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PAPER

Gas-phase generation and cyclisation reactions of imidoyl radicals†

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Some 1,2-diarylimidoyl radicals were generated in the gas-phase by intramolecular radical translocation from *ortho*-imino-aryloxyl radicals, in turn generated under flash vacuum pyrolysis (FVP) conditions. The imidoyls reacted with XR *ortho*′-substituents in the *N*-aryl group to give (in most cases) modest yields of cyclisation products. Depending on the nature of the bridging atom (X), the formation of these products was initiated either by a further hydrogen atom translocation (X = CH_2), or by *ipso*-attack onto the aryl group (R = Ph), or by direct substitution at the heteroatom (X = S). With XR = N(Me)Ph, the major reaction product was probably the result of a competing pathway not involving the corresponding imidoyl.

Introduction

Imidoyl radicals **1** are carbon-centred intermediates whose spin-bearing carbon atom belongs to a carbon-nitrogen double bond (Fig. 1). The substituents at either C or N sides of the iminic bond can be alkyls, aryls, or, mainly in the case of R^2, even heteroatom-containing moieties (*e.g.* alkoxyls, sulfanyls, stannyls, silyls). Although plenty of data have been reported concerning their behaviour in solution and the resultant synthetic applications,[1] currently there are no general, direct gas-phase routes to imidoyl radicals. However, generation of the isomeric iminyls **2** under flash vacuum pyrolysis (FVP) conditions is well known,[2] and much is known of their chemical behaviour.[3]

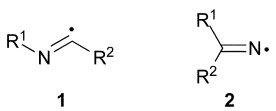
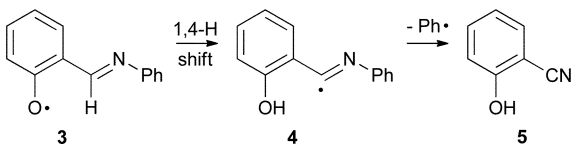


Fig. 1 Generic formula of imidoyl radicals **1** and isomeric iminyls **2**.

In an earlier paper, we discovered that generation of phenoxyl radical **3** by FVP gave 2-cyanophenol **5** as the major product and we rationalised this reaction as a hydrogen atom translocation followed by β-cleavage, with formation of the intermediate imidoyl **4** (Scheme 1).[3b,4] Phenoxyl radicals are known to be efficient hydrogen atom scavengers under FVP conditions.[2] In the work described in this paper, we have extended these ideas as a general method to generate imidoyls in the gas phase: furthermore, by

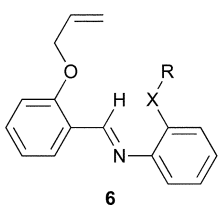


Scheme 1

incorporating an *ortho*-substituted aryl moiety as the imine R^1 group we have studied some reactivities of those imidoyls under these conditions, hence reporting the first examples of cyclisation reactions of imidoyls in the gas-phase.

Results and discussion

Aryl allyl ethers are well-known precursors of phenoxyl radicals under short contact time conditions in the gas-phase;[2,4] radical cleavage of the *O*-allyl bond is complete at 650 °C in our apparatus. The starting materials **6a–f** (Fig. 2) were therefore chosen to provide suitable *ortho*-substituted aryl groups in the imine function consisting, first, of a methyl group (**6a**) and, second, of X-aryl groups linked, respectively by X = CH_2 (**6b**), X = CO (**6c**), X = S (**6d**), X = O (**6e**), and X = NMe (**6f**). All substrates **6** were made by condensation of the appropriate amine with 2-(allyloxy)benzaldehyde.[4]



a: X = CH_2, R = H
b: X = CH_2, R = Ph
c: X = C(O), R = Ph
d: X = S, R = Ph
e: X = O, R = Ph
f: X = NMe, R = Ph

Fig. 2 Aryl allyl ethers **6** synthesised as precursors of imidoyl radicals.

In most cases (**6a**,**b**,**d**,**e**), the equilibrium was positioned well on the side of the imines, which could therefore be obtained in high purity and characterised by standard methods. This was not the

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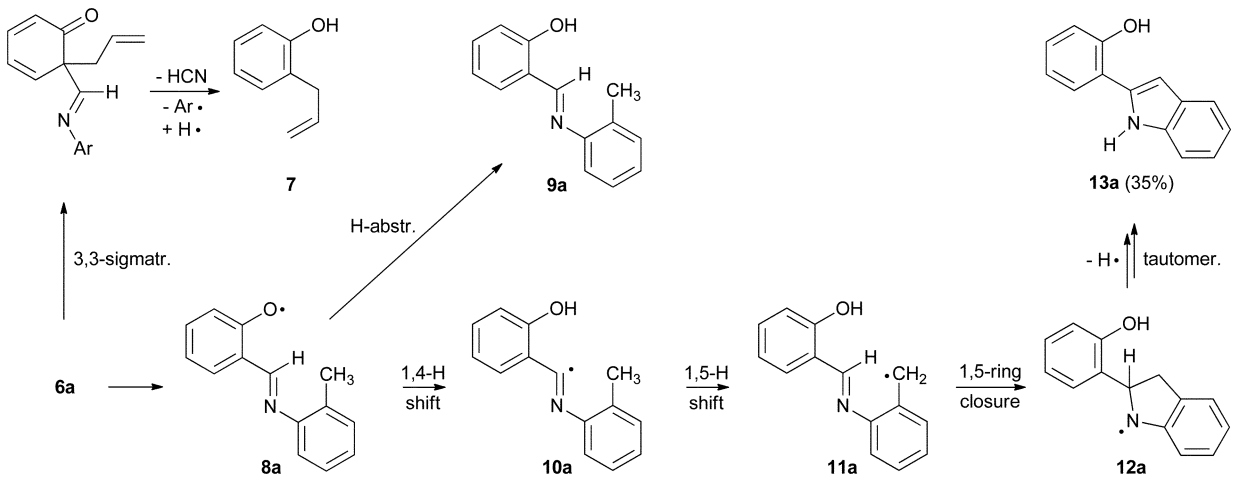
† Most of this research was carried out at the University of Edinburgh by our beloved friend Hamish McNab (1949–2010), whose premature death did not allow publication of these results during his life. This paper is lovingly dedicated to his memory.



Scheme 2

case for compounds **6c**,**f**, which were nonetheless sufficiently pure for pyrolysis purposes, but were not fully characterised.

FVP of compound 6a

FVP of the *ortho*-tolyl compound **6a** at 650 °C gave 2-(2-hydroxyphenyl)indole **13a** as the major product (35%), identified by comparison with an authentic sample (Scheme 2). Two minor products isolated after dry-flash chromatography were iminophenol **9a** (7%) – an expected[2] result of intermolecular hydrogen capture by the corresponding phenoxyl – and 2-allylphenol **7** (5%). The latter product proved to be a common minor component of the pyrolyses in this series, though we did not observe its formation in previous studies on phenoxyls under FVP conditions. A likely mechanism involves sigmatropic rearrangement to the site of the substituent, followed by radical cleavage of the substituent and eventual hydrogen capture (Scheme 2).

A likely mechanism for the formation of indole **13a** entails initial formation of imidoyl **10a** by 1,4-H-transfer to phenoxyl **8a**, followed by a second 1,5-H-shift to provide benzyl **11a**. Cyclisation of the latter onto the imine function to give the cyclic aminyl **12a**, loss of a hydrogen atom by β-fragmentation, and eventual tautomerism provided indole **13a** (Scheme 2). With compound **6a** no evidence was achieved of a possible, competitive β-scission of **12a**, involving loss of a 2-hydroxyphenyl radical, with formation of 2-unsubstituted indole. This was probably due to the significant presence of intermolecular hydrogen-capturing species (*e.g.* phenoxyls)[2] that favoured loss of a hydrogen atom rather than an aryl radical.

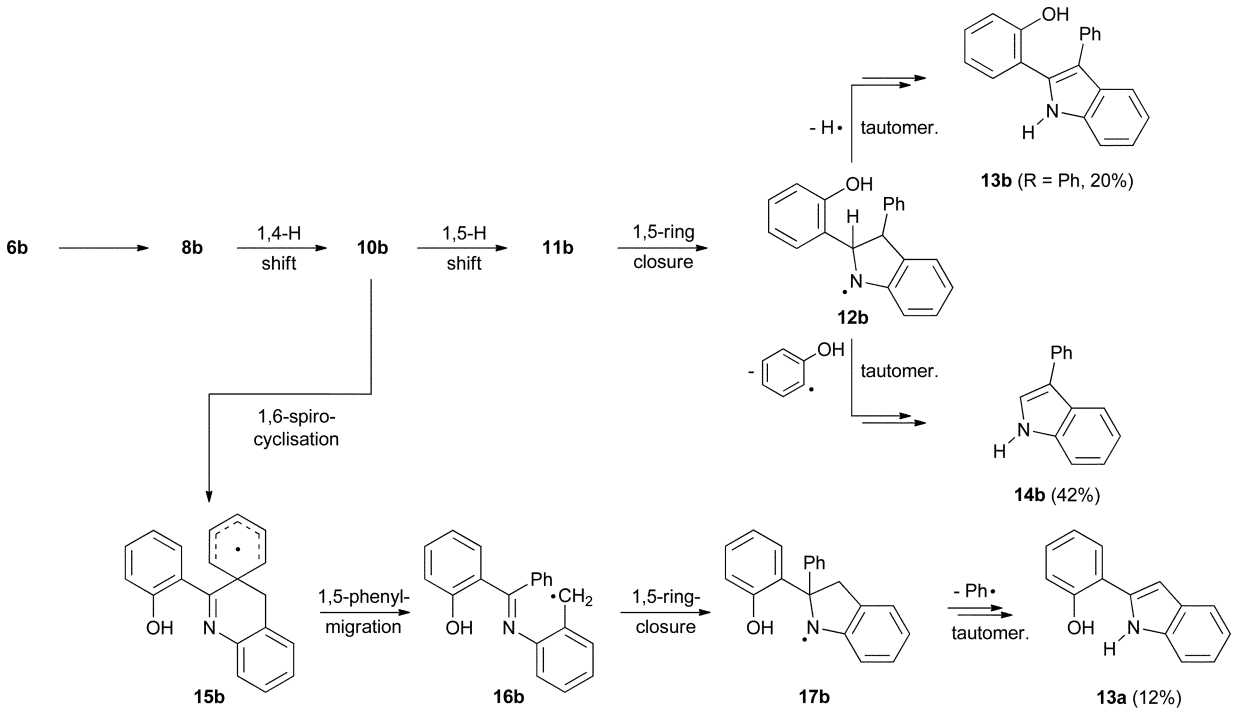
FVP of compound 6b

FVP of the analogous benzyl compound **6b** surprisingly provided three indoles, *viz.* 3-phenylindole **14b** (42%), 2-(2-hydroxyphenyl)-3-phenylindole **13b** (20%), and again indole **13a** (12%), together with traces of fluorene (2%).[5] The identity of **14b** was readily confirmed by comparison with literature data, which also excluded the presence of the isomeric 2-phenylindole (Scheme 3).[6]

Assignment of the structure of the third indole as **13b** [and not the isomeric 3-(2-hydroxyphenyl)-2-phenylindole] was made by a combination of NMR methods. Thus, the TOCSY spectrum showed the presence of two 4-spin systems and one 5-spin system, due, respectively, to the carbocyclic ring of the indole, the 2-hydroxyphenyl group and the unsubstituted phenyl group. The ^{1}H NMR spectrum showed the presence of an NH at δ_H 8.43, but analysis was complicated by the overlap of the two *ortho*-protons of the phenyl group and the signal due either to the 4- or the 7-proton of the indole at around δ_H 7.5. However, the NOESY spectrum showed correlation between the *other* indole 7/4-proton (δ_H 7.86) and the peak at δ_H 7.5, which shows that the phenyl group can only be in the 3-position. This assignment was confirmed by the presence of a NOESY interaction between a doublet of the other 4-spin system (the 2-hydroxyphenyl group) and the NH proton.

The mechanism of formation of indoles **14b** and **13b** follows directly from the above discussion on compound **6a**. Indeed, sequential 1,4- and 1,5-hydrogen atom shifts, followed by cyclisation onto the imine function, generate a 2,3-diarylindol-1-yl radical **12b**, which, contrary to **12a**, can apparently collapse by β-cleavage of either the C–(2-hydroxyphenyl)- or the C–H bond to give indoles **14b** and **13b**, respectively (Scheme 3). Since loss of β-hydrogen atoms from radical intermediates is substantially a bimolecular process,[2] the presence of the phenyl group in the 3-position probably hinders H-abstraction in radical **12b** in such a way as to favour release of 2-hydroxyphenyl radical, hence promoting formation of indole **14b** at the expense of **13b**.

It is worth noting that the presence of the benzyl substituent (namely, the phenyl group) allows the possibility of another reaction pathway, which can account for the formation of indole **13a**. Hence, *ipso*-attack of imidoyl **10b** at the benzyl group provides spirodienyl intermediate **15b**, which can fragment to benzyl radical **16b** through a 1,5-phenyl radical migration (Scheme 3). Spirodienyl rearrangements are common in the gas-phase chemistry of substituted aryl species,[2,3b] and have also been observed with some imidoyl radicals in solution.[7] Attack of the benzyl radical at the imine function gives 2,2-diarylindol-1-yl radical **17b**, which can collapse by (apparently selective) cleavage of the C–Ph bond to provide **13a**. Formation of 2-phenylindole by competitive fragmentation of the C–(2-hydroxyphenyl) bond was weirdly not observed. Since the two involved C–aryl β-bonds of **17b** should be of comparable strength, we suggest that



Scheme 3

the observed selectivity could be the result of some stabilising intramolecular H-bond interaction between the heterocyclic nitrogen of indolyl radical **17b** and the phenolic moiety, which might slow down fragmentation of the C–(2-hydroxyphenyl) bond (Fig. 3).[8]

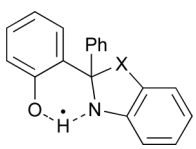
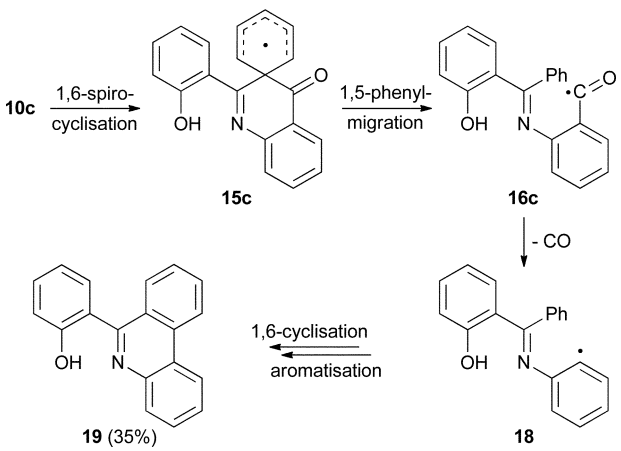


Fig. 3 Stabilising intramolecular H-bond interaction in phenol-substituted indolyl radicals.



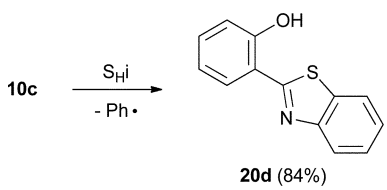
Scheme 4

FVP of compound 6c

The benzoyl derivative **6c** was not obtained pure, and some of the products found in the complex pyrolysate (*e.g.* 2-aminobenzophenone) were undoubtedly carried over from the initial preparation. Phenanthridine **19** (*ca.* 35%) was the only cyclised product and it was characterised by comparison with published data (Scheme 4).[3b] By analogy with the above discussion (Scheme 3), the most likely mechanism for the formation of **19** entails 1,5-phenyl radical translocation from the acyl to the imidoyl carbon of **10c** to give acyl radical **16c**, followed by decarbonylation to aryl radical **18** and eventual cyclisation onto the unsubstituted phenyl ring. Similar decarbonylation/cyclisation reactions have been observed.[9] The selectivity of the ring closure step is perhaps surprising, but may be due to rapid cyclisation prior to potential imine *E*/*Z*-isomerisation. The latter process could be also significantly slowed down by the intramolecular O-H-*N*-bonding stabilisation discussed above (Fig. 3).

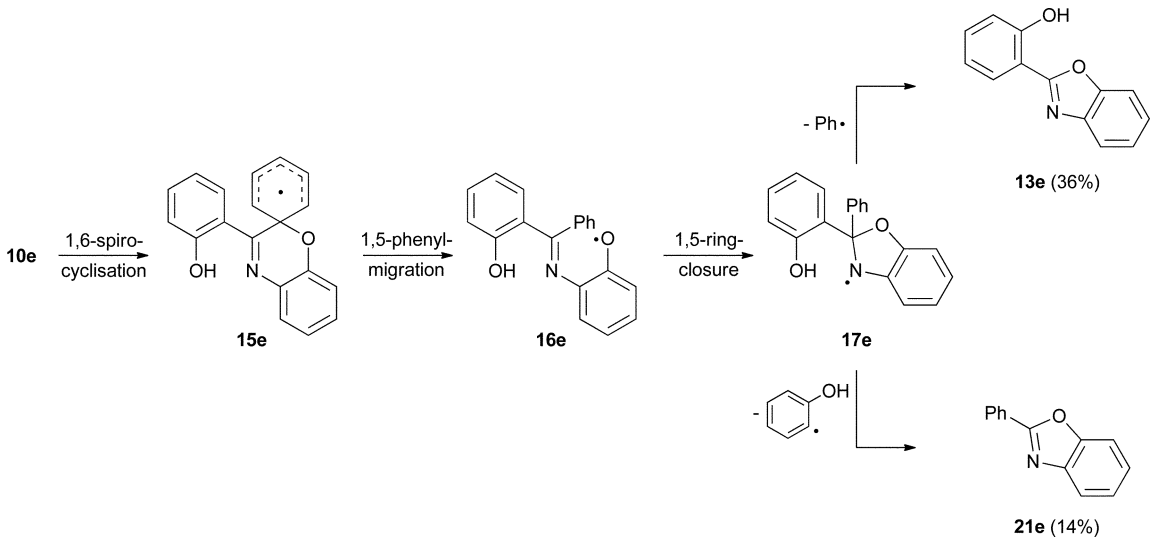
FVP of compound 6d

FVP of the phenylthio compound **6d** gave by far the cleanest reaction of this series: 2-(2-hydroxyphenyl)benzothiazole **20d**[10] was by far the major component (84% isolated yield) (Scheme 5).



Scheme 5

The most reasonable mechanism, involving homolytic intramolecular substitution (S_Hi) at the sulfur atom with release



Scheme 6

of a phenyl radical, follows the behaviour of analogous imidoyls in solution.[11,12] Only a trace of biphenyl (2%) was isolated, but phenyl radicals are known to couple very inefficiently under FVP conditions.[2] The hydrogen capture product **9d** was also detected and confirmed by comparison with an authentic sample (see Experimental section). Although product **20d** could be in principle the outcome of 1,5-phenyl migration from sulfur to the imidoyl carbon followed by 1,5-cyclisation of the resulting thiophenoxyl, the very high yield of **20d** associated with the complete absence of any other thiophenoxyl-derived products[13] suggest a more efficient pathway such as a direct S_Hi onto the sulfide moiety.

FVP of compound 6e

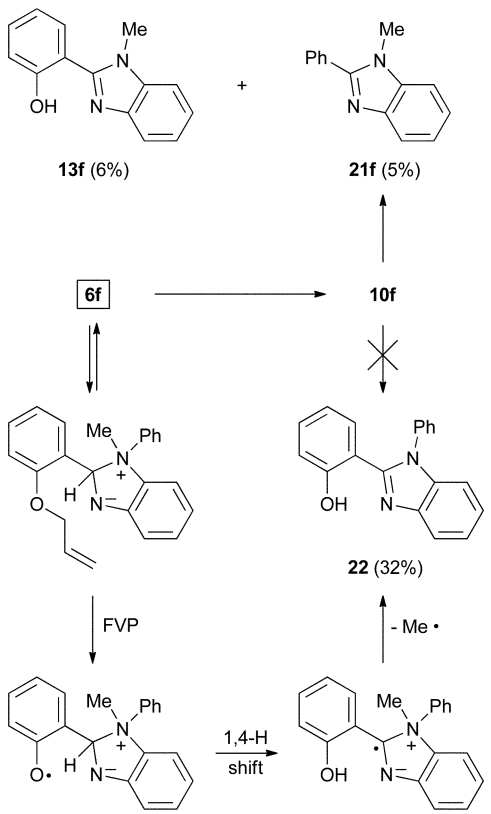
Two cyclised products, *i.e.* 2-(2-hydroxyphenyl)benzoxazole **13e** (36%) and 2-phenylbenzoxazole **21e** (14%) were obtained by FVP of the phenoxy compound **6e**. The mechanism of formation of those benzoxazoles is probably once more a sequence of 1,5-phenyl migration, cyclisation of phenoxyl **16e** to indolyl radical **17e**, and eventual release of an aryl radical (Scheme 6). Preferential formation of **13e** may be due again to H-bonding stabilisation of indolyl **17e**, in analogy with what suggested above for the fate of congener **17b**. Direct homolytic substitution at oxygen to afford **13e**, which could compete with the translocation pathway hence increasing the **13e**/**21e** ratio, should be discarded. Indeed, only heavier elements from the p-block (sulfur, selenium, silicon, phosphorous, and tellurium) usually undergo efficient homolytic substitution reactions.[14] Second period p-block elements such as oxygen require very weak bonds (and this is definitely not the case of a phenylether moiety), and S_Hi reactions can only be encountered with peroxides or organometallic complexes, whereas carbon-based groups give such a reaction only in the presence of very strained structures (*e.g.* cyclopropanes).

FVP of compound 6f

As far as reaction of compound **6f** is concerned, this gave the most puzzling results. First, although 1,6-hydrogen atom transfer from the *N*-methyl group of imidoyl **10f** is possible,[15] no products were apparently formed by this route. Second, 2-(2-hydroxyphenyl)-1-methyl-benzimidazole **13f** (6%) and 1-methyl-2-phenylbenzimidazole **21f** (5%) were obtained in comparable (although very low) yields, with no noticeable preference for retaining the 2-hydroxyphenyl moiety, as observed with other substrates (**6b**,**e**) (Scheme 7). Finally, the major cyclised product was 2-(2-hydroxyphenyl)-1-phenylbenzimidazole **22** (32%), a compound that does not fit with any conceivable pathway already described, with the only possible exception of a direct S_Hi onto the nitrogen moiety (see formation of product **20d** in Scheme 5).

Indeed, FVP-induced direct homolysis of the N–Me bond is known *not* to be a viable process under our experimental conditions,[16] although generation of the corresponding aminyl radical followed by cyclisation and eventual hydrogen abstraction could easily account for the formation of **22**. In addition, cyclisation of that aminyl radical onto the C=N bond would afford a benzimidazolyl radical that should fragment by competing releases of *both* hydrogen *and* 2-hydroxyphenyl radical, hence yielding *two* phenylbenzimidazole derivatives (see formation of compounds **13b** and **14b** from **6b**, Scheme 3).

Although the N–Me bond of the amino moiety of **6f** is not expected to be a strong one, especially under FVP conditions, we remain nonetheless convinced that it is not weak enough to make a direct S_Hi of imidoyl **10f** onto the nitrogen atom very likely,[14] even in the supposed absence of viable alternative pathways. A very recent paper has shown that such a *formal* process might occur in cyclisations of acyl radicals onto dialkylamino groups.[17] Nevertheless, those authors have proved that their mechanism is not a simple homolytic substitution reaction, since multiorbital interactions including donation of the nitrogen lone-pair into the π* orbital of the acyl radicals complicate the overall process. Actually, to account for the eventual cyclisation products, they have put forward an alternative mechanism entailing nucleophilic ring closure of the amino function onto a ketene moiety, followed by radical fragmentation. In our case, we might propose a similar mechanism involving occurrence of a nucleophilic cyclisation prior (or concomitant) to radical generation, followed by intramolecular hydrogen abstraction and eventual release of methyl radical



Scheme 7

(Scheme 7). This pathway, not entailing generation of imidoyl **10f**, can easily explain the effective formation of **22** without claiming any unusual S_Hi process at nitrogen; it also gives a reliable explanation for selective loss of the 2-hydrogen atom and hence for production of a unique 1-phenylbenzimidazole.

Conclusions

Hydrogen atom transfer from imines to phenoxyls can be regarded as a general, easy route to generate imidoyl radicals under FVP conditions. In almost all the cases studied, cyclised products were obtained through the intermediacy of imidoyls **10**. Three main product-forming routes have been identified. First, a further radical translocation can occur if the imine group contains an *ortho* CH moiety: in this case the resulting benzyl radical can cyclise onto the imine to provide the indole nucleus (compounds **13a**,**b** and **14b**, Schemes 2 and 3). Second, *ipso*-attack at the X-aryl group promotes a rearrangement *via* spirodienyl radicals that provides 5-membered cyclised products by subsequent attack at the novel imine function generated by the translocation process (compounds **13a**, **13e**,**f**, and **21e**,**f**, Schemes 3 and 6). With X = CO (imidoyl **10c**), a phenanthridine derivative (**19**) was formed through decarbonylation of the translocated radical and subsequent cyclisation of an aryl radical (Scheme 4). It is worth pointing out that the spirodienyl route was observed with four out of the five phenyl-substsituted structural types studied; it competes even in the presence of other in principle more viable pathways such as abstraction of the benzhydrylic hydrogen of imidoyl **10b**.[18] Finally, efficient homolytic substitution at sulfur can take place (compound **20d**), as already found for certain imidoyls in solution (Scheme 5). The relative importance of the three routes is highly dependent on the nature of the bridging atom X (see Table 1 for product distribution). We suggest that formation of imidoyl **10f** was instead somewhat hindered in favor of a competing nucleophilic ring closure of the amine group onto the imine function of the starting material **6f** (Scheme 7). This could account for the formation of 1-phenylbenzimidazole **22** without involving an unlikely S_Hi mechanism on nitrogen.

Table 1 Product distribution for reactions of imines **6a–f**

Imine	1,5-H shift + ring closure	Spiro-cyclisation	S_Hi
6a	**13a** (35%)	—	—
6b	**13b** (20%) + **14b** (42%)	**13a** (12%)	—
6c	—	**19** (35%)	
6d	—	—	**20d** (84%)
6e	—	**13e** (36%) + **21e** (14%)	—
6f	—	**13f** (6%) + **21f** (5%)	**22** (32%)[a]

[a] Formal product of S_Hi not involving imidoyl **10f**.

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 obtained under electron impact conditions. Column chromatography was carried out on silica gel using hexane–ethyl acetate or hexane-diethyl ether gradients as eluent. Previously reported compounds were identified by mp and/or spectral comparison with authentic samples. Elemental analyses were carried out for all new products, with the exception of compounds **6c**,**f**, which could not be suitably purified and were reacted as they were.

N-(2-Allylbenzylidene)aniline derivatives – general method

A 1 : 1 mixture of 2-allyloxybenzaldehyde[4] and the appropriate amine in ethanol (3 cm^3) was stirred at room temperature until equilibrium was reached (determined by ratio of imine H: aldehyde H in the ^1H NMR spectrum). The solvent was removed *in vacuo* and the residue subjected to Kugelrohr distillation (0.04–0.009 Torr) to give the imine as a yellow oil.

***N*-(2-Allyloxybenzylidene)-2-methylbenzenamine (6a).** After 10 min 2-allyloxybenzaldehyde (0.511 g, 3.1 mmol) and *o*-toluidine (0.332 g, 3.1 mmol) yielded *N*-(2-allyloxybenzylidene)-2-methylbenzenamine **6a** (0.500 g, 64%), bp 115–120 °C (0.5 Torr) (Found: M^+, 251.1310. $C_{17}H_{17}NO$ requires *M* 251.1310. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.2; H, 6.8; N, 5.6. Found: C, 81.0; H, 6.8; N, 5.6.); δ_H 8.86 (1H, s), 8.23 (1H, m), 7.43 (1H, m), 7.25–6.92 (6H, m), 6.08 (1H, m), 5.47–5.27 (2H, m), 4.64–4.61 (2H, m) and 2.37 (3H, s); δ_C 158.33 (quat), 155.36, 151.74 (quat), 132.79, 132.28, 131.69 (quat), 130.00, 127.55, 126.54, 125.21, 125.09 (quat), 120.97, 117.89, 117.63, 112.30, 69.05 and 17.78; *m*/*z* 251 (M^+, 31%), 210 (21), 145 (83), 106 (100), 91 (85) and 41 (68).

***N*-(2-Allyloxybenzylidene)-2-benzylbenzenamine (6b).** After 10 min 2-allyloxybenzaldehyde (0.444 g, 2.7 mmol) and

2-aminodiphenylmethane (0.490 g, 2.7 mmol) yielded *N*-(2-allyloxybenzylidene)-2-benzylbenzenamine **6b** (0.552 g, 63%), bp 105–110 °C (9×10^{-3} Torr) (Found: M^+, 327.1629. $C_{23}H_{21}NO$ requires *M* 327.1623. Anal. Calcd for $C_{23}H_{21}NO$: C, 84.4; H, 6.5; N, 4.3. Found: C, 84.2; H, 6.4; N, 4.3.); δ_H 8.91 (1H, s), 8.25 (1H, dd, ^3J 7.7, ^4J 1.8), 7.48–6.95 (12H, m), 6.09 (1H, m), 5.49–5.31 (2H, m), 4.65–4.62 (2H, m) and 4.21 (2H, s); δ_C 158.32 (quat), 155.51, 151.08 (quat), 141.36 (quat), 135.05 (quat), 132.75, 132.28, 129.68, 128.94, 128.08. 127.56, 127.11, 125.53, 125.04 (quat), 120.90, 118.01, 117.57, 112.30, 69.00 and 37.24 (one CH signal overlapping); *m/z* 327 (M^+, 37%), 286 (31), 183 (100), 91 (84) and 41 (68).

[2-(2-Allyloxybenzylideneamino)phenyl](phenyl)methanone (6c). After stirring for 4 days and three distillations of the product from 2-allyloxybenzaldehyde (0.448 g, 2.8 mmol) and 2-aminobenzophenone (0.556 g, 2.8 mmol) a complex mixture of components was obtained of which *ca.* 80% was [2-(2-allyloxybenzylideneamino)phenyl](phenyl)methanone **6c** (0.338 g, *ca.* 36%), bp 125–130 °C (2.3×10^{-2} Torr) (Found: M^+, 341.1412. $C_{23}H_{19}NO_2$ requires *M*, 341.1416); δ_H 8.81 (1H, s), 7.83–7.80 (2H, m), 7.64–7.18 (9H, m), 6.84–6.74 (2H, m), 6.13–5.95 (1H, m), 5.49–5.25 (2H, m) and 4.57–4.54 (2H, m); δ_C 197.69 (quat), 158.29 (quat), 156.76, 150.99 (quat), 138.05 (quat), 133.61 (quat), 132.53, 132.39, 131.36, 129.68, 128.90, 127.60, 125.14, 114.48 (quat), 120.67, 118.98, 117.56, 112.00, and 68.94 (two CH signals overlapping); *m/z* 341 (M^+, 12%), 300 (8), 196 (100), 120 (56), and 77 (64). Unreacted starting material was also present (identified by comparison with authentic samples). Compound **6c** was not pure enough for an elemental analysis and was reacted without further purification attempts.

***N*-(2-Allyloxybenzylidene)-2-phenylthiobenzenamine (6d).** After 10 min 2-allyloxybenzaldehyde (0.484 g, 3.0 mmol) and 2-phenylthioaniline (0.601 g, 3.0 mmol) yielded *N*-(2-allyloxybenzylidene)-2-phenylthiobenzenamine **6d** (0.886 g, 85%), bp 120–130 °C (1.7×10^{-2} Torr) (Found: M^+, 345.1184. $C_{22}H_{19}NOS$ requires *M* 345.1187. Anal. Calcd for $C_{22}H_{19}NOS$: C, 76.5; H, 5.5; N, 4.05. Found: C, 76.3; H, 5.4; N, 4.1.); δ_H 8.91 (1H, s), 8.23 (1H, m), 7.52–6.93 (12H, m), 6.35 (1H, m), 5.98–5.30 (2H, m) and 4.63–4.59 (2H, m); δ_C 158.38 (quat), 156.16, 150.31 (quat), 133.14 (quat), 133.27, 132.72, 132.60, 132.20 (quat), 129.09, 128.34. 127.89, 127.57, 126.69, 125.84, 124.67 (quat), 120.91, 118.19, 117.56, 112.16 and 68.96; *m/z* 345 (M^+, 5%), 304 (2), 201 (100) and 77 (22).

***N*-(2-Allyloxybenzylidene)-2-phenoxybenzenamine (6e).** After 30 min 2-allyloxybenzaldehyde (0.542 g, 3.4 mmol) and 2-phenoxyaniline (0.619 g, 3.4 mmol) yielded *N*-(2-allyloxybenzylidene)-2-phenoxybenzenamine **6e** (0.748 g, 67%), bp 115–120 °C (2×10^{-2} Torr) (Found: M^+, 329.1415. $C_{22}H_{19}NO_2$ requires *M* 329.1416. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.2; H, 5.8; N, 4.25. Found: C, 80.0; H, 5.7; N, 4.3.); δ_H 8.99 (1H, s), 7.97 (1H, dd, ^3J 7.7, ^4J 1.7), 7.40–6.87 (12H, m), 6.05 (1H, m), 5.51–5.27 (2H, m) and 4.60–4.57 (2H, m); δ_C 158.32 (quat), 158.04 (quat), 157.64, 148.44 (quat), 144.91 (quat), 132.73, 132.45, 129.27, 127.67, 126.13. 124.85 (quat), 124.50, 122.15, 121.30, 120.80, 117.55, 117.48, 112.13 and 68.95 (one CH signal overlapping); *m/z* 329 (M^+, 23%), 288 (5), 185 (100) and 77 (28).

***N*-(2-Allyloxybenzylidene)-*N*′-methyl-*N*′-phenylbenzene-1,2-diamine (6f).** Reaction of 2-allyloxybenzaldehyde with *N*-(2-aminophenyl)-*N*-methylaniline under Dean and Stark conditions gave *N*-(2-allyloxybenzylidene)-*N*′-methyl-*N*′-phenylbenzene-1,2-diamine **6f** (Found: M^+, 342.1738. $C_{23}H_{22}N_2O$ requires *M* 342.1732); δ_H 9.03 (1H, s), 8.09 (1H, m), 7.48–6.81 (12H, m) 6.17–6.06 (1H, m), 5.55–5.38 (2H, m), 4.70–4.60 (2H, m), and 3.43 (3H, s); δ_C 157.97 (quat), 156.06, 149.77 (quat), 149.37 (quat), 140.44 (quat), 132.54, 132.10, 128.68, 128.33, 128.04, 127.37, 126.10, 125.89, 124.73 (quat), 120.53, 120.46, 117.17, 116.92, 113.74, 111.93, and 39.16 (CH_3); *m/z* 342 (M^+, 100%), 301 (62), 209 (36), 195 (43), 180 (42), 167 (40), 91 (20) and 77 (36). This starting material was only *ca.* 90% pure and its elemental analysis was not carried out; it was reacted without further purification attempts.

General method for the preparation of (iminomethyl)phenol derivatives 9a,d

A 1 : 1 mixture of 2-salicylaldehyde and the corresponding amine in ethanol (3 cm^3) was stirred at room temperature until equilibrium was reached (determined by ratio of imine H: aldehyde H). The solvent was then removed *in vacuo* and the residue distilled (0.023–0.024 Torr) to give a yellow oil in all cases.

2-[(*o*-Tolylimino)methyl]phenol (9a). After 10 min salicylaldehyde (0.122 g, 1.1 mmol) and *o*-toluidine (0.108 g, 1.1 mmol) yielded 2-[(*o*-tolylimino)methyl]phenol **9a** (0.172 g, 82%), bp 90–95 °C (2.3×10^{-2} Torr); (Found: M^+, 211.0999. $C_{14}H_{13}NO$ requires *M* 211.0997. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.6; H, 6.2; N, 6.6. Found: C, 79.4; H, 6.0; N, 6.8.); δ_H 13.57 (1H, br s), 8.57 (1H, s), 7.45–6.95 (8H, m) and 2.45 (3H, s); δ_C 161.92, 160.97 (quat), 147.13 (quat), 132.85, 132.85 (quat), 132.07, 131.97, 130.46, 126.77, 119.09 (quat), 117.78, 117.44, 116.95 and 17.99 (CH_3); *m/z* 211 (M^+, 100%), 118 (79), 91 (62), 65 (48) and 39 (28).

2-[(2-Phenylthio)phenylimino]methylphenol (9d). After 10 min 2-salicylaldehyde (0.182 g, 1.5 mmol) and 2-phenylsulfanylphenylamine (0.305 g, 1.5 mmol) yielded 2-[(2-phenylthio)phenylimino]methylphenol **9d** (0.356 g, 78%), bp 120–125 °C (2.4×10^{-2} Torr); (Found: M^+, 305.0872. $C_{19}H_{15}NOS$ requires *M* 305.0874. Anal. Calcd for $C_{19}H_{15}NOS$: C, 74.7; H, 4.95; N, 4.6. Found: C, 74.5; H, 4.9; N, 4.6.); δ_H 12.53 (1H, s), 8.56 (1H, s) and 7.45–6.89 (13H, m); δ_C 162.19 (quat), 160.91 (quat), 146.42 (quat), 133.40 (quat), 133.18, 132.62, 132.20, 129.82, 129.15, 127.62, 127.20, 118.96 (quat), 118.83, 117.78 and 117.6 (two CH overlapping); *m/z* 305 (M^+ 100%), 212 (45) and 77 (31).

FVP experiments

The substrates were distilled under reduced pressure into the empty silica furnace tube (35 × 2.5 cm) which was maintained at the appropriate temperature by an electrical furnace. Products were quenched in a U-tube cooled with liquid nitrogen located at the exit point of the furnace. At the end of the pyrolysis the products were removed from the trap with solvent, which was subsequently removed *in vacuo*. The crude products were purified as described below. The quantity of precursor, furnace temperature (T_f), inlet temperature (T_i), pressure range (*P*) and pyrolysis time (*t*) are indicated in parenthesis.

FVP of *N*-(2-allyloxybenzylidene)-2-methylbenzenamine 6a. FVP of **6a** (0.325 g, 1.3 mmol, T_f 650 °C, T_i 120 °C, *P* 0.02 Torr, *t* 20 min) gave three products. These were purified by dry-flash chromatography (hexane-ethyl acetate eluent) to give, first, 2-(2-hydroxyphenyl)indole **13a** (0.095 g, 35%) mp 168–169 °C, (lit.,[19] 167 °C) mixed mp 167–169 °C; δ_H 9.31 (1H, br s) and 7.71–6.85 (10H, m); δ_C 151.92 (quat), 136.27 (quat), 134.85 (quat), 128.71, 128.14, 122.01, 121.33, 120.26, 119.94, 118.93 (quat), 116.46, 110.90 and 99.88 (one quaternary carbon not apparent); *m/z* 209 (M^+, 100%), 180 (47), 152 (16) and 77 (37). The second component was 2-allylphenol **7** (0.009 g, 5%) from its ^{1}H NMR spectrum; δ_H 7.13–7.05 (2H, m), 6.90–6.74 (2H, m), 5.92 (1H, m), 4.96–5.13 (3H, m) and 3.39 (2H, m), consistent with literature data.[10] The third component was 2-[(*o*-tolylimino)methyl]phenol **9a** (0.020 g, 7%); δ_H 13.53 (1H, br s), 8.57 (1H, s), 7.47–6.93 (8H, m) and 2.40 (3H, s); δ_C 162.11, 161.06 (quat), 147.30 (quat), 133.00, 132.19 (quat), 132.06, 130.57, 126.90, 126.74, 119.19 (quat), 118.93, 117.60, 117.09 and 18.10; *m/z* 211 (M^+, 58), 118 (100), 91 (82), 65 (64) and 39 (57). Spectra were identical with the authentic sample made using the procedure described above.

FVP of *N*-(2-allyloxybenzylidene)-2-benzylbenzenamine 6b. FVP of **6b** (0.408 g, 1.2 mmol, T_f 650 °C, T_i 120–130 °C, *P* 0.009 Torr, *t* 20 min) gave four products. These were purified by dry-flash chromatography (hexane-ether eluent) to give, first, fluorene (0.005 g, 2%); δ_H 7.75–7.51 (2H, d, ^3J 6.6), 7.58–7.45 (2H, m), 7.38–7.24 (4H, m), 3.83 (2H, s); *m/z* 166 (M^+, 100%) and 83 (38). The ^{1}H NMR spectrum was consistent with literature data.[10] The second was 3-phenylindole **14b** (0.100 g, 42%), mp 84–87 °C (lit.,[6] 85–87 °C); δ_H 8.17 (1H, br s), 8.01 (1H, m), 7.74–7.69 (2H, m) and 7.53–7.24 (8H, m); δ_C 136.47 (quat), 135.41 (quat), 128.64, 127.33, 125.84, 125.54 (quat), 122.24, 121.69, 120.16, 119.65, 118.07 (quat) and 111.30; *m/z* 193 (M^+, 100%), 165 (46), 139 (10), 96 (20) and 43 (7). The NMR spectra were consistent with literature data.[6] The third component was 2-(2-hydroxyphenyl)-3-phenylindole **13b** (0.070 g, 20%); (Found: M^+, 285.1156. $C_{20}H_{15}NO$ requires *M* 285.1154. Anal. Calcd for $C_{20}H_{15}NO$: C, 84.2; H, 5.3; N, 4.9. Found: C, 84.0; H, 5.2; N, 5.0.); δ_H (360 MHz) 8.43 (1H, br s), 7.86 (1H, d ^3J 8.0), 7.51–7.48 (3H, m), 7.46–7.39 (3H, m), 7.36–7.29 (3H, m), 7.27–7.24 (1H, m), 7.03–6.98 (1H, m), 6.95–6.92 (1H, m) and 5.42 (1H, m); δ_C 153.45 (quat), 136.79 (quat), 134.40 (quat), 130.93, 130.60, 130.22 (quat), 129.56, 129.31, 128.89 (quat), 127.28, 123.52, 121.31, 121.12, 120.12, 119.42 (quat), 116.88, 116.36 (quat) and 111.52; *m/z* 285 (M^+). The fourth component was 2-(2-hydroxyphenyl)indole **13a** (0.030 g, 12%); δ_H 9.43 (1H, br s), 7.73–7.65 (2H, m) and 7.50–6.86 (8H, m); δ_C 151.80 (quat), 136.08 (quat), 134.72 (quat), 128.58, 128.04, 121.87, 121.15, 120.18, 119.84, 118.82 (quat), 116.45, 110.90 and 99.61 (one quaternary carbon not apparent); *m/z* 209 (M^+, 100%), 180 (74), 152 (44) and 77 (48) (data consistent with those reported above).

FVP of [2-(2-allyloxybenzylideneamino)phenyl](phenyl) methanone 6c. FVP of **6c** (0.504 g, 1.5 mmol, T_f 650 °C, T_i 155–160 °C, *P* 0.023 Torr, *t* 25 min) gave a complex pyrolysate from which three products were identified. These were purified by dry-flash chromatography (hexane-ether eluent) to give, first, 6-(2-hydroxyphenyl)phenanthridine **19** (0.140 g, 35%); δ_H (360 MHz) 8.76 (1H, d, ^3J 8.3), 8.65 (1H, dd, ^3J 8.1, ^4J 1.5), 8.56 (1H, dd, ^3J 8.4), 8.16 (1H, m), 7.95 (1H, ddd, ^3J 8.3 and 7.1, ^4J 1.4), 7.83–7.71 (4H, m), 7.46 (1H, ddd, ^3J 7.3 and 6.6, ^4J 1.6), 7.26 (1H, dd, ^3J 8.2, ^4J 1.1) and 7.07 (2H, td, ^3J 8.0, ^4J 1.3); δ_C 159.69 (quat), 158.46 (quat), 141.93 (quat), 134.91 (quat), 132.21, 131.53, 129.64, 129.52, 129.36, 127.77 (quat), 127.69, 124.02, 122.98, 122.47, 121.72 (quat), 119.22 and 118.63. All spectra were consistent with reported data.[3b] The second component was unreacted *o*-aminobenzophenone (0.035 g, 12%) identified by comparison with an authentic sample. A trace of 2-allylphenol **7** was also detected (data as above).[10]

FVP of *N*-(2-allyloxybenzylidene)-2-phenylthiobenzenamine 6d. FVP of **6d** (0.540 g, 1.6 mmol, T_f 650 °C, T_i 150–155 °C, *P* 0.013 Torr, *t* 15 min) gave three significant products. These were purified by dry-flash chromatography (hexane-ethyl acetate eluant) to give, first, biphenyl (0.005 g, 2%); δ_H 7.64–7.62 (4H, m), 7.55–7.46 (4H, m) and 7.38–7.30 (2H, m); δ_C 141.67 (quat), 129.16, 127.66 and 127.45; *m/z* 154 (M^+, 100%) and 77 (34). The NMR spectra were consistent with literature data.[10] The second component was 2-(2-hydroxyphenyl)benzothiazole **20d** (0.300 g, 84%) mp 130–133 °C (lit.,[20] 132–135 °C); δ_H 12.51 (1H, br s), 7.94–7.92 (1H, m), 7.74–7.72 (1H, m) and 7.56–6.97 (7H, m); δ_C 169.19 (quat), 157.76 (quat), 151.64 (quat) 132.58, 132.40 (quat), 128.24, 126.51, 125.37, 121.99, 121.34, 119.35, 117.69 and 116.60 (quat); *m/z* 227 (M^+, 100%), 201 (86), 167 (29), 109 (25), 65 (50) and 39 (66). Spectra were consistent with literature data.[20] The third component was 2-allylphenol **7** (0.019 g, 9%); δ_H 7.14–7.06 (2H, m), 6.93–6.72 (2H, m), 6.08–5.94 (1H, m), 5.18–5.01 (2H, m) and 3.41 (2H, m); δ_C 153.82 (quat), 136.34, 130.21, 127.63, 125.31 (quat), 120.59, 116.13, 115.54 and 34.82 (spectra consistent with literature data[10]). A trace of 2-[(2-phenylthio)phenylimino]methylphenol **9d** was detected by comparison with an authentic sample (made as described above).

FVP of *N*-(2-allyloxybenzylidene)-2-phenoxybenzenamine 6e. FVP of **6e** (0.480 g, 1.46 mmol, T_f 650 °C, T_i 130–140 °C, *P* 0.01 Torr, *t* 25 min) gave three products. These were separated by dry-flash chromatography (hexane-diethyl ether eluent) to give, first, 2-(2-hydroxyphenyl)benzoxazole **13e** (0.110 g, 36%) mp 121–124 °C (lit.,[21] 125–126 °C); δ_H 11.49 (1H, s), 8.03–7.98 (1H, m), 7.73–7.69 (1H, m), 7.61–7.54 (1H, m), 7.48–7.32 (3H, m), 7.15–7.10 (1H, m) and 7.04–6.96 (1H, m); δ_C 162.77 (quat), 158.62 (quat), 148.99 (quat), 139.89 (quat), 133.38, 126.97, 125.21, 124.83, 119.39, 119.09, 117.27, 110.47 and 110.42; *m/z* 211 (M^+, 100%), 183 (39), 154 (19), 92 (24) and 63 (33). The NMR spectra were consistent with literature data.[21] The second component was 2-phenylbenzoxazole **21e** (0.040 g, 14%); δ_H 8.28–8.22 (2H, m), 7.79–7.74 (1H, m), 7.60–7.47 (4H, m) and 7.38–7.31 (2H, m); δ_C 162.89 (quat), 150.59 (quat), 141.93 (quat), 131.39, 128.77, 127.48, 126.99 (quat), 124.98, 124.44, 119.94 and 110.46. The NMR spectra were consistent with literature data.[10] The third component was 2-allylphenol **7** (0.012 g, 6%) (data as above).[10]

FVP of *N*-(2-allyloxybenzylidene)-*N′*-methyl-*N′*-phenylbenzene-1,2-diamine 6f. FVP of **6f** (0.50 g, 1.46 mmol, T_f 650 °C, T_i 150 °C, *P* 0.01 Torr, *t* 180 min) gave a yellow liquid which was separated by dry flash chromatography using hexane-ethyl acetate as eluants. The products were 2-(2-hydroxyphenyl)-1-phenylbenzimidazole **22** (0.13 g, 32%) m.p. 116–119 °C (lit.,[22] 119 °C); δ_H 13.56 (1H, br. s), 7.82 (1H, m), 7.67–7.57 (3H, m), 7.45–7.08 (7H, m), 6.86 (1H, m) and 6.54 (1H, m) (consistent

with literature data[22]); δ_C 159.46 (quat), 150.60 (quat), 139.81 (quat), 136.33 (quat), 131.24, 129.37, 127.71, 127.12, 123.58, 118.46, 117.84, 112.15 and 110.21; *m/z* 286 (M^+, 96%), 285 (100), 269 (31), 257 (18), 256 (16), 167 (8), 166 (7), 128 (9) and 77 (30). The second component was 2-(2-hydroxyphenyl)-1-methylbenzimidazole **13f** (0.020 g, 6%) δ_H 7.86–7.69 (2H, m), 7.43–7.31 (5H, m), 7.00 (1H, m) and 4.04 (3H, s); δ_C 158.87, 140.25 (quat), 135.54, 131.40, 130.41 (quat), 129.50 (quat), 126.97, 123.18, 122.88, 118.49, 118.00, 113.01 (quat), 109.40 and 31.47; *m/z* 224 (M^+, 100%), 223 (89), 207 (45), 198 (57), 195 (32) and 169 (15) (^{1}H NMR and mass spectra consistent with literature data[23]). The third component was 1-methyl-2-phenylbenzimidazole **21f** (0.015 g, 5%) δ_H 7.82–7.72 (3H, m), 7.52–7.25 (6H, m) and 3.86 (3H, s); δ_C (non-quaternary signals only) 129.76, 129.32, 128.60, 122.81, 122.52, 119.49, 109.57 and 31.55 (CH_3) (NMR spectra consistent with literature data[24]); *m/z* 208 (M^+, 39%), 207 (49), 182 (42), 105 (100) and 77 (64).

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