.9, 6-H), 9.00 (1H, dd, *J* 1.2 and 8.6, 1-H), 9.10 (1H, dd, *J* 0.8 and 8.9, 5-H) and 10.53 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 34.3 (NCH_3), 109.1 (10-C), 115.7 (7-C)[a], 119.7 (4a-C)[b], 119.9 (5-C and 8-C)[a], 122.3 (6-C)[a], 122.7 (6a-C)[b], 123.0 (7a-C)[b], 123.8 (9-C)[c], 125.4 (3-C)[c], 128.7 (2-C)[c], 130.5 (4-C)[d], 131.6 (10a-C)[d], 135.2 (1a-C)[e], 140.6 (11a-C)[e] and 193.6 (CHO); *m*/*z* 259 (M^+, 100%), 231 (86), 230 (39), 216 (38), 202 (14), 129 (13) and 115 (15).

3-Methoxy-11-methyl-11*H*-benzo[*a*]carbazole 11c. The desired *product* **11c** (103 mg, 52%) was isolated as a pale yellow oil that crystallised on standing; mp 169–171 °C (ethyl acetate) (Found: M^+ 261.1156. $C_{18}H_{15}NO$ requires *M*, 261.1154); $\nu_{max}(CHCl_3)/cm^{-1}$ 3009 (ArC–H), 2853 (OCH_3), 1622 and 1568 (ArC=C), 1208 (C–O) and 855 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 3.91 (3H, s, OCH_3), 4.12 (3H, s, NCH_3), 7.16 (1H, dd, *J* 2.5 and 9.3, 2-H), 7.24–7.28 (1H, m, 10-H), 7.30 (1H, d, *J* 2.5, 4-H), 7.40–7.43 (2H, m, 8-H and 9-H), 7.48 (1H, d, *J* 8.5, 5-H), 8.06 (1H, d, *J* 8.5, 6-H), 8.07 (1H, dd, *J* 1.2 and 7.4, 7-H) and 8.47 (1H, d, *J* 9.3, 1-H); δ_C (100.625 MHz; $CDCl_3$) 33.8 (NCH_3), 55.3 (OCH_3), 108.4 (10-C)[a], 108.8 (2-C)[a], 116.8 (4-C)[a], 117.5 (4a-C)[b], 117.6 (7a-C)[b], 119.3 (7-C)[c], 119.4 (8-C)[c], 119.5 (5-C)[c], 119.7 (6-C)[c], 123.1 (6a-C)[b], 123.6 (1-C)[d], 124.2 (9-C)[d], 135.2 (10a-C)[e], 135.9 (1a-C)[e], 140.5 (11a-C)[e] and 156.6 (3-C); *m*/*z* 261 (M^+, 100%), 246 (4), 218 (45), 130 (13) and 108 (10).

11-Benzyl-11*H*-benzo[*a*]carbazole 11d. The *product* **11d** (56 mg, 37%) was isolated as a colourless solid; mp 145–147 °C (ethyl acetate–hexane) (Found: M^+ 307.1378. $C_{23}H_{17}N$ requires *M*, 307.1361); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020 (ArC–H), 1523 (ArC=C), 1424 (C–N) and 787 (ArH oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 6.01 (2H, s, NCH_2Ph), 7.23–7.41 (7H, m, 7 × ArH), 7.42–7.47 (3H, m, 3 × ArH), 7.69 (1H, d, *J* 8.5, 6-H)[a], 8.00 (1H, ddd, *J* 0.6, 1.3 and 8.0, 4-H), 8.20 (1H, dd, *J* 0.8 and 7.7, 7-H), 8.22 (1H, d, *J* 8.5, 5-H)[a] and 8.25 (1H, dd, *J* 0.6 and 8.6, 1-H); δ_C (100.625 MHz; $CDCl_3$) 49.7 (NCH_2Ph), 109.3 (10-C), 119.1 (7-C)[a], 119.4 (4a-C)[b], 119.7 (8-C)[a], 120.0 (5-C)[a], 120.9 (6-C)[a], 122.0 (1-C)[a], 122.1 (7a-C)[b], 123.3 (6a-C)[b], 124.6 (3-C)[c], 125.1 (9-C)[c], 125.4 (2-C)[c], 126.0 (2 × ArCH), 127.5 (ArCH), 129.1 (2 × ArCH), 129.4 (4-C), 133.6 (10a-C)[d], 135.3 (1a-C)[d], 137.5 (ArC)[d] and 141.1 (11a-C)[d]; *m*/*z* 307 (M^+, 100%), 306 (4), 216 (89) and 91 (78).

***tert*-Butyl 1*H*-indole-1-carboxylate 15a.** Indole (2.00 g, 17.11 mmol) was dissolved in THF (150 cm^3) and treated with 4-dimethylaminopyridine (21 mg, 0.17 mmol) and di-*tert*-butyl dicarbonate (4.11 g, 18.82 mmol). The mixture was stirred at room temperature under an atmosphere of nitrogen for 16 h. The solvent was then removed under reduced pressure and the crude residue was purified by chromatography (10% ethyl acetate–hexane) to afford the *product* **15a** (3.72 g, 100%) as a clear oil identical in all respects with that described in the literature;[26] δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.67 [9H, s, $CO_2C(CH_3)_3$], 6.56 (1H, d, *J* 3.8, 3-H), 7.21–7.25 (1H, m, 5-H), 7.27–7.31 (1H, m, 6-H) and 7.53–7.58 (1H, m, 4-H); δ_C (100.625 MHz; $CDCl_3$) 28.2 [$CO_2C(CH_3)_3$], 83.6 [$CO_2C(CH_3)_3$], 107.2 (3-C), 115.1 (7-C), 120.9 (5-C)[a], 122.6 (6-C)[a], 124.1 (4-C)[a], 125.8 (2-C)[a], 130.5 (3a-C)[b], 135.2 (7a-C)[b] and 149.8 [$CO_2C(CH_3)_3$].

***tert*-Butyl 5-methoxy-1*H*-indole-1-carboxylate 15b.** 5-Methoxyindole (1.06 g, 7.10 mmol) was dissolved in THF (70 cm^3) and treated with dimethylaminopyridine (9 mg, 0.07 mmol) and di-*tert*-butyldicarbonate (1.70 g, 7.81 mmol). The mixture was stirred at room temperature under an atmosphere of nitrogen for 16 h. The solvent was then removed under reduced pressure and the crude residue was purified by chromatography (5% ethyl acetate–hexane) to afford the *product* **15b** (1.76 g, 100%) as a clear oil which crystallised on standing, identical in all respects with that decribed in the literature;[27] mp 74–76 °C (ethyl acetate–hexane) [lit.,[27] 75–76 °C (methanol)]; δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.65 [9H, s, $CO_2C(CH_3)_3$], 3.83 (3H, s, OCH_3), 6.48 (1H, d, *J* 3.7, 3-H), 6.92 (1H, dd, *J* 2.5 and 9.0, 6-H), 7.01 (1H, d, *J* 2.5, 4-H), 7.55 (1H, d, *J* 3.7, 2-H) and 8.02 (1H, br d, *J* 9.0, 7-H); δ_C (50.32 MHz; $CDCl_3$) 28.1 [$CO_2C(CH_3)_3$], 55.6 (OCH_3), 83.4 [$CO_2C(CH_3)_3$], 103.4 (3-C)[a], 107.0 (6-C)[a], 112.9 (4-C)[a], 115.8 (7-C)[a], 126.4 (2-C), 129.9 (7a-C)[b], 131.3 (3a-C)[b], 149.5 (5-C) and 155.8 [$CO_2C(CH_3)_3$].

General method for the preparation of indoleboronic acids

Typically, tetramethylpiperidine (5.15 mmol) in THF (10 cm^3) was cooled to −78 °C under an atmosphere of nitrogen and treated with *n*-butyllithium (4.3 cm^3, 5.85 mmol). The mixture was stirred at −78 °C for 10 min, then warmed to 0 °C within 30 min. The mixture was again cooled to −78 °C and the lithium tetramethylpiperidide generated was treated with *tert*-butyl 1*H*-indole-1-carboxylate **15a** or *tert*-butyl 5-methoxy-1*H*-indole-1-carboxylate **15b** (4.68 mmol) in THF (20 cm^3). The mixture was stirred at −78 °C for 80 min. Freshly distilled triisopropyl borate (7.02 mmol) in THF (10 cm^3) was then added, and the reaction mixture was stirred for 30 min at −78 °C before being warmed to room temperature. The reaction mixture was quenched with water (50 cm^3), acidified with an aqueous 10% hydrochloric acid solution, and extracted into ethyl acetate (3 × 50 cm^3). The combined organic phases were dried with magnesium sulfate and the solvent was evaporated under reduced pressure to afford off-white crystalline materials in quantitative yields, which were used without further purification or characterisation. 1-(*tert*-Butoxycarbonyl)-1*H*-indol-2-

ylboronic acid **14a** and 1-(*tert*-butoxycarbonyl)-5-methoxy-1*H*-indol-2-ylboronic acid **14b** were prepared by this method.

tert-Butyl 2-(3-methyl-2-pyridyl)-1*H*-indole-1-carboxylate 17a

A deoxygenated solution of 1-(*tert*-butoxycarbonyl)-1*H*-indol-2-ylboronic acid **14a** (489 mg, 1.87 mmol) and 2-bromo-3-methylpyridine **16** (226 mg, 1.25 mmol) in DME (15 cm^3) was added to $Pd(PPh_3)_4$ (10%, 144 mg, 0.12 mmol) under a nitrogen atmosphere with stirring. To this was added a deoxygenated aqueous sodium carbonate solution (2 M, 2.6 cm^3, 556 mg, 5.2 mmol). The mixture was then heated at reflux for 18 h. After this time the mixture was cooled to room temperature and quenched with water (15 cm^3). The organic material was extracted into dichloromethane (3 × 30 cm^3) and the combined organic extracts dried with sodium sulfate. The solvent was evaporated under reduced pressure and the resulting residue subjected to column chromatography (10–30% ethyl acetate–hexane) to afford the *product* **17a** (383 mg, 99%) as a clear oil (Found: M^+ 308.1513. $C_{19}H_{20}N_2O_2$ requires *M*, 308.1525); ν_{max}(film)/cm^{-1} 2980 (ArC–H), 1734 (CO_2R), 1586 and 1561 (ArC=C) and 1337 (C–O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.25 [9H, s, $CO_2C(CH_3)_3$], 2.24 (3H, s, $ArCH_3$), 6.61 (1H, s, 3-H), 7.19 (1H, dd, *J* 4.8 and 7.7, 5′-H), 7.22–7.25 (1H, m, 5-H), 7.34 (1H, ddd, *J* 1.1, 7.3 and 8.4, 6-H), 7.52 (1H, dd, *J* 0.8 and 7.7, 4′-H), 7.56 (1H, d, *J* 7.7, 4-H), 8.27 (1H, d, *J* 8.4, 7-H) and 8.48 (1H, dd, *J* 0.8 and 4.8, 6′-H); δ_C (100.625 MHz; $CDCl_3$) 18.9 ($ArCH_3$), 27.4 [$CO_2C(CH_3)_3$], 82.9 [$CO_2C(CH_3)_3$], 109.9 (3-C), 115.3 (5′-C)[a], 120.6 (5-C)[a], 122.6 (6-C)[a], 122.7 (4′-C)[a], 124.4 (4-C)[a], 129.0 (2-C)[b], 132.6 (3a-C)[b], 136.6 (7a-C)[b], 137.2 (7-C), 137.6 (3′-C), 146.1 (6′-C), 149.6 (2′-C) and 153.2 [$CO_2C(CH_3)_3$]; *m*/*z* 308 (M^+, 17%), 235 (6), 208 (100), 207 (64) and 57 (46).

tert-Butyl 5-methoxy-2-(3-methyl-2-pyridyl)-1*H*-indole-1-carboxylate 17b

A deoxygenated solution of 1-(*tert*-butoxycarbonyl)-5-methoxy-1*H*-indol-2-ylboronic acid **14b** (303 mg, 1.04 mmol) and 2-bromo-3-methylpyridine **16** (126 mg, 0.69 mmol) in DME (5 cm^3) was added to $Pd(PPh_3)_4$ (10%, 80 mg, 0.07 mmol) under a nitrogen atmosphere with stirring. To this was added a deoxygenated aqueous sodium carbonate solution (2 M, 1.5 cm^3, 309 mg, 2.9 mmol). The mixture was then heated at reflux for 18 h. After this time the mixture was cooled to room temperature and quenched with water (10 cm^3). The organic material was extracted into ethyl acetate (3 × 30 cm^3) and the combined organic extracts dried with magnesium sulfate. The solvent was evaporated under reduced pressure and the crude residue purified by column chromatography (10–20% ethyl acetate–hexane) to afford the *product* **17b** (182 mg, 77%) as a clear oil (Found: M^+ 338.1640. $C_{20}H_{22}N_2O_3$ requires *M*, 338.1630); ν_{max}(film)/cm^{-1} 2980 (ArC–H), 2848 (OCH_3), 1729 (CO_2R), 1625 and 1586 (ArC=C), 1235 (C–O) and 850 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.25 [9H, s, $CO_2C(CH_3)_3$], 2.24 (3H, s, $ArCH_3$), 3.86 (3H, s, OCH_3), 6.54 (1H, s, 3-H), 6.96 (1H, dd, *J* 2.4 and 9.0, 6-H), 7.04 (1H, d, *J* 2.4, 4-H), 7.21 (1H, dd, *J* 4.8 and 7.7, 5′-H), 7.55 (1H, dd, *J* 0.6 and 7.7, 4′-H), 8.15 (1H, dd, *J* 0.6 and 9.0, 7-H) and 8.49 (1H, dd, *J* 0.6 and 4.8, 6′-H); δ_C (50.32 MHz; $CDCl_3$) 18.9 ($ArCH_3$), 27.5 [$CO_2C(CH_3)_3$], 55.6 (OCH_3), 82.9 [$CO_2C(CH_3)_3$], 103.1 (3-C), 109.8 (6-C), 113.3 (4-C), 116.2 (5′-C), 122.7 (4′-C), 129.9 (2-C)[a], 131.4 (7a-C)[a], 132.7 (3a-C)[a], 137.2 (7-C), 138.3 (3′-C), 146.2 (6′-C), 149.6 (5-C)[b], 153.4 (2′-C)[b] and 155.9 [$CO_2C(CH_3)_3$]; *m*/*z* 338 (M^+, 18%), 265 (4), 238 (100), 223 (34), 130 (11), 119 (13), 69 (54) and 57 (68).

2-(3-Methyl-2-pyridyl)-1*H*-indole 18a

tert-Butyl 2-(3-methyl-2-pyridyl)-1*H*-indole-1-carboxylate **17a** (256 mg, 0.83 mmol) was dissolved in dichloromethane (50 cm^3) and adsorbed onto silica gel 60 (70–230 mesh, 8 g). The flask containing the mixture was then placed in an alumina bath and irradiated with microwave radiation from a conventional 700 W microwave oven on 100% power for 3 min. The product was washed from the silica with ethyl acetate (3 × 30 cm^3) and acetone (3 × 30 cm^3) and the solvent was evaporated under reduced pressure. The resulting residue was subjected to column chromatography (10% ethyl acetate–hexane) to afford the *product* **17a** (165 mg, 96%) as a pale yellow solid; mp 162–163.5 °C (methanol) (Found: M^+ 208.0990. $C_{14}H_{12}N_2$ requires *M*, 208.1001); ν_{max}($CHCl_3$)/cm^{-1} 3112 (NH), 3019 (ArC–H), 1586 and 1522 (ArC=C), 1419 (C–N) and 794 (ArH oop); δ_H (400 MHz; $CDCl_3$ and DMSO-d_6; Me_4Si) 2.64 (3H, s, $ArCH_3$), 6.97 (1H, s, 3-H), 7.08 (1H, dd, *J* 4.6 and 7.7, 5′-H), 7.10–7.12 (1H, m, 6-H), 7.20–7.24 (1H, m, 5-H), 7.39 (1H, dd, *J* 0.8 and 8.2, 4-H), 7.53 (1H, dd, *J* 0.9 and 7.7, 4′-H), 7.67 (1H, dd, *J* 0.7 and 7.9, 7-H), 8.47 (1H, dd, *J* 0.9 and 4.6, 6′-H) and 10.00 (1H, br s, NH); δ_C (50.32 MHz; $CDCl_3$ and DMSO-d_6) 21.5 ($ArCH_3$), 104.3 (3-C), 111.1 (7-C)[a], 119.8 (5-C)[a], 121.3 (6-C)[a], 121.6 (2-C), 123.3 (4-C)[a], 129.4 (5′-C)[a], 130.7 (3′-C)[a], 135.5 (4′-C), 136.1 (3a-C), 139.3 (6′-C), 146.4 (7a-C) and 148.7 (2′-C); *m*/*z* 208 (M^+, 99%), 207 (100), 180 (9) and 103 (13).

5-Methoxy-2-(3-methyl-2-pyridyl)-1*H*-indole 18b

tert-Butyl 5-methoxy-2-(3-methyl-2-pyridyl)-1*H*-indole-1-carboxylate **17b** (176 mg, 0.52 mmol) was dissolved in dichloromethane (30 cm^3) and adsorbed onto silica gel 60 (70–230 mesh, 5 g). The flask containing the mixture was then placed in an alumina bath and irradiated with microwave radiation from a conventional 700 W microwave oven on 100% power for 3 min. The product was washed from the silica with ethyl acetate (3 × 30 cm^3) and acetone (3 × 30 cm^3) and the solvent was evaporated under reduced pressure. The resulting residue was subjected to column chromatography (10–20% ethyl acetate–hexane) to afford the *product* **18b** (106 mg, 86%) as an off-white solid; mp 122–123 °C (methanol) (Found: M^+ 238.1115. $C_{15}H_{14}N_2O$ requires *M*, 238.1106); ν_{max}($CHCl_3$)/cm^{-1} 3446 (NH), 3008 (ArC–H), 1585, 1572 and 1535 (ArC=C), 1441 (C–N), 1208 (OCH_3) and 839 (ArH oop); δ_H (200 MHz; $CDCl_3$ and DMSO-d_6; Me_4Si) 2.63 (3H, s, $ArCH_3$), 3.86 (3H, s, OCH_3), 6.89 (1H, dd, *J* 2.5 and 8.8, 6-H), 6.91 (1H, dd, *J* 0.7 and 2.5, 4-H), 7.08 (1H, dd, *J* 4.7 and 7.7, 5′-H), 7.12 (1H, s, 3-H), 7.28 (1H, dd, *J* 0.7 and 8.8, 7-H), 7.53 (1H, dd, *J* 1.7 and 7.7, 4′-H), 7.46 (1H, dd, *J* 1.7 and 4.7, 6′-H) and 9.94 (1H, br s, NH); δ_C (100.625 MHz; $CDCl_3$) 21.4 ($ArCH_3$), 55.8 (OCH_3), 102.4 (3-C)[a], 103.8 (4-C)[a], 111.9 (6-C)[a], 113.9 (5′-C)[a], 121.4 (7-C)[a], 129.6 (2-C)[b], 130.5 (3a-C)[b], 130.9 (7a-C)[b], 136.7 (3′-C)[b], 139.3 (4′-C), 146.3 (6′-C), 148.7 (2′-C)[c] and 154.1 (5-C)[c]; *m*/*z* 238 (M^+, 100%), 223 (63), 195 (31), 168 (6), 119 (7) and 97 (5).

2-(3-Methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde 19a

Phosphorus oxychloride (0.08 cm^3, 0.87 mmol) was added dropwise to dry DMF (0.27 cm^3, 3.49 mmol) at 0 °C. The resulting mixture was warmed to room temperature and treated with 2-(3-methyl-2-pyridyl)-1*H*-indole **18a** (165 mg, 0.79 mmol) in DMF (3 cm^3). The mixture was heated to 35 °C and left stirring at this temperature under a nitrogen atmosphere for 1 h. After this time, ice was added and the mixture was made basic with 2 M aqueous sodium hydroxide. The mixture was then heated at reflux for 30 min. Once the mixture had cooled, the organic material was extracted into chloroform (3 × 30 cm^3) and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting residue was subjected to column chromatography (20% ethyl acetate–hexane followed by 10% methanol–ethyl acetate) to afford the *product* **19a** (171 mg, 91%) as an off-white solid; mp 203–204.5 °C (methanol) (Found: M^+ 236.0960. $C_{15}H_{12}N_2O$ requires *M*, 236.0950); ν_{max}($CHCl_3$)/cm^{-1} 3450 (NH), 3019 (ArC–H), 1656 (CHO), 1583 and 1522 (ArC=C), 1448 (C–N) and 850 (ArH oop); δ_H (400 MHz; $CDCl_3$ and DMSO-d_6; Me_4Si) 2.39 (3H, s,

$ArCH_3$), 7.25–7.31 (2H, m, 5-H and 6-H), 7.37 (1H, dd, *J* 4.3 and 7.7, 5′-H), 7.49–7.51 (1H, m, 4-H), 7.71 (1H, d, *J* 7.7, 4′-H), 8.29–8.31 (1H, m, 7-H), 8.58 (1H, d, *J* 4.3, 6′-H), 9.83 (1H, s, CHO) and 11.89 (1H, br s, NH); δ_C (100.625 MHz; $CDCl_3$ and DMSO-d_6) 18.5 ($ArCH_3$), 111.3 (5′-C)[a], 114.8 (3-C)[b], 120.9 (5-C)[a], 121.8 (6-C)[a], 123.0 (4′-C)[a], 123.2 (4-C)[a], 124.5 (2-C)[b], 133.0 (3a-C)[b], 135.4 (7a-C)[b], 137.8 (7-C)[c], 146.2 (6′-C)[c], 146.3 (3′-C)[d], 148.3 (2′-C)[d] and 185.5 (CHO); *m*/*z* 236 (M^+, 41%), 208 (62), 207 (100), 180 (10), 103 (11) and 89 (6).

5-Methoxy-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde 19b

Phosphorus oxychloride (0.04 cm^3, 0.46 mmol) was added dropwise to dry DMF (0.14 cm^3, 1.83 mmol) at 0 °C. The resulting mixture was warmed to room temperature and treated with 5-methoxy-2-(3-methyl-2-pyridyl)-1*H*-indole **18b** (99 mg, 0.42 mmol) in DMF (3 cm^3). The mixture was heated to 35 °C and left stirring at this temperature under a nitrogen atmosphere for 1 h. After this time, ice was added and the mixture was made basic with 2 M aqueous sodium hydroxide. The mixture was then heated at reflux for 30 min. Once the mixture had cooled, the organic material was extracted into chloroform (3 × 30 cm^3) and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting residue was subjected to column chromatography (20% ethyl acetate–hexane followed by 10% methanol–ethyl acetate) to afford the *product* **19b** (93 mg, 84%) as a pale yellow solid; mp 181–182 °C (methanol) (Found: M^+ 266.1053. C, 72.60; H, 5.30; N, 10.40%. $C_{16}H_{14}N_2O_2$ requires *M*, 266.1055. C, 72.20; H, 5.30; N, 10.50%); ν_{max}($CHCl_3$)/cm^{-1} 3443 (NH), 3019 (ArC–H), 1653 (CHO), 1522 (ArC=C), 1423 (C–N), 1220 (C–O) and 772 (ArH oop); δ_H (400 MHz; $CDCl_3$ and DMSO-d_6; Me_4Si) 2.40 (3H, s, $ArCH_3$), 3.89 (3H, s, OCH_3), 6.92 (1H, dd, *J* 2.5 and 8.8, 6-H), 7.35–7.40 (2H, m, 5′-H and 7-H), 7.71 (1H, d, *J* 7.5, 4′-H), 7.82 (1H, d, *J* 2.5, 4-H), 8.58 (1H, d, *J* 3.7, 6′-H), 9.81 (1H, s, CHO) and 11.68 (1H, br s, NH); δ_C (50.32 MHz; $CDCl_3$ and DMSO-d_6) 18.7 ($ArCH_3$), 55.1 (OCH_3), 102.5 (6-C)[a], 112.3 (5′-C)[a], 113.6 (4-C)[a], 115.0 (3-C), 123.3 (7-C)[a], 125.5 (2-C)[b], 130.5 (7a-C)[b], 133.2 (3a-C)[b], 138.0 (4′-C), 146.4 (6′-C), 148.6 (2′-C and 3′-C)[c], 155.8 (5-C)[c] and 185.8 (CHO); *m*/*z* 266 (M^+, 86%), 251 (3), 238 (64), 237 (20), 223 (100) and 195 (38).

1-Methyl-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde 13a

2-(3-Methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde **19a** (171 mg, 0.73 mmol) was dissolved in THF (5 cm^3) and cooled to −78 °C. Potassium hexamethyldisilazide (KHMDS, 0.5 M solution in toluene, 2.2 cm^3, 1.09 mmol) was added dropwise and the reaction mixture stirred at −78 °C for 30 min. Methyl iodide (0.11 cm^3, 1.81 mmol) was added and the reaction mixture stirred for a further 30 min at −78 °C. After this time the mixture was warmed to room temperature and stirred for 30 min. The mixture was then quenched with water (20 cm^3) and extracted with diethyl ether (3 × 30 cm^3). The organic fractions were combined and dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude residue was purified by chromatography (10% methanol–ethyl acetate) to afford the *product* **13a** (168 mg, 93%) as a clear oil (Found: M^+ 250.1094. $C_{16}H_{14}N_2O$ requires *M*, 250.1106); ν_{max}(film)/cm^{-1} 3011 (ArC–H), 1655 (CHO), 1612, 1579 and 1535 (ArC=C), 1468 (C–N) and 753 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.21 (3H, s, $ArCH_3$), 3.57 (3H, s, NCH_3), 7.33–7.43 (4H, m, 4-H, 5-H, 5′-H and 6-H), 7.71 (1H, dd, *J* 0.9 and 7.8, 4′-H), 8.36–8.42 (1H, m, 7-H), 8.63 (1H, dd, *J* 0.9 and 4.8, 6′-H) and 9.64 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 18.9 ($ArCH_3$), 30.7 (NCH_3), 109.8 (7-C), 115.8 (3-C), 122.2 (5-C)[a], 123.2 (6-C)[a], 124.0 (4-C)[a], 124.4 (5′-C)[a], 125.0 (2-C)[b], 134.8 (3a-C)[b], 137.4 (7a-C)[b], 138.3 (4′-C), 147.5 (6′-C), 148.0 (2′-C)[c], 148.1 (3′-C)[c] and 185.3 (CHO); *m*/*z* 250 (M^+, 100%), 249 (6), 235 (9), 222 (45), 221 (100), 207 (22) and 130 (17).

5-Methoxy-1-methyl-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde 13b

5-Methoxy-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde **19b** (93 mg, 0.35 mmol) was dissolved in THF (5 cm^3) and cooled to −78 °C. Potassium hexamethyldisilazide (KHMDS, 0.5 M solution in toluene, 1.1 cm^3, 0.52 mmol) was added dropwise and the reaction mixture stirred at −78 °C for 30 min. Methyl iodide (0.05 cm^3, 0.87 mmol) was added and the reaction mixture stirred for a further 30 min at −78 °C. After this time the mixture was warmed to room temperature and stirred for 30 min. The mixture was then quenched with water (20 cm^3) and extracted with ethyl acetate (3 × 30 cm^3). The organic fractions were combined and dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude residue was purified by chromatography (20–30% ethyl acetate–hexane) to afford the *product* **13b** (81 mg, 83%) as a clear oil (Found: M^+ 280.1212. $C_{15}H_{10}N_2$ requires *M*, 280.1212); ν_{max}(film)/cm^{-1} 2934 (ArC–H), 2832 (OCH_3), 1655 (CHO), 1618, 1584 and 1526 (ArC=C), 1479 (C–N) and 797 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.25 (3H, s, $ArCH_3$), 3.57 (3H, s, NCH_3), 3.93 (3H, s, OCH_3), 7.01 (1H, dd, *J* 2.5 and 8.9, 6-H), 7.31 (1H, d, *J* 8.9, 7-H), 7.39 (1H, dd, *J* 4.8 and 7.8, 5′-H), 7.71 (1H, dd, *J* 1.6 and 7.8, 4′-H), 7.88 (1H, d, *J* 2.5, 4-H), 8.64 (1H, dd, *J* 1.6 and 4.8, 6′-H) and 9.59 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 18.9 ($ArCH_3$), 30.8 (NCH_3), 55.7 (OCH_3), 103.4 (6-C)[a], 110.7 (4-C)[a], 114.4 (5′-C)[a], 115.6 (3-C), 124.3 (7-C)[a], 125.7 (2-C)[b], 132.3 (3a-C)[b], 134.7 (7a-C)[b], 138.3 (4′-C), 147.5 (6′-C), 148.1 (2′-C and 3′-C), 156.9 (5-C)[c] and 185.3 (CHO); *m*/*z* 280 (M^+, 100%), 279 (7), 265 (19), 252 (49), 251 (86), 237 (42), 209 (16) and 160 (11).

1-Benzyl-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde 13c

2-(3-Methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde **19a** (158 mg, 0.67 mmol) was dissolved in THF (10 cm^3) and cooled to −78 °C. Potassium hexamethyldisilazide (KHMDS, 0.5 M solution in toluene, 2.0 cm^3, 1.00 mmol) was added dropwise and the reaction mixture stirred at −78 °C for 30 min. Benzyl bromide (0.12 cm^3, 1.00 mmol) was added and the reaction mixture stirred for a further 30 min at −78 °C. After this time the mixture was warmed to room temperature and stirred for 30 min. The mixture was then quenched with water (20 cm^3) and extracted with diethyl ether (3 × 30 cm^3). The organic fractions were combined and dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude residue was purified by chromatography (10% methanol–ethyl acetate) to afford the *product* **13c** (162 mg, 77%) as a clear oil (Found: M^+ 326.1422. $C_{22}H_{18}N_2O$ requires *M*, 326.1419); ν_{max}(film)/cm^{-1} 3058 (ArC–H), 1657 (CHO), 1611, 1576 and 1535 (ArC=C), 1458 (C–N) and 750 (ArH oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.97 (3H, s, $ArCH_3$), 5.23 (2H, d, *J* 2.4, NCH_2Ph), 6.90–6.92 (2H, m, 2 × ArH), 7.12–7.16 (3H, m, 3 × ArH), 7.28–7.35 (3H, m, 5′-H, 5-H and 6-H), 7.38–7.40 (1H, m, 4′-H), 7.55 (1H, ddd, *J* 0.6, 1.5 and 7.8, 4-H), 8.40–8.43 (1H, m, 7-H), 8.62 (1H, dd, *J* 1.2 and 4.7, 6′-H) and 9.67 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 18.7 ($ArCH_3$), 47.6 (NCH_2Ph), 110.5 (7-C), 116.0 (3-C), 122.1 (4-C), 123.2 (5′-C)[a], 124.1 (6-C)[a], 124.3 (5-C)[a], 125.0 (2-C), 126.7 (2 × ArCH), 127.7 (ArCH), 128.5 (2 × ArCH), 135.0 (3a-C)[b], 136.0 (ArC)[b], 138.2 (4′-C), 147.4 (6′-C), 147.7 (3′-C)[c], 148.0 (2′-C)[c] and 185.3 (CHO); *m*/*z* 326 (M^+, 72%), 325 (4), 311 (26), 298 (11), 297 (24), 235 (100), 221 (27), 207 (44) and 91 (66).

11-Methyl-11*H*-pyrido[2,3-*a*]carbazole 20a

1-Methyl-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde **13a** (80 mg, 0.32 mmol) was dissolved in dry DMF (15 cm^3). Potassium *tert*-butoxide (143 mg, 1.27 mmol) was added to the reaction mixture, which was heated under nitrogen at 80 °C and irradiated with a high-pressure mercury lamp through a quartz filter for 10 min. The reaction mixture was quenched with water

(50 cm^3) and the organic material extracted into diethyl ether (3 × 50 cm^3). The organic layer was dried with magnesium sulfate and filtered. The diethyl ether was then evaporated under reduced pressure to afford a pale residue which was subjected to chromatography (20% ethyl acetate–hexane) to afford the *product* **20a** (58 mg, 78%) as a pale yellow solid; mp 129–130.5 °C (ethyl acetate–hexane) (Found: M$^+$, 232.1000. C, 82.70; H, 5.20; N, 12.00%. $C_{16}H_{12}N_2$ requires *M*, 232.1001. C, 82.73; H, 5.20; N, 12.05%); ν_{max}($CHCl_3$)/cm^{-1} 3019 (ArC–H), 1604 and 1522 (ArC=C), 1211, 772 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 4.66 (3H, s, NCH_3), 7.29–7.34 (1H, m, 10-H), 7.34 (1H, dd, *J* 4.3 and 8.3, 3-H), 7.46 (1H, d, *J* 8.5, 6-H), 7.50–7.53 (2H, m, 8-H and 9-H), 8.14 (1H, d, *J* 8.5, 5-H), 8.11–8.21 (2H, m, 4-H and 7-H) and 8.87 (1H, dd, *J* 1.8 and 4.3, 2-H); δ_C (100.625 MHz; $CDCl_3$) 30.8 (NCH_3), 109.3 (10-C), 118.5 (6-C)[a], 119.5 (3-C)[a], 119.7 (5-C)[a], 119.8 (7-C)[a], 119.9 (9-C)[a], 121.0 (7a-C)[b], 122.6 (10a-C)[b], 125.2 (8-C), 127.7 (4a-C)[b], 134.4 (6a-C)[c], 136.1 (4-C), 139.4 (11a-C)[c], 140.9 (1a-C)[c] and 147.3 (2-C); *m*/*z* 232 (M$^+$, 75%), 231 (100), 204 (7), 116 (11) and 102 (8).

8-Methoxy-11-methyl-11*H*-pyrido[2,3-*a*]carbazole 20b

5-Methoxy-1-methyl-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde **13b** (76 mg, 0.27 mmol) was dissolved in dry DMF (15 cm^3). Potassium *tert*-butoxide (122 mg, 1.08 mmol) was added to the reaction mixture, which was heated under nitrogen at 80 °C and irradiated with a high-pressure mercury lamp through a quartz filter for 10 min. The reaction mixture was quenched with water (50 cm^3) and the organic material extracted into diethyl ether (3 × 50 cm^3). The organic layer was separated, dried with magnesium sulfate and filtered. The diethyl ether was then evaporated under reduced pressure to afford a pale residue which was subjected to chromatography (5–10% ethyl acetate–hexane) to afford the desired *product* **20b** (55 mg, 77%) as an off-white solid; mp 122–123 °C (ethyl acetate–hexane) (Found: M$^+$, 262.1097. C, 77.40; H, 5.20; N, 10.20%. $C_{17}H_{14}N_2O$ requires *M*, 262.1106. C, 77.80; H, 5.40; N, 10.70%); ν_{max}($CHCl_3$)/cm^{-1} 3019 (ArC–H), 1602, 1578 and 1522 (ArC=C), 1220 (C–O) and 772 (ArH oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 3.92 (3H, s, NCH_3), 4.61 (3H, s, OCH_3), 7.14 (1H, dd, *J* 2.4 and 8.8, 9-H), 7.33 (1H, dd, *J* 4.3 and 8.2, 3-H), 7.40 (1H, d, *J* 8.8, 10-H), 7.40 (1H, d, *J* 8.4, 6-H), 7.55 (1H, d, *J* 2.4, 7-H), 8.07 (1H, d, *J* 8.4, 5-H), 8.16 (1H, dd, *J* 1.8 and 8.2, 4-H) and 8.85 (1H, dd, *J* 1.8 and 4.3, 2-H); δ_C (50.32 MHz; $CDCl_3$) 33.0 (NCH_3), 56.0 (OCH_3), 101.9 (7-C), 110.1 (10-C)[a], 115.0 (9-C), 118.0 (6-C)[a], 119.6 (3-C), 119.9 (5-C), 120.7 (7a-C)[b], 122.8 (10a-C)[b], 127.7 (4a-C)[b], 134.8 (6a-C)[c], 136.0 (4-C and 11a-C)[c], 139.5 (1a-C)[c], 147.2 (2-C) and 154.0 (8-C); *m*/*z* 262 (M$^+$, 100%), 261 (28), 248 (10), 247 (56), 219 (32) and 218 (27).

11-Benzyl-11*H*-pyrido[2,3-*a*]carbazole 20c

1-Benzyl-2-(3-methyl-2-pyridyl)-1*H*-indole-3-carbaldehyde **13c** (148 mg, 0.46 mmol) was dissolved in dry DMF (15 cm^3). Potassium *tert*-butoxide (205 mg, 1.83 mmol) was added to the reaction mixture, which was heated under nitrogen at 80 °C and irradiated with a high-pressure mercury lamp through a quartz filter for 10 min. The reaction mixture was quenched with water (50 cm^3) and the organic material extracted into diethyl ether (3 × 50 cm^3). The organic layer was dried with magnesium sulfate and filtered. The diethyl ether was then evaporated under reduced pressure to afford a pale residue which was subjected to chromatography (5–10% ethyl acetate–hexane) to afford the desired *product* **20c** (105 mg, 75%) as a white solid; mp 110–111 °C (ethyl acetate) (Found: M$^+$, 308.1317. $C_{22}H_{16}N_2$ requires *M*, 308.1314); ν_{max}($CHCl_3$)/cm^{-1} 3020 (ArC–H), 1573 and 1524 (ArC=C) and 787 (ArH oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 6.66 (2H, s, NCH_2Ph), 7.11–7.21 (5H, m, 5 × ArCH), 7.29 (1H, ddd, *J* 0.9, 7.0 and 7.8, 8-H), 7.33 (1H, dd, *J* 4.2 and 8.2, 3-H), 7.42 (1H, ddd, *J* 1.0, 7.0 and 8.2, 9-H), 7.48 (1H, d, *J* 8.2, 10-H), 7.53 (1H, d, *J* 8.3, 6-H), 8.16 (1H, d, *J* 7.8, 7-H), 8.19 (1H, dd, *J* 1.7 and 8.2, 4-H), 8.20 (1H, d, *J* 8.3, 5-H) and 8.80 (1H, dd, *J* 1.7 and 4.2, 2-H); δ_C (100.625 MHz; $CDCl_3$) 49.1 (NCH_2Ph), 110.3 (10-C), 119.6 (6-C), 119.8 (3-C and 9-C)[a], 120.0 (5-C)[a], 121.4 (7a-C)[b], 123.1 (10a-C)[b], 125.4 (9-C), 126.8 (3 × ArCH), 127.8 (4a-C)[b], 128.4 (2 × ArCH), 134.1 (6a-C)[c], 136.1 (4-C), 139.2 (11a-C)[c], 139.2 (ArCH)[c], 140.5 (1a-C) and 147.6 (2-C); *m*/*z* 308 (M$^+$, 97%), 307 (32), 232 (21), 231 (100), 217 (16), 154 (14) and 91 (38).

11*H*-Pyrido[2,3-*a*]carbazole 21

11-Benzyl-11*H*-pyrido[2,3-*a*]carbazole **20c** (50 mg, 0.16 mmol) in dry benzene (2.5 cm^3) was added to aluminium trichloride (87 mg, 0.65 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 40 min, and then stirred for a further 2 h at room temperature. After this time the reaction mixture was quenched with water (10 cm^3) and the organic material extracted into ethyl acetate (3 × 15 cm^3). The organic layer was washed successively with 5% aqueous sodium hydrogen carbonate (30 cm^3) and a saturated sodium chloride solution (30 cm^3), dried with magnesium sulfate and filtered. The diethyl ether was then evaporated under reduced pressure and the crude residue was subjected to chromatography (10–30% ethyl acetate–hexane) to afford the desired *product* **21** (28 mg, 80%) as a white solid; mp 171–172 °C (toluene) (lit.,[28] 172–173 °C) (Found: M$^+$, 218.0843. *M*, $C_{15}H_{10}N_2$ requires *M*, 218.0844); ν_{max}($CHCl_3$)/cm^{-1} 3299 (NH), 3030 (ArC–H), 1611, 1591 and 1526 (ArC=C), 1373 (C–N) and 754 (ArH oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.21–7.44 (3H, m, 8-H, 9-H and 10-H), 7.46 (1H, dd, *J* 4.3 and 8.2, 3-H), 7.57 (1H, d, *J* 8.5, 6-H), 8.15 (1H, dd, *J* 0.5 and 7.9, 7-H), 8.21 (1H, d, *J* 8.5, 5-H), 8.31 (1H, dd, *J* 1.6 and 8.2, 4-H), 8.93 (1H, dd, *J* 1.6 and 4.3, 2-H) and 11.60 (1H, br s, NH); δ_C (100.625 MHz; $CDCl_3$) 111.6 (10-C), 118.5 (9-C)[a], 119.7 (3-C)[a], 120.2 (6-C)[a], 120.4 (7-C)[a], 120.5 (8-C)[a], 121.4 (7a-C)[b], 123.7 (10a-C)[b], 125.5 (5-C), 127.1 (4a-C)[b], 135.4 (6a-C)[c], 136.9 (4-C), 137.4 (11a-C)[c], 139.3 (1a-C)[c] and 148.1 (2-C); *m*/*z* 218 (M$^+$, 100%), 217 (13), 201 (3) and 190 (6).

Acknowledgements

This work was supported by the National Research Foundation (NRF) and the University of the Witwatersrand. A. L. R. would like to thank the AECI for additional financial support. Mrs S. Heiss of this University and Dr P. Boshoff (Cape Technikon) are thanked for recording NMR spectra and mass spectra respectively.

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