Synthesis of Azapyrrolo[3,2,1-*jk*]carbazoles, Azaindolo[3,2,1-*jk*]carbazoles, and Carbazole-1-carbonitriles by Gas-Phase Cyclization of Aryl Radicals

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Abstract: Flash vacuum pyrolysis of *N*-(2-nitroheteroaryl)indoles or -carbazoles at 875 °C gave aza analogues of strained pyrrolo[3,2,1-*jk*]carbazole (50–55%) and indolo[3,2,1-*jk*]carbazole (55–85%) ring systems, respectively, through generation of aryl radicals and cyclization. The corresponding reactions of *N*-(2-nitroheteroaryl)indazoles and -benzimidazoles at 850 °C, on the other hand, gave carbazole-1-carbonitrile derivatives (56–64%) by a mechanism involving radical ring opening and hydrogen atom rearrangement.

Key words: gas-phase reactions, cyclizations, heterocycles, pyrolysis, nitro compounds

In previous papers,[1,2] we have shown that flash vacuum pyrolysis (FVP) of aromatic nitro compounds provides aryl radical intermediates that, in appropriate frameworks, cyclize efficiently to provide the strained pyrrolo[3,2,1-*jk*]carbazole **1** or indolo[3,2,1-*jk*]carbazole **2** ring systems (Figure 1) in just two steps from commercially available starting materials.

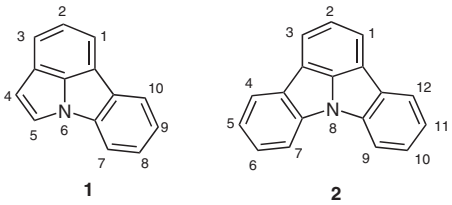
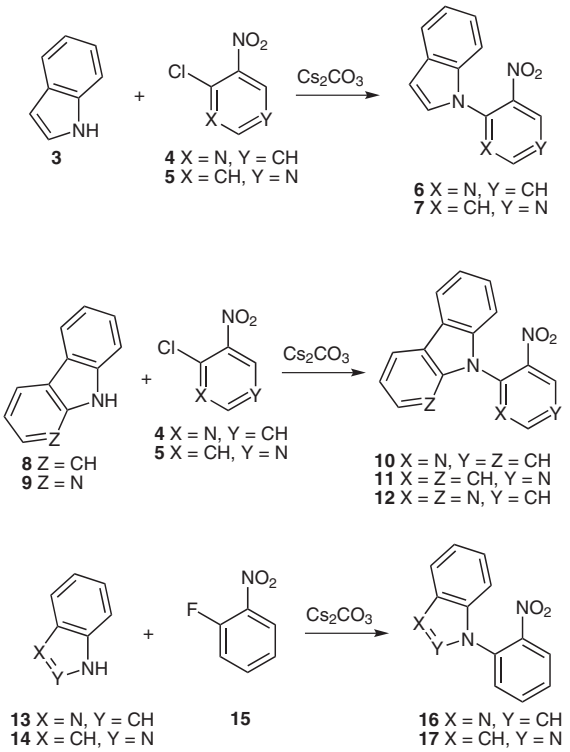


Figure 1

Because the indolo[3,2,1-*jk*]carbazoles **2**, in particular, show interesting properties under electrooxidation conditions,[2] we examined the effects on the ring synthesis of nitrogen atoms at various positions in the five- and six-membered rings of the precursors. When the heteroatom is present in a six-membered ring, the method provides useful synthetic routes to azapyrrolo[3,2,1-*jk*]carbazoles and azaindolo[3,2,1-*jk*]carbazoles. When a second heteroatom is present in the five-membered ring, ring opening and rearrangement take place under the FVP conditions to give carbazole-1-carbonitriles regiospecifically.

S_NAr reactions of N-heterocyclic nucleophiles with carbonate bases in dipolar aprotic solvents are well known.[1–3] However, the reactions of indole **3**, carbazole **8**, or 9*H*-pyrido[2,3-*b*]indole (**9**; α-carboline) with chloro(nitro)pyridines **4** or **5** required individual optimization because of the poor reactivity of the nucleophile and the sensitivity of the halo compound; details are given in the experimental section. In general, the most effective base was cesium carbonate, and anhydrous dimethyl sulfoxide or acetonitrile was the optimal solvent. Yields of products **6**, **7**, and **10–12** varied from 50 to 80% after chromatography (Scheme 1). At a late stage in the project, the use of palladium-catalyzed coupling[4] was studied for one case, and this proved to be at least as efficient as the S_NAr methods. Reactions of benzimidazole **13** or indazole **14** with 1-fluoro-2-nitrobenzene (**15**) at 125 °C in *N*,*N*-dimethylformamide provided the nitroaryl derivatives **16** and **17** in yields of 81 and 57%, respectively (Scheme 1).



Scheme 1

FVP of the nitro derivatives **6**, **7**, and **10–12** took place cleanly at 875 °C to provide the parent azapyrrolo[3,2,1-*jk*]carbazoles **18–19** (50–55%) and azaindolo[3,2,1-*jk*]carbazoles **20–22** (55–85%), all of which are new het-

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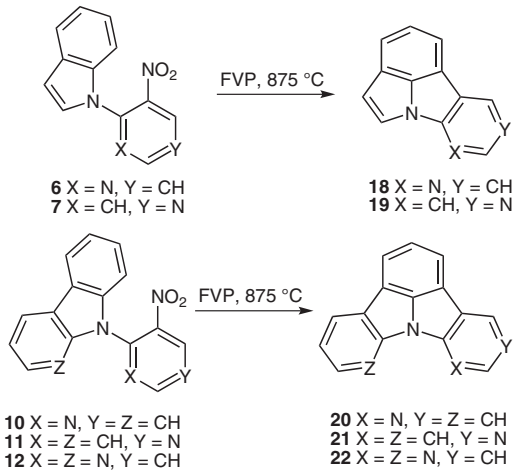
erocyclic systems (Scheme 2). Because of the reactivity of the nitrogen oxide byproducts, some modifications to the normal FVP trapping systems were required,[1,2] and these are described in the experimental section. Therefore, the increased strain in the azapyrrolo[3,2,1-*jk*]carbazole and azaindolo[3,2,1-*jk*]carbazole systems compared with **1** and **2**, which is the result of the presence of short C–N bonds in the six-membered ring(s), can clearly be accommodated, and the systems are stable even at 875 °C.



6 X = N, Y = CH
7 X = CH, Y = N

18 X = N, Y = CH
19 X = CH, Y = N

10 X = N, Y = Z = CH
11 X = Z = CH, Y = N
12 X = Z = N, Y = CH

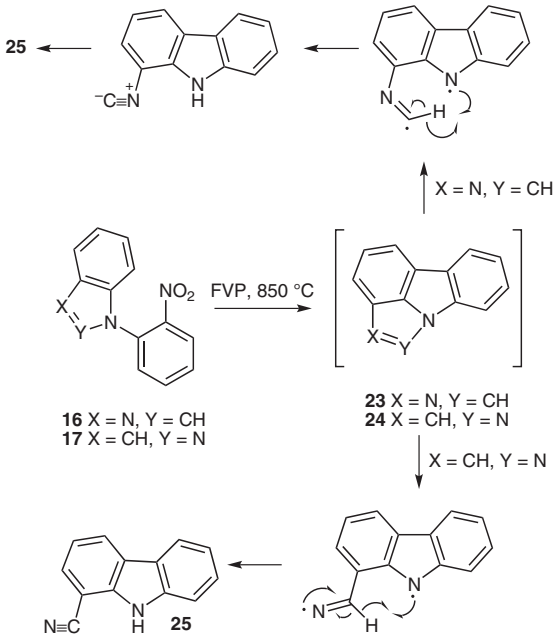
20 X = N, Y = Z = CH
21 X = Z = CH, Y = N
22 X = Z = N, Y = CH

Scheme 2

In contrast, FVP at 850 °C of the parent benzimidazole **16** and indazole **17** both gave carbazole-1-carbonitrile (**25**) (57% and 64%, respectively) as the sole product that was obtained in a significant yield. It is likely that the imidazolocarbazole (**23**) and the pyrazolocarbazole (**24**) are formed as intermediates, but these are too strained to survive the pyrolysis temperatures needed to break the C–NO_2 bond. Radical cleavage of the five-membered ring followed by hydrogen transfer gives the carbazole. In the benzimidazole series, the initial formation of an isocyanide may be followed by thermal rearrangement to the nitrile (Scheme 3),[5] although rearrangement at the imidoyl radical stage is also possible.

To explore the synthetic utility of this regiospecific route to carbazole-1-carbonitriles, we briefly studied the FVP reactions of the substituted benzimidazole precursors **26**–**29** (made by the method shown in Scheme 1). The sites of the substituents on the benzimidazole were chosen to avoid regiochemical problems at the arylation stage; those on the aryl ring (including the heteroatom) were chosen to avoid similar problems due to hydrogen atom rearrangements at the aryl radical stage.[6] In each case, the corresponding substituted carbazole-1-carbonitrile **30**–**33** was obtained as the major product. Carbazole-1-carbonitriles are relatively uncommon, and this synthetic route complements those involving stepwise functional group interconversions,[7] cycloaddition reactions,[8] or Friedel–Crafts-type processes.[9]

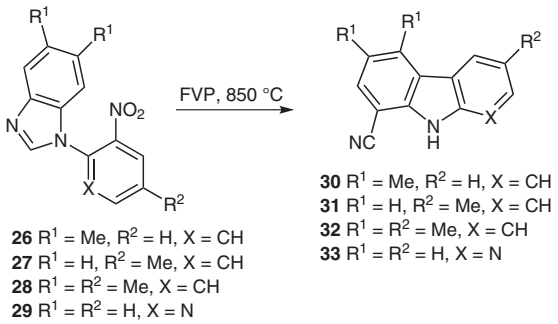
In conclusion, the parent members of new azapyrrolo[3,2,1-*jk*]carbazole and azaindolo[3,2,1-*jk*]carbazole



16 X = N, Y = CH
17 X = CH, Y = N

23 X = N, Y = CH
24 X = CH, Y = N

Scheme 3



26 R^1 = Me, R^2 = H, X = CH
27 R^1 = H, R^2 = Me, X = CH
28 R^1 = R^2 = Me, X = CH
29 R^1 = R^2 = H, X = N

30 R^1 = Me, R^2 = H, X = CH
31 R^1 = H, R^2 = Me, X = CH
32 R^1 = R^2 = Me, X = CH
33 R^1 = R^2 = H, X = N

Scheme 4

ring systems have been made by FVP of nitro-substituted pyridinylcarbazoles and -indoles. These results provide further examples of the effectiveness of this strategy for the formation of strained rings. In contrast to the thermal stability of these systems, the five-membered rings of **23** and **24** cleaved under the conditions required for their formation. Nevertheless, such reactions provide regiospecific routes to a range of carbazole-1-carbonitrile derivatives.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX250 spectrometer operating at 250 MHz and 63 MHz respectively. Chemical shifts are given in ppm relative to TMS. Mass spectra were recorded on a Kratos MS50 instrument under electron impact conditions, unless stated otherwise. All solvents were dried over molecular sieves. Starting materials were purchased from Aldrich. Melting points were recorded on a Gallenkamp apparatus and are uncorrected.

N-Arylation Reactions

Method 1: The indole (**3**) or carbazole (**8**) (6 mmol) and a chloronitropyridine (0.95 g, 6 mmol) were dissolved in dry DMSO (20 mL). Cs_2CO_3 (2.15 g, 6.6 mmol) was added to the soln with stirring. The suspension was stirred for 18 h at 100 °C then cooled and diluted with brine (50 mL). The mixture was extracted with CH_2Cl_2

(4 × 100 mL) and the organic layers were combined and washed with H_2O (2 × 100 mL) then dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was pre-adsorbed onto silica gel. The product was purified by dry flash chromatography (hexane–EtOAc).

Method 2: Carbazole (**8**) (0.500 g, 3.0 mmol), a chloronitropyridine **4** or **5** (0.475 g, 3.0 mmol), and K_2CO_3 (8.270 g, 60.00 mmol) were weighed and mixed. A soln of $Pd(OAc)_2$ (0.027 g, 4 mol%) and *rac*-BINAP (0.075 g, 4 mol%) in toluene (10 mL) was stirred for 10 min under argon and then added to the pyridine–carbazole mixture under argon. The remainder of the catalyst mix was washed into the reaction mixture with toluene (15 mL). The mixture was refluxed for 24 h, then cooled to r.t., diluted with CH_2Cl_2, and washed with H_2O (2 × 50 mL). The extracts were filtered through a pad of Celite and then dried ($MgSO_4$). The soln was concentrated onto silica gel for purification by dry flash chromatography (hexane–EtOAc).

Method 3: The carbazole or indole (6.3 mmol) and a chloronitropyridine **4** or **5** (1.50 g, 9.5 mmol) were dissolved in MeCN (30 mL), and Cs_2CO_3 (2.50 g, 7.7 mmol) was added to the soln with stirring. The suspension was stirred for 30 h at reflux, the MeCN was concentrated under reduced pressure, and the residue was redissolved in EtOH. This soln was pre-adsorbed onto silica gel for separation by dry flash chromatography (hexane–EtOAc).

Method 4: The appropriate benzimidazole or indazole (10 mmol), K_2CO_3 (10.2 mmol), and the appropriate 1-fluoro-2-nitrobenzene (10 mmol) were heated at 125 °C in DMF (30 mL) for 8 h. H_2O (100 mL) was added to the cooled soln, which was extracted with Et_2O (3 × 100 mL). The combined organic fractions were washed with H_2O (3 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure.

1-(3-Nitropyridin-2-yl)-1*H*-indole (6)

Prepared by Method 1 from indole (**3**; 1.05 g, 9.0 mmol) and 2-chloro-3-nitropyridine (**4**; 1.56 g, 9.9 mmol); yield: 1.72 g (80%); mp 110–111 °C.

^{1}H NMR ($CDCl_3$): δ = 8.64 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1 H), 8.23 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 1 H), 7.57 (m, 1 H), 7.40 (m, 1 H), 7.28–7.10 (m, 4 H), 6.67 (d, ^3J = 3.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 152.31 (CH), 144.27 (C_q), 139.18 (C_q), 135.06 (C_q), 134.70 (CH), 129.81 (C_q), 126.37 (CH), 123.46 (CH), 121.93 (CH), 121.32 (CH), 121.20 (CH), 118.81 (CH), 107.09 (CH).

MS: *m/z* (%) = 239 (100) [M$^+$], 181 (42), 154 (14), 89 (16), 63 (17).

HRMS: *m/z* [M$^+$] calcd for $C_{13}H_9N_3O_2$: 239.0821; found: 239.0822.

1-(3-Nitropyridin-4-yl)-1*H*-indole (7)

Prepared by Method 3 from indole (**3**; 1.05 g, 9.0 mmol), 4-chloro-3-nitropyridine (**5**) (1.56 g, 9.9 mmol), and Cs_2CO_3 (3.51 g, 10.76 mmol); yield: 1.51 g (70%); mp 117–118 °C.

^{1}H NMR ($CDCl_3$): δ = 9.40 (s, 1 H), 9.03 (d, ^3J = 5.4 Hz, 1 H), 7.85 (m, 1 H), 7.75 (d, ^3J = 5.4 Hz, 1 H), 7.45-7.35 (m, 3 H), 7.28 (d, ^3J = 3.5 Hz, 1 H), 6.97 (d, ^3J = 3.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 154.18 (CH), 147.28 (CH), 140.58 (C_q), 139.93 (C_q), 135.12 (C_q), 129.63 (C_q), 126.62 (CH), 123.72 (CH), 122.06 (CH), 121.73 (CH), 121.50 (CH), 109.47 (CH), 107.49 (CH).

MS: *m/z* (%) = 239 (100) [M$^+$], 194 (97), 166 (35), 154 (35), 139 (46), 89 (49), 63 (37).

Anal. Calcd for $C_{13}H_9N_3O_2$: C, 65.3; H, 3.8; N, 17.6. Found: C, 65.75; H, 3.7; N, 17.15.

9-(3-Nitropyridin-2-yl)-9*H*-carbazole (10)

Prepared by Method 1 by using carbazole (**8**; 1.00 g, 6 mmol) and 2-chloro-3-nitropyridine (**4**; 0.95 g, 6 mmol); yield: 0.87–1.04 g (50–60%); mp 143–144 °C.

Application of Method 2 also gave **10**; yield: 0.649 g (75%); mp 144–145 °C. In practice, the product was easier to purify by using Method 2 than by Method 1.

^{1}H NMR (DMSO-d_6): δ = 9.06 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1 H), 8.82 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 2 H), 8.27 (m, 1 H), 7.90 (dd, ^3J = 8.2 Hz, ^3J = 4.8 Hz, 1 H), 7.49–7.33 (m, 6 H).

^{13}C NMR (DMSO-d_6): δ = 154.10 (CH), 142.48 (C_q), 141.78 (C_q), 139.09 (2 C_q), 136.24 (CH), 126.69 (2 CH), 124.52 (CH), 123.69 (2 C_q), 121.56 (2 CH), 120.83 (2 CH), 110.07 (2 CH).

MS: *m/z* (%) = 289 (100) [M$^+$], 242 (89), 215 (15), 189 (5), 167 (19), 140 (6), 121 (26).

Anal. Calcd for $C_{17}H_{11}N_3O_2$: C, 70.6; H, 3.8; N, 14.55. Found: C, 70.85; H, 3.9; N, 14.5.

9-(3-Nitropyridin-4-yl)-9*H*-carbazole (11)

Prepared by Method 3 from carbazole (**8**; 1.05 g, 6.29 mmol) and 4-chloro-3-nitropyridine (**5**; 1.50 g, 9.46 mmol); yield: 1.45 g (80%); mp 181–182 °C, after chromatography.

^{1}H NMR (DMSO-d_6): δ = 9.50 (s, 1 H), 9.16 (d, ^3J = 5.3 Hz, 1 H), 8.30 (d, ^3J = 7.6 Hz, 1 H), 8.11 (d, ^3J = 5.3 Hz, 1 H), 7.51–7.32 (m, 7 H).

^{13}C NMR (DMSO-d_6): δ = 156.03 (CH), 147.04 (CH), 141.97 (C_q), 139.12 (2 C_q), 137.81 (C_q), 126.89 (2 CH), 124.73 (CH), 123.75 (2 C_q), 121.61 (2 CH), 121.00 (2 CH), 109.45 (2 CH).

MS: *m/z* (%) = 289 (100) [M$^+$], 242 (52), 215 (24), 140 (5), 107 (23).

Anal. Calcd for $C_{17}H_{11}N_3O_2$: C, 70.6; H, 3.8; N, 14.55. Found: C, 71.15; H, 3.95; N, 14.4.

9-(3-Nitropyridin-2-yl)-9*H*-pyrido[2,3-*b*]indole (12)

9*H*-Pyrido[2,3-*b*]indole (**9**, α-carboline; 0.328 g, 1.96 mmol) and 2-chloro-3-nitropyridine (**4**; 0.464 g, 6 mmol) were dissolved in dry DMF (10 mL). Cs_2CO_3 (0.763 g, 2.34 mmol) was added to the soln with stirring. The suspension was stirred for 18 h at 125 °C before being cooled and diluted with brine (50 mL). The suspension that formed was extracted with CH_2Cl_2 (4 × 50 mL). The CH_2Cl_2 layers were combined, washed with H_2O (2 × 50 mL), and dried ($MgSO_4$). The CH_2Cl_2 soln was pre-adsorbed onto silica gel for separation by dry flash chromatography (hexane–EtOAc) to give **12**; yield: 0.209 g (37%); mp 167–169 °C.

^{1}H NMR (DMSO-d_6): δ = 8.79 (dd, ^3J = 6.4 Hz, ^4J = 1.7 Hz, 1 H), 8.47 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 1 H), 8.28–8.23 (m, 2 H), 8.01 (dq, ^3J = 7.8 Hz, ^4J = 1.5 Hz, ^5J = 0.7 Hz, 1 H), 7.88 (dq, ^3J = 8.1 Hz, ^4J = 1.7 Hz, ^5J = 0.8 Hz, 1 H), 7.51–7.39 (m, 2 H), 7.32 (td, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1 H), 7.17 (dd, ^3J = 7.5 Hz, ^3J = 4.5 Hz, 1 H).

^{13}C NMR (DMSO-d_6): δ = 155.48 (C_q), 152.17 (CH), 150.35 (C_q), 145.81 (CH), 142.72 (C_q), 138.00 (C_q), 134.64 (CH), 128.53 (CH), 127.46 (CH), 122.31 (CH), 122.22 (C_q), 122.05 (CH), 120.90 (CH), 117.61 (CH), 117.43 (C_q), 112.33 (CH).

MS: *m/z* (%) = 290 (3) [M$^+$], 190 (100), 168 (48), 155 (71), 128 (13), 78 (7).

HRMS: *m/z* [M$^+$] calcd for $C_{16}H_{10}N_4O_2$: 290.0804; found: 290.0802.

1-(2-Nitrophenyl)-1*H*-benzimidazole (16)

Application of Method 4 gave **16**; yield; 1.94 g (81%); mp 80–81 °C (Lit.[10] 80–82 °C).

^{1}H NMR ($CDCl_3$): δ = 8.14 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1 H), 8.01 (s, 1 H), 7.54–7.89 (m, 4 H), 7.10–7.38 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 145.97 (C_q), 143.23 (C_q), 142.32 (CH), 134.17 (CH), 129.90 (CH), 129.62 (CH), 129.27 (C_q), 125.84 (CH), 124.09 (CH), 123.07 (CH), 120.66 (CH), 109.32 (CH) (one C_q not apparent).

MS: *m/z* (%) = 239 (61) [M$^+$], 222 (7), 192 (23), 181 (60), 140 (17), 77 (20).

1-(2-Nitrophenyl)-1*H*-indazole (17)
Application of Method 4 gave **17**; yield; 1.37 g (57%); mp 151–152 °C [Lit.[11] 152–153 °C].

^{1}H NMR ($CDCl_3$): δ = 8.22 (s, 1 H), 7.22–8.03 (m, 8 H).

^{13}C NMR ($CDCl_3$): δ = 142.85 (C_q), 139.45 (C_q), 136.89 (CH), 133.14 (CH), 132.72 (C_q), 128.16 (CH), 127.66 (CH), 127.15 (CH), 125.53 (CH), 124.95 (C_q), 122.02 (CH), 121.49 (CH), 109.19 (CH).

MS: *m/z* (%) = 239 (100) [M$^+$], 222 (86), 192 (54), 166 (49), 140 (37), 118 (63), 91 (50), 77 (60).

5,6-Dimethyl-1-(2-nitrophenyl)-1*H*-benzimidazole (26)
Application of Method 4 gave **26**; yield: 2.54 g (>95%); mp 155 °C.

^{1}H NMR ($CDCl_3$): δ = 8.13 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H), 7.90 (s, 1 H), 7.81 (td, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H), 7.68 (ddd, ^3J = 7,9, 7.6 Hz, ^4J = 1.4 Hz, 1 H), 7.63 (s, 1 H), 7.56 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H), 6.91 (s, 1 H), 2.38 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 146.20 (C_q), 142.34 (C_q), 142.00 (CH), 134.61 (CH), 133.94 (C_q), 133.27 (C_q), 132.59 (C_q), 130.14 (CH), 130.06 (CH), 126.28 (CH), 121.14 (CH), 109.96 (CH), 20.94 (CH_3), 20.63 (CH_3) (one C_q not apparent).

MS: *m/z* (%) = 267 (41) [M$^+$], 255 (100), 254 (82), 209 (25), 73 (97), 43 (96).

HRMS: *m/z* [M$^+$] calcd for $C_{15}H_{13}N_3O_2$: 267.10023; found: 267.10043.

1-(4-Methyl-2-nitrophenyl)-1*H*-benzimidazole (27)
Application of Method 4 on a 3.3 mmol scale gave **27**; yield: 0.81 g (95%), mp 96 °C.

^{1}H NMR ($CDCl_3$): δ = 7.90 (apparent d, 2 H), 7.80 (d, ^3J = 7.8 Hz, 1 H), 7.53 (d, ^3J = 7.3 Hz, 1 H), 7.36 (d, ^3J = 8.0 Hz, 1 H), 7.19–7.26 (m, 2 H), 7.05 (d, ^3J = 7.8 Hz, 1 H), 2.50 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 146.24 (C_q), 143.06 (C_q), 141.54 (C_q), 135.23 (CH), 129.97 (CH), 127.17 (C_q), 126.58 (CH), 124.48 (CH), 123.44 (CH), 121.13 (CH), 109.90 (CH), 21.53 (CH_3) (one CH overlapping and one C_q not apparent).

MS: *m/z* (%) = 253 (100) [M$^+$], 211 (31), 195 (83), 183 (25), 91 (22), 77 (96).

HRMS: *m/z* [M$^+$] calcd for $C_{14}H_{11}N_3O_2$: 253.08458; found: 253.08481.

5,6-Dimethyl-1-(4-methyl-2-nitrophenyl)-1*H*-benzimidazole (28)
Application of Method 4 on a 3.3 mmol scale gave **28**; yield: 0.49 g (53%); mp 182 °C.

^{1}H NMR ($CDCl_3$): δ = 7.87 (d, ^4J = 1.1 Hz 1 H), 7.81 (s, 1 H), 7.51 (m, 2 H), 7.36 (d, ^3J = 8.1 Hz, 1 H), 6.81 (s, 1 H), 2.50 (s, 3 H), 2.31 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 145.37 (C_q), 141.65 (CH), 140.65 (C_q), 134.61 (CH), 133.16 (C_q), 132.91 (C_q), 131.88 (C_q), 129.30 (CH), 126.85 (C_q), 125.87 (CH), 120.45 (CH), 109.44 (CH), 20.90 (CH_3), 20.32 (CH_3), 20.93 (CH_3) (one C_q not apparent).

MS: *m/z* (%) = 281 (100) [M$^+$], 239 (33), 223 (56), 219 (21), 208 (18).

HRMS: *m/z* [M$^+$] calcd for $C_{16}H_{15}N_3O_2$: 281.11588; found: 281.11571.

1-(3-Nitropyridin-2-yl)-1*H*-benzimidazole (29)
Application of Method 4 on a 5.0 mmol scale gave **29**; yield: 0.39 g (33%); mp 45 °C.

^{1}H NMR ($CDCl_3$): δ = 8.79 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1 H), 8.44 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 1 H), 8.21 (s, 1 H), 7.82 (m, 1 H), 7.54 (m, 1 H), 7.33–7.19 (m, 3 H).

^{13}C NMR ($CDCl_3$) (CH signals only): δ = 152.97, 141.61, 135.06, 124.51, 123.77, 123.26, 120.98, 110.34.

MS: *m/z* (%) = 240 (25) [M$^+$], 195 (100), 194 (43), 169 (38), 118 (56).

HRMS: *m/z* [M$^+$] calcd for $C_{12}H_8N_4O_2$: 240.06418; found: 240.06430.

FVP Reactions of *N*-(2-Nitrophenyl) Heterocycles[1,2]
The nitro compound was sublimed under vacuum through a silica furnace tube (35 × 2.5 cm). The solid product(s) were collected on a cold-finger trap cooled with a dry-ice/acetone mixture and positioned at the exit point of the furnace. A U-tube trap, cooled with liquid N_2, was placed between the cold finger and the pump to trap the NO_x byproducts. Upon completion of the pyrolysis, N_2 gas was released through the system, which was then dismantled. The U-tube was allowed to warm to r.t. in a fume cupboard. Pyrolysis conditions are quoted as follows: substrate, quantity, furnace temperature (T_f), inlet temperature (T_i), pressure range (P), pyrolysis time (t), and product(s). Each pyrolysate was dissolved in CH_2Cl_2 and pre-adsorbed onto silica gel for purification by dry flash chromatography.

Note that for small-scale reactions (< 100 mg), a standard U-tube trap[12] at the exit point of the furnace gives satisfactory results.

Pyrido[2,3-*b*]pyrrolo[3,2,1-*hi*]indole (7-Azapyrrolo[3,2,1-*jk*]carbazole) (18)
The pyrolysate obtained by FVP of 1-(3-nitropyridin-2-yl)-1*H*-indole [**6**, 0.500 g (2.09 mmol), T_f = 875 °C, T_i = 170 °C, $P = 2.4 \times 10^{-2}$ Torr, t = 40 min] was purified by dry flash chromatography (hexane–EtOAc) to give **18**; yield: 0.221 g (55%); mp 99–100 °C.

^{1}H NMR ($CDCl_3$): δ = 8.42 (dd, ^3J = 5.1 Hz, ^4J = 1.6 Hz, 1 H), 8.29 (dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1 H), 7.93 (d, ^3J = 3.5 Hz, 1 H), 7.86 (d, ^3J = 7.4 Hz, 1 H), 7.83 (d, ^3J = 7.4 Hz, 1 H), 7.53 (t, ^3J = 7.4 Hz, 1 H), 7.24 (dd, ^3J = 7.7 Hz, ^3J = 5.1 Hz, 1 H), 6.91 (d, ^3J = 3.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 145.25 (C_q), 140.17 (CH), 130.66 (C_q), 124.55 (C_q), 123.83 (CH), 122.41 (C_q), 122.14 (CH), 122.01 (C_q), 121.95 (CH), 117.90 (CH), 117.69 (CH) 115.95 (CH), 110.84 (CH).

MS: *m/z* (%) = 192 (100) [M$^+$], 164 (31), 138 (12), 96 (38), 82 (21), 69 (10).

Anal. Calcd for $C_{13}H_8N_2$: C, 81.25; H, 4.2; N, 14.6. Found: C, 81.0; H, 4.25; N, 14.5.

Pyrido[4,3-*b*]pyrrolo[3,2,1-*hi*]indole (9-Azapyrrolo[3,2,1-*jk*]carbazole) (19)
The pyrolysate obtained by FVP of 1-(3-nitropyridin-4-yl)-1*H*-indole [**7**, 0.506 g (2.12 mmol), T_f = 875 °C, T_i = 140 °C, $P = 4.0 \times 10^{-2}$ Torr, t = 35 min] was purified by dry flash chromatography (hexane–EtOAc) to give **19**; yield: 0.203 g (50%); mp 122–123 °C.

^{1}H NMR ($CDCl_3$): δ = 9.25 (d, ^4J = 0.9 Hz, 1 H), 8.62 (d, ^3J = 5.7 Hz, 1 H), 7.91 (d, ^3J = 7.4 Hz, 1 H), 7.79 (d, ^3J = 7.4 Hz, 1 H), 7.67

(d, ^3J = 3.2 Hz, 1 H), 7.54 (t, ^3J = 7.4 Hz, 1 H), 7.52 (d, ^3J = 5.7 Hz, 1 H), 6.91 (d, ^3J = 3.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 146.73 (CH), 144.25 (CH), 143.33 (C_q), 140.78 (C_q), 126.77 (C_q), 124.36 (CH), 122.38 (CH), 121.90 (CH), 121.50 (C_q), 118.28 (CH), 116.27 (C_q), 111.89 (CH), 106.87 (CH).

MS: *m/z* (%) = 192 (100) [M$^+$], 164 (72), 138 (55), 114 (22), 96 (54), 83 (70), 63 (44), 50 (24).

HRMS: *m/z* [M$^+$] calcd for $C_{13}H_8N_2$: 192.0688; found: 192.0690.

Pyrido[3′,2′:4,5]pyrrolo[3,2,1-*jk*]carbazole (20)

FVP of 9-(3-nitropyridin-2-yl)-9*H*-carbazole [**10**, 0.500 g (1.73 mmol), T_f = 875 °C, T_i = 170 °C, $P = 2.4 \times 10^{-2}$ Torr, t = 40 min] gave a pyrolysate that was purified by dry flash chromatography (hexane–EtOAc) to give **20**; yield: 0.356 g (85%); mp 149–150 °C.

^{1}H NMR ($CDCl_3$): δ = 8.53 (dd, ^3J = 5.1 Hz, ^4J = 1.4 Hz, 1 H), 8.33 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1 H), 8.28 (dd, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 1 H), 8.10 (d, ^3J = 7.8 Hz, 1 H), 8.05 (d, ^3J = 7.5 Hz, 1 H), 7.98 (d, ^3J = 7.5 Hz, 1 H), 7.60 (m, 2 H), 7.39 (td, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1 H), 7.31 (dd, ^3J = 7.8 Hz, ^3J = 5.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 149.92 (C_q), 145.11 (CH), 142.57 (C_q), 137.81 (C_q), 130.86 (CH), 129.95 (C_q), 127.13 (CH), 123.70 (C_q), 123.30 (CH), 122.74 (CH), 122.66 (CH) 120.21 (CH), 119.68 (CH), 118.94 (C_q), 116.91 (C_q), 115.49 (CH), 113.92 (CH).

MS: *m/z* (%) = 242 (100) [M$^+$], 214 (20), 188 (7), 167 (15), 139 (3), 121 (52), 93 (17), 81 (6).

HRMS: *m/z* [M$^+$] calcd for $C_{17}H_{10}N_2$: 242.0843; found: 242.0842.

Pyrido[3′,4′:4,5]pyrrolo[3,2,1-*jk*]carbazole (21)

The pyrolysate obtained by FVP of 9-(3-nitropyridin-4-yl)-9*H*-carbazole [**11**, 0.492 g (1.70 mmol), T_f = 875 °C, T_i = 150–190 °C, $P = 3.0 \times 10^{-2}$ Torr, t = 60 min] was purified by dry flash chromatography (hexane–EtOAc) to give **21**; yield: 0.227 g (55%); mp 155–156 °C.

^{1}H NMR ($CDCl_3$): δ = 9.25 (s, 1 H), 8.63 (d, ^3J = 5.6 Hz, 1 H), 8.02 (d, ^3J = 7.8 Hz, 1 H), 7.95 (d, ^3J = 7.5 Hz, 1 H), 7.93 (d, ^3J = 7.5 Hz, 1 H), 7.73 (d, ^3J = 7.8 Hz, 1 H), 7.63 (d, ^3J = 5.6 Hz, 1 H), 7.54 (t, ^3J = 7.5 Hz, 1 H), 7.50 (td, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1 H), 7.35 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 146.37 (CH), 144.39 (CH), 143.26 (C_q), 142.09 (C_q), 137.88 (C_q), 130.40 (C_q), 126.89 (CH), 125.81 (C_q), 123.87 (CH), 123.11 (CH), 122.78 (CH), 120.01 (CH), 119.76 (CH), 118.52 (C_q), 115.89 (C_q), 112.55 (CH), 107.22 (CH).

MS: *m/z* (%) = 242 (100) [M$^+$], 214 (14), 187 (5), 121 (17), 107 (17) 93 (11).

HRMS: *m/z* [M$^+$] calcd for $C_{17}H_{10}N_2$: 242.0843; found: 242.0847.

Pyrido[2,3-*b*]pyrido[3′,2′:4,5]pyrrolo[3,2,1-*hi*]indole (22)

The pyrolysate obtained by FVP of 9-(3-nitropyridin-2-yl)-9*H*-pyrido[2,3-*b*]indole [**12**, 0.073 g (0.25 mmol), T_f = 875 °C, T_i = 80–120 °C, $P = 4.0 \times 10^{-2}$ Torr, t = 20 min] was purified by dry flash chromatography (hexane–EtOAc) to give **22**; yield: 0.37 g (60%); mp 152–153 °C.

^{1}H NMR ($CDCl_3$): δ = 8.62 (dd, ^3J = 5.0 Hz, ^4J = 1.6 Hz, 2 H), 8.35 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 2 H), 8.02 (d, ^3J = 7.5 Hz, 2 H), 7.61 (t, ^3J = 7.5 Hz, 1 H), 7.80 (dd, ^3J = 7.6 Hz, ^3J = 5.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 150.16 (2 C_q), 146.63 (2 CH), 141.67 (C_q), 130.75 (2 CH), 123.69 (2 C_q), 123.67 (CH), 120.72 (2 CH), 117.93 (2 CH), 116.34 (2 C_q).

MS: *m/z* (%) = 243 (30) [M$^+$], 190 (72), 156 (100), 128 (26), 78 (15).

HRMS: *m/z* [M$^+$] calcd for $C_{16}H_9N_3$: 243.0797; found: 243.0797.

9*H*-Carbazole-1-carbonitrile (25)

Method 1: The pyrolysate obtained by FVP of 1-(2-nitrophenyl)-1*H*-benzimidazole [**16**, 0.500 g (2.09 mmol), T_f = 850 °C, T_i = 160–180 °C, P = 0.0034 Torr, t = 20 min] was subjected to dry flash chromatography (silica gel, hexane–EtOAc) to give **25**; yield: 0.26 g (64%); mp 189–190 °C (Lit.[13] 188–189 °C) (NMR data as below).

Method 2: The pyrolysate obtained by FVP of 1-(2-nitrophenyl)-1*H*-indazole [**17**, 0.350 g (1.46 mmol), T_f = 850 °C, T_i = 250–270 °C, P = 0.013 Torr, t = 30 min] was subjected to dry flash chromatography (silica gel, hexane–EtOAc) to give **25**; yield: 0.16 g (57%); mp 189–190 °C (Lit.[13] 188–189 °C).

^{1}H NMR ($CDCl_3$): δ = 9.00 (br s, 1 H), 8.27 (dt, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1 H), 8.08 (ddd, ^3J = 6.9 Hz, ^4J = 1.7 Hz, ^5J = 0.9 Hz, 1 H), 7.68 (dd, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1 H), 7.45–7.57 (m, 2 H), 7.29 (dd, ^3J = 6.5 Hz, ^4J = 1.4 Hz, 1 H), 7.25 (t, ^3J = 7.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 140.49 (C_q), 139.38 (C_q), 129.06 (CH), 127.18 (CH), 125.07 (CH), 124.23 (C_q), 122.42 (C_q), 120.55 (2 CH), 119.18 (CH), 117.25 (C_q), 111.20 (CH), 93.50 (C_q).

MS: *m/z* (%) = 192 (100) [M$^+$], 164 (15), 138 (5), 96 (7).

3,4-Dimethyl-9*H*-carbazole-1-carbonitrile (30)

The pyrolysate obtained by FVP of 5,6-dimethyl-1-(2-nitrophenyl)-1*H*-benzimidazole [**26**, (0.442 g (1.66 mmol), T_f = 850 °C, T_i = 160–180 °C, P = 0.04 Torr, t = 40 min] was subjected to dry flash chromatography (silica gel, hexane–EtOAc) to give **30**; yield: 0.215 g (59%); mp 215 °C.

^{1}H NMR ($CDCl_3$): δ = 8.51 (br s, 1 H), 8.15 (d, ^3J = 8.1 Hz, 1 H), 7.38–7.43 (m, 3 H), 7.30 (m, 1 H), 2.77 (m, 3 H), 2.40 (m, 3 H).

MS: *m/z* (%) = 220 (100) [M$^+$], 205 (97), 194 (51), 180 (42), 73 (37).

HRMS: *m/z* [M$^+$] calcd for $C_{15}H_{12}N_2$: 220.09950; found: 220.09845.

6-Methyl-9*H*-carbazole-1-carbonitrile (31)

The pyrolysate obtained by FVP of 1-(4-methyl-2-nitrophenyl)-1*H*-benzimidazole [**27**, 26 mg (0.10 mmol), T_f = 850 °C, T_i = 150 °C, P = 0.065 Torr, t = 15 min) gave **31**; yield: 13 mg (60%); mp 185 °C.

^{1}H NMR ($CDCl_3$): δ = 8.58 (s, 1 H), 8.16 (d, ^3J = 7.5 Hz, 1 H), 8.05 (s, 1 H), 7.59 (dd, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 1 H), 7.40–7.15 (m, 3 H), 2.47 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ (non-C_q signals only) = 129.03, 125.22, 128.68, 120.53, 119.12, 110.72, 18.55 (CH_3).

MS: *m/z* (%) = 206 (100) [M$^+$], 205 (83), 177 (8), 151 (8), 103 (10).

HRMS: *m/z* [M$^+$] calcd for $C_{14}H_{10}N_2$: 206.08385; found: 206.08340.

3,4,6-Trimethyl-9*H*-carbazole-1-carbonitrile (32)

The pyrolysate obtained by FVP of 5,6-dimethyl-l-(4-methyl-2-nitrophenyl)-1*H*-benzimidazole [**28**, 55 mg (0.20 mmol), T_f = 850 °C, T_i = 170–185 °C, P = 0.018 Torr, t = 15 min] gave **32**; yield: 27 mg (58%); mp 228 °C.

^{1}H NMR ($CDCl_3$): δ = 8.42 (br s, 1 H), 7.92 (s, 1 H), 7.40–7.27 (m, 3 H), 2.78 (s, 3 H), 2.51 (s, 3 H), 2.38 (s, 3 H).

MS: *m/z* (%) = 234 (100) [M$^+$], 233 (40), 220 (16), 219 (45), 109 (8).

HRMS: *m/z* [M$^+$] calcd for $C_{16}H_{14}N_2$: 234.11515; found: 234.11490.

9*H*-Pyrido[2,3-*b*]indole-8-carbonitrile (33)
The pyrolysate obtained by FVP of (3-nitropyridin-2-yl)-1*H*-benzimidazole [**29**, 303 mg (1.26 mmol), T_f = 850 °C, T_i = 180–200 °C, P = 0.075 Torr, t = 40 min] gave **33**; yield: 136 mg (56%).

^{1}H NMR (DMSO-d_6): δ = 12.76 (br s, 1 H), 8.79 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1 H), 8.50–8.55 (m, 2 H), 7.90 (dd, ^3J = 4.5 Hz, ^4J = 1.7 Hz, 1 H), 7.40–7.27 (m, 2 H).

^{13}C NMR (DMSO-d_6): δ (CH signals only, from HSQC spectrum) = 147.64 (CH), 131.06 (CH), 129.45 (CH), 126.60 (CH), 119.60 (CH), 116.34 (CH).

MS: *m/z* (%) = 193 (100) [M$^+$], 166 (46), 164 (33), 139 (46), 138 (21), 88 (17).

HRMS: *m/z* [M$^+$] calcd for $C_{12}H_7N_3$: 193.06345; found: 193.06431.

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