# Reactions of 2-(pyrrol-1-yl)benzyl radicals and related species under flash vacuum pyrolysis conditions†

**J. I. G. Cadogan,*[a] Bernard A. J. Clark,‡[b] Daniel Ford,[c] Ranald J. MacDonald,[c] Andrew D. MacPherson,[c] Hamish McNab,*[c] Iain S. Nicolson,[c] David Reed[c] and Craig C. Sommerville[c]**

***Received 23rd July 2009, Accepted 14th September 2009***
***First published as an Advance Article on the web 21st October 2009***
**DOI: 10.1039/b914965a**

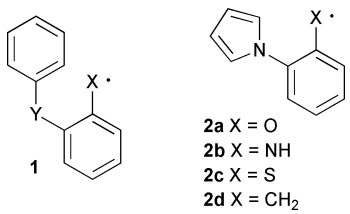


2-(Pyrrol-1-yl)phenoxyl, aminyl, thiophenoxyl and benzyl radicals **2a–2d**, respectively, were generated in the gas-phase under flash vacuum pyrolysis conditions. In all cases except the phenoxyl, cyclisation took place providing acceptable synthetic routes to the fused heterocycles **11**, **14** and **15**, respectively. Only sigmatropic rearrangement products were isolated, in low yields, from the phenoxyl **2a**. The pyrrolo[1,2-*a*]benzimidazole **11** adopts the 1*H*-tautomer exclusively in chloroform solution. Electrophilic substitution reactions of pyrrolo[2,1-*b*]benzothiophene **14** were studied, including protonation, deuterium exchange, Vilsmeier formylation and reaction with dimethyl acetylenedicarboxylate. 2-(2,5-Diarylpyrrol-1-yl)thiophenoxyl, phenoxyl and aminyl radicals **23a–f**, were also generated in the gas-phase under similar conditions. The thiophenoxyls **23a/b** gave extremely complex pyrolysate mixtures in which primary cyclisation products were formed by attack of the radical at the pyrrrole ring and attack at the *ipso*-, *ortho*- and *meta*- positions of the aryl ring. Secondary pyrolysis products were obtained by specific sigmatropic shifts of the *N*-aryl group. The 2,5-di(thien-2-yl)thiophenoxyl radical **23c** gave the pyrrolobenzothiazole **31c** as the only cyclisation product in low yield. FVP of the phenoxyl and aminyl radical generators **26d** and **26f**, respectively, gave 3-arylpyrrolo[1,2-*f*]phenanthridines **46d** and **46f**, respectively, by a hydrogen transfer-cyclisation mechanism.

## Introduction

We have previously studied the interactions of phenoxyl, aminyl, thiophenoxyl and benzyl radicals, with *ortho*-substituted aromatic functionalities (*e.g.* **1** X, Y = O, NH, S, $CH_2$).[1-4] The radicals were generated in the gas-phase by flash vacuum pyrolysis (FVP). Reactions of soft radicals **1** (X = $CH_2$ or S) are dominated by *ipso*-attack to provide a 5-membered ring intermediate, leading to rearranged cyclised products.[2] In contrast, hard radicals **1** (X = O or NH) tend to undergo inter- or intra-molecular hydrogen atom capture processes.[3,4] Although these reactions provided an unexpectedly rich mechanistic tapestry, their synthetic utility was disappointing.

In order to overcome these synthetic disadvantages, the radicals **2** were designed so that attack to give a 5-membered ring might lead to products directly without the complications of *ipso* attack and rearrangement. These substrates were also attractive




because relatively few radical reactions of pyrrole nuclei have been reported, even in solution;[5] we hoped our reactions would help establish the reactivity of pyrroles with radical centres in the gas-phase and, if successful, lead to a new synthetic approach to bridgehead nitrogen heterocycles. In the second part of the paper, we describe our work on the reactivity of 2-(2,5-diarylpyrrol-1-yl) species, in which the radicals can in principle collapse to products *via* reaction at the π-system of pyrrole ring or at its 2(5)-substitutent.

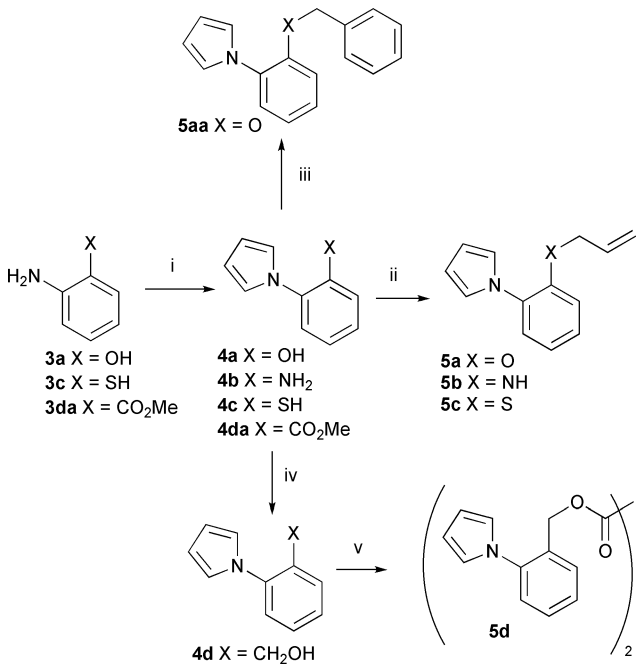
## Results and discussion

As before,[6] we employed allyl or benzyl precursors to phenoxyl, aminyl and thiophenoxyl radicals **2a-c**, and an oxalate precursor to the benzyl radical **2d**. The allyl precursors **5a-c**, the *O*-benzyl precursor **5aa** and the oxalate precursor **5d** were made by the standard methods shown in Scheme 1. In order to establish whether other azole derivatives show similar reactivity, the related pyrazole **7** was synthesised by two-step reductive amination of the amino-compound **6** (Scheme 2).

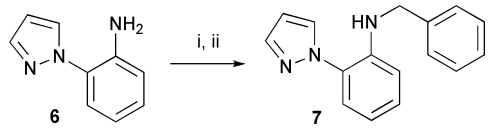
[a]*Department of Chemistry, University of Wales Swansea, Swansea, UK SA2 3PP*
[b]*Kodak European Research and Development, Headstone Drive, Harrow, Middlesex, UK HA1 4TY*
[c]*School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ. E-mail: H.McNab@ed.ac.uk; Fax: +44 131 650 4743; Tel: +44 131 650 4718*

† Electronic supplementary information (ESI) available: Experimental, NOE results. See DOI: 10.1039/b914965a

‡ Current address: c/o Dr Christopher Moore, Kodak European Research, 332 Science Park, Cambridge, UK CB4 0WN.

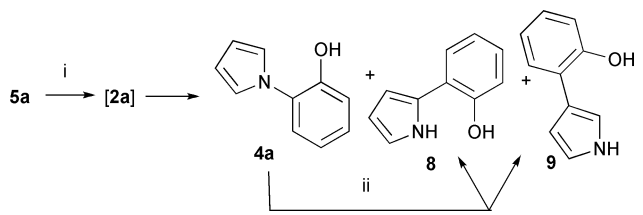



**Scheme 1** *Reagents and conditions:* (i) 2,5-dimethoxytetrahydrofuran, HOAc, dioxane, reflux; (ii) allyl bromide, $K_2CO_3$, DMF, 20 °C; (iii) benzyl bromide, $K_2CO_3$, DMF, 20 °C; (iv) $LiAlH_4$, 37 °C; (v) oxalyl chloride. $Et_3N$, 0 °C.




**Scheme 2** *Reagents and conditions:* (i) PhCHO, EtOH, 20 °C; (ii) $NaBH_4$, MeOH, 65 °C.

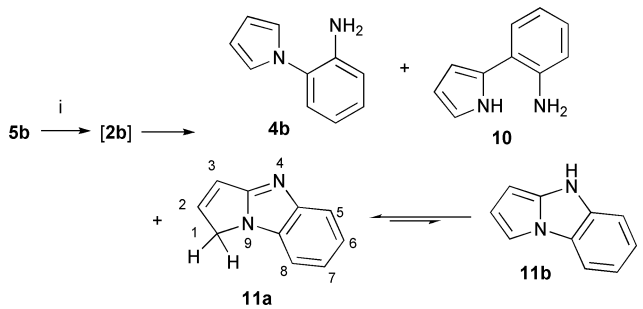
FVP of the *o*-allyloxy and *o*-benzyloxy compounds **5a** and **5aa** at 650 and 750 °C respectively gave disappointing results. No evidence of cyclisation products could be detected and the only products isolated after chromatography were the hydrogen capture product **4a** and the rearranged phenols **8** and **9** (from **5a**, 48, 16 and 0% yields, respectively; from **5aa**, 11, 20 and 10% yields, respectively), obtained by 1,5-sigmatropic shift of the *N*-aryl group, followed by hydrogen capture (Scheme 3). Hydrogen capture is a well-known property of phenoxyl radicals generated under FVP conditions.[4,6] Surprisingly, the temperature required for the formation of the rearranged products is significantly lower than expected for 1,5-sigmatropic shifts in pyrrole systems in our apparatus. Indeed synthesis of authentic samples of **8** and **9** by FVP of **4a** required a furnace temperature of 900 °C for




**Scheme 3** *Reagents and conditions:* (i) FVP (650 °C, 0.005 Torr); (ii) FVP (900 °C, 0.005 Torr).

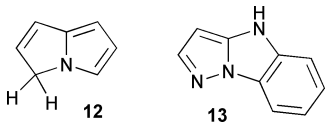
reasonable conversion. This suggests either that the formation of the radical is accompanied by chemical activation[7] or that there is a radical induced acceleration of the sigmatropic shift. There has been speculation that radical acceleration of 3,3-sigmatropic shifts may be observed,[8] but the evidence may not be unequivocal.[9]

The $^1$H NMR spectrum of the crude pyrolysate from the *N*-allyl compound **5b** is dominated by an apparent triplet at $\delta_H$ 4.59 ($J$ 1.9 Hz) but only the hydrogen capture product **4b** (16%) and a sigmatropic shift product **10** (7%) could be isolated by chromatography (Scheme 4). However, detailed NMR analysis of the crude pyrolysate showed that the major product is in fact the 1*H* tautomer of pyrrolo[1,2-*a*]benzimidazole **11a** and that the apparent triplet is due to approximately equal $^3J$ and $^4J$ coupling between the $CH_2$ group and the 2- and 3-protons, a well-known feature of the spectrum of pyrrolizine **12** and related systems.[10] The NOESY spectrum of **11a** confirmed that a signal at $\delta_H$ 7.05 is due to the 2-proton and the COSY spectrum showed that the signal due to the 3-proton resonates at $\delta_H$ 6.90. The yield of **11a** estimated from the NMR spectrum was *ca.* 49%. The expected cyclisation product, the 4*H* tautomer **11b** has been reported[11] (mp[11] 98–100 °C) from a reaction involving nitrene insertion following nitro-group deoxygenation, but characterisation details are sketchy. In view of our results on the stable tautomer of **11**, it is possible that the 2-amino compound **4b** (mp[12] 98–99 °C) may have been isolated instead, by the earlier workers.




**Scheme 4** *Reagents and conditions:* (i) FVP (750 °C, 0.005 Torr).

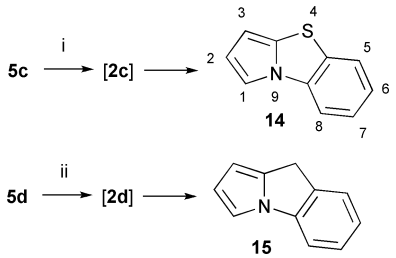
As a second example of aminyl radical cyclisation, the known pyrazolo[1,5-*a*]benzimidazole **13**[13] was obtained in 20% yield as its 4*H*-tautomer, by FVP of the benzylamino compound **7**. The general principle has therefore been established, that radical cyclisation reactions onto azole nuclei can take place under FVP conditions.




FVP of the allylthio compound **5c** provided the known pyrrolo[2,1-*b*]benzothiophene **14**[14] in 87% yield on a multi-gram scale (Scheme 5). Cyclisation of the thiophenoxyl onto the 2-position of the pyrrole therefore takes place with great efficiency, as found for benzenoid systems.[2] The overall yield of **14** is 63%, in 3 steps from commercially available starting materials. This method therefore provides a potentially useful, reagent free, alternative to previous solution-phase routes to **14**.[15]

The well-known pyrroloindole **15**[16] was obtained in 85% yield by FVP of the oxalate **5d** at 750 °C. The overall yield for the 4 steps

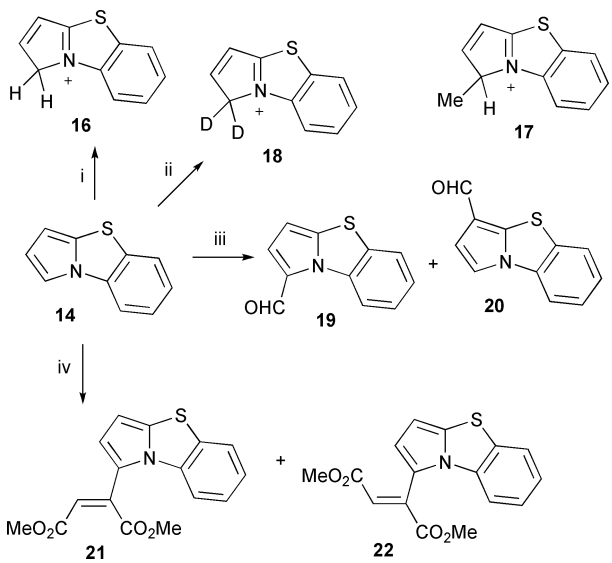
 




**Scheme 5** *Reagents and conditions:* (i) FVP (650 °C, 0.005 Torr); (ii) FVP (750 °C, 0.005 Torr).

of the synthetic route is 49%, comparable to a recent literature method (2 steps, 41% overall yield).[17] Taken together with the above example, it is clear that efficient cyclisation of soft radical species at the 2-position of pyrrole can occur, leading to workable synthetic routes to fused heterocycles exemplified by **14** and **15**.

With the availability of the pyrrolobenzothiazole **14**, its reactivity with mild electrophiles was briefly investigated (Scheme 6). It is smoothly protonated at the 1-position in TFA solution to give **16**. The position of protonation was established by corresponding reaction of the 1-methyl derivative;[18] in the protonated species **17** the 1-methyl group occurs as a doublet ($^3J$ 7.2 Hz) due to coupling with the 1-proton. The protonated species are stable in TFA solution for at least 2 weeks. In [$^2$H]TFA, the dideuteriated compound **18** is formed instantly, which suggests that the initial monodeuteriated species is in rapid equilibrium with the free base. A second pyrrole-type proton also exchanges with a half life of *ca.* 10 min, but the position of this reaction was not established unambiguously.




**Scheme 6** *Reagents and conditions:* (i) TFA, 20 °C; (ii) DTFA, 20 °C; (iii) DMF, $POCl_3$ 20 °C; (iv) DMAD, 20 °C.

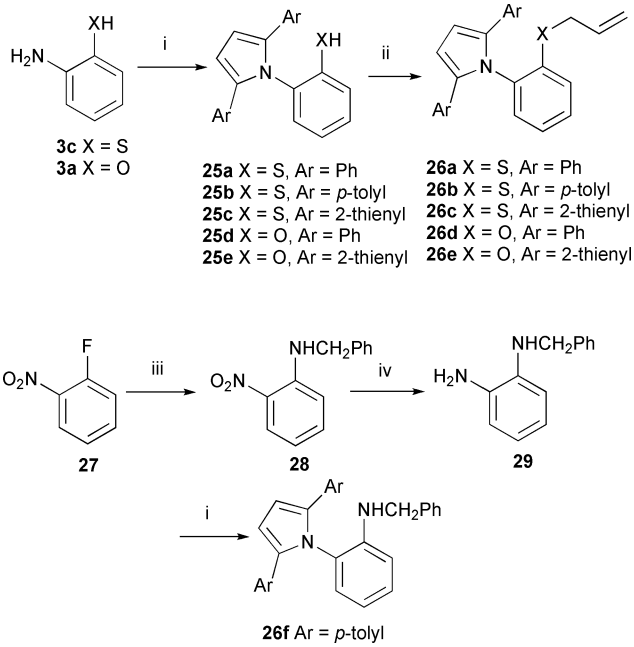
*In situ* Vilsmeier–Haack formylation of **14** has been previously reported to provide an 8 : 1 ratio of the 1- and 3-isomers **19** and **20** respectively. In our hands, both products were obtained, though in very low yield (5% and 7% respectively) (Scheme 6) which may be a consequence of the work-up. Key NOE enhancements which confirm previous assignments[19] are shown in the ESI.†

Compound **14** reacted with dimethyl acetylenedicarboxylate (DMAD) exclusively by conjugate addition at the 1-position. Both *Z*- and *E*- isomers **21** (20%) and **22** (33%), respectively, were obtained (Scheme 6) and NOE data leading to the assignment of the *Z*-isomer are shown in the ESI.† The predominance of *Z*-isomer over *E*-isomer is in accord with the work of Tsuge *et al.*[20] who obtained analogous results by the reaction of 2-phenylpyrrolo[2,1-*b*]benzothiazole with DMAD.


**23a** X = S, Ar = Ph
**23b** X = S, Ar = *p*-tolyl
**23c** X = S, Ar = 2-thienyl
**23d** X = O, Ar = Ph
**23e** X = O, Ar = 2-thienyl
**23f** X = NH, Ar = *p*-tolyl

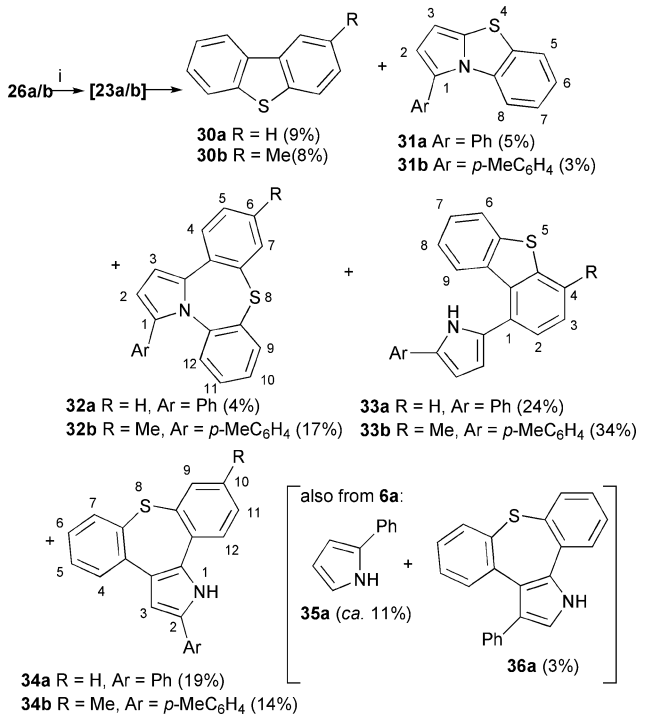
**24**

In the second part of this paper, we consider the generation and reactions of thiophenoxyl, phenoxyl and aminyl radicals **23**. These studies show the effect on the cyclisation process of blocking the 2,5-positions of the pyrrole ring by aryl groups; the properties of the 2,5-dialkyl analogues **24** will be the subject of a future paper. The radicals were again generated by FVP of their allyl or benzyl derivatives **26**. Most of these precursors were synthesised from 2-substituted anilines **3a/c** by a two-step method (Scheme 7); the aminyl precursor **26f** was made *via N*-benzyl-*o*-phenylenediamine **29** (Scheme 7).




**Scheme 7** *Reagents and conditions:* (i) $ArCO(CH_2)_2COAr$, benzene or toluene/acetic acid, reflux; (ii) allyl bromide, $K_2CO_3$, DMF, 20 °C; (iii) $PhCH_2NH_2$, $K_2CO_3$, 0 °C; (iv) $H_2$, Pd/C, MeOH.

FVP of the *S*-allyl compound **26a** at 750 °C gave a complex pyrolysate (Scheme 8) from which seven compounds could be separated by dry-flash chromatography. The structure of the minor products **30a** (9%) and **35a** (11%) followed by literature comparison (see Experimental section); the constitution of **31a**




**Scheme 8** *Reagents and conditions:* (i) FVP (substrate **26a** 750 °C; substrate **26b** 650 °C).

was apparent from its mass spectrum (loss of Ph$^{\bullet}$ From **23a**) and from the two 'pyrrole' peaks ($\delta_H$ 6.52 and 6.32, $^3J$ 3.6 Hz) whose coupling constant is consistent with the assignment as H-2 and H-3 (*c.f.* data for **14**). This mode of reaction, which gives by far the major product from **2c** is now reduced to a very minor pathway, due to the high heat of formation of the phenyl radical.[6]

The structure of the seven-membered ring **32a** (4%) follows from the NOE data shown in the ESI† and from its mass spectrum, recorded under FAB conditions [*m/z* 326, $(M+H)^+$]. (Under EI conditions, an intense peak was observed at *m/z* 293 due to loss of S from the molecular ion—see below.) Significant enhancements observed between the 7- and 9-positions would suggest that the seven-membered ring is butterfly-shaped, as found for related structures.[21] This is an unusual example of stable seven-membered rings being formed by radical cyclisation under FVP conditions.[22]

Two compounds isomeric with **32a** were identified as **34a** (19%) and **36a** (3%) as follows. Both showed NH signals at *ca.* $\delta_H$ 9.1 so it was clear that sigmatropic rearrangements had occurred. The pyrrole CH proton of **34a** ($\delta_H$ 7.58; resolved at 360 MHz in [$^2H_6$]acetone solution) shows NOE interaction with the *ortho*-protons of the phenyl group and one other aromatic proton (ESI†). Its NH proton is also close in space to the phenyl group and to a different single aromatic proton. Irradiation of the NH proton of **36a** causes enhancement of a proton at $\delta_H$ 7.94, part of a 4-spin system and to a single proton at $\delta_H$ 7.10 ($J$ 2.6 Hz) which was itself adjacent to the phenyl group. The connectivities shown are therefore established. It is clear that the 2-phenyl group of **34a** has undergone sigmatropic rearrangement to the 3-position, *en route* to formation of **36a**.

The major product of the reaction, **33a** (24%), was shown by mass spectrometry to be isomeric with **32a**, **34a** and **36a** but it had a very different structure. Two pyrrole-like protons ($\delta_H$ 6.49 and 6.68) showed evidence of coupling to each other and to an NH (at $\delta_H$ 8.68). A phenyl ring was still present, and the remaining seven protons were contained in one 4-spin system and one 3-spin system [$\delta_H$ ([$^2H_6$]acetone) 7.99, 7.54 and 7.49] whose coupling constants were typical of a 1,2,3-trisubstituted aromatic. NOE data (ESI†) between the NH and a proton of the 4-spin system serve to identify the product as the 1-substituted dibenzothiophene **33a** rather than its 4-substituted isomer.

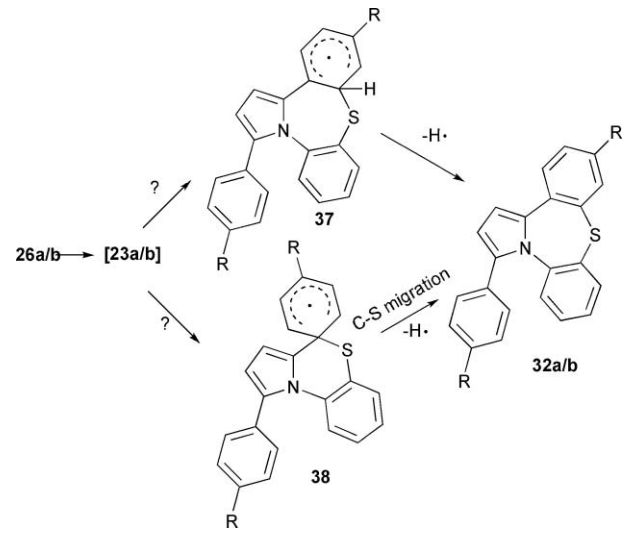
A number of mechanisms can be drawn for the formation of these products so the *p*-tolyl precursor **26b** was synthesised in order to help define the connectivities of the bond forming processes. FVP of **26b** was carried out at 650 °C to minimise the occurrence of fragmentation products (such as **35a**) and secondary rearrangement products (such as **36a**). Five products were isolated and identified (Scheme 8). It was clear that these were closely related to corresponding products from **26a**, except that the cleavage product (*c.f.* **35a**) and the multiple rearrangement product (*c.f.* **36a**) were indeed not isolated in this case. Significantly, only one isomer of the ring systems **30b**–**34b** was isolated. Structures of the 2-methyldibenzothiophene **30b** (8%) and the aryl-cleavage product **31b** (3%) were readily assigned by comparison with an authentic sample and by analogy with the formation of **31a**, respectively.

Location of the position of the methyl group(s) in **32b**–**34b** was of particular importance and NOE/NOESY data are presented in the ESI.† All showed the presence of an unreacted *p*-tolyl group which is ignored in the following discussion. For compound **32b**, the other methyl group was located on the tri-substituted benzene ring and correlations could be traced in one direction, to the pyrrole ring, and in the other to the 9-proton of the 4-spin system. The location of the methyl group of compound **33b** is defined by its correlation with one of the two protons of a two-spin system, whose other proton correlates with a pyrrole proton. The NOESY spectrum of **34b** showed interactions between the NH and the *p*-tolyl group in one direction, and a tri-substituted benzene ring in the other; the methyl group showed NOESY interactions with both of the other protons of this 3-spin system, which defines the substitution pattern as shown (ESI†).

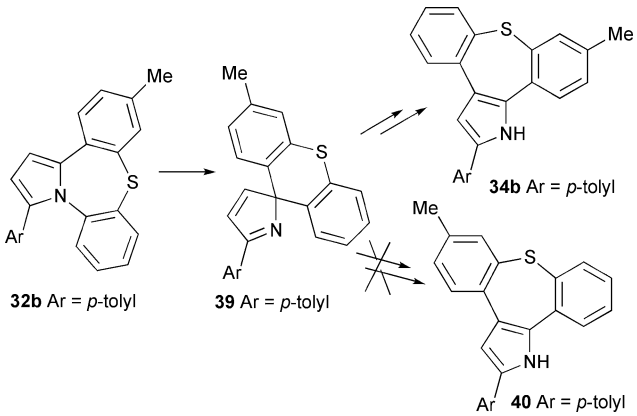
Mechanistically, only the formation of **31a/b** by attack at the 2(5)-position of the pyrrole ring and loss of the aryl radical, follows the general precedent set by reactions reported in the first part of this paper. In principle, compounds **32** may be formed by two mechanisms, either direct attack at the *ortho*-position of the aryl substituent or by attack at the *ipso*-position and migration (Scheme 9). The latter is observed in related cases (*e.g.* 2-benzylthiophenoxyl[2]) and results in the formation of two isomeric products. In this case, the formation of only one isomer **32b** suggests either direct attack *via* **37**, or formation of the spirodienyl intermediate **38** followed by exclusive migration of the sulfur substituent.

In principle, the simplest route to the sigmatropic shift products **34a/b** is by rearrangement of the thiazepines **32a/32b**. However, there is no obvious reason why the remote methyl group in the 2,2-diaryl intermediate **39** should have such an influence on the subsequent migration such that **40** is not formed (Scheme 10). To form **34b**, the *N*-aryl group, which initially migrates to the 2-position, continues to migrate to the 3-position. Alternatively, if the sigmatropic shift of a radical species is favoured,[8,9] the exclusive formation of **34b** becomes easy to understand (Scheme 11). The

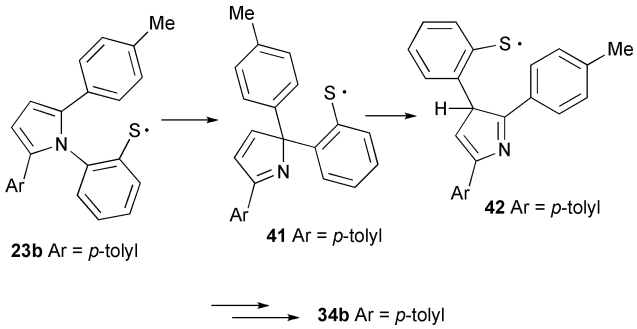
 




Scheme 9



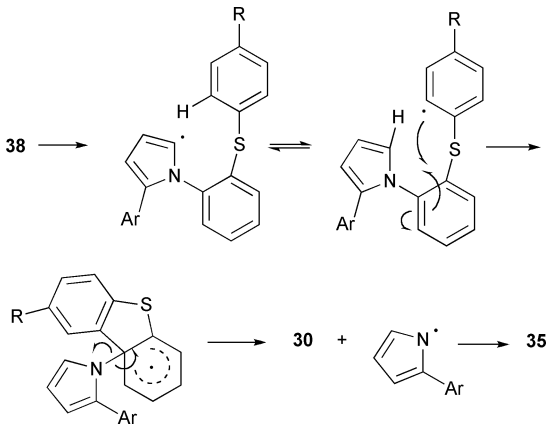

Scheme 10




Scheme 11

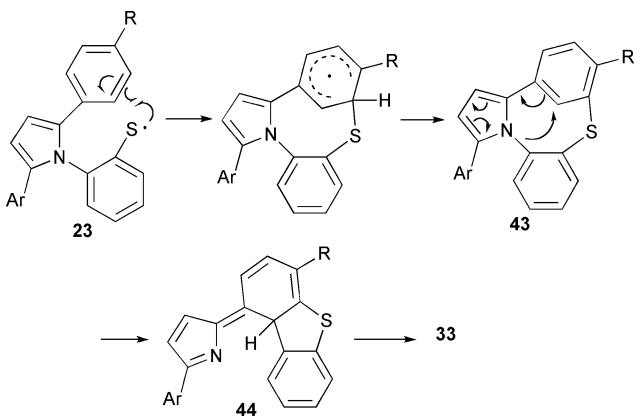
initial formation of **41** is followed by continued migration of the aryl group bearing the thiophenoxyl radical to provide **42**, which gives **34b** by cyclisation, loss of a hydrogen atom and multiple 1,5-H shifts (Scheme 11). Other sigmatropic shifts presumably rationalise the formation of the trace of **36a** formed in the pyrolysis of **26a**.

The two dibenzothiophenes, **30a/b** and **33a/b**, must be formed by different mechanisms, since the substitution pattern in **30b** and **33b** is different. In **30b**, the methyl group is *para* to the sulfur atom, suggesting that collapse of the *ipso*-intermediate **38** may be involved. A possible mechanism, involving translocation of the aryl group, hydrogen atom shift and cyclisation, is shown in Scheme 12. The co-product can abstract a hydrogen atom to provide 2-arylpyrrole, which was the identified species **35a** from FVP of **26a**.



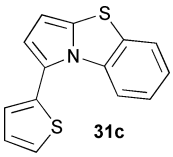

Scheme 12

The connectivity formed in **33b** suggests that the mechanism for the formation of the major products, **33**, requires thiophenoxyl **23a/b** to attack at the position *meta* to the pyrrole ring in **23b** to provide the 8-membered *m*-cyclophane intermediate **43**. Pericyclic ring closure creates **44** which provides **33** after H-shifts and aromatisation (Scheme 13).



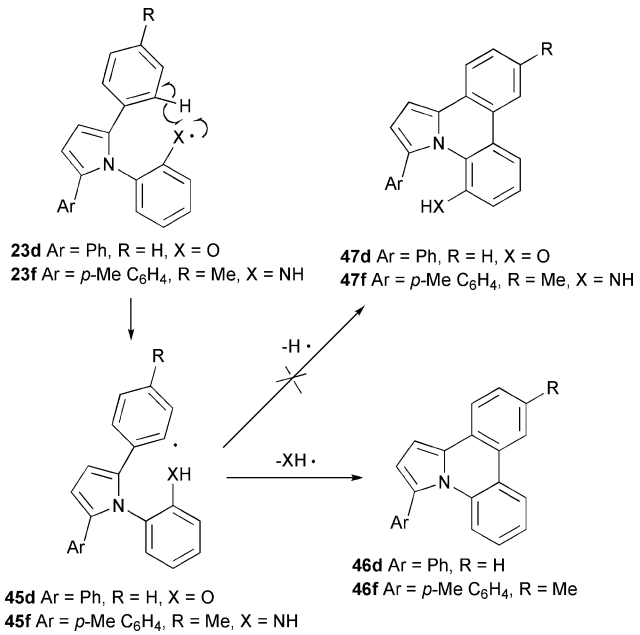

Scheme 13

Thus, significant primary pyrolysis products are formed from the radicals **23a/b** by attack at the pyrrole ring, attack at the *ipso* position of the aryl ring, attack at the *ortho*-position of the aryl ring (or at the *ipso*-position followed by rearrangement) and at the *meta* position of the aryl ring. In contrast, FVP of the 2,5-di(thien-2-yl) compound **26c** was disappointing. Changing the geometrical and electronic requirements of the system in this way gave a complex pyrolysate from which only low yields of **31c** could be isolated (23%) (formed by ejection of a thiophen-2-yl radical) together with the thiophenol **25c** (61%). Hydrogen abstraction by thiophenoxyl radicals is unusual,[6] but other reaction pathways appear to be even less feasible in this system.




**31c**

In contrast, hydrogen atom abstraction by phenoxyl and aminyl radicals is a common reaction pathway under FVP conditions.[1,3,4] Radicals **23d–23f** offer the possibility of hydrogen atom abstraction from the 2-aryl group, though only *via* a (potentially disfavoured) 8-membered transition state. In practice, this mode of reaction proved to be an efficient process for **23d** whose FVP at 650 °C gave 3-phenylpyrrolo[1,2-*f*]phenanthridine **46d** as essentially the only product in 60% isolated yield. None of the phenol **47d** was formed, so the aryl radical **45d** obtained by intramolecular hydrogen atom transfer cyclises exclusively with loss of OH• rather than by loss of H• (Scheme 14). This behaviour is in contrast to that of 2-benzylphenoxyl radicals[4] (which cyclise after hydrogen transfer with exclusive loss of H•). The greater steric requirements of intermediates leading to **47d/f** may be involved. Only the trivial intermolecular hydrogen abstraction product **25e** (76%) could be isolated from the FVP of the 2,5-dithienyl precursor **26e**.




**Scheme 14**

FVP of the *N*-benzyl precursor **26f** required 800 °C for complete removal of the benzyl group and gave a complex set of products, from which only bibenzyl and the 3-arylpyrrolo[1,2-*f*]phenanthridine **46f** (19%) could be isolated. The latter was clearly the major product from the NMR spectrum of the crude pyrolysate. In broad terms, therefore, phenoxyl and aminyl radicals show similar properties in this series of compounds.

## Conclusions

In conclusion, FVP of the *S*-allyl compound **5c** and of the oxalate **5d** provides good yields of the bridgehead heterocycles **14** and **15** *via* the soft radicals **2c** and **2d**. This work establishes that the 2-position of pyrrole is capable of attack by soft radical species. Although the same conclusion may hold for the aminyl **2b**, the situation is complicated by the chemical instability of the cyclised product and the formation of minor impurities. Nevertheless, this is the first authentic report of the parent pyrazolo[1,5-*a*]benzimidazole, which exists as the 1*H* tautomer in chloroform solution. Extension to the pyrazole series was successful in principle, though the isolated yield of **13** was low. Only the phenoxyl **2a** gave no useful cyclisation products, though the occurrence of 1,5-sigmatropic shifts at unexpectedly low temperatures may indicate that the rearrangement is accelerated by the presence of the radical centre. Meanwhile, the FVP reactions of 2-(2,5-diarylpyrrol-1-yl) thiophenoxyl species have been shown to be extremely complex with at least five reaction pathways taking place in competition. Surprisingly, the major product is formed by attack of the thiophenoxyl *meta*- to the site of the pyrrolyl substituent. There is some further evidence for accelerated migration aptitude in 1,5-aryl shift reactions, of aryl groups bearing a radical centre. Reactions of related phenoxyls and aminyls are instead dominated by intramolecular hydrogen atom transfer and cyclisation of the resulting phenyl radical, with loss of the resulting $OH/NH_2$ substituents.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded at 200 (or 250) and 50 (or 63) MHz respectively for solutions in [$^2H$]chloroform unless otherwise stated. Coupling constants are quoted in Hz. Mass spectra were recorded under electron impact conditions.

### *N*-[2-(Allyloxy)phenyl]pyrrole 5a

A mixture of 2-aminophenol **3a** (3.60 g, 33 mmol), 2,5-dimethoxytetrahydrofuran (3.96 g, 30 mmol) and glacial acetic acid (15 $cm^3$) in dioxane (30 $cm^3$) was heated under reflux for 4 h. The volatiles were then removed on a rotary evaporator and the residue was taken up between ether (60 $cm^3$) and 3% aqueous sodium hydroxide (90 $cm^3$). The aqueous phase was separated, acidified (pH 4) and extracted with chloroform (3 × 50 $cm^3$). The combined extracts were washed with sodium hydrogen carbonate (1 M, 50 $cm^3$), dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. The crude product was then purified by bulb to bulb distillation to give *N*-(2-hydroxyphenyl)pyrrole **4a** (2.95 g, 61%), bp 138–140 °C (0.03 Torr) (lit.,[23] mp 45-47 °C) [Found: $M^+$ 159.0687. $C_{10}H_9NO$ requires *M* 159.0684]; $\delta_H$ 7.35-7.26 (2H, m), 7.11-6.98 (2H, m), 6.94 (2H, t, $^3J$ and $^4J$ 2.2) and 6.44 (2H, t, $^3J$ and $^4J$ 2.2); $\delta_C$ 150.16 (quat), 128.70, 128.22 (quat), 126.58, 121.86, 120.79, 116.81 and 110.12; *m/z* 159 ($M^+$, 100%), 158 (11), 131 (27), 130 (41), 103 (10) and 51 (21).

A suspension of anhydrous potassium carbonate (2.29 g, 16.6 mmol) in DMF (20 $cm^3$) was stirred for 10 min. *N*-(2-Hydroxyphenyl)pyrrole **4a** (2.64 g, 16.6 mmol) and allyl bromide (2.41 g, 19.9 mmol) were added and the mixture stirred until t.l.c. showed the disappearance of the *N*-arylpyrrole. Water (40 $cm^3$) was added and the mixture was extracted with ether (3 × 15 $cm^3$). The combined extracts were washed with water (3 × 30 $cm^3$) and dried ($MgSO_4$). The solvent was removed on a rotary evaporator to yield the crude product which was purified by bulb to bulb distillation to give *N*-[2-(allyloxy)phenyl]pyrrole **5a** (2.74 g,

83%), bp 110-115 °C (0.005 Torr) (Found: C, 78.6; H, 6.75; N, 7.0. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.05%); $\delta_H$ 7.42-7.27 (2H, m), 7.16 (2H, t, $^3J$ and $^4J$ 2.3), 7.13-7.05 (2H, m), 6.43 (2H, t, $^3J$ and $^4J$ 2.3), 6.05 (1H, m), 5.40 (2H, m) and 4.61 (2H, m); $\delta_C$ 151.50 (quat), 132.78, 130.69 (quat), 127.19, 125.62, 122.00, 121.29, 117.32, 114.19, 108.77 and 69.44; *m/z* 199 ($M^+$, 58%), 198 (19), 184 (12), 172 (14), 170 (14), 159 (14), 158 (100), 132 (11), 130 (12), 103 (14), 80 (10), 77 (27) and 51 (17).

The other products made by this method are described in the ESI.†

### FVP reactions

FVP experiments were carried out by distillation of the substrate *in vacuo* through an electrically heated silica furnace tube (35 × 2.5 cm). Products were trapped in a U-tube situated at the exit point of the furnace and cooled with liquid nitrogen. Pyrolysis conditions are quoted as follows: substrate, quantity, furnace temperature ($T_f$), inlet temperature ($T_i$), pressure range ($P$), pyrolysis time ($t$) and products.

### FVP of *N*-[2-(allyloxy)phenyl]pyrrole 5a

The crude pyrolysate from the FVP of *N*-[2-(allyloxy)phenyl]-pyrrole **5a** (0.200 g, 1 mmol), ($T_f$ 650 °C, $T_i$ 80–100 °C, $P$ 0.005 Torr, $t$ 10 min) was washed from the trap with dichloromethane and extracted with sodium hydrogen carbonate (1 M). The basic fraction was then acidified with hydrochloric acid (2 M) and extracted with ether. The acidic products were then separated by dry-flash chromatography. This gave *N*-(2-hydroxyphenyl)pyrrole **4a** (0.076 g, 48%) bp 145–150 °C (0.05 Torr), identified by comparison of NMR spectra with that reported above and 2-(2-hydroxyphenyl)pyrrole[24] **8** (0.025 g, 16%) bp 140–145 °C (0.05 Torr) (Found: $M^+$ 159.0686. $C_{10}H_9NO$ requires $M$ 159.0684) $\delta_H$ 9.63 (1H, br. s), 7.56 (1H, dd), 7.12–6.80 (4H, m), 6.63 (1H, m) and 6.33 (1H, m); $\delta_C$ 151.06 (quat), 128.96 (quat), 126.92, 126.80, 121.12, 119.58 (quat), 118.25, 116.19, 108.96 and 105.94; *m/z* 159 ($M^+$, 100%), 158 (11), 131 (49), 130 (73), 104 (13), 103 (21), 102 (11), 78 (10), 77 (30) and 51 (71).

### FVP of *N*-[2-(Benzyloxy)phenyl]pyrrole 5aa

The crude pyrolysate from the FVP of *N*-[2-(benzyloxy)phenyl]-pyrrole **5aa** (0.553 g, 2 mmol), ($T_f$ 750 °C, $T_i$ 140–160 °C, $P$ 0.005 Torr, $t$ 10 min) was worked up as described for **5a** and the products were separated by dry-flash chromatography to give *N*-(2-hydroxyphenyl)pyrrole **4a** (0.040 g, 11%), 2-(2-hydroxyphenyl)pyrrole[24] **8** (0.071 g, 20%), bp 150–155 °C (0.1 Torr) (Found: $M^+$ 159.0686. $C_{10}H_9NO$ requires $M$ 159.0684), $^1$H NMR and mass spectra compatible with those reported above; and 3-(2-hydroxyphenyl)pyrrole **9** (0.035 g, 10%),[24] bp 155–160 °C (0.1 Torr) (Found: 159.0684. $C_{10}H_9NO$ requires $M$ 159.0684); $\delta_H$ 8.50 (1H, br. s), 7.63-6.89 (6H, m) and 6.44 (1H, m); $\delta_C$ 152.64 (quat), 129.25, 127.53, 122.59 (quat), 120.42, 119.43 (quat), 119.24, 116.34, 115.16 and 108.25; *m/z* 159 ($M^+$, 79%), 131 (38), 130 (57), 103 (37), 102 (32), 86 (31), 84 (43), 77 (100), 65 (33), 63 (62) and 51 (86).

### *N*-(2-Hydroxyphenyl)pyrrole 8 and *N*-(3-hydroxyphenyl)pyrrole 9

FVP of *N*-(2-hydroxyphenyl)pyrrole **4a** (0.495 g, 3.1 mmol), ($T_f$ 900 °C, $T_i$ 80–100 °C, $P$ 0.005 Torr, $t$ 30 min) gave a mixture of three products which were separated by dry-flash chromatography to give recovered *N*-(2-hydroxyphenyl)pyrrole **4a** (0.042 g, 8%), 2-(2-hydroxyphenyl)pyrrole **8** (0.034 g, 7%), ($^1$H NMR and mass spectra compatible with those reported above) and 3-(2-hydroxyphenyl)pyrrole **9** (0.069 g, 14%), ($^1$H NMR and mass spectra compatible with those reported above).

### FVP of *N*-[2-(allylamino)phenyl]pyrrole 5b

The $^1$H NMR spectrum of the crude pyrolysate from FVP of *N*-[2-(allylamino)phenyl]pyrrole **5b** (0.511 g, 2.58 mmol), ($T_f$ 750 °C, $T_i$ 60–80 °C, $P$ 0.005 Torr, $t$ 10 min) showed a clear signal at $\delta_H$ 4.59 (t, $J$ 1.9). Attempted separation by chromatography on 6% deactivated alumina gave only *N*-(2-aminophenyl)pyrrole **4b** (0.065 g, 16%), mp 92–94 °C (lit.,[12] 98–99 °C) (Found: $M^+$ 158.0843. $C_{10}H_{10}N_2$ requires $M$ 158.0844); $\delta_H$ 7.20-7.12 (2H, m); 6.84-6.75 (4H, m); 6.35 (2H, t, $^3J$ 2.1) and 3.62 (2H, br); *m/z* 158 ($M^+$, 100%), 157 (91), 156 (13), 131 (16), 130 (35) and 65 (14); and 2-(2-aminophenyl)pyrrole **10** (0.030 g, 7%), mp 121-126 °C (Found: $M^+$ 158.0843. $C_{10}H_{10}N_2$ requires $M$ 158.0844) $\delta_H$ 8.70 (1H, br. s), 7.24 (1H, m), 7.09 (1H, m), 6.88-6.74 (3H, m), 6.43 (1H, m), 6.32 (1H, m) and 4.80 (2H, br. s); $\delta_C$ 143.23 (quat), 129.45 (quat), 128.32, 127.69, 119.60 (quat), 118.96, 117.87, 116.35, 109.21 and 107.21; *m/z* 158 ($M^+$,100%), 157 (29), 131 (14), 130 (81), 103 (11) and 77 (17).

In a repeat pyrolysis (68.7 mg, 0.35 mmol), ($T_f$ 750 °C, $T_i$ 60-80 °C, $P$ 0.01 Torr, $t$ 10 min) the major product was identified as 1*H*-pyrrolo[1,2-*a*]benzimidazole **11a** (*ca.* 49%) from the NMR spectra of the crude reaction mixture, but was not purified; $\delta_H$ 7.78 (1H, m), 7.39 (1H, m), 7.24 (2H, m), 7.05 (1H, dt, $^3J$ 6.1, $^3J$ 1.9) 6.90 (1H, dt $^3J$ 6.1, $^4J$ 1.9) and 4.59 (2H, t, $^3J$ and $^4J$ 1.9); $\delta_C$ 139.83, 128.30 (quat), 122.27 (2CH), 121.55, 120.49, 118.96 (quat), 116.35 (quat), 108.88 and 49.16 ($CH_2$); *m/z* 156 ($M^+$, 6%), 109 (63), 84 (100), and 67 (51).

### FVP of 1-(2-benzylaminophenyl)pyrazole 7

FVP of 1-(2-benzylaminophenyl)pyrazole **7** (0.41 g, 1.6 mmol), ($T_f$ 750 °C, $T_i$ 100 °C, $P$ 0.004 Torr, $t$ 90 min) gave products that were separated by gravity chromatography on alumina (grade III) eluting with a mixture of *n*-hexane and ethyl acetate, to provide 4*H*-pyrazolo[1,5-*a*]benzimidazole **13** (0.05 g, 20%), mp 216–218 °C (lit.,[13] 220 °C) $\delta_H$ ([$^2H_6$]acetone) 10.44 (1H, br s), 7.76 (1H, m), 7.69 (1H, d, $^3J$ 2.1), 7.46 (1H, m), 7.28 (1H, td, $^3J$ 7.6, $^4J$ 1.3), 7.21 (1H, td, $^3J$ 7.6, $^4J$ 1.2) and 5.77 (1H, d, $^3J$ 2.1); $\delta_C$ 143.54 (quat), 143.05, 135.10, 125.48 (quat), 122.45 (quat), 119.39, 111.11, 108.99 and 78.80; *m/z* 157 ($M^+$, 94%), 156 (16), 149 (100), 119 (10), 104 (10), 103 (26) and 81(16), and bibenzyl (0.14 g, 48%), $\delta_H$ ([$^2H_6$]acetone) 6.68-7.12 (10H, m) and 2.65 (4H, s).

### FVP of *N*-[2-(allylthio)phenyl]pyrrole 5c

FVP of *N*-[2-(allylthio)phenyl]pyrrole **5c** (2.12 g, 9.87 mmol), ($T_f$ 650 °C, $T_i$ 100 °C, $P$ 0.005 Torr, $t$ 20 min) gave pyrrolo[2,1-*b*]benzothiophene **14**, which was washed from the trap with dichloromethane and purified by bulb to bulb distillation (1.47 g,

87%), bp 90–100 °C (0.05 Torr) mp 52–54 °C (from hexane–ethyl acetate) (lit.,[14] 52 °C) (Found: C, 69.0; H, 4.2; N, 8.1. $C_{10}H_7NS$ requires C, 69.35; H, 4.05; N, 8.1%); $\delta_H$ 7.61-7.51 (2H, m), 7.45 (1H, dd, $^3J$ 2.9 and $^4J$ 1.3), 7.35 (1H, m), 7.21 (1H, m), 6.61 (1H, dd, $^3J$ 3.6 and 2.9) and 6.24 (1H, dd, $^3J$ 3.6 and $^4J$ 1.3); $\delta_C$ 134.42 (quat), 131.40 (quat), 127.49 (quat), 125.23, 123.67, 123.44, 114.57, 111.46, 110.08 and 98.62; *m/z* 173 ($M^+$, 100%) and 39 (34).

### FVP of bis-[2-(pyrrol-1-yl)benzyl] oxalate 5d

FVP of bis-[2-(pyrrol-1-yl)benzyl] oxalate **5d** (0.50 g, 1.25 mmol), ($T_f$ 750 °C, $T_i$ 160–180 °C, $P$ 0.005 Torr, $t$ 20 min) gave 9*H*-pyrrolo[1,2-*a*]indole **15**, which was washed from the trap with dichloromethane and purified by bulb to bulb distillation (0.33 g, 85%), bp 60–65 °C (0.3 Torr), mp 89–91 °C (from ethanol) [lit.,[16] bp 60–65 °C (0.2 Torr), mp 90–91 °C] (Found: $M^+$ 155.0731 $C_{11}H_9N$ requires $M$ 155.0735); $\delta_H$ 7.41–7.24 (3H, m), 7.13–7.04 (2H, m), 6.39 (1H, t, $^3J$ 3.0), 6.12 (1H, m) and 3.84 (2H, d, $^4J$ 0.4); $\delta_C$ 141.06 (quat), 135.37 (quat), 134.84 (quat), 127.29, 125.73, 122.94, 113.01, 109.61 (2 CH), 101.57 and 28.92; *m/z* 155 ($M^+$, 81%), 154 (100), 153 (10), 127 (12) and 77 (15).

### Protonation and deuterium exchange reactions of pyrrolo[2,1-*b*]benzothiophene 14

Pyrrolo[2,1-*b*]benzothiophene **14** was dissolved in trifluoroacetic acid. Protonation occured at the 1-position to give $\delta_H$ (80 MHz) 8.27-7.84 (4H, m), 7.50 (1H, m), 5.54 (2H, m) and 5.25 (1H, s).

1-Methylpyrrolo[2,1-*b*]benzothiophene[18] was dissolved in trifluoroacetic acid. Protonation occured at the 1-position to give **17** $\delta_H$ (80 MHz) 8.20–7.81 (4H, m), 7.43 (1H, dd), 5.76 (1H, q, $^3J$ 7.2), 5.24 (1H, s) and 1.98 (3H, d, $^3J$ 7.2).

Pyrrolo[2,1-*b*]benzothiophene **14** was dissolved in [$^2$H]trifluoroacetic acid. Exchange took place initially at the 1-position over a period of less than 2 min, followed by exchange of another proton (2- or 3-position) over a period of 30–40 min.

### Formylation of pyrrolo[2,1-*b*]benzothiophene 14

Phosphoryl chloride (2 $cm^3$) was dissolved in DMF (20 $cm^3$). A solution of pyrrolo[2,1-*b*]benzothiophene **14** (0.173 g, 1 mmol) in DMF (10 $cm^3$), was added dropwise. The mixture was stirred until t.l.c. showed the disappearance of the starting material and the appearance of two products of lower $R_f$ value. The reaction mixture was neutralised with sodium hydroxide (2 M), extracted with ether (3 × 25 $cm^3$), and the combined organic fractions were washed with water (3 × 50 $cm^3$) and dried ($MgSO_4$). The crude products were then pre-adsorbed onto silica and separated by dry-flash chromatography to give 1-formylpyrrolo[2,1-*b*]benzothiophene **19** (0.010 g, 5%), mp 127–130 °C (lit.,[19] 132–132.5 °C) (Found: $M^+$ 201.0243. $C_{11}H_7NOS$ requires $M$ 201.0248); $\delta_H$ 9.48 (1H, s); 9.33 (1H, d, $^3J$ 8.1), 7.63 (1H, dd, $^3J$ 7.7, $^4J$ 0.9), 7.51–7.30 (2H, m), 7.35 (1H, d, $^3J$ 4.4) and 6.47 (1H, d, $^3J$ 4.4); $\delta_C$ 175.15, 140.86 (quat), 135.72 (quat), 131.73, 130.65 (quat), 128.75 (quat), 126.00, 124.95, 122.89, 118.18 and 102.24; *m/z* 201 ($M^+$, 100%), 200 (67), 173 (18), 172 (32), 145 (13), 69 (42), 63 (17) and 50 (25) and 3-formylpyrrolo[2,1-*b*]benzothiophene **20** (0.014 g, 7%), mp 128–131 °C (lit.,[19] 133.5–134 °C) (Found: $M^+$ 201.0248. $C_{11}H_7NOS$ requires $M^+$ 201.0248); $\delta_H$ 9.83 (1H, s), 7.78-7.68 (2H, m), 7.52-7.34 (2H, m), 7.46 (1H, d, $^3J$ 3.3) and 6.99 (1H, d, $^3J$ 3.3); $\delta_C$ 183.97, 132.95 (quat), 131.47 (quat), 126.37, 125.08, 124.28, 116.01 (quat), 115.64, 113.11, and 112.54, one quaternary not apparent; *m/z* 201 ($M^+$, 86), 200 (100), 192 (16), 179 (11), 178 (34), 172 (13), 128 (13), 91 (14), 87 (11), 69 (27) and 45 (16).

### Reaction of pyrrolo[2,1-*b*]benzothiophene 14 with dimethyl acetylenedicarboxylate

Pyrrolo[2,1-*b*]benzothiophene **14** (0.173 g, 1 mmol) was dissolved in dichloromethane (10 $cm^3$). Dimethyl acetylenedicarboxylate (0.142 g, 0.122 $cm^3$, 1 mmol) was added and the mixture was stirred at room temperature until t.l.c. showed the disappearance of the starting material and the appearance of two products of lower $R_f$ value. The crude products were then pre-adsorbed onto silica and separated by dry-flash chromatography to give methyl *Z*-[3-carbomethoxy-3-(pyrrolo[2,1-*b*]benzothiophen-1-yl]propenoate **21** (0.063 g, 20%), bp 165-170 °C (0.1 Torr) (Found: $M^+$ 315.0556 $C_{16}H_{13}NO_4S$ requires $M^+$ 315.0565) $\delta_H$ 7.60 (1H, d), 7.32-7.19 (3H, m), 7.11 (1H, s), 6.66 (1H, d, $^3J$ 3.9), 6.31 (1H, d, $^3J$ 3.9), 3.72 (3H, s) and 3.58 (3H, s); $\delta_C$ 166.59 (quat), 165.25 (quat), 134.89 (quat), 134.30 (quat), 131.41 (quat), 130.92 (quat), 128.88, 125.23, 123.71, 123.38, 119.36, 118.52 (quat), 112.60, 99.36, 53.08 and 51.84; *m/z* 315 ($M^+$, 100%), 257 (17), 256 (94), 255 (14), 241 (16), 198 (13), 197 (63), 196 (21), and 153 (10) and methyl *E*-[3-carbomethoxy-3-(pyrrolo[2,1-*b*]benzothiophen-1-yl]propenoate **22** (0.103 g, 33%), bp 160-165 °C (0.1 Torr) (Found: $M^+$ 315.0556 $C_{16}H_{13}NO_4S$ requires $M$ 315.0565) $\delta_H$ 7.92 (1H, d, $^3J$ 8.0), 7.60 (1H, m), 7.38-7.25 (2H, m), 6.70 (1H, d, $^3J$ 4.0), 6.33 (1H, d, $^3J$ 4.0), 6.20 (1H, s). 3.92 (3H, s) and 3.80 (3H, s); $\delta_C$ 167.17 (quat), 165.58 (quat), 125.25, 124.14, 123.94, 121.50, 115.66, 114.00, 101.04, 52.83 and 51.88, five quaternaries not assigned: *m/z* 315 ($M^+$, 100%), 257 (17), 256 (94), 255 (14), 241 (16), 198 (13), 197 (63), 196 (21), and 153 (10).

### 2,5-Diaryl-*N*-arylpyrrole derivatives 25 – general method

A solution of the appropriate 2-(substituted)aniline **3** (13 mmol), a 1,2-diaroylethane (13 mmol) and acetic acid (30 $cm^3$) in benzene (30 $cm^3$) was heated under reflux while water was removed by a Dean and Stark trap until t.l.c. showed the disappearance of the 1,2-diaroylethane. Appropriate precautions were taken when using benzene. The volatiles were removed on a rotary evaporator. The residue was dissolved in dichloromethane (100 $cm^3$) and washed with sodium hydrogen carbonate (1 M, 3 × 50 $cm^3$) and the organic fraction dried ($MgSO_4$). The solvent was removed to yield the crude product, which was purified by dry-flash chromatography. Other products made by this method are described in the ESI.†

### 2,5-Diphenyl-*N*-(2-mercaptophenyl)pyrrole 25a

2-Aminothiophenol **3c** (1.42 g, 13 mmol) and 1,2-dibenzoylethane (3.09 g, 13 mmol) gave 2,5-diphenyl-*N*-(2-mercaptophenyl)pyrrole **25a** (4.16 g, 98%), mp 120–124 °C (from ethanol) (lit.,[25] 139 °C) (Found: $M^+$ 327.1077. $C_{22}H_{17}NS$ requires $M$ 327.1081) $\delta_H$ 7.28-7.09 (14H, m), 6.59 (2H, s) and 3.14 (1H, s); $\delta_C$ 136.44 (quat), 135.48 (quat), 133.42 (quat), 132.58 (quat), 130.73, 129.19, 128.62, 127.98, 127.82, 126.38, 125.63 and 110.05; *m/z* 327 ($M^+$, 100%), 326 (24), 325 (11), 250 (20), 115 (18) and 77 (14).

### 2,5-Diaryl-*N*-[2-(allylthio)phenyl]pyrroles and 2,5-diaryl-*N*-[2-(allyloxy)phenyl]pyrroles 26

Using the method reported above, the derivatives **26** were made by treatment of the appropriate *N*-arylpyrrole (1 equivalent) and allyl bromide (1.1 equivalents) with a suspension of potassium carbonate (1.1 equivalents) in DMF (10 $cm^3$ per gram of pyrrole). After TLC showed the absence of starting material, the product was isolated by aqueous work-up and purified by bulb to bulb distillation. Other products made by this method are described in the ESI.†

### 2,5-Diphenyl-*N*-[2-(allylthio)phenyl]pyrrole 26a

2,5-Diphenyl-*N*-(2-mercaptophenyl)pyrrole **25a** (3.27 g, 0.01 mol) gave 2,5-diphenyl-*N*-[2-(allylthio)phenyl]pyrrole **26a** (3.52 g, 96%), mp 120–122 °C (from ethanol) (Found. C, 81.3; H, 5.6; N, 3.65. $C_{25}H_{21}NS$ requires C, 81.7; H, 5.75; N, 3.8%); $\delta_H$ 7.27–7.05 (14H, m), 6.56 (2H, s), 5.57 (1H, m), 5.02-4.93 (2H, m) and 3.29 (2H, m); $\delta_C$ 137.50 (quat), 137.05 (quat), 135.87 (quat), 133.01, 132.69, 130.74 (quat), 130.48, 128.32, 128.11 (4CH), 127.65 (4CH), 126.07 (2CH), 125.36, 117.68, 109.48 (2CH) and 34.80; *m/z* 367 ($M^+$, 100%), 327 (17), 326 (72), 223 (15), 119 (40) and 115 (11).

### FVP of 2,5-diphenyl-*N*-[2-(allylthio)phenyl]pyrrole 26a

FVP of 2,5-diphenyl-*N*-[2-(allylthio)phenyl]pyrrole **26a** [0.98 g, (2.7 mmol) $T_f$ 750 °C, $T_i$ 220 °C, *P* 0.01 Torr, *t* 40 min] gave a mixture which was separated by dry-flash chromatography (hexane). The following seven products were identified: dibenzothiophene **30a** (0.046 g, 9%) mp 95–98 °C (lit.,[26] 99.7 °C) $\delta_H$ 8.22-8.14 (2H, m), 7.94–7.85 (2H, m) and 7.53–7.46 (4H, m); $\delta_C$ 139.32 (quat), 135.43 (quat), 126.60, 124.25, 122.71 and 121.48; (NMR spectra consistent with literature data[27]); *m/z* 184 ($M^+$, 100%), 139 (22), 92 (38) and 79 (19): 1-phenylpyrrolo[2,1-*b*]benzothiazole **31a** (0.033 g, 5%) mp 110–113 °C (Found: $M^+$ 249.0612. $C_{16}H_{11}NS$ requires *M* 249.0612) $\delta_H$ 7.60–7.09 (9H, m), 6.52 (1H, d, $^3J$ 3.6) and 6.32 (1H, d, $^3J$ 3.6); $\delta_C$ 135.09 (quat), 132.79 (quat), 131.73 (quat), 129.33, 128.53 (quat), 128.26, 127.55, 124.62, 123.56, 123.16, 115.66, 113.46 and 99.00 (one quaternary overlapping); *m/z* 249 ($M^+$, 59%), 248 (100), 125 (18), 124 (30) and 115 (30): 1-phenyldibenzo[*b*,*f*]pyrrolo[1,2-*d*]-1,4-thiazepine **32a** (0.038 g, 4%) mp 89–93 °C [Found (FAB): $(M+H)^+$ 326.1003. $C_{22}H_{16}NS$ requires *M* 326.1003] $\delta_H$ 8.34–8.24 (2H, m), 8.07 (1H, dd, $^3J$ 7.7, $^4J$ 1.2), 7.57–7.11 (10H, m), 7.08 (1H, d, $^3J$ 3.9) and 6.69 (1H, d, $^3J$ 3.9); $\delta_C$ 135.54 (quat), 133.89 (quat), 131.47 (quat), 131.38 (quat), 128.82, 128.50, 128.05, 127.31, 126.98, 126.62 (quat), 125.83, 125.19 (quat), 123.85, 123.52, 122.98 (quat), 122.54, 122.27, 118.92, 115.94 and 102.04; *m/z* (FAB) 326 [$(M+H)^+$, 100%]: 4-(5-phenylpyrrol-2-yl)dibenzothiophene **33a** (0.210 g, 24%) mp 115–118 °C (Found: $M^+$ 325.0911. $C_{22}H_{15}NS$ requires *M* 325.0925) $\delta_H$ 8.68 (1H, br. s), 7.88 (2H, m), 7.55-7.22 (10H, m), 6.78 (1H, m) and 6.49 (1H, m); $\delta_C$ 140.01 (quat), 139.49 (quat), 135.10 (quat), 132.40 (quat), 131.41 (quat), 130.00 (quat), 128.85, 128.20, 127.91 (quat), 127.62, 126.38, 126.21, 125.85, 124.24, 123.58, 122.52, 109.83 and 107.00 (two CH signals overlapping); *m/z* 325 ($M^+$, 100%), 323 (23), 220 (11) and 163 (13): mixture of which the main component was 2-phenylpyrrole **35a** (0.043 g, *ca.* 11%) (Found: $M^+$ 143.0735. $C_{10}H_9N$ requires *M* 143.0735) $\delta_H$ 8.43 (1H, br. s), 7.70–7.15 (5H, m), 6.83 (1H, m), 6.56 (1H, m) and 6.33 (1H, m); *m/z* 143 ($M^+$, 100%), 116 (16) and 115 (47) (spectra consistent with literature data[28]): 2-phenyl-1*H*-dibenzo[2,3:6,7]thiepino[4,5-*b*]pyrrole **34a** (0.163 g, 19%) mp 124–127 °C $\delta_H$ 9.15 (1H, br. s), 8.69 (2H, m), 8.26 (1H, d, $^3J$ 8.0), 8.04 (1H, d, $^3J$ 7.9) and 7.77-7.33 (10H, m); $\delta_C$ 135.43 (quat), 132.30 (quat), 129.27 (quat), 128.94, 128.27 (quat), 127.08, 126.71, 126.47, 126.02 (quat), 124.60, 124.15, 123.90, 123.67 (quat), 123.34, 123.27, 122.79 (quat), 122.10 (quat), 119.61 and 100.37 (2 CH signals overlapping); *m/z* (FAB) 326 [$(M+1)^+$, 8%), 294 [$(M+1-32)]^+$ 100: 1-phenyl-2*H*-dibenzo[2,3:6,7]thiepino[4,5-*c*]pyrrole **36a** (0.026 g, 3%) mp 130–135 °C $\delta_H$ 9.11 (1H, br. s), 8.73-8.65 (2H, m), 8.12 (1H, m), 7.94 (1H, m), 7.65-7.32 (9H, m) and 7.10 (1H, d, $^3J$ 2.6); $\delta_C$ 137.02 (quat), 130.05, 128.88 (quat), 128.23, 126.72, 126.50, 126.16, 124.66, 123.76 (2 CH), 123.33, 122.93 (quat), 122.21 (quat), 120.97 and 119.50 (1 CH and 4 quaternaries not assigned); *m/z* 293 [$(M-32)^+$, 2%], 205 (7), 143 (9), 98 (6), 97 (9), 94 (33), 86 (100), 84 (33) and 83 (42).

### FVP of 2,5-di-*p*-tolyl-*N*[2-(allylthio)phenyl]pyrrole 26b

FVP of 2,5-di-*p*-tolyl-*N*[2-(allylthio)phenyl]pyrrole **26b** [0.80 g, (2.0 mmol), $T_f$ 650 °C, $T_i$ 235 °C, *P* 0.005 Torr, *t* 15 min] gave a mixture of products which were initially separated by dry-flash column chromatography (1% ethyl acetate–hexane: 2.5% gradient) to give the first and last components of the mixture. The other fractions were combined and re-columned (1% ethyl acetate–hexane: no gradient). The following products were obtained: 2-methyldibenzothiophene **30b** (0.032 g, 8%) mp 78–81 °C (lit.,[29] 86 °C); $\delta_H$ 8.13 (1H, m), 7.97 (1H, m), 7.85 (1H, m), 7.74 (1H, d, $^3J$8.2), 7.48–7.41 (2H, m), 7.28 (1H, m) and 2.55 (3H, s); $\delta_C$ 139.67 (quat), 136.26 (quat), 135.56 (quat), 135.30 (quat), 133.97 (quat), 128.08, 126.39, 124.06, 122.69, 122.28, 121.64, 121.33 and 21.37 (spectra compatible with literature values[30]); *m/z* 198 ($M^+$, 100%), 195 (19), 152 (13) and 98 (13): 1-*p*-tolylpyrrolo[2,1-*b*]benzothiazole **31b** (0.015 g, 3%) (Found: $M^+$, 263.0776. $C_{17}H_{13}NS$ requires *M* 263.0769); $\delta_H$ (360 MHz) 7.61 (1H, m), 7.48–7.43 (2H, m), 7.33–7.30 (3H, m), 7.21–7.11 (2H, m), 6.50 (1H, d, $^3J$ 3.6), 6.32 (1H, d, $^3J$ 3.7) and 2.49 (3H, s); $\delta_C$ (90 MHz) 138.01 (quat), 135.77 (quat), 132.34 (quat), 130.46 (quat), 129.91, 129.52, 128.83 (quat), 128.71 (quat), 125.15, 124.07, 123.64, 115.91, 114.03, 99.41 and 30.75; *m/z* 263 ($M^+$, 100%), 261 (34), 205 (22), 130 (18), 129 (18), 128 (21) and 91 (12): 6-methyl-1-*p*-tolyldibenzo[*b*,*f*]pyrrolo[1,2-*d*]-1,4-thiazepine **32b** (0.12 g, 17%) (Found: $M^+$, 353.1236. $C_{24}H_{19}NS$ requires *M* 353.1238); $\delta_H$ (360 MHz) 8.30 (1H, m), 8.03 (1H, s), 7.92 (1H, d, $^3$J 8.1), 7.52–7.08 (8H, m), 6.96 (1H, m), 6.59 (1H, m), 2.51 (3H, s) and 2.44 (3H, s); $\delta_C$ (90 MHz) 137.58 (quat), 135.88 (quat), 134.75 (quat), 133.41 (quat), 131.94 (quat), 131.74 (quat), 129.92, 129.75, 129.36, 127.37, 125.72 (quat), 124.93 (quat), 124.29, 124.80 (quat) 123.89, 123.06, 122.88, 119.41, 116.17, 101.80, 22.24 and 21.79; *m/z* 353 ($M^+$, 75%), 321 (100), 305 (21), 193 (27), 152 (23), 119 (30) and 91 (21): 4-methyl-1-(5-*p*-tolylpyrrol-2-yl)dibenzothiophene) **33b** (0.24 g, 34%) (Found: $M^+$, 353.1233. $C_{24}H_{19}NS$ requires *M* 353.1238); $\delta_H$ (360 MHz) 8.46 (1H, br. s), 7.91 (1H, d, $^3J$ 7.9), 7.47-7.20 (9H, m), 6.72 (1H, t, $^3J$ 3.1), 6.47 (1H, t, $^3J$ 3.0), 2.69 (3H, s) and 2.40 (3H, s); $\delta_C$ (90 MHz) 140.65 (quat), 139.83 (quat), 136.44 (quat), 134.09 (quat), 132.93 (quat), 132.47 (quat), 131.64 (quat), 130.37 (quat), 130.06, 128.53, 128.27 (quat), 126.76, 126.73, 124.88, 124.80, 124.12,

123.08, 110.22, 106.96, 21.55 and 20.94 (one quaternary signal overlapping); *m/z* 353 ($M^+$, 100%), 337 (20), 321 (19), 226 (51), 91 (30) and 77 (20): 10-methyl-2-*p*-tolyl-1*H*-dibenzo[2,3:6,7]thiepino[4,5-*b*]pyrrole **34b** (0.10 g, 14%) (Found: $M^+$, 353.1240. $C_{24}H_{19}NS$ requires *M* 353.1238); $\delta_H$ (360 MHz) 9.20 (1H, s), 8.68 (1H, d, $^3J$ 8.3), 8.50 (1H, s), 8.25 (1H, d, $^3J$ 7.9), 7.99 (1H, d, $^3J$ 8.0), 7.68-7.63 (3H, m), 7.57 (1H, m), 7.42 (1H, d, $^3J$ 8.0), 7.30-7.26 (3H, m), 2.63 (3H, s) and 2.43 (3H, s) $\delta_C$ 136.71 (quat), 133.85 (quat), 129.54, 128.42 (quat), 128.15 (quat), 126.82 (quat), 126.47, 124.48, 123.82, 123.70, 123.26, 123.18, 121.38 (quat), 120.69 (quat), 119.73, 99.57, 21.91 and 20.94 (one CH and three quaternary signals overlapping); *m/z* 353 ($M^+$, 9%), 321 (100) and 160 (20).

### FVP of 2,5-di(thien-2-yl)-*N*-[(2-allylthio)phenyl]pyrrole 26c

FVP of 2,5-di(thien-2-yl)-*N*-[(2-allylthio)phenyl]pyrrole **26c** [168 mg (0.44 mmol), $T_f$ 650 °C, $T_i$ 150 °C, *P* 0.018 Torr, *t* 75 min] gave a pyrolysate (103 mg) which was separated by dry flash chromatography (2% ethyl acetate/hexane) to give 2,5-di-(thien-2-yl)-*N*-(2-mercaptophenyl)pyrrole **25c** (63 mg, 61%); $\delta_H$ 7.38 (3H, m), 7.22 (1H, m), 7.04 (2H, dd, $^3J$ 5.0, $^4J$ 1.1), 6.84 (2H, dd, $^3J$ 3.5, 5.0), 6.61 (2H, dd, $^3J$ 3.5, $^4J$ 1.1), 6.60 (2H, s) and 3.06 (1H, s); $\delta_C$ 135.60 (quat), 134.98 (quat), 134.01 (2 quat), 131.25, 130.10, 129.41, 128.97 (2 quat), 126.94 (2 CH), 126.14, 123.82 (2 CH), 123.55 (2 CH) and 110.08 (2 CH). *m/z* 339 ($M^+$, 100%), 306 (30), 217 (20), 195 (22), 194 (28), 150 (30) and 111 (29) (compatible with data reported in ESI†): 1-(thien-2-yl)-2*H*-pyrrolo[2,1-*b*]benzothiazole **31c** (*ca.* 24 mg, 23%); (Found: $M^+$, 255.01720. $C_{14}H_9NS_2$ requires *M* 255.01709); $\delta_H$ 7.56 (1H, dd, $^3J$ 7.4, $^4J$ 1.0), 7.44 (1H, dd, $^3J$ 5.2, $^4J$ 1.2), 7.10–7.25 (5H, m), 6.44 (1H, d, $^3J$ 3.6) and 6.28 (1H, d, $^3J$ 3.6); $\delta_C$ 135.05 (quat), 133.48 (quat), 131.59 (quat), 128.70, 127.08, 126.72, 124.95, 123.56, 123.38, 117.89, 113.30 and 98.95 (2 quaternary signals not apparent). *m/z* 255 ($M^+$ 100%), 254 (27), 210 (7), 127 (9), 71 (8), 57 (11) and 43 (32).

### FVP of 2,5-diphenyl-*N*-[2-(allyloxy)phenyl]pyrrole 26d

FVP of 2,5-diphenyl-*N*-[2-(allyloxy)phenyl]pyrrole **26d** [0.540 g, (1.54 mmol), $T_f$ 650 °C, $T_i$ 160–180 °C, *P* 0.01 Torr, *t* 20 min] gave one major product which was purified by dry-flash chromatography on silica (2% ethyl acetate–hexane) to give 3-phenylpyrrolo[1,2-*f*]phenanthridine **46d** (0.27 g, 60%) mp 85–90 °C (Found: $M^+$ 293.1211. $C_{22}H_{15}N$ requires *M* 293.1204) $\delta_H$ 8.34–8.24 (2H, m), 8.06 (1H, m), 7.56–7.10 (10H, m), 7.07 (1H, d, $^3J$ 3.9) and 6.68 (1H, d, $^3J$ 3.9); $\delta_C$ 135.50 (quat), 133.84 (quat), 133.40 (quat), 131.33 (quat), 128.76, 128.44, 127.98, 127.24, 126.90, 126.56 (quat), 125.76, 125.13 (quat), 123.78, 123.44, 122.93 (quat), 122.48, 122.20, 118.85, 115.97 and 102.01; *m/z* 293 ($M^+$, 100%), 292 (19), 291 (38) and 146 (23).

### FVP of 2,5-di(thien-2-yl)-*N*-[(2-allyloxy)phenyl]pyrrole 26e

FVP of 2,5-di(thien-2-yl)-*N*-[(2-allyloxy)phenyl]pyrrole **26e** [128 mg, (0.35 mmol) $T_f$ 650 °C, $T_i$ 150 °C, *P* 0.026 Torr, *t* 45 min] gave a pyrolysate (70 mg) which was mainly 2,5-di(thien-2-yl)-*N*-(2-hydroxyphenyl)pyrrole **25e** (*ca.* 76%) by comparison with the authentic sample reported in ESI;† $\delta_H$ 7.40 (1H, m), 7.20 (1H, dd, $^3J$ 7.8, $^4J$ 1.7), 7.06–6.95 (4H, m), 6.80 (2H, dd, $^3J$ 3.8, 5.0), 6.58 (2H, dd, $^3J$ 3.8, $^4J$ 1.2) and 6.59 (2H, s); $\delta_C$ 134.06 (2 quat), 131.28, 130.72, 130.07 (2 quat), 127.04 (2 CH), 124.15 (2 CH), 123.72 (2 CH), 121.02, 116.65 and 110.43 (2 CH) (2 quaternary signals not apparent).

### FVP of 2,5-di-*p*-tolyl-*N*-[2-(benzylamino)phenyl]pyrrole 26f

FVP of 2,5-di-*p*-tolyl-*N*-[2-(benzylamino)phenyl]pyrrole **26f** [750 mg, (1.75 mmol) $T_f$ 800 °C, $T_i$ 200 °C, *P* 0.02 Torr, *t* 20 min] gave a pyrolysate (700 mg) which was initially separated by fractional distillation to give bibenzyl [bp 90 °C (1.5 Torr)] followed by 10-methyl-3-*p*-tolylpyrrolo[1,2-*f*]phenanthridine **46f** [bp 150 °C (1.5 Torr)] (133 mg, 19%); (Found: $M^+$, 321.15104. $C_{24}H_{19}N$ requires *M* 321.15120); $\delta_H$ 8.29 (1H, dd, $^3J$ 8.2, $^4J$ 1.5), 8.04 (1H, s), 7.92 (1H, d, $^3J$ 8.1), 7.50 (1H, dd, $^3J$ 8.5, $^4J$ 1.0), 7.38 (2H, dt, $^3J$ 8.1, $^4J$ 1.7), 7.21–7.33 (4H, m), 7.11 (1H, ddd, $^3J$ 7.2, 8.6, $^4J$ 1.5), 6.97 (1H, d, $^3J$ 3.8), 6.59 (1H, d, $^3J$ 3.8), 2.51 (3H, s) and 2.44 (3H, s); $\delta_C$ 137.05 (quat), 135.37 (quat), 134.17 (quat), 132.79 (quat), 131.37 (quat), 131.19 (quat), 125.16 (quat), 124.35 (quat), 122.97 (quat), 129.38, 129.20 (2 CH), 128.79 (2 CH), 126.83, 123.74, 123.35, 122.51, 122.34, 118.57, 115.57, 101.19, 21.72 and 21.26; *m/z* 321 ($M^+$, 100%), 305 (13), 195 (25), 192 (16), 119 (22) and 91 (22).

## Acknowledgements

We are grateful to British Petroleum for a Research Studentship (to A. D. MacP.), to Kodak Ltd and the EPSRC for a Research Studentship (to C. C. S.) and to The University of Edinburgh for funding.

## Notes and references

1 J. I. G. Cadogan, H. S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1407–1411.
2 J. I. G. Cadogan, H. S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2875–2879.
3 J. I. G. Cadogan, C. L. Hickson, H. S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1991, 377–384.
4 J. I. G. Cadogan, C. L. Hickson, H. S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1991, 385–393.
5 S. M. Allin, W. R. S. Barton, W. R. Bowman, E. Bridge, M. R. J. Elsegood, T. McInally and V. McKee, *Tetrahedron*, 2008, **64**, 7745–7758, and references therein.
6 J. I. G. Cadogan, C. L. Hickson and H. McNab, *Tetrahedron*, 1986, **42**, 2135–2165.
7 For example, C. Wentrup, *Reactive Molecules*, Wiley, New York, 1984, p. 225.
8 E. J. Enholm, K. M. Moran, P. E. Whitley and M. A. Battiste, *J. Am. Chem. Soc.*, 1998, **120**, 3807–3808.
9 (*a*) D. P. Curran and Y. Nishii, *J. Am. Chem. Soc.*, 1999, **121**, 8955–8956; (*b*) E. J. Enholm, M. A. Battiste, M. Gallagher, K. M. Moran, A. Alberti, M. Guerra and D. Macciantelli, *J. Org. Chem.*, 2002, **67**, 6579–6581.
10 W. Flitsch, R. Heidhues and H. Paulsen, *Tetrahedron Lett.*, 1968, **9**, 1181–1184.
11 J. M. Lindley, I. M. McRobbie, O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2194–2204.
12 G. W. H. Cheeseman and M. Rafiq, *J. Chem. Soc. C*, 1971, 2732–2734.
13 M. A. Khan and V. L. T. Ribeiro, *Heterocycles*, 1977, **6**, 979–981.
14 D. K. Bates, R. T. Winters and J. A. Picard, *J. Org. Chem.*, 1992, **57**, 3094–3097.
15 *c.f.* L.-C. Chen, H. M. Wang and I.-J. Kang, *Heterocycles*, 1999, **51**, 1437–1441.
16 V. J. Mazzola, K. F. Bernady and R. W. Frank, *J. Org. Chem.*, 1967, **32**, 486–489.
17 I. A. Kashulin and I. E. Nifant'ev, *J. Org. Chem.*, 2004, **69**, 5476–5479.
18 A. D. MacPherson, Ph.D. Thesis, The University of Edinburgh, 1994.

19 D. K. Bates, B. A. Sell and J. A. Picard, *Tetrahedron Lett.*, 1987, **28**, 3535–3538.
20 O. Tsuge, M. Tanaka, H. Shimoharada and M. Noguchi, *Heterocycles*, 1981, **16**, 1705–1712.
21 J. A. G. Drake and D. W. Jones, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1982, **38**, 200–203.
22 *c.f.*M. Black, J. I. G. Cadogan and H. McNab, *J. Chem. Soc., Chem. Commun.*, 1990, 395–396.
23 M. Artico, G. C. Poretta and G. De Martino, *J. Heterocycl. Chem.*, 1971, **8**, 283–287.
24 J. Kurita, H. Sakai, S. Yamada and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1987, 285.
25 R. Rips, C. Derappe and N. P. Buu-Hoï, *J. Org. Chem.*, 1960, **25**, 390–393.
26 A. Luttringhaus and K. Hauschild, *Ber. Dtsch. Chem. Ges. B*, 1940, **73**, 145–153.
27 J. Pouchert and J. Behnke, *The Aldrich Library of $^{13}C$ and $^{1}H$ NMR Spectra*, edn 1, Aldrich Chemical Company Inc., 1993.
28 C. L. Hickson and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1988, 339–342.
29 S. Oae, K. Iida, K. Shinhama and T. Takata, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2374–2378.
30 J. I. G. Cadogan, H. S. Hutchison and H. McNab, *Tetrahedron*, 1992, **48**, 7747–7762.