Synthesis of functionalised indolines by radical-polar crossover reactions

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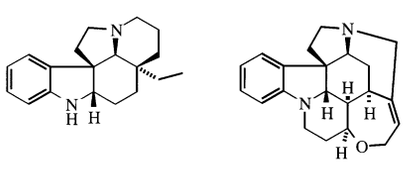
Functionalised indolines have been prepared by treating tetrathiafulvalene (TTF) with 2-(*N*-acyl-*N*-allylamino)benzenediazonium tetrafluoroborates. *N*-Benzoyl-protected substrates afford complex reaction mixtures due to competing radical cyclisation onto the benzoyl group. Acetamides react more efficiently affording good yields of product alcohols when the reactions are carried out in moist acetone

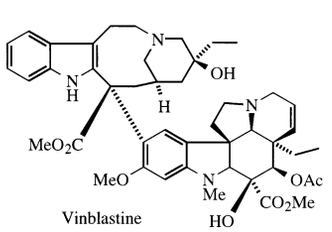
Introduction

Indolines feature abundantly in Nature and many of these compounds are of pharmaceutical interest. The family includes the complex alkaloids aspidospermidine, strychnine and vinblastine which pose many intriguing challenges to the synthetic chemist. The synthesis of naturally occurring indolines is therefore a very active field, and one of the most popular recent approaches has involved the use of radicals[1–7] as precursors. However, despite all these developments, our recently discovered radical-polar crossover reactions could have unique and important advantages, not only in avoiding the troublesome and toxic tin radicals but also, more especially, in controlling stereochemistry of more complex polycyclic indolines. A preparative strategy for complex indoline skeletons, such as **4**, present in many medicinally important indoline alkaloids, would involve formation of the aryl radical **1** from the corresponding diazonium salt by treatment with tetrathiafulvalene (TTF), and cyclisation of **1** to a new radical **2** which then undergoes radical-polar crossover ultimately leading to the cation **3**.[8] A *cis* ring junction can be predicted in formation of **2** leaving the side-chain containing the group N′HR so disposed as to favour the all-*cis* stereochemistry of the desired product **4**. The stereocontrol in the final cyclisation is totally dependent on unimolecular substitution *via* a mandatory carbocation intermediate **3**. Prior trapping of the radical **2** (*e.g.* leading to an iodide)[1] from the less hindered face would afford[9] product **5** (X = I), and this would either suffer direct closure of the fourth ring with inversion of configuration, affording the wrong stereochemistry or, at the least, require two sequential inversions at the neopentyl carbon bearing the iodine, firstly by an intermolecular nucleophile and then by N′HR in order to incorporate the desired stereochemistry in the fourth ring.



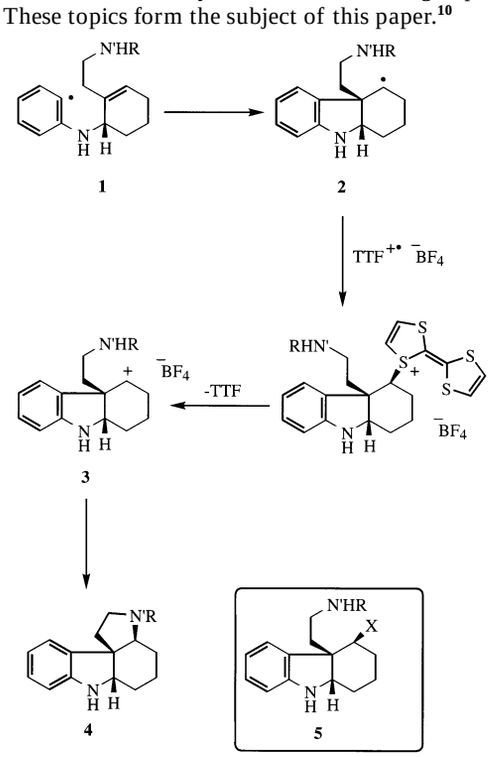
Aspidospermidine

Strychnine



Vinblastine

However, before embarking on complex syntheses, it was necessary to investigate if *simple* indolines could be formed using the radical-polar crossover approach, and how such chemistry would be affected by the choice of nitrogen-protecting group. These topics form the subject of this paper.[10]



Scheme 1

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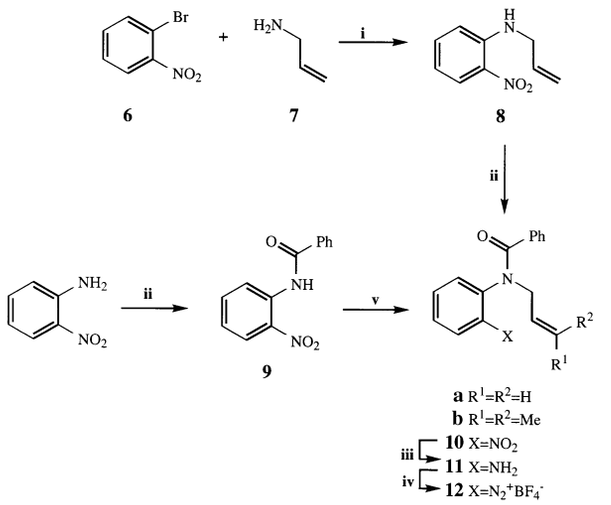
Benzamide derivatives

Nucleophilic aromatic substitution of 2-bromonitrobenzene **6** with prop-2-enylamine **7** led to **8**, which was benzoylated to afford **10a** as microanalytically pure, pale yellow needles. Reduction to **11a** followed by diazotisation furnished **12a** as a fine, colourless powder.

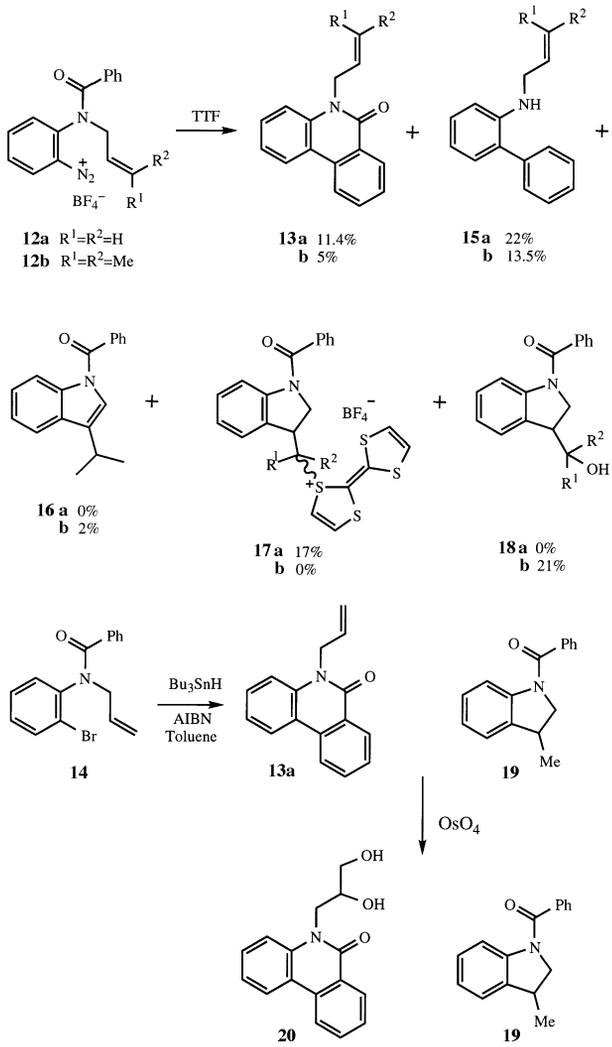
In parallel, synthesis of **12b** was also undertaken to compare whether the product ratio would be altered by changing the terminus of the radical acceptor C=C bond. A different synthetic approach was adopted in this case. Benzoylation of 2-nitroaniline afforded **9** as yellow needles. Subsequent deprotonation by sodium hydride was conveniently achieved in tetrahydrofuran and followed by alkylation with 2-methyl-4-bromobut-2-ene (prenyl bromide) to give **10b**. Reduction to **11b** followed by diazotisation afforded **12b**, the cyclisation precursor, as a pale yellow powder.



Scheme 2 *Reagents and conditions:* i reflux, 48 h, 87%; ii PhCOCl, DMAP, py; (**a**) at 80 °C 84%; (**b**) at RT 93%; iii $Cu(acac)_2$, $NaBH_4$, EtOH, 3 h; (**a**) 75%; (**b**) 77%; iv Aq. HBF_4, isoamyl nitrite, EtOH; (**a**) and (**b**) 80%; v NaH, THF, 0 °C then prenyl bromide; 73%

Reaction of **12a** and **12b** with TTF in moist acetone afforded the products shown in Scheme 3. The product distributions here were of particular interest because Togo[3] had observed the *exclusive* formation of **13a** (100%) when the bromo compound **14** analogous to **12a** was subjected to standard reductive conditions (Bu_3SnH–AIBN) in toluene. This reaction has assumed further importance since it fits into a picture[11] in which the intriguing regioselectivity of certain anilide aryl radical addition reactions could be neatly rationalised. Our reactions afforded a greater variety of products and (as pointed out by a reviewer) since the same radical features in both cases, the fact that we observed formation of an indoline, whereas Togo did not, was surprising. To probe this point, we have now repeated the experiment of Togo on many occasions. The crude NMR spectrum consistently shows *two* products, compound **13a** and *N*-benzoyl-3-methylindoline **19** in a 73:27 ratio (as well as the tin by-products). Separation of these two compounds from each other is non-trivial although they can be separated from the tin residues without difficulty; the mixture of the two compounds clearly shows all the signals later identified as the indoline. Dihydroxylation of the mixture with osmium tetroxide affords the polar diol **20** which is easily separated from the indoline **19**. The isolation of indoline **19** from these experiments makes it clear that the same radical can feature in both our reactions and those of Togo.

The mechanisms of formation of the products derived from reaction of **12a,b** are worthy of consideration. The biphenylamines **15a,b** were formed *via ipso* cyclisation of the aryl radical onto the aromatic ring.[12–14] In this case, after the initial cyclisation of the radicals derived from **12a,b**, **22** is formed as an intermediate radical which either rearranges to **21** by a neophyl rearrangement or rearomatises leading to the amidoyl radical **23** (Scheme 4). Radicals of this type are known to be quite stable and cannot rapidly decarbonylate[5] to give an aminyl radical **26**.

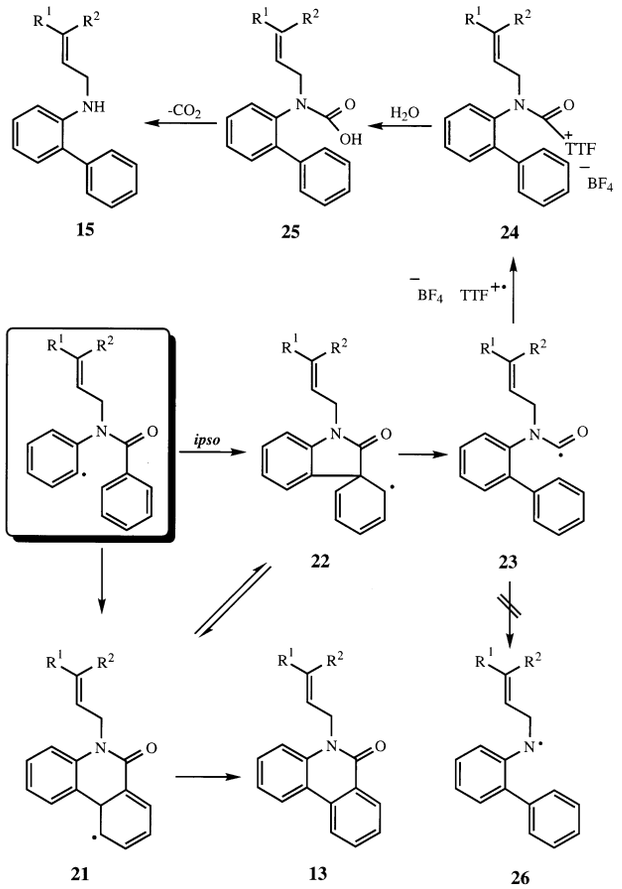


Scheme 3

Hence, it was concluded that $TTF^{\bullet+}$ must be playing an active role in decarbonylation in order to produce **15**. Combination of $TTF^{\bullet+}$ with **23** would give **24** (see Scheme 4), which would then be readily attacked by water to give the carbamic acid **25**. This could now readily decarboxylate, the entropic driving force leading to the formation of carbon dioxide and **15**.

Formation of **13a,b** may arise by *ipso* addition giving **22** followed by arrangement or, alternatively, by direct formation of the 6-membered ring in **21**. Hey[13] and Grimshaw[14] have studied cyclisations of similar aryl radicals generated photochemically and electrolytically. In their substrates the amide group is transposed, *i.e.* with the radical being generated on the benzoyl ring; they also observed products arising from cyclisations to 5- and 6-membered rings.

In addition to the products described above, the other products which have been characterised can all be rationalised from the intermediates **17a** or **17b**. The ^{1}H NMR spectrum of **17a**, formed from reaction of **12a** with TTF in 17% yield, was difficult to interpret. This was not surprising due to the expected presence of diastereoisomers as well as the rotamers around the amide bond. Attempts to obtain a ^{1}H NMR spectrum of **17a** at elevated temperatures in deuteriated dimethyl sulfoxide were



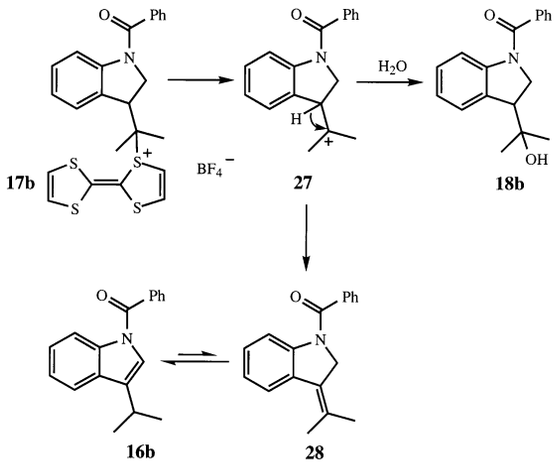
Scheme 4

fruitless. Decomposition products were observed as the temperature was raised. The sulfonium tetrafluoroborate **17a** was formed *via* the aryl radical cyclising onto the pendant alkene to afford an intermediate alkyl radical, which was then trapped by $TTF^{\bullet+}$. As predicted, no sign of the corresponding alcohol **18a** was observed. This would require substitution by an S_N1 reaction,[8] which is not possible since it would require the intermediacy of a primary cation.

Reaction of **12b** with TTF afforded **18b** as the major product. The ^{1}H NMR spectrum revealed broadened signals at room temperature in $CDCl_3$ due to the hindered rotation about the amide bond. To aid interpretation both the ^{1}H and ^{13}C NMR spectra were recorded in deuteriated dimethyl sulfoxide at 353 K. In contrast to **17a** the corresponding sulfonium salt **17b** was not isolated. In addition, a minor product was isolated in the reaction of **12b** and this was fully characterised as the indole **16b** which displayed a characteristic indole ring singlet at 7.03 ppm in the ^{1}H NMR spectrum. The indole **16b** arises through the mechanism shown in Scheme 5. Loss of TTF from **17b** gives the carbocation **27** which can react with residual moisture present in acetone to give **18b** or can lose a proton to give **28** which isomerises to **16b**.

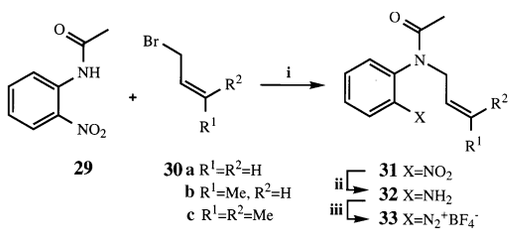
Acetamide precursors

In view of the complications observed in the benzoyl case, a series of precursors **33a–c** featuring acetyl protecting groups[2] were synthesised. 2-Nitroacetanilide[15] **29** was obtained as a yellow, crystalline solid in 94% yield by acylation of 2-nitroaniline. Deprotonation followed by alkylation with the commercially available, appropriately substituted, alkenyl bromides **30a–c** furnished **31a–c** in good to excellent yields as deep orange, viscous oils. In general, the NMR spectra of these indicated the existence of rotameric mixtures at ambient temperatures. Hence, their ^{1}H NMR spectra were recorded in deuteriated dimethyl sulfoxide at 398 K and could then be conveniently interpreted. In the case of **31c**, the ^{1}H NMR spectrum at 398 K



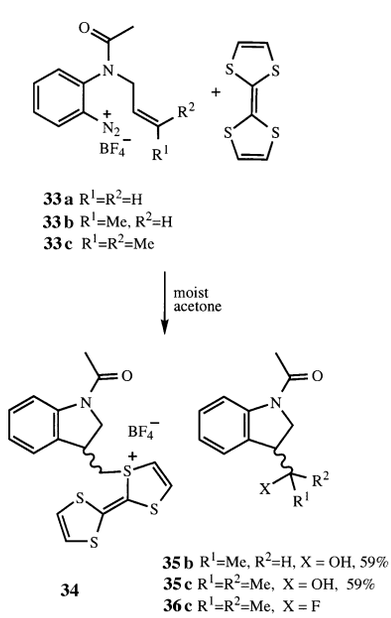
Scheme 5

gave broader signals with loss of resolution, hence the spectrum recorded at 298 K has been quoted. The corresponding amines **32a–c** were isolated as stable, colourless powders with sharp melting points.



Scheme 6 *Reagents and condtitions:* i NaH, THF, **27** then **28** 16 h; (**a**) 68%; (**b**) 83%; (**c**) 78%; ii $Cu(acac)_2$, $NaBH_4$, EtOH, 3 h; (**a**) 97%; (**b**) 72%; (**c**) 65%; iii HBF_4, isoamyl nitrite, EtOH, 0 °C; (**a**) 73%; (**b**) 85%; (**c**) 91%

The diazonium tetrafluoroborates **33a–c** were prepared by the usual method in good yields as crystalline solids. The next step was cyclisation with TTF and this was performed in moist acetone as before.



Scheme 7

With **33a**, reaction with TTF gave a product tentatively identified as **34**, a yellow powder obtained by precipitation from diethyl ether, as the sole product of the reaction. ^{13}C NMR spectroscopy indicated the compound to be present as a pair of diastereoisomers. The diastereotopic protons α to the sulfur

appeared at 3.94 (1 H, dd, *J* 13, 6.7 Hz) and 4.02 (1 H, dd, *J* 13, 6.7 Hz), respectively. The benzylic proton and those α to the acetamide nitrogen were observed as complex multiplets. The signals at 6.98 (major isomer), 6.84 (minor isomer), 7.38, 7.43, 8.23 and 8.12 (minor isomer) ppm were attributable to the TTF portion of the molecule. The ^{13}C NMR spectrum was similar to that of **17a**. Repeated efforts to purify this compound fully by column chromatography were unsuccessful.

The reaction of **33b** with TTF afforded only **35b** as a 1:1 diastereoisomeric mixture as the only product of the reaction in 59% yield.

Finally, **33c** was treated with TTF in moist acetone and two products in the ratio of 1:12 were isolated after chromatography. The more polar product was indeed the alcohol **35c** as was expected, isolated as a pale waxy solid (mp 108–111 °C) in good yield. Its NMR data were easy to analyse due to the absence of diastereoisomers. A molecular ion which fitted the proposed formula was observed by electron impact mass spectrometry (Found: M^+, 219.1258. $C_{13}H_{17}NO_2$ requires *M*, 219.1259).

The less polar product was isolated in 5% yield as a pale powder. Extensive purification by chromatography was required on this product as it co-migrated with TTF by-products. The ^{1}H NMR spectrum recorded at 400 MHz was significantly different from that of **35c**. Signals at 1.24 and 1.39 (3 H, d, *J* 21.4 Hz) ppm were attributed to the methyl protons and a signal at 2.25 ppm to the methyl of the acetyl group. The doublet structure for two of the methyl groups suggested that the compound was the fluoride **36c**. This, indeed, was seen to be the case. In the ^{13}C spectrum, the two methyl carbons at 23.1 ($^2J_{CF}$ 24.1 Hz) and 24.5 ($^2J_{CF}$ 24.2 Hz) ppm as well as the methine carbon at 49.7 ($^2J_{CF}$ 24.2 Hz) ppm all appeared as doublets. In addition, the methylene carbon at 51.1 ppm also appeared as a doublet ($^3J_{CF}$ 7.7 Hz). Particularly noticeable was the quaternary carbon at 96.8 ppm appearing as a doublet ($^1J_{CF}$ 170 Hz). Mass spectrometry gave a molecular ion for the proposed molecular formula (Found: MH^+, 222.1292. $C_{13}H_{16}FNO$ requires *M*H, 222.1294). Further evidence to confirm the structure of **36c** came from the undecoupled ^{19}F spectrum recorded at 235 MHz using deuteriated chloroform as solvent with $CFCl_3$ (0.2%) as the internal reference. The two broad multiplets at −75.7 (minor) and −76.47 (major) ppm were attributable to the fluorine coupling to the benzyl and methyl protons. The presence of two signals also indicates that the compound exhibits hindered rotation about the amide bond. Formation of the fluoride **36c** is analogous to the Schiemann reaction which involves heating of an arenediazonium tetrafluoroborate to produce aryl fluorides.

Conclusion

Functionalised indolines can indeed be prepared using the 'radical-polar crossover' approach. The nature of the protecting group is important. Whereas complications are experienced with *N*-benzoyl protection, the use of acetamide protection proceeds smoothly. These results suggest that the methodology may indeed be useful for the synthesis of complex natural indolines. We are currently investigating this approach.

Experimental

General procedures

Mps were carried out on a Kofler hot-stage apparatus and are uncorrected. Microanalyses were determined using a Perkin-Elmer 240B elemental analyser. IR spectra were obtained on a Perkin-Elmer 1720-X FTIR or Pye-Unicam SP3-100 spectrometer. 'Disc' refers to spectra that were recorded from compounds prepared in a KBr disc.

Mass spectra were recorded on an AE1 MS-902 or a MM-701 CF instrument using either electron impact ionisation (EI at 70 eV), fast-atom bombardment (FAB) or ionspray (IS) techniques at the University of Nottingham. High-resolution FAB or CI mass spectra were recorded on a JLSX 102 instrument (SB). Alternatively, the high-resolution FAB spectra were also recorded on a VG-AUTOSPEC instrument (at 25 kV) and the CI spectra were obtained on a VG ZAB-E instrument (at 8 kV) using peak-matching techniques at the EPSRC Mass Spectrometry Centre, Swansea.

^{1}H NMR spectra were recorded at 250 MHz on a Bruker WM250, at 270 MHz on a JEOL EX270 or at 400 MHz on a Bruker AM400 machine. ^{13}C NMR spectra were similarly recorded at 67.5 MHz on a JEOL EX270 or at 100 MHz on a Bruker AM400 machine. NMR experiments were in general carried out in deuteriochloroform ($CDCl_3$), unless otherwise specified, using tetramethylsilane (TMS) as the internal reference for ^{1}H and chloroform as standard for the ^{13}C NMR. ^{13}C NMR spectra were acquired on a broad band decoupled mode with the multiplicities obtained using a DEPT sequence. The alternative deuteriated solvents employed were [$^2H_6$]acetone or [$^2H_6$]dimethyl sulfoxide, the latter used to conduct variable-temperature studies. Chemical shifts (δ) are quoted in parts per million (ppm) from TMS as the internal standard. The following abbreviations are used for the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, app = apparent, br = broad and m = multiplet. Coupling constants (*J*) are reported in Hz. Where mixtures of isomers are obtained, they are distinguished in the NMR spectra by using the word 'minor' to denote less prevalent isomer(s). In cases where superimposition of two or more isomers occurred, the signals have been reported as multiplets (m), unless coupling constants for each isomer could be ascertained.

The ^{19}F NMR spectrum for **36c** was recorded at 235 MHz on a Bruker WM250 machine in $CDCl_3$ using $CFCl_3$ (0.2%) as the internal reference.

Flash chromatography was performed using Sorbisil C60 (May and Baker), Merck silica Keiselgel 60 (Art 9385) or Kieselgel HF_{254} silica gels. Thin layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} pre-coated plastic plates. Visualisation was achieved under UV light and the plates developed with methanolic phosphomolybdic acid (10–20%, w/v) or acidic *p*-anisaldehyde (10% v/v) or acidic ethanolic vanillin solutions.

Where necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under nitrogen. Unless otherwise stated, LP refers to light petroleum (bp 40–60 °C). Diethyl ether, cyclohexene, toluene and benzene were dried over sodium wire. Other solvents were dried by distillation from the following: tetrahydrofuran (sodium–benzophenone); dichloromethane, *N*,*N*-dimethylformamide, dimethyl sulfoxide and pyridine (calcium hydride); methanol (magnesium methoxide) and prop-2-enylamine (potassium hydroxide). In experiments where sodium hydride (60% suspension in mineral oil) has been utilised as a base, it was washed with THF at least twice prior to use.

All reactions requiring anydrous conditions were performed in flame- or oven-dried apparatus under a nitrogen or argon atmosphere. Organic extracts were, in general, dried over anhydrous magnesium sulfate ($MgSO_4$) or sodium sulfate (Na_2SO_4).

N-(2-Nitrophenyl)-*N*-prop-2-enylamine 8

Freshly distilled prop-2-enylamine (7.5 ml, 5.7 g, 100 mmol) was added to 2-bromonitrobenzene (8.24 g, 41 mmol) and the mixture heated at reflux for 48 h.[15] After cooling, the deep brown residue was dissolved in ethyl acetate (350 ml) and the organic phase separated and washed with water (3 × 400 ml). The aqueous phase was back-washed with ethyl acetate (3 × 300 ml) and the combined organic phase was concentrated *in vacuo* to yield a brown, viscous oil. The crude compound was further purified by column chromatography on silica gel using LP–ethyl

acetate (90:10) as eluent to afford the title compound **8** as a bright orange oil (6.31 g, 35 mmol, 87%) (Found: C, 60.57; H, 5.69; N, 15.61; M^+, 178.0732. $C_9H_{10}N_2O_2$ requires C, 60.64; H, 5.66; N, 15.72%; *M*, 178.0756); ν_{max}(film)/cm^{-1} 3386, 3086, 3009, 2984, 2855, 1618, 1574, 1511, 1351, 1331, 995, 923 and 743; δ_H(270 MHz) 1.58 (1 H, br s, NH), 3.98 (2 H, br d, *J* 5, CH_2), 5.23 (2 H, m, HC=CH_2), 5.96 (1 H, m, *H*C=CH_2), 6.66 (1 H, dd, *J* 7, 7, ArH), 6.82 (1 H, d, *J* 9, ArH), 7.45 (1 H, dd, *J* 7, 7, ArH) and 8.17 (1 H, d, *J* 9, ArH); δ_C(67.5 MHz) 45.27 (CH_2), 114.07 (CH), 115.51 (CH), 117.07 (CH_2), 126.85 (CH), 133.2 (CH), 136.12 (CH) and 145.32 (2C); *m/z* (EI) 178 (M^+, 100%), 130 (90), 119 (58), 105 (100), 91 (23), 77 (40) and 55 (38).

N-(2-Nitrophenyl)-*N*-(prop-2-enyl)benzamide[16] 10a

To a stirred solution of *N*-(2-nitrophenyl)-*N*-prop-2-enylamine **8** (6.31 g, 35 mmol) in dry pyridine (50 ml) cooled to 0 °C was added 4-(*N*,*N*-dimethylamino)pyridine (500 mg, 4 mmol). Benzoyl chloride (4.5 ml, 4.92 g, 39 mmol) was added to the reaction mixture which was then heated at reflux (3 h). After cooling, the mixture was concentrated by removal of the excess pyridine by evaporation under reduced pressure; the residue was then taken up in ethyl acetate. The solution was subsequently washed with sulfuric acid (1 M; 3 × 500 ml), saturated aqueous sodium hydrogen carbonate (3 × 500 ml), water (3 × 500 ml) and brine (2 × 500 ml), dried and evaporated under reduced pressure to yield a deep brown residue. This was chromatographed on silica gel eluting with LP–ethyl acetate (90:10) to yield the title compound **10a** as bright yellow needles (8.36 g, 30 mmol, 84%), mp 83–84 °C (lit.,[16] 88–89 °C from ethyl acetate–LP) (Found: C, 67.98; H, 4.96; N, 9.80; M^+, 282.0992. $C_{16}H_{14}N_2O_3$ requires C, 68.08; H, 5.00; N, 9.92%; *M*, 282.1004); ν_{max}(disc)/cm^{-1} 3084, 2922, 2835, 1651, 1605, 1526, 1345, 1309, 996 and 741; δ_H(CD_3COCD_3, 270 MHz) spectrum indicated the presence of two rotameric forms: 4.13 (1 H, br m, CH_2), 4.36 (1 H, br m, CH_2), 5.13 (2 H, m, HC=CH_2), 6.05 (1 H, m, *H*C=CH_2) and 7.20–8.05 (9 H, br m, ArH); δ_C(CD_3COCD_3, 100 MHz), 53.3 (CH_2), 118.9 (CH_2), 126.2 (CH), 128.9 (CH), 129.4 (CH), 129.9 (CH), 130.7 (CH), 133.1 (CH), 134.1 (CH), 134.9 (CH), 136.6 (C), 137.7 (C), 147.2 (C) and 169.8 (C); *m/z* (EI) 282 (M^+, 11%), 252 (45), 236 (35), 160 (20), 131 (53), 105 (100) and 77 (100).

N-(2-Nitrophenyl)benzamide[17] 9

To a stirred solution of 2-nitroaniline (3.04 g, 22 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (245 mg, 2 mmol) in dry pyridine (100 ml) at 0 °C was added benzoyl chloride (3.8 ml, 4.64 g, 33 mmol) under nitrogen over a period of 0.5 h; the solution was then warmed to room temperature. Excess of pyridine was removed *via* rotary evaporation and the residue dissolved in dichloromethane. The solution was washed with aqueous sulfuric acid (1 M; 3 × 500 ml), saturated aqueous sodium hydrogen carbonate (3 × 500 ml), water (3 × 500 ml) and brine (2 × 500 ml), dried and evaporated under reduced pressure to yield the title compound **9** as fine yellow crystals (4.96 g, 20.5 mmol, 93%), mp 93.5–94 °C (lit.,[17] 92–94 °C, from ethanol) (Found: C, 64.12; H, 4.07; N, 11.31. $C_{13}H_{10}N_2O_3$ requires C, 64.46; H, 4.16; N, 11.56%); ν_{max}($CHCl_3$)/cm^{-1} 3358, 1687, 1609, 1588 and 1342; δ_H(400 MHz) 7.22 (2 H, ddd, *J* 7.5, 7.5, 1.3, ArH), 7.57 (2 H, m, ArH), 7.72 (1 H, ddd, *J* 8.7, 8.7, 1.5, ArH), 8.01 (2 H, dd, *J* 8.8, 1.5, ArH), 8.27 (1 H, dd, *J* 8.5, 1.5, ArH), 9.02 (1 H, dd, *J* 7.5, 1.1, ArH) and 9.18 (1 H, br s, NH); δ_C(100 MHz) 122.0 (CH), 123.2 (CH), 125.8 (CH), 127.3 (CH), 128.9 (CH), 129.2 (CH), 133.9 (C), 135.2 (C), 136.1 (CH), 136.3 (C) and 165.6 (C).

N-(2-Nitrophenyl)-*N*-(3-methylbut-2-enyl)benzamide 10b

To a slurry of washed sodium hydride (60% suspension in mineral oil; 396 mg, 10 mmol) in dry tetrahydrofuran (200 ml) was added compound **9** (1.51 g, 6 mmol) portionwise over a period of 10 min under nitrogen; the mixture was then stirred for 0.5 h leading to the development of a deep red colouration. 4-Bromo-2-methylbut-2-ene (1.2 ml, 0.93 g, 10.4 mmol) was then added dropwise to the mixture after which it was stirred in the dark (12 h). Excess of tetrahydrofuran was removed by evaporation under reduced pressure, after which the yellow residue was partitioned between ethyl acetate and water (50 : 50, v/v; 300 ml) the aqueous phase was separated and further extracted with ethyl acetate (2 × 150 ml). The combined organic extracts were dried and concentrated *in vacuo* to furnish the *title compound* **10b** as a crystalline, yellow solid (1.41 g, 4.6 mmol, 73%), mp 80.5–82.5 °C (from ethyl acetate–LP) (Found: C, 69.52; H, 5.83; N, 8.76%; MH^+, 311.1411. $C_{18}H_{18}N_2O_3$ requires C, 69.66; H, 5.85; N, 9.03%; *M*H, 311.1396); ν_{max}($CHCl_3$)/cm^{-1} 2935, 2858, 1648, 1603, 1580, 1534, 1350 and 966; δ_H(CD_3SOCD_3, 400 MHz at 405 K) 1.35 (3 H, s, CH_3), 1.55 (3 H, s, CH_3), 4.33 (2 H, d, *J* 6.3, CH_2), 5.23 (1 H, m, HC=C), 7.25 (5 H, m, ArH), 7.44 (2 H, m, ArH), 7.63 (1 H, ddd, *J* 8, 8, 1.5, ArH) and 7.86 (1 H, dd, *J* 7, 1.2, ArH); δ_C(67.5 MHz), 17.5 (CH_3), 25.7 (CH_3), 47.7 (CH_2), 118.5 (CH), 125.4 (CH), 127.3 (CH), 127.4 (CH), 128.0 (CH), 129.9 (CH), 132.2 (CH), 133.6 (CH), 135.5 (C), 137.8 (C), 146.4 (C), 146.5 (C) and 169.8 (C); *m/z* (FAB) 311 [(MH^+), 36%], 105 (100) and 77 (35).

N-(2-Aminophenyl)-*N*-prop-2-enylbenzamide 11a

Sodium boranuide (1.67 g, 44 mmol) was added to a rapidly stirred solution of copper(II) acetylacetonate (744 mg, 2.9 mmol) in ethanol (250 ml) to give a brown suspension. Stirring was continued until a dark solid was precipitated and the opaque solution turned clear. Compound **10a** (4.06 g, 14 mmol)[18] was then added as a solution in ethanol (10 ml) to the mixture over 20 min. After being stirred for 3 h the reaction mixture was poured into water (200 ml), filtered and concentrated to low volume under reduced pressure. The aqueous phase was extracted with dichloromethane (3 × 150 ml) and the combined extracts were dried and evaporated under reduced pressure to yield the crude amine. After work-up the crude amine (660 mg) was purified by chromatography on silica gel using LP–ethyl acetate–isopropylamine (80:18:2) as eluent, to afford the *title compound* **11a** as a fine, colourless powder (2.72 g, 11 mmol, 75%), mp 76–78 °C (from diethyl ether–LP) (Found: M^+, 252.1247. $C_{16}H_{16}N_2O$ requires *M*, 252.1262); ν_{max}($CHCl_3$)/cm^{-1} 3402, 3342, 3068, 3034, 2973, 2931, 2871, 1616, 1572, 1504, 1351, 1001, 968, 926, 791, 746 and 724; δ_H(250 MHz) 3.91 (2 H, br s, NH_2), 4.12 (1 H, dd, *J* 14, 7, CH_2), 4.56 (1 H, dd, *J* 14.3, 6, CH_2), 5.21 (2 H, m, HC=CH_2), 6.03 (1 H, m, *H*C=CH_2), 6.52 (1 H, dd, *J* 7, 7, ArH), 6.65 (1 H, d, *J* 8, ArH), 6.70 (1 H, d, *J* 8, ArH), 7.0 (1 H, dd, *J* 7, 7, ArH), 7.18 (3 H, m, ArH) and 7.35 (2 H, d, *J* 7, ArH); δ_C(67.5 MHz) 51.1 (CH_2), 115.9 (CH), 118.1 (CH), 118.6 (CH_2), 127.5 (CH), 127.7 (CH), 128.5 (CH), 128.6 (CH), 129.8 (CH), 132.7 (CH), 135.5 (C), 142.5 (2C) and 171.2 (C); *m/z* (EI) 252 (M^+, 19%), 250 (25), 234 (100), 105 (58) and 77 (42).

N-(2-Aminophenyl)-*N*-(3-methylbut-2-enyl)benzamide 11b

Sodium boranuide (395 mg, 10.4 mmol) was added to a rapidly stirred solution of copper(II) acetylacetonate (220 mg, 0.83 mmol) in ethanol (250 ml) to give a brown suspension. Stirring was continued until a dark solid was precipitated and the opaque solution turned clear. Compound **10b** (1.02 g, 3.3 mmol) was then added as a solution in ethanol (10 ml) to the mixture over 20 min. After being stirred for 3 h the reaction mixture was poured into water (200 ml), filtered and concentrated to low volume under reduced pressure. The aqueous phase was extracted with dichloromethane (3 × 150 ml), and the combined extracts were dried and evaporated under reduced pressure to yield the crude amine. This was recrystallised to afford the *title compound* **11b** as a colourless, crystalline solid (711 mg, 2.5 mmol, 77%), mp 142.5–144 °C (from diethyl ether–LP) (Found: MH^+, 281.1661. $C_{18}H_{20}N_2O$ requires *M*H, 281.1654); ν_{max}($CHCl_3$)/cm^{-1} 3490, 3394, 1633, 1577, 908 and 860; δ_H(400 MHz) spectrum shows this compound to be a mixture of rotamers: 1.46 (3 H, s, CH_3), 1.60 (3 H, s, CH_3), 3.91

(2 H, br s, NH_2), 4.14 (1 H, dd, *J* 14, 8, CH_2), 4.51 (1 H, dd, *J* 13, 7.3, CH_2), 5.46 (1 H, m, HC=C), 6.50 (1 H, dd, *J* 7.5, 7.5, ArH), 6.63 (1 H, d, *J* 7.2, ArH), 6.68 (1 H, d, *J* 8.3, ArH), 6.98 (1 H, dd, *J* 7.3, 7.3, ArH), 7.20 (3 H, m, ArH) and 7.36 (2 H, d, *J* 7, ArH); δ_C(67.5 MHz) 17.5 (CH_3), 25.6 (CH_3), 45.9 (CH_2), 115.7 (CH), 118.2 (CH), 118.9 (CH), 127.5 (CH), 127.7 (CH), 128.4 (CH), 128.7 (C), 129.6 (CH), 130.4 (CH), 135.8 (C), 136.9 (C), 142.6 (C) and 171.2 (C); *m/z* (FAB) 281 (MH^+), (36%), 213 (36), 195 (16), 119 (100), 105 (100), 89 (13) and 77 (26).

2-(*N*-Benzoyl-*N*-prop-2-enylamino)benzenediazonium tetrafluoroborate 12a

Compound **11a** (2.64 g, 10.5 mmol) was dissolved in ethanol (3 ml) and aqueous fluoroboric acid (48% solution; 2 ml, 32 mmol) was added to the solution; the mixture was then cooled to −5 °C. Isoamyl nitrite (1.7 ml, 1.48 g, 13 mmol) was added dropwise to the mixture and stirring continued for 0.5 h. Dilution of the mixture with diethyl ether (50 ml) led to precipitation of the *title compound* **12a** as a fine, colourless powder (2.95 g, 8.4 mmol, 80%), mp 102–103 °C (decomp., from acetone–diethyl ether) (Found: C, 54.48; H, 4.04; N, 12.17. $C_{16}H_{14}BF_4N_3O$ requires C, 54.73; H, 4.02; N, 11.97%) (Found: M^+, 264.1145. $C_{16}H_{14}N_3O$ requires *M*, 264.1145); ν_{max}(disc)/cm^{-1} 3084, 2924, 2853, 2263, 1657, 1586, 968, 951, 769 and 730; δ_H(CD_3COCD_3, 250 MHz) 4.79 (2 H, ddd, *J* 6, 2, 2, CH_2), 5.20 (2 H, m, HC=CH_2), 6.02 (1 H, m, *H*C=CH_2), 7.48–7.63 (3 H, br m, ArH), 7.73 (2 H, ddd, *J* 7, 7, 2, ArH), 7.95 (1 H, ddd, *J* 8, 8, 2, ArH), 8.11 (1 H, dd, *J* 8, 2, ArH), 8.43 (1 H, ddd, *J* 8, 8, 2, ArH), 8.86 (1 H, dd, *J* 8, 2, ArH); δ_C(CD_3COCD_3, 67.5 MHz) 55.2 (CH_2), 113.1 (C), 119.9 (CH_2), 128.6 (CH), 129.3 (CH), 129.3 (CH), 129.5 (CH), 132.2 (CH), 134.3 (CH), 134.9 (CH), 143.6 (CH), 145.2 (2C) and 172.1 (C); *m/z* (FAB) 264 (M^+, 43%), 236 (100), 195 (12), 105 (84), 89 (33) and 73 (66).

2-(*N*-Benzoyl-*N*-3-methylbut-2-enylamino)benzenediazonium tetrafluoroborate 12b

Compound **11b** (640 mg, 2.3 mmol) was dissolved in ethanol (1.4 ml) and aqueous fluoroboric acid (48% solution; 1.4 ml, 7 mmol) was added to the solution; the mixture was then cooled to −5 °C. Isoamyl nitrite (380 μl, 331 mg, 2.78 mmol) was added dropwise to the mixture and stirring was continued for 0.5 h. Dilution of the mixture with diethyl ether (50 ml) led to precipitation of the title compound **12b** (695 mg, 1.8 mmol, 80%) as a pale yellow powder, mp 109–111 °C (decomp., from acetone–diethyl ether); ν_{max}($CHCl_3$)/cm^{-1} 2927, 2853, 2268, 1658, 1588 and 1000; δ_H(CD_3COCD_3, 400 MHz) 1.44 (3 H, s, CH_3), 1.63 (3 H, s, CH_3), 4.71 (2 H, d, *J* 7, CH_2), 5.4 (1 H, br m, HC=C), 7.55 (3 H, m, ArH), 7.71 (2 H, m, ArH), 7.94 (1 H, dd, *J* 8.4, 8.4, ArH), 8.08 (1 H, d, *J* 8.4, ArH), 8.41 (1 H, dd, *J* 8, 8, ArH) and 8.83 (1 H, dd, *J* 8.4, 1.3, ArH); compound decomposed in solution during acquisition of the ^{13}C spectrum; *m/z* (IS) 292.4 (M^+, 12%).

Reaction of compound 12a with tetrathiafulvalene

Tetrathiafulvalene (376 mg, 1.84 mmol) in acetone (2.5 ml) was added dropwise to a solution of compound **12a** (460 mg, 1.72 mmol) in degassed acetone (2 ml) and the mixture was stirred at room temperature for 5 min. It was then concentrated to low volume and poured into diethyl ether to precipitate a dark solid (380 mg) which was collected by filtration, under a nitrogen atmosphere and retained. The filtrate was evaporated under reduced pressure to yield a deep brown oil (564 mg). Column chromatography of this oil on silica gel eluting with LP–dichloromethane (80:20) separated the products, 5-prop-2-enyl-phenanthridin-6-one **13a** and *N*-prop-2-enylbiphenyl-2-amine **15a**, which were further purified by chromatography as indicated below.

Compound **13a**[3] was purified by column chromatography eluting with LP–ethyl acetate, the solvent polarity being gradually increased (98:2, 95:5, 90:10, 80:20 and 50:50) to furnish the phenanthridinone (46 mg, 0.2 mmol, 11.4%) as a pale yellow oil, which solidified with time, mp 94–96 °C (lit.,[3] 98–100 °C) (Found: M^+, 235.0976. $C_{16}H_{13}NO$ requires *M*, 235.0976); ν_{max}($CHCl_3$)/cm^{-1} 1640, 1610, 1587 and 977; δ_H(250 MHz) 5.07 (2 H, d, *J* 4.4, CH_2), 5.20 (1 H, d, *J* 17.5, HC=CH_2) 5.24 (1 H, d, *J* 10.4, HC=CH_2), 6.03 (1 H, ddt, *J* 17.5, 10.3, 4.5, *H*C=CH_2), 7.34 (2 H, m, ArH), 7.51 (2 H, m, ArH), 7.77 (1 H, dd, *J* 7.3, 7.3, ArH), 8.28 (2 H, d, *J* 8, ArH) and 8.55 (1 H, d, *J* 8, ArH); δ_C(67.5 MHz) 45.1 (CH_2), 115.8 (CH_2), 116.9 (CH), 119.5 (C), 121.6 (CH), 122.5 (CH), 123.3 (CH), 125.5 (C), 127.9 (CH), 129.0 (CH), 129.4 (CH), 131.9 (CH), 132.5 (CH), 133.8 (C), 138.4 (C) and 161.0 (C); *m/z* (EI) 235 (M^+, 38%), 220 (100), 195 (12) and 178 (17).

The second product **15a** was chromatographed twice on silica gel with LP–dichloromethane (80:20) to give *compound* **15a** (73 mg, 0.35 mmol, 22%) as a pale yellow oil (Found: M^+, 209.1222. $C_{15}H_{15}N$ requires *M*, 209.1204); ν_{max}(film)/cm^{-1} 3429, 3077, 2918, 1645, 1604, 748 and 704; δ_H(250 MHz) 3.73 (2 H, br d, *J* 5, CH_2), 5.08–5.25 (2 H, m, HC=CH_2), 5.81–5.97 (1 H, m, *H*C=CH_2), 6.68 (1 H, d, *J* 8, ArH), 6.78 (1 H, dd, *J* 7.4, 7.4, ArH), 7.08 (1 H, dd, *J* 6, 1.4, ArH), 7.24 (1 H, dd, *J* 8, 8, ArH), 7.32 (1 H, m, ArH) and 7.43 (4 H, m, ArH); δ_C(67.5 MHz) 46.4 (CH_2), 110.7 (CH), 115.9 (CH_2), 117.1 (CH), 127.2 (CH), 127.6 (C), 128.6 (CH), 128.9 (CH), 129.4 (CH), 130.2 (CH), 135.3 (CH), 139.4 (C) and 144.8 (C); *m/z* (EI) 209 (M^+, 100%), 182 (45), 167 (34), 152 (20) and 77 (15).

The dark solid from the initial precipitation, was purified by chromatography twice on silica gel eluting with dichloromethane–acetone (66:34) to furnish 1-(1-*benzoyl*-2,3-*dihydroindol*-3-*ylmethyl*)*tetrathiafulvalen*-1-*ium tetrafluoroborate* **17a** as a yellow powder (129 mg, 0.29 mmol, 17%), mp 112–115 °C (from acetone–diethyl ether) (Found: M^+, 440.0273. $C_{22}H_{18}NOS_4$ requires *M*, 440.0271); ν_{max}(disc)/cm^{-1} 1634, 1558, 1084 and 663; δ_H(CD_3COCD_3, 400 MHz: NMR shows this compound to be a mixture of diastereoisomers) 3.77 (d, *J* 5.6, CH_2S minor), 3.87 (2 H, m, CH_2S major), 4.13 (2 H, m, CH_2N), 4.39 (1 H, br m, C*H*Ar), 6.80 (1 H, d, *J* 6, CHS major), 6.86 (d, *J* 6, CHS minor), 7.07 (2 H, m, ArH), 7.19 (1 H, d, *J* 6, CHS), 7.32 (1 H, d, *J* 6, CHS), 7.38–7.60 (7 H, m, ArH), 8.17 (1 H, d, *J* 6, CHS) and 8.21 (1 H, d, *J* 6, CHS); δ_C(CD_3COCD_3, 100 MHz) 37.1 (CH), 37.7 (CH), 52.6 (CH_2), 53.0 (CH_2), 55.5 (CH_2), 56.0 (CH_2), 84.9 (C), 85.1 (C), 110.8 (CH), 112.8 (CH), 111.1 (2CH), 122.7 (CH), 123.4 (CH), 123.9 (CH), 125.0 (CH), 125.7 (CH), 126.0 (CH), 127.7 (CH), 127.9 (CH), 129.3 (CH), 129.4 (CH), 129.7 (CH), 131.2 (CH), 132.2 (CH), 137.8 (C), 137.9 (C), 143.7 (C), 143.8 (C), 145.1 (CH), 145.7 (CH), 161.9 (C), 164.0 (C) and 169.2 (C); *m/z* (FAB) 440 (M^+, 12%), 235 (95), 204 (89), 105 (73), 89 (45) and 77 (53).

Reaction of compound 12b with tetrathiafulvalene

Compound **12b** (300 mg, 0.8 mmol) was treated with tetrathiafulvalene (176 mg, 0.86 mmol) in degassed acetone (4 ml) and the resultant solution was poured into diethyl ether (100 ml) to precipitate a black solid. The filtrate was evaporated under reduced pressure to a yellow oil, which was adsorbed onto silica gel (from acetone) and chromatographed eluting with LP–dichloromethane (90:10) to separate the following products **13b**, **15b**, **16b** and **18b**.

***N*-(3-Methylbut-2-enyl)phenanthridin-6-one 13b.** This was further purified by chromatography eluting with LP–ethyl acetate (90:10) to give a pale oil (9.5 mg, 0.04 mmol, 5%) which solidified to a waxy solid upon refrigeration, mp 78–81 °C (Found: MH^+, 264.1380. $C_{18}H_{17}NO$ requires *M*H, 264.1388); ν_{max}(film)/cm^{-1} 2856, 1640, 1610 and 1586; δ_H(400 MHz) 1.74 (3 H, s, CH_3), 1.93 (3 H, s, CH_3), 5.03 (2 H, d, *J* 5.5, CH_2), 5.22 (1 H, br t, *J* 6, HC=C), 7.30 (1 H, ddd, *J* 8, 8, 1, ArH), 7.38 (1 H, d, *J* 8.4, ArH), 7.52 (1 H, ddd, *J* 7.2, 7.2, 1.4, ArH), 7.58 (1 H, ddd, *J* 8, 8, 1, ArH), 7.75 (1 H, ddd, *J* 8.4, 8.4, 1.7, ArH), 8.30 (2 H, dd, *J* 7, 7, ArH) and 8.55 (1 H, dd, *J* 8, 1, ArH); δ_C(100 MHz) 18.4 (CH_3), 25.6 (CH_3), 41.3 (CH_2), 119.5 (C), 119.7

(CH), 121.6 (CH), 122.3 (CH), 123.3 (CH), 125.6 (C), 127.9 (CH), 128.9 (CH), 129.4 (CH), 132.4 (CH), 132.4 (CH), 133.6 (C), 135.8 (C), 137.4 (C) and 161.3 (C); *m/z* (FAB) 264 [(MH^+), 12%], 196 (10), 91 (6), 77 (23), 69 (72) and 55 (96).

***N*-(3-Methylbut-2-enyl)biphenyl-2-amine 15b.** This was purified by column chromatography on silica gel eluting with LP–ethyl acetate (97:3) to give a pale yellow oil (25.4 mg, 0.11 mmol, 13.5%) (Found: M^+, 237.1516. $C_{17}H_{19}N$ requires *M*, 237.1517); ν_{max}(film)/cm^{-1} 3419, 3057, 2969, 2926, 2854, 1674, 1603, 1581, 770, 747 and 703; δ_H(250 MHz) 1.66 (3 H, s, CH_3), 1.69 (3 H, s, CH_3), 3.65 (2 H, d, *J* 6.5, CH_2), 3.88 (1 H, br s, NH), 5.21 (1 H, tm, *J* 6.5, HC=C), 6.68 (1 H, d, *J* 8.2, ArH), 6.76 (1 H, ddd, *J* 7.4, 7.4, 1.1, ArH), 7.09 (1 H, dd, *J* 7.5, 1.6, ArH), 7.24 (1 H, ddd, *J* 8, 8, 1.6, ArH), 7.35 (1 H, m, ArH) and 7.45 (4 H, m, ArH); δ_C(67.5 MHz) 18.0 (CH_3), 25.1 (CH_3), 42.0 (CH_2), 110.6 (CH), 116.9 (CH), 121.7 (CH), 127.1 (CH), 127.6 (C), 128.6 (CH), 128.8 (CH), 129.3 (CH), 130.2 (CH), 135.3 (C), 139.5 (C) and 145.1 (C); *m/z* (EI) 237 (M^+, 60%), 222 (20), 180 (17), 169 (100) and 77(5).

1-Benzoyl-3-isopropylindole 16b. This was chromatographed on silica gel eluting with LP–ethyl acetate (40:1) to yield a pale oil (4.4 mg, 0.02 mmol, 2%) (Found: MH^+, 264.1367. $C_{18}H_{17}NO$ requires *M*H, 264.1388); ν_{max}($CHCl_3$)/cm^{-1} 2929, 2854, 1679 and 1603; δ_H(400 MHz) 1.31 (6 H, d, *J* 6.9, $2CH_3$), 3.12 (1 H, septet, *J* 7, CH), 7.03 (1 H, s, N-CH), 7.20–7.45 (2 H, m, ArH), 7.53 (2 H, dd, *J* 7, 7, ArH), 7.60 (2 H, ddd, *J* 7.4, 7.4, 1.5, ArH), 7.71 (2 H, dd, *J* 7, 1.6, ArH) and 8.36 (1 H, d, *J* 8, ArH); δ_C(100 MHz) 22.5 ($2CH_3$), 25.3 (CH), 116.6 (CH), 119.4 (CH), 122.1 (CH), 123.53 (CH), 124.85 (CH), 128.56 (CH), 129.02 (CH), 129.50 (C), 130.51 (C), 131.6 (CH), 135.00 (C), 136.7 (C) and 168.5 (C); *m/z* (FAB) 264 [(MH^+), 59%], 220 (11), 196 (59), 105 (100), 91 (15), 77 (34), 69 (84) and 55 (65).

1-Benzoyl-2,3-dihydro-3-(2-hydroxypropan-2-yl)indole 18b. This was isolated from the initial elution without the need for further purification as a pale oil (42 mg, 0.16 mmol, 21%), which solidified with time to a beige powder, mp 109–111 °C (Found: MH^+, 282.1512. $C_{18}H_{19}NO_2$ requires *M*H, 282.1494); ν_{max}($CHCl_3$)/cm^{-1} 3378, 2930, 2853, 1684, 1636 and 1595; δ_H(CD_3SOCD_3, 400 MHz at 353 K) 0.99 (3 H, s, CH_3), 1.13 (3 H, s, CH_3), 3.26 (1 H, dd, *J* 9, 4.3, CH), 4.00 (2 H, m, N-CH_2), 7.00 (1 H, ddd, *J* 7.5, 7.5, 1.1, ArH), 7.13 (1 H, dd, *J* 8, 8, ArH), 7.39 (1 H, d, *J* 7.6, ArH) and 7.39–7.54 (6 H, m, ArH); δ_C(100 MHz) 25.4 (CH_3), 26.4 (CH_3), 50.5 (CH), 52.4 (CH_2), 70.6 (C), 115.7 (CH), 122.7 (CH), 125.9 (CH), 126.3 (CH), 126.8 (CH), 128.05 (CH), 129.6 (CH), 133.1 (C), 136.8 (C), 142.95 (C) and 167.3 (C); *m/z* (FAB) 282 [(MH^+), 8%], 223 (6), 147 (7) and 105 (33).

Tributyltin hydride-mediated radical cyclisation of the bromide 14

The bromide **14** (0.104 g, 0.328 mmol) in toluene (1.6 ml) was heated under reflux whilst AIBN (0.010 g, 0.0678 mmol) and tributyltin hydride (0.124 g, 0.427 mmol) were added in toluene (2 ml) to the mixture using a syringe pump over 1 h. The resulting solution was heated under reflux for 2 h after which evaporation of toluene led to a mixture which was shown by ^{1}H NMR spectroscopy to contain tributyltin residues as well as a mixture of phenanthridinone **13a** and 1-benzoyl-3-methyl-2,3-dihydroindole **19** in a 73:27 ratio. Column chromatography eluting with (hexane–ethyl acetate, 16:1) removed the tributyltin residues. Authentic dihydroindole was then isolated as below.

Separation of compound 19. A mixture of phenanthridinone **13a** and compound **19** (0.07 g, 0.297 mmol) from the above experiment was added in a mixture of acetone and water (9:1; 20 ml) to osmium tetroxide (0.8 ml of a solution in Bu^tOH, 0.0297 mmol). 4-Methylmorpholine *N*-oxide (0.0418 g, 0.0357 mmol) was added to the mixture which was then stirred for 24 h at room temperature. After this, solid sodium metabisulfite (1 g) was added to the mixture followed by aqueous sodium metabisulfite [0.7 g in water (5 ml)]; the mixture was then stirred for 45 min. After this the orange solution was filtered through Kieselguhr to remove osmium residues and then most of the acetone was removed *in vacuo*. The resulting solution was extracted with dichloromethane (3 × 10 ml), dried ($MgSO_4$), filtered and evaporated to dryness to give a pale yellow oil. This was subjected to column chromatography eluting with hexane–ethyl acetate (4:1) and gave compound **19** as a white solid (18 mg) together with dihydroxylation derivative **20** (42 mg) also as a white solid.

1-Benzoyl-3-methyl-2,3-dihydroindole 19. Mp 101–102 °C. (diethyl ether–LP) (lit.,[19] 101–102 °C); ν_{max}(KBr)/cm^{-1} 1638, 1478 and 1393; δ_H(250 MHz) 1.48 (d, 3 H, *J* 7, Me), 3.48 and 3.50 (m, 1 H, CHMe), 3.60 (br s, 1 H, NCH_2), 4.23 (br s, 1 H, NCH_2) and 7.06–8.26 (m, 9 H, ArH); *m/z* (EI) 237 (M^+, 10%), 130 (10) and 105 (100).

5-(2,3-Dihydroxypropyl)phenanthridin-6-one 20. Mp 147–148 °C; ν_{max}(KBr)/cm^{-1} 3381, 3335, 2923, 2853 and 1640; δ_H(250 MHz) 3.34 (br s, 2 H, 2 × OH), 3.50 (dd, 1 H, *J* 11.2, 2.2, NCH_2), 3.62 (dd, 1 H, *J* 11.2, 3.2, NCH_2), 4.05 (m, 1 H, OCH), 4.25 (dd, 1 H, *J* 13.5, 5.5, OCH_2), 4.25 (dd, 1 H, *J* 13.5, 7.5, OCH_2), 7.18–7.56 (m, 4 H, ArH), 7.73 (t, 1 H, *J* 8, ArH), 8.25 (t, 2 H, *J* 8, ArH) and 8.45 (d, 1 H, *J* 8); δ_C(CD_3COCD_3, 62.9 MHz), 46.7 (CH_2), 65.0 (CH_2), 71.4 (CH), 117.2 (CH), 120.2 (C), 123.0 (CH), 123.6 (CH), 124.4 (CH), 126.2 (C), 128.9 (CH), 129.3 (CH), 130.6 (CH), 133.8 (CH), 134.9 (C), 138.9 (C) and 163.1 (C).

N-(2-Nitrophenyl)acetamide[20] 29

To a warmed solution of 2-nitroaniline (10.4 g, 75 mmol) in benzene (10 ml), ethanoic anhydride (8 ml, 8.7 g, 85 mmol) was added dropwise followed by concentrated sulfuric acid (0.5 ml); this led to a vigorous reaction causing the benzene to reflux. The resulting mixture was warmed at reflux for 4 h, after which it was cooled and evaporated *in vacuo* to furnish the title compound **29** as yellow needles (12.9 g, 71.6 mmol, 94.5%), mp 93–95 °C (lit.,[20] 92–93 °C, from dilute, aqueous ethanol) (Found: M^+, 180.0497. $C_8H_8N_2O_3$ requires *M*, 180.0535); ν_{max}(disc)/cm^{-1} 3372, 3090, 2926, 1703, 1611, 1586, 1510, 1343, 836, 795 and 751; δ_H(270 MHz) 2.30 (3 H, s, CH_3), 7.10 (1 H, dd, *J* 8, 8, ArH), 7.65 (1 H, dd, *J* 8, 8, ArH), 8.20 (1 H, d, *J* 8, ArH), 8.75 (1 H, d, *J* 8, ArH) and 10.34 (1 H, br s, NH); δ_C(67.5 MHz) 25.2 (CH_3), 128.1 (CH), 122.9 (CH), 125.3 (CH), 134.5 (C), 135.5 (CH), 136.0 (C) and 168.8 (C); *m/z* (EI) 180 (M^+, 17%), 138 (100) and 92 (36).

N-(2-Nitrophenyl)-*N*-prop-2-enylacetamide 31a

To a slurry of washed sodium hydride (60% suspension in mineral oil; 213 mg, 5 mmol) in dry tetrahydrofuran (15 ml) was added compound **29** (525 mg, 2.92 mmol), portionwise over a period of 10 min under nitrogen; the mixture was then stirred for 0.5 h. Prop-2-enyl bromide **30a** (500 μl, 358 mg, 5 mmol) was then added dropwise to the mixture after which it was stirred in the dark (12 h). Excess of tetrahydrofuran was then removed from the mixture by evaporation under reduced pressure, and the yellow residue was partitioned between ethyl acetate and water (50:50, v/v; 300 ml) the aqueous phase was further extracted with ethyl acetate (2 × 150 ml). The combined organic extracts were dried, filtered and evaporated to yield a yellow oil, which was adsorbed onto silica gel (from dichloromethane) and chromatographed using LP–dichloromethane–methanol (70:20:10) as eluent to furnish the *title compound* **31a** (412 mg, 2 mmol, 68%) as an orange oil (Found: MH^+, 221.0927. $C_{11}H_{12}N_2O_3$ requires *M*H, 221.0926); ν_{max}(film)/cm^{-1} 3081, 3012, 2983, 2931, 1672, 1604, 1579, 1530, 1457, 1436, 1353, 1098, 993, 929 and 850; δ_H(CD_3SOCD_3, 400 MHz at 398 K; the spectrum shows this compound to be a 5:1 rotameric mixture) 1.86 (3 H, s, CH_3), 4.19 (2 H, br m, CH_2), 5.09 (2 H, m, HC=CH_2), 5.83 (1 H, m, *H*C=CH_2), 7.32 (1 H, dd, *J* 7, 2, ArH), 7.61 (1 H, ddd, *J* 7.6, 7.6, 1.5, ArH), 7.76 (1 H, ddd, *J* 7.6, 7.6, 1.5, ArH) and 8.02 (1 H, dd, *J* 7.2, ArH); δ_C(67.5 MHz) 21.4 (CH_3 minor), 21.9 (CH_3), 51.3 (CH_2), 54.2 (CH_2 minor), 117.6

(CH_2 minor), 118.7 (CH_2), 124.5 (CH minor), 125.0 (CH), 125.4 (CH minor), 129.2 (CH minor), 129.8 (CH), 131.6 (CH), 131.8 (CH), 132.3 (CH minor), 133.5 (CH minor), 133.9 (CH), 134.4 (C), 135.1 (C minor), 146.0 (C minor), 146.6 (C), 169.1 (C) and 170.7 (C minor); *m/z* (FAB) 221 [(MH^+), 100%], 179 (69), 145 (32), 133 (25), 119 (15), 105 (12), 91 (8) and 77 (15).

***N*-(2-Nitrophenyl)-*N*-but-2-enylacetamide 31b**

In a manner analogous to that for the preparation of **31a**, compound **29** (2.06 g, 11.4 mmol), sodium hydride (60% suspension in mineral oil; 680 mg, 17.7 mmol) and 4-bromobut-2-ene **30b** (1.3 ml, 1.73 g, 12.9 mmol) were allowed to react in dry tetrahydrofuran (10 ml). The resulting crude yellow oil was adsorbed onto silica gel (from dichloromethane) and chromatographed using LP–dichloromethane–methanol (70:20:10) as eluent to furnish the *title compound* **31b** (2.10 g, 9.5 mmol, 83%) as a mustard coloured oil (Found: C, 61.95; H, 6.06; N, 11.79%; MH^+, 235.1086. $C_{12}H_{14}N_2O_3$ requires C, 61.53; H, 6.02; N, 11.96%; *M*H, 235.1004); ν_{max}(film)/cm^{-1} 3010, 2967, 2919, 2857, 1666, 1602, 1578, 1530, 1352, 1005 and 754; δ_H(CD_3SOCD_3, 400 MHz at 398 K; the spectrum shows the compound to be a 3:1 rotameric mixture) 1.56 (3 H, d, *J* 5, CH_3), 1.84 (3 H, s, CH_3), 4.12 (2 H, br m, NCH_2), 5.46 (2 H, m, HC=CH), 7.45 (1 H, dd, *J* 8, 1.2, ArH), 7.48 (d, *J* 8, ArH, minor), 7.60 (1 H, dd, *J* 7.8, 7.8, ArH), 7.78 (1 H, ddd, *J* 7.7, 7.7, 1.5, ArH) and 8.00 (1 H, dd, *J* 8, 1.5, ArH); δ_C(67.5 MHz) 12.3 (CH_3 minor), 17.6 (CH_3), 21.9 (CH_3 minor), 22.6 (CH_3), 44.9 (CH_2 minor), 51.2 (CH_2), 123.7 (CH minor), 124.8 (CH), 125.1 (CH minor), 125.3 (CH), 128.0 (CH minor), 129.4 (CH), 131.0 (CH), 132.1 (CH), 133.8 (CH minor), 134.0 (CH), 135.7 (C), 136.1 (C minor), 146.0 (C minor), 147.6 (C), 169.6 (C) and 171.0 (C minor); *m/z* (FAB) 235 [(MH^+), 56%], 191 (11), 139 (35), 119 (14), 91 (23), 77 (25), 55 (100) and 43 (85).

***N*-(2-Nitrophenyl)-*N*-(3-methylbut-2-enyl)acetamide 31c**

In a manner analogous to that for the preparation of **31a**, compound **29** (2.48 g, 14 mmol), sodium hydride (60% suspension in mineral oil; 846 mg, 56.4 mmol) and 4-bromo-2-methylbut-2-ene **30c** (3.3 ml, 28 mmol) were allowed to react in dry tetrahydrofuran (100 ml). The resulting crude yellow oil was adsorbed onto silica gel (from dichloromethane) and chromatographed using LP–dichloromethane–methanol (70:20:10) as eluent to furnish the *title compound* **31c** (2.58 g, 10.4 mmol, 78%) as an orange oil (Found: C, 62.70; H, 6.63; N, 11.06%; MH^+, 249.1240. $C_{13}H_{16}N_2O_3$ requires C, 62.89; H, 6.50; N, 11.28%; *M*H, 249.1239); ν_{max}(film)/cm^{-1} 2973, 2933, 1672, 1602, 1578, 1353 and 734; δ_H(CD_3SOCD_3, 400 MHz at 298 K; the spectrum showed this compound to be a rotameric 4:1 mixture) 1.23 (3 H, s, CH_3), 1.49 (s, CH_3 minor), 1.53 (3 H, s, CH_3), 1.64 (s, CH_3 minor), 1.73 (3 H, s, CH_3), 2.14 (s, CH_3, minor), 4.09 (2 H, d, *J* 7.6, CH_2), 4.96 (1 H, br t, *J* 6, CH major), 5.34 (br t, *J* 6, CH minor), 7.45 (m, ArH minor), 7.56 (1 H, dd, *J* 7.8, 1.4, ArH), 7.66 (1 H, ddd, *J* 7.8, 7.8, 1.3, ArH), 7.71 (dd, *J* 8, 8, ArH minor), 7.79 (1 H, ddd, *J* 7.6, 7.6, 1.5, ArH), 7.91 (d, *J* 8, ArH minor) and 8.04 (1 H, dd, *J* 8, 1.5, ArH); δ_C(67.5 MHz) 16.7 (CH_3), 17.2 (CH_3 minor), 21.2 (CH_3), 21.5 (CH_3 minor), 25.2 (CH_3), 45.7 (CH_2), 49.6 (CH_2 minor), 117.7 (CH), 118.7 (CH minor), 124.6 (CH minor), 124.9 (CH), 127.6 (CH minor), 129.2 (CH), 129.7 (CH minor), 131.7 (CH), 133.4 (CH minor), 133.8 (CH), 135.2 (C), 135.8 (C minor), 136.5 (C minor), 137.8 (C), 146.3 (C minor), 147.2 (C), 169.2 (C) and 170.5 (C minor); *m/z* (FAB) 249 [(MH^+), 57%], 205 (9), 181 (19), 139 (42), 91 (17) and 77 (19).

***N*-(2-Aminophenyl)-*N*-prop-2-enylacetamide 32a**

Sodium boranuide (154 mg, 4 mmol) was added to a rapidly stirred solution of copper(II) acetylacetonate (70 mg, 0.3 mmol) in ethanol (25 ml) to give a brown suspension. Stirring was continued until a dark solid was precipitated and the opaque solution turned clear. Compound **31a** (260 mg, 1.3 mmol) was then added as a solution in ethanol over 20 min to the reaction which was then stirred for 3 h. After this it was poured into water (200 ml), filtered and concentrated to low volume under reduced pressure. The aqueous phase was extracted with dichloromethane, dried and evaporated under reduced pressure to yield the crude amine which was recrystallised to afford the *title compound* **32a** as a yellow powder (from diethyl ether–LP) (215 mg, 1.21 mmol, 97%) (Found: M^+, 190.1115. $C_{11}H_{14}N_2O$ requires *M*, 190.1106); ν_{max}(film)/cm^{-1} 3437, 3349, 3078, 3037, 2978, 2928, 1651, 1583, 988, 926 and 748; δ_H(250 MHz; the spectrum showed this compound to be a 9:1 rotameric mixture) 1.85 (s, CH_3 minor), 1.88 (3 H, s, CH_3), 3.87 (2 H, br s, NH_2), 3.97 (1 H, dd, *J* 14, 7, CH_2), 4.44 (1 H, dd, *J* 14, 7, CH_2), 5.11 (1 H, dt, *J* 16, 1, HC=C*H*$_2$), 5.11 (1 H, dt, *J* 9, 1, HC=C*H*$_2$), 5.91 (1 H, m, *H*C=CH_2), 6.80 (2 H, m, ArH), 6.94 (1 H, d, *J* 8, ArH) and 7.12 (1 H, dd, *J* 8, 8, ArH); δ_C(67.5 MHz) 21.0 (CH_3 minor), 21.9 (CH_3), 48.7 (CH_2 minor), 50.3 (CH_2), 116.1 (CH), 118.4 (CH_2), 121.8 (CH minor), 127.7 (C), 129.0 (CH), 129.2 (CH), 129.3 (CH), 132.8 (CH), 143.0 (C) and 171.4 (C); *m/z* (EI) 190 (M^+, 74%), 172 (50), 147 (36), 119 (71), 107 (100), 92 (18) and 77 (18).

***N*-(2-Aminophenyl)-*N*-but-2-enylacetamide 32b**

Sodium boranuide (305 mg, 12.7 mmol) was added to a rapidly stirred solution of copper(II) acetylacetonate (309 mg, 1.17 mmol) in ethanol (100 ml) to give a brown suspension. Stirring was continued until a dark solid was precipitated and the opaque solution turned clear. Compound **31b** (735 mg, 3.14 mmol) was then added as a solution in ethanol to the mixture over 20 min. After the reaction mixture had been stirred for 3 h it was poured into water (200 ml), filtered and concentrated to low volume under reduced pressure. The aqueous phase was extracted with dichloromethane and the extract dried and evaporated under reduced pressure to yield the crude amine. After work-up the crude amine was recrystallised to yield the *title compound* **32b** as a colourless, low density powder (457 mg, 2.2 mmol, 72%), mp 96–97 °C (from diethyl ether–LP) (Found: MH^+, 205.1333. $C_{12}H_{16}N_2O$ requires *M*H, 205.1341); ν_{max}($CHCl_3$)/cm^{-1} 3491, 3398, 2919, 2855, 1649, 1615, 970 and 640; δ_H(400 MHz; the spectrum shows this compound to be a rotameric mixture) 1.63 (3 H, d, *J* 5, CH_3), 1.85 (3 H, s, CH_3), 3.88 (2 H, br s, NH_2), 3.92 (1 H, dd, *J* 13.3, 5.5, CH_2), 4.32 (1 H, dd, *J* 13, 5.1, CH_2), 5.56 (2 H, m, *H*C=C*H*), 6.72 (1 H, ddd, *J* 7.6, 7.6, 1.3, ArH), 6.78 (1H, dd, *J* 8, 1.2, ArH), 6.93 (1 H, dd, *J* 7.8, 1.5, ArH) and 7.13 (1 H, ddd, *J* 7.8, 7.8, 1.5, ArH); δ_C(67.5 MHz) 17.6 (CH_3), 22.0 (CH_3), 49.6 (CH_2), 116.0 (CH), 118.5 (CH), 125.5 (CH), 128.0 (C), 129.1 (CH), 129.4 (CH), 130.0 (CH), 143.1 (C) and 171.3 (C); *m/z* (FAB) 205 [(MH^+), 100%], 187 (13), 161 (27), 119 (23), 77 (15) and 55 (34).

***N*-(2-Aminophenyl)-*N*-(3-methylbut-2-enyl)acetamide 32c**

Sodium boranuide (384 mg, 10 mmol) was added to a rapidly stirred solution of copper(II) acetylacetonate (234 mg, 0.9 mmol) in ethanol (100 ml) to give a brown suspension. Stirring was continued until a dark solid was precipitated and the opaque solution turned clear. Compound **31c** (803 mg, 3.24 mmol) was then added as a solution in ethanol to the mixture over 20 min. After the reaction mixture had been stirred for 3 h it was poured into water (200 ml), filtered and concentrated to low volume under reduced pressure. The aqueous phase was extracted with dichloromethane (3 × 50 ml) and the extract dried and evaporated under reduced pressure to yield the crude amine. After work-up the crude amine was recrystallised to yield the *title compound* **32c** as a cream powder (460 mg, 2.1 mmol, 65%), mp 122.5–124 °C (from diethyl ether–LP) (Found: MH^+, 219.1475. $C_{13}H_{18}N_2O$ requires *M*H, 219.1419); ν_{max}($CHCl_3$)/cm^{-1} 3493, 3398, 1642, 1615, 858 and 637; δ_H(400 MHz) 1.45 (3 H, s, CH_3), 1.67 (3 H, s, CH_3), 1.84 (3 H, s, CH_3), 3.79 (2 H, br s, NH_2), 4.09 (1 H, dd, *J* 14, 7.8, CH_2), 4.30 (1 H, dd, *J* 14, 7.3, CH_2), 5.28 (1 H, m, HC=C), 6.71 (2 H, m, ArH),

6.93 (1 H, dd, *J* 7.8, 1.5, ArH) and 7.13 (1 H, ddd, *J* 8, 8, 1.5, ArH); δ_C(100 MHz), 17.5 (CH_3), 22.0 (CH_3), 25.6 (CH_3), 44.9 (CH_2), 115.9 (CH), 118.5 (CH), 119.0 (CH), 128.1 (C), 129.00 (CH), 129.3 (CH), 138.8 (C), 143.00 (C) and 171.2 (C); *m/z* (FAB) 219 [(MH^+), 100%], 203 (10), 175 (48), 151 (73), 133 (36), 119 (38), 109 (54), 93 (22) and 77 (16).

2-(*N*-Acetyl-*N*-prop-2-enylamino)benzenediazonium tetrafluoroborate 33a

Compound **32a** (133 mg, 0.75 mmol) and aqueous fluoroboric acid (48% solution; 200 μl, 0.1 mmol) were mixed in ethanol (1 ml) and the mixture was cooled to −5 °C. Isoamyl nitrite (120 μl, 105 mg, 0.9 mmol) was added dropwise to the mixture and the stirring continued for 0.5 h. Dilution of the mixture with diethyl ether (50 ml) resulted in precipitation of the *title compound* **33a** as a yellow solid (151 mg, 0.55 mmol, 73%), mp 90.5–92 °C (decomp., from acetone–diethyl ether) (Found: M^+, 202.0987. $C_{11}H_{12}N_3O$ requires *M*, 202.0980); ν_{max}(disc)/cm^{-1} 3081, 3010, 2926, 2266, 1673, 1586, 974 and 772; δ_H(CD_3COCD_3, 400 MHz) 2.44 (3 H, s, CH_3), 4.73 (2 H, br m, CH_2), 5.33 (2 H, br m, HC=CH_2), 6.17 (1 H, m, *H*C=CH_2), 7.85 (2 H, m, ArH), 8.38 (1 H, dd, *J* 7, 7, ArH) and 8.75 (1 H, d, *J* 8, ArH); δ_C compound decomposed in solution during acquisition of the ^{13}C spectrum; *m/z* (FAB) 202 (M^+, 100%) and 174 (48).

2-(*N*-Acetyl-*N*-but-2-enylamino)benzenediazonium tetrafluoroborate 33b

In a procedure similar to that described for the preparation of **33a**, compound **32b** (230 mg, 1.1 mmol), aqueous fluoroboric acid (48% solution; 700 μl, 350 mg, 4 mmol) and isoamyl nitrite (250 μl, 105 mg, 1.8 mmol) were allowed to react in ethanol (1 ml) to furnish the *title compound* **33b** (295 mg, 1 mmol, 85%) as a cream solid mp 73–75 °C (decomp., from acetone–diethyl ether), ν_{max}($CHCl_3$)/cm^{-1} 2274, 1679, 1590 and 969; δ_H(CD_3COCD_3, 400 MHz) 1.70 (3 H, d, *J* 5, CH_3), 2.84 (3 H, br s, CH_3), 4.66 (2 H, br m, CH_2), 5.80 (2 H, br m, *H*C=C*H*), 7.89 (1 H, dd, *J* 7.4, 7.4, ArH), 7.98 (1 H, d, *J* 8.4, ArH), 8.38 (1 H, dd, *J* 8.4, 8.4, ArH) and 8.76 (1 H, d, *J* 8, ArH); δ_C compound decomposed in solution during acquisition of the ^{13}C spectrum; *m/z* (IS) 216.2 (M^+, 20%).

2-[*N*-Acetyl-*N*-(3-methylbut-2-enyl)amino]benzenediazonium tetrafluoroborate 33c

In a procedure similar to that described for the preparation of **33a**, compound **32c** (392 mg, 1.8 mmol), aqueous fluoroboric acid (48% solution; 800 μl, 4 mmol) and isoamyl nitrite (320 μl, 279 mg, 2.3 mmol) were allowed to react in ethanol (2 ml) to afford the *title compound* **33c** as a pale yellow powder (523 mg, 1.6 mmol, 91%), mp 87–89.5 °C (decomp., from acetone–diethyl ether); ν_{max}($CHCl_3$)/cm^{-1} 2273, 1678, 1590 and 1003; δ_H(CD_3COCD_3, 400 MHz) 1.68 (br s, CH_3 minor), 1.72 (6 H, br s, 2 CH_3), 2.83 (3 H, br s, CH_3), 4.69 (2 H, br m, CH_2), 5.48 (1 H, br m, HC=C), 7.89 (1 H, dd, *J* 6, 6, ArH), 7.94 (1 H, d, *J* 8.3, ArH), 8.40 (1 H, ddd, *J* 8.5, 8.5, 1.3, ArH) and 8.75 (1 H, d, *J* 8, ArH); δ_C compound decomposed in solution during acquisition of the ^{13}C spectrum; *m/z* (IS) 230.2 (M^+, 5%).

1-(1-Acetyl-2,3-dihydroindol-3-ylmethyl)tetrathiafulvalen-1-ium tetrafluoroborate 34

Tetrathiafulvalene (46.3 mg, 0.23 mmol) was added in one portion to compound **31a** (52.5 mg, 0.19 mmol) in dry degassed acetone (2 ml) and the mixture stirred for 5 min; it was then poured into diethyl ether (50 ml) to precipitate a dark solid, which was filtered off. Purification of this solid by column chromatography was carried out twice on silica gel eluting with dichloromethane–acetone (66:33) to give a dark brown waxy solid. This was dissolved in acetone and precipitated from diethyl ether to afford the *title compound* **34** (31.2 mg, 0.13 mmol, 68%) as a bright yellow powder, mp 107–110 °C (from acetone–diethyl ether); ν_{max}(disc)/cm^{-1} 2925, 1684, 1654, 1596, 1084 and 758; δ_H(CD_3COCD_3, 400 MHz; the spectrum shows this compound to be a mixture of diastereoisomers) 2.08 (s, CH_3 minor), 2.18 (3 H, s, CH_3), 3.77 (d, *J* 13, CH_2S minor), 3.94 (1 H, dd, *J* 13, 6.7, CH_2S), 4.02 (1 H, dd, *J* 13, 6.7, CH_2S), 4.26 (1 H, m, CH), 4.40 (m, CH_2N minor), 4.53 (2 H, m, CH_2N), 6.84 (d, *J* 6, CHS minor), 6.98 (1 H, d, *J* 6, CHS), 7.01 (1 H, d, *J* 8, ArH), 7.16–7.28 (3 H, m, ArH), 7.38 (1 H, d, *J* 7.3, CHS), 7.43 (1 H, d, *J* 7.4, CHS), 8.12 (d, *J* 7.3, CHS minor) and 8.23 (1 H, d, *J* 6, CHS); δ_C(CD_3COCD_3, 100 MHz) 24.2 (CH_3), 37.5 (2 CH), 53.8 (CH_2), 53.9 (CH_2), 85.2 (C), 85.6 (C), 112.5 (CH), 117.6 (CH), 117.7 (CH), 122.5 (CH), 122.8 (CH), 123.2 (CH), 123.6 (CH), 124.2 (CH), 125.5 (CH), 125.6 (CH), 129.6 (CH), 129.8 (CH), 131.0 (C), 144.2 (C), 145.3 (CH), 145.5 (CH), 163.0 (C), 163.7 (C) and 169.2 (2C); *m/z* (FAB) 378 (M^+, 22%), 307 (13), 204 (61), 174 (16) and 77 (48).

1-Acetyl-2,3-dihydro-3-(1-hydroxyethyl)indole 35b

Compound **33b** (20 mg, 0.07 mmol) and tetrathiafulvalene (14.4 mg, 0.07 mmol) were allowed to react in a degassed acetone–water mixture (99:1 v/v; 1 ml) which was stirred at room temperature for 5 min. Evaporation and chromatography of the mixture gave a deep brown residue which on silica gel eluting with LP–dichloromethane of gradually increasing polarity (90:10, 80:20, 50:50) and then ethyl acetate led to the *title compound* **35b** (8.3 mg, 0.04 mmol, 59%) as a pale yellow oil, which solidified to a waxy yellow solid, mp 75–77 °C (Found: M^+, 205.1103. $C_{12}H_{15}NO_2$ requires *M*, 205.1103); ν_{max}($CHCl_3$)/cm^{-1} 3381, 2854, 1652, 1597 and 806; δ_H(400 MHz; the spectrum shows this compound to be a 1:1 diastereoisomeric mixture) 1.10 (3 H, d, *J* 6.3, CH_3), 1.26 (3 H, d, *J* 6.3, CH_3), 2.23 (3 H, s, CH_3), 3.40 (1 H, m, C*H*Ar), 3.51 (1 H, m, C*H*Ar), 4.10 (3 H, m, CH_2, C*H*OH, overlapping), 7.03 (1 H, m, ArH), 7.23 (2 H, m, ArH) and 8.19 (1 H, d, *J* 8.1, ArH); δ_C(67.5 MHz) 18.7 (CH_3), 20.5 (CH_3), 24.1 (CH_3), 46.7 (CH), 47.3 (CH), 49.8 (CH_2), 50.7 (CH_2), 68.7 (CH), 69.8 (CH), 116.9 (CH), 123.5 (2CH), 124.3 (CH), 124.9 (CH), 128.2 (CH), 128.3 (CH), 131.6 (2C), 143.2 (C), 143.6 (C), 168.7 (C) and 168.9 (C); *m/z* (CI) 205 [(M^+), 5%].

Reaction of compound 33c with tetrathiafulvalene

Compound **33c** (145.3 mg, 0.46 mmol) and tetrathiafulvalene (107 mg, 0.52 mmol) were allowed to react in a degassed acetone–water mixture (99:1, v/v). The deep red residue was adsorbed onto silica gel (from acetone) and then chromatographed on silica gel eluting first with LP–dichloromethane (90:10) and then with mixtures of gradually increasing polarity (75:25, 50:50, 25:75, 100% dichloromethane) and then ethyl acetate (100%) to separate two products **35c** and **36c**.

Compound **35c** was further purified by chromatography on silica gel using ethyl acetate–dichloromethane (50:50) as eluent to afford N-*acetyl*-2,3-*dihydro*-3-(2-*hydroxypropan*-2-*yl*)*indole* as a pale waxy solid (58 mg, 0.26 mmol, 59%), mp 108–111 °C (Found: M^+, 219.1258. $C_{13}H_{17}NO_2$ requires *M*, 219.1259); ν_{max}($CHCl_3$)/cm^{-1} 3370, 2992, 2930, 2854, 1652, 1594 and 642; δ_H(400 MHz) 1.18 (3 H, s, CH_3), 1.27 (3 H, s, CH_3), 1.65 (1 H, br s, OH), 2.25 (3 H, s, CH_3), 3.36 (1 H, dd, *J* 8.1, 5, *H*C-Ar), 4.06 (2 H, m, CH_2), 7.01 (1 H, ddd, *J* 7.5, 7.5, 1, ArH), 7.25 (1 H, ddd, *J* 7, 7, 0.7, ArH), 7.32 (1 H, d, *J* 7.5, ArH) and 8.23 (1 H, d, *J* 8, ArH); δ_C(100 MHz) 24.2 (CH_3), 26.0 (CH_3), 27.1 (CH_3), 51.1 (CH), 51.6 (CH_2), 72.8 (C), 117.0 (CH), 123.3 (CH), 125.8 (CH), 128.3 (CH), 131.3 (C), 143.6 (C) and 168.5 (C); *m/z* (EI) 219 (M^+, 5%), 201 (2), 161 (25), 118 (100), 91 (15), 77 (5) and 59 (22).

Compound **36c** was further purified by column chromatography on silica gel using LP–ethyl acetate (50:50) as eluent to furnish N-*acetyl*-2,3-*dihydro*-3-(2-*fluoropropan*-2-*yl*)*indole* as a cream powder (5 mg, 0.02 mmol, 5%), mp 103–105.5 °C (Found: MH^+, 222.1292. $C_{13}H_{16}FNO$ requires *M*H, 222.1294); ν_{max}($CHCl_3$)/cm^{-1} 2934, 1652, 1596, 1402 and 1341; δ_H(400 MHz) 1.24 (3 H, d, $^3J_{HF}$ 21.4, CH_3), 1.39 (3 H, d, $^3J_{HF}$ 22, CH_3),

2.25 (3 H, s, CH_3), 3.63 (1 H, m, CH), 3.96 (1 H, dd, *J* 11.2, 4, CH_2), 4.06 (1 H, dd, *J* 11.2, 4, CH_2), 7.01 (1 H, dd, *J* 7.4, 7.4, ArH), 7.28 (2 H, m, ArH) and 8.22 (1 H, d, *J* 8.2, ArH); δ_F[235 MHz, $CDCl_3$ with $CFCl_3$ (0.2%) as internal reference] spectrum showed this compound to be a mixture of rotamers: −75.73 (m, minor) and −76.5 (m, major); δ_C(100 MHz) 23.1 (d, $^2J_{CF}$, 24.1, CH_3), 24.2 (CH_3), 24.5 (d, $^2J_{CF}$ 24.2, CH_3), 49.7 (d, $^2J_{CF}$ 24.2, CH), 51.1 (d, $^3J_{CF}$ 7.7, CH_2), 96.8 (d, $^1J_{CF}$ 170, C), 117.1 (CH), 123.5 (CH), 125.5 (CH), 128.7 (CH), 130.1 (C), 143.5 (C) and 168.4 (C); *m/z* (FAB) 222 [(MH^+), 68%], 178 (5), 144 (11), 128 (7), 118 (45), 91 (31), 69 (66) and 55 (95).

Acknowledgements

We thank the EPSRC for support and EPSRC and SmithKline Beecham for a CASE studentship. We also thank the EPSRC Mass Spectrometry Service Centre, Swansea, for mass spectra. We thank the Alliance Programme for Anglo-French cooperation for the award of a grant (S. G.) and Nadeem Bashir for assistance.

References

1 A. L. J. Beckwith and W. B. Gara, *J. Chem. Soc., Perkin Trans. 2*, 1975, 593, 795. A. L. J. Beckwith and G. F. Meijs, *J. Org. Chem.*, 1987, **52**, 1922.
2 J. P. Dittami and H. Ramanathan, *Tetrahedron Lett.*, 1988, **29**, 45.
3 H. Togo and O. Kikuchi, *Tetrahedron Lett.*, 1988, **29**, 4133; H. Togo and O. Kikuchi, *Heterocycles*, 1989, **28**, 373.
4 A. J. Clark and K. Jones, *Tetrahedron*, 1992, **48**, 6875; K. Jones and J. M. D. Storey, *J. Chem. Soc., Chem. Commun.*, 1992, 1766; K. Jones, T. C. T. Ho and J. Wilkinson, *Tetrahedron Lett.*, 1995, **36**, 6743.
5 G. B. Gill, G. Pattenden and S. J. Reynolds, *J. Chem. Soc., Perkin Trans. 1*, 1994, 369.
6 D. L. Boger and J. A. McKie, *J. Org. Chem.*, 1995, **60**, 1271.
7 D. P. Curran, H. Yu and H. Liu, *Tetrahedron*, 1994, **50**, 7343.
8 J. A. Murphy, C. Lampard and N. Lewis, *J. Chem. Soc., Chem. Commun.*, 1993, 295; R. Fletcher, C. Lampard, J. A. Murphy and N. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1995, 623.
9 T. J. Mills and J. A. Murphy, unpublished results.
10 For a preliminary account, see: J. A. Murphy, C. Lampard, F. Rasheed, N. Lewis, M. B. Hursthouse and D. E. Hibbs, *Tetrahedron Lett.*, 1994, **35**, 8675.
11 K. Jones and J. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1992, 1767; D. P. Curran and N. C. DeMello, *J. Chem. Soc., Chem. Commun.*, 1993, 1314.
12 N. S. Narasimhan and I. S. Aidhen, *Tetrahedron Lett.*, 1988, **29**, 2987; L. Friedman, *Tetrahedron Lett.*, 1961, **7**, 238; W. B. Motherwell, A. M. K. Pennell and F. Uzzainwalla, *J. Chem. Soc., Chem. Commun.*, 1992, 1067; W. B. Motherwell and A. M. K. Pennell, *J. Chem. Soc., Chem. Commun.*, 1991, 877; A. Citterio, R. Sebastiano, A. Maronati, R. Santi and F. Bergamini, *J. Chem. Soc., Chem. Commun.*, 1994, 1517.
13 D. H. Hey, C. W. Rees and A. R. Todd, *J. Chem. Soc. C*, 1967, 1518; D. H. Hey, G. H. Jones and M. J. Perkins, *J. Chem. Soc. C*, 1971, 116.
14 (*a*) J. Grimshaw, R. J. Haslett and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans 1*, 1977, 2448; (*b*) J. Grimshaw and R. J. Haslett, *J. Chem. Soc., Perkin Trans 1*, 1980, 657.
15 L. F. Fieser and E. L. Martin, *J. Am. Chem. Soc.*, 1935, **57**, 1835.
16 F. Mandyuk and R. V. Sendega, *Zh. Org. Khim.*, 1974, **10**, 364.
17 P. Ruggli and J. Rohner, *Helv. Chim. Acta*, 1942, 1533.
18 K. Hanaya, T. Muramitsu and H. Kudo, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2409.
19 D. E. Armes, H. R. Ansari, A. D. G. France, A. C. Lovesey, B. Novitt and R. Simpson, *J. Chem. Soc. C*, 1971, 3088.
20 L. F. Fieser and E. L. Martin, *J. Am. Chem. Soc.*, 1935, **57**, 1835.

Paper 6/07060D
Received 16*th October* 1996
Accepted 27*th January* 1997