The oxidative rearrangement of furan-2-carboximidamides: preparation and properties of 2-acylaminofurans

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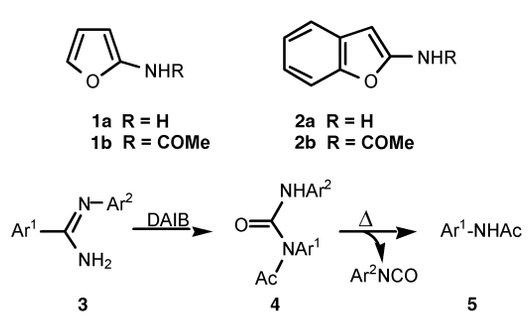
Oxidation of furan-2-carboximidamides **8** by (dicarboxyiodo)benzenes gives N^1-acyl-N^1-(2-furyl)ureas **9** *via* rearrangement to a carbodiimide. Thermolysis of eleven ureas **9** gave the corresponding 2-acylaminofurans **10**, which cannot be made from the free amines owing to their high instability. When oxidation of the corresponding benzo[*b*]furan derivatives **12** was investigated a new type of product was isolated, in addition to the expected ureas **14**, and these were shown to be benzo[4,5]furo[2,3-*d*]pyrimidine derivatives **15**. The mechanism of formation of these products must involve reaction of the carbodiimide intermediate with the amidine precursor and cyclisation of the resulting guanidine derivatives **19**. The corresponding tetraphenylguanidine **21** was prepared and underwent thermal cyclisation but the quinazoline derivative formed **23** was shown to occur *via* an alternative cyclisation mechanism. The structures of cyclisation products **15** and **23** were confirmed by X-ray crystallography. *N*-(2-Furyl)acetamide **10a** readily undergoes cycloaddition reactions with electron-deficient alkynes to give phenols after spontaneous ring opening. Observed regioselectivity is in agreement with the results of AM1 molecular orbital calculations. Reaction of the amide **10a** with Lawesson's reagent gave the thioamide **26**.

Introduction

2-Aminofuran **1a** and 2-aminobenzofuran **2a** are too unstable to be isolated or even trapped as *in situ* intermediates.[1] However, simple amide derivatives (*e.g.* **1b** and **2b**) are sufficiently stable to be prepared and characterised[2–4] while at the same time retaining the high reactivity expected for an activated furan ring. [4+2]-Cycloadditions and electrophilic substitutions of these amide derivatives (*i.e.* **1**; R = COR′) are therefore of potential synthetic value. In fact, the use of Diels–Alder reactions of 2-aminofuran derivatives in synthesis has been elegantly demonstrated by Padwa and co-workers in recent studies of methyl 5-aminofuroates[5] and related derivatives including carbamates.[6]

Since these amides (**1**; R = COR′) cannot be prepared *via* the unstable amines, access to derivatives that do not contain a stabilising electron-withdrawing group (*e.g.* NO_2, CO_2Me) on the furan ring is difficult. A limited number of 2-acylaminofurans (**1**; R = COR′) have been made by Curtius rearrangement of the acyl azide prepared from 2-furoic acid followed by reaction of the isocyanate with a Grignard reagent or cyanocuprate.[2,7] Padwa and co-workers have also made the carbamate derivative (**1**; R = tBuOCO) in good yield from 2-furoic acid, diphenoxyphosphoryl azide and tBuOH.[6] However, conversion of 2-carbamates to 2-acylamino derivatives, which cannot be done *via* the free amine, has not been described. Similar, but even more limited studies, have also been reported for 3-acylaminofurans.[8,9]

We have recently described a novel oxidative rearrangement of *C,N*-diarylamidines **3** to *N*-acetylureas **4** mediated by (diacetoxyiodo)benzene (DAIB).[4] Thermolysis of these ureas **4** results in elimination of an aryl isocyanate and formation of an *N*-arylacetamide **5** (Scheme 1). The amidines we studied



Scheme 1

previously included the 2-furyl derivative **3** (Ar^1 = 2-furyl, Ar^2 = Ph) and the results demonstrated a preparative route to the amide **1b** from readily available furfural, *via* 2-furonitrile. In order to evaluate this alternative route to synthetically useful 2-acylaminofurans (**5**; Ar^1 = 2-furyl derivatives) (Scheme 1), we have investigated the generality of the method and have studied some reactions of the amide **1b**. We now report the results of this study.

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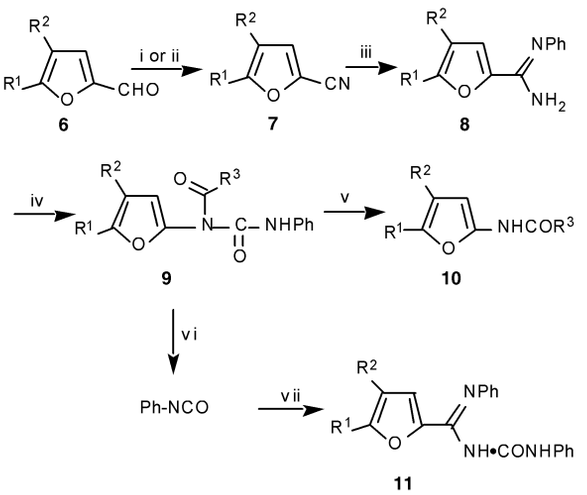
Results and discussion

Since furfural and various substituted derivatives **6** are readily available we have found them convenient starting materials that are readily converted to the corresponding nitriles **7**. Most of the nitriles used in this study were made in good yield by treatment of the aldehydes **6** with hydroxylamine hydrochloride in the presence of pyridine and acetic anhydride. The 4,5-dimethyl derivative **7h** was conveniently prepared by oxidation of the N^1,N^1-dimethylhydrazone using MCPBA. The amidines **8** were all prepared in good yield by reaction of the nitriles **7** with aniline and aluminium chloride at room temperature in CH_2Cl_2 solution, and were fully characterised after recrystallisation.

Reaction of the amidines **8** with diacetoxyiodobenzene (DAIB) in toluene at 60 or 80 °C gave the *N*-acetylureas **9** in moderate yields together with the *N*-phenylcarbamoyl derivatives **11** (Scheme 2). The mechanisms of formation of these



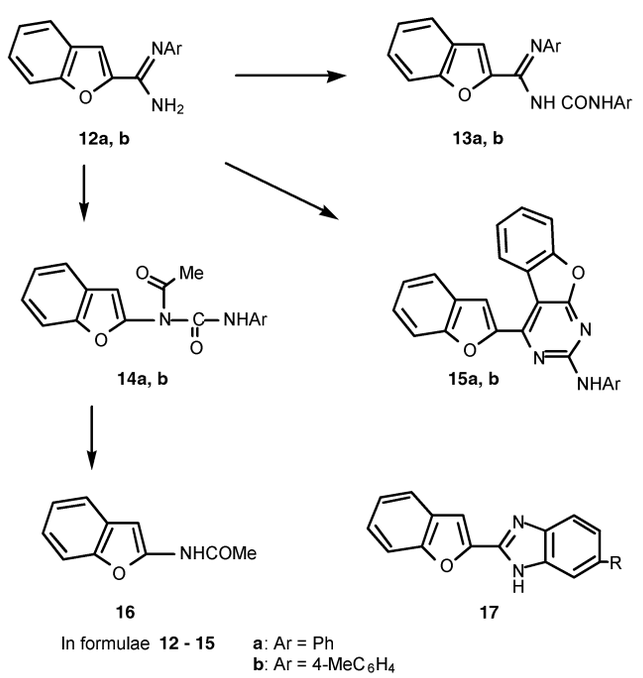
Scheme 2 *Reagents*: i, $HONH_2$·HCl–Ac_2O–pyridine; ii, Me_2NNH_2–MCPBA; iii, $PhNH_2$–$AlCl_3$; iv, $PhI(O_2CR^3)_2$ at 80 °C; v, 110 °C + $PhNH_2$; vi, heat; vii, amidine **8**.

products have been described elsewhere.[4] The optimum conditions for formation of the *N*-acetylureas **9** (R^3 = Me) are critical and vary for individual derivatives. If the temperature is too high the desired products **9** eliminate phenyl isocyanate which reacts with the amidine precursors **8** to give the unwanted *N*-phenylcarbamoyl products **11**. At 110 °C the derivatives **11** are the only products. Occasionally, very high yields of the ureas **9** were obtained but reproducing the conditions proved to be difficult. We have found that addition of one equivalent of triethylamine, to neutralise the acetic acid formed, consistently leads to some yield enhancement (*ca*. 5–15%). Some, but not all, of the urea preparations were repeated using this procedure.

Commercially available DAIB can be converted to other dicarboxyiodine(III) reagents [*i.e.* $(MeCO_2)_2IPh \longrightarrow (R^3CO_2)_2$-IPh] in almost quantitative yield from the appropriate carboxylic acid (R^3CO_2H) using the method of Merkushev.[10] This provides the opportunity of preparing a wider range of amide derivatives **10**. In this way we have prepared the ureas **9i**–**k** demonstrating that aromatic and heteroaromatic, as well as aliphatic, substituents can be incorporated. It is significant to note that in all cases the acyl group (R^3CO) rearranges to give the N^1-acyl-N^1-(2-furyl) product and we detected no formation of the N^2-acyl-N^2-phenyl regioisomers. For compound **9a** we have previously interpreted this selectivity in terms of the relative basicities of the two nitrogen atoms in the intermediate carbodiimide.[4]

We have also investigated the oxidation of furan-2-carboxamide under identical conditions to those used for amidine oxidation. This reaction was undertaken in expectation that a rearrangement–addition–elimination sequence analogous to that shown in Scheme 1 would occur to give the amide **1b** but that carbon dioxide instead of aryl isocyanate would be eliminated in the final step giving a much more convenient procedure. This mode of reaction with DAIB has been described for benzamides[11] but, surprisingly, we isolated only starting material in two independent investigations of furan-2-carboxamide.

When we investigated the oxidative rearrangement of the benzo[*b*]furancarboximidamides **12a**,**b** a new type of product, isolated in low yield (*ca*. 5%) as yellow crystals, was obtained in addition to the desired ureas **14a**,**b** and the *N*-arylcarbamoyl derivatives **13a**,**b** (Scheme 3). These new products were of a type



Scheme 3

that we had not obtained from any of the amidines previously studied and unambiguous assignment of a structure to these products was difficult until an X-ray study of the product formed from **12b** showed that it was the benzo[4,5]furo[2,3-*d*]-pyrimidine derivative **15b**. The ^{1}H and ^{13}C NMR and other spectra are all entirely consistent with the structures **15a**,**b**. For compound **15b**, which shows a molecular ion at *m*/*z* 391, the ^{1}H NMR shows a total of seventeen protons only one of which occurs as a singlet (δ 7.85) corresponding to the proton at the 3-position of the benzo[*b*]furyl substituent: the ^{13}C NMR spectrum shows eleven quaternary carbon atoms.

Fig. 1 shows a perspective view and atom labeling of the crystal structure of compound **15b**. The molecular geometry of **15b** compares well with what one would expect. The structure of **15b** may be considered to be composed of three ring-based moieties, where the benzofuran-2-yl and benzo[4,5]furo[2,3-*d*]-pyrimidine components are coplanar with respect to one another and collectively form a twist angle of 42.08(3)° with the *p*-tolylamine group. The supramolecular structure is comprised

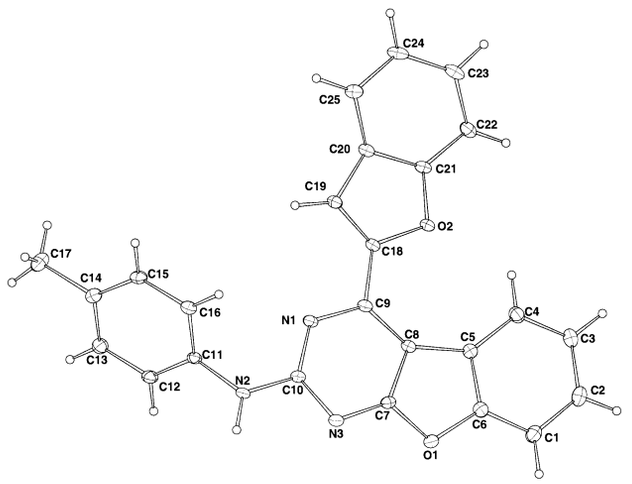
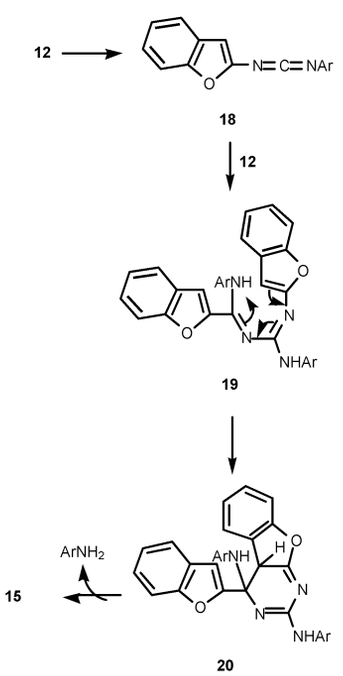


Fig. 1 The molecular structure of 2-(4-methylphenylamino)-4-(benzo[*b*]furan-2-yl)benzo[4,5]furo[2,3-*d*]pyrimidine **15b**.

of hydrogen bonded dimers, where the molecules A and B associate between N2A–H2A · · · N3B and N2B–H2B · · · N3A (N2–N3 = 3.088 Å and N2–H2 · · · N3 = 175°).

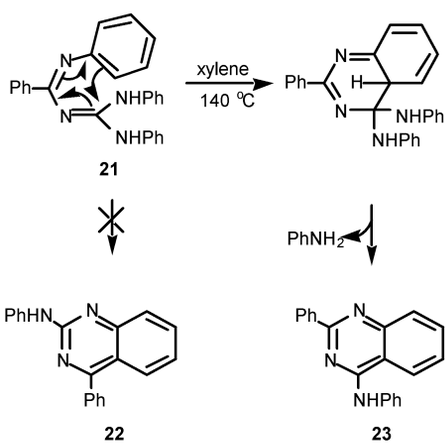
The formation of the pyrimidine derivatives **15** is consistent with our mechanistic proposal that I^{III} oxidation of amidines leads to carbodiimide intermediates. In this case the carbodiimide **18** presumably reacts with the amidine precursor **12** to give a guanidine derivative **19** which then undergoes thermal cyclisation and arylamine elimination to give the isolated product (Scheme 4). Although ring formation is represented as



Scheme 4

a concerted electrocyclic reaction in Scheme 4, we recognise that cyclisation may involve an addition–elimination mechanism involving different tautomers. The reason why reaction of the carbodiimide with the amidine competes with addition of acetic acid for these benzofuran derivatives is not clear but may be related to the electron-rich nature of this heterocyclic substituent, which makes the amidine a better nucleophile. We have previously described[4] the formation of the tosylate salt of the phenyl analogue **21** of the intermediate **19** by oxidation of N^2-phenylbenzamidine (**3**; $Ar^1 = Ar^2 = Ph$) with [methoxy-(tosyloxy)iodo]benzene (MTIB). In this case the acid anion (TsO^-) is less nucleophilic than acetate and the carbodiimide reacts exclusively with the amidine precursor. We therefore anticipated that oxidation of the amidines **12** with MTIB would lead to increased yields of the pyrimidine derivatives **15** but this was not the case and only complex mixtures, containing some of the desired products **15**, were obtained.

When the guanidine derivative **21** was heated in xylene at reflux temperature for two days a product was obtained (78% yield) which we initially assumed was the 2-phenylamino-4-phenylquinazoline **22** formed *via* a mechanism analogous to that shown in Scheme 4. However, a close examination of the ^{13}C NMR spectrum revealed that this product did not have a signal at *ca*. δ 170.5 analogous to that shown by the amino-pyrimidine carbon at position 2 of compound **15a**. It seemed possible, therefore, that the provisional structural assignment **22** was incorrect and that the product was the isomeric 4-phenylamino-2-phenylquinazoline **23**. To resolve this question we determined the crystal structure of this compound by X-ray analysis and this confirmed that the product is the isomer **23**. The formation of this product can be rationalised by the alternative mode of cyclisation shown in Scheme 5. In this



Scheme 5

mechanism, and in contrast to the benzo[*b*]furan mechanism (Scheme 4), the eliminated arylamine comes from the guanidine fragment and not from the amidine. Clearly the nature of the rearranged aryl substituent (Ar^1 in Scheme 1) profoundly influences the ease of the cyclisation mechanism shown in Scheme 4, which occurs at 60 °C for benzo[*b*]furan-2-yl. In contrast, no analogous reaction occurs for the phenyl compound **21** even at 140 °C in xylene (Scheme 5). The mode of reaction shown in Scheme 5 is consistent with the formation of similar products by thermal cyclisation of *N*-phenylcarbamoyl and *N*-phenylthiocarbamoylbenzamidines.[12]

Fig. 2 shows a perspective view and atom labeling for the crystal structure of compound **23**. The geometry of the structure **23** is in accordance with expected values. The quinazoline fragment in this molecule is planar, within experimental error, and forms a twist angle of 40.80(6)° with the phenylamine group. Intermolecular hydrogen bonding forms a supramolecular assembly of infinite two-dimensional chains. Molecules associate by means of a bifurcated hydrogen bond to a single acceptor (N2), with one interaction considerably stronger than the other (N3–H3 · · · N2 and C14–H14 · · · N2, D · · · A = 3.071, 3.432 Å and D–H · · · A = 162, 166° respectively).

Formation of the *p*-tolyl derivatives **13b**–**15b** was accompanied by a low yield (6%) of the benzimidazole derivative **17** (R= Me). We have previously encountered benzimidazole formation in similar oxidations and have discussed the mechanism of formation and the influence of temperature and leaving-group on this mode of reaction.[4]

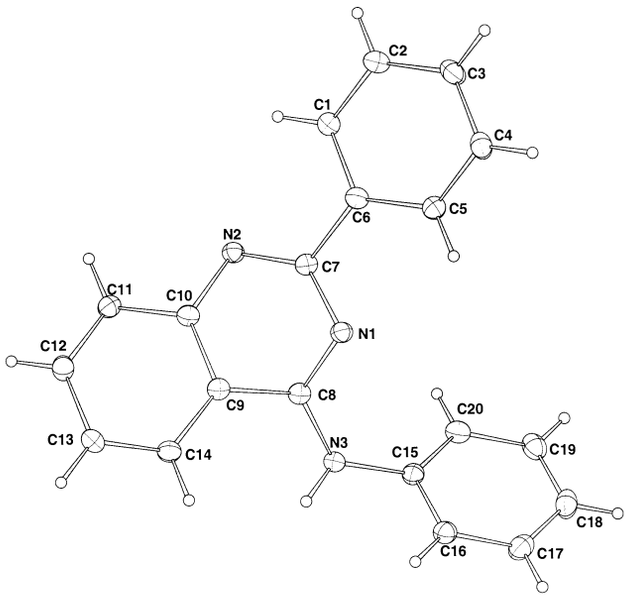
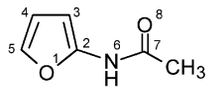


Fig. 2 The molecular structure of 2-phenyl-4-phenylaminoquinazoline **23**.

Thermolysis of the ureas **9a**–**k** in toluene at 110 °C, in the presence of one equivalent of aniline to trap the liberated phenyl isocyanate, gave the *N*-(2-furyl)carboxamides **10a**–**k** in moderate to good yield after chromatographic separation and recrystallisation. All these amides were stable, crystalline compounds and the structures were fully supported by their spectroscopic properties. The amide **10k** is of interest in that it contains both an *N*-(2-furyl) and a furan-2-carboxamide fragment. In the ^{1}H NMR spectrum, as expected, the *N*-(2-furyl) ring protons at positions 3 and 4 come at a higher field (δ 6.2 and 6.4, $J_{3,4}$ 3.2 Hz) than the corresponding protons on the furan-2-carboxamide ring (δ 6.6 and 7.3, $J_{3',4'}$ 3.4 Hz).

N-(2-Furyl)acetamide **10a** readily underwent reaction with dimethyl butynedioate in acetonitrile at room temperature to give the phenol **25**. This reaction, which demonstrates the high reactivity of these 2-aminofuran derivatives towards electron-deficient dienophiles, presumably proceeds *via* initial formation of the cycloadduct **24** which readily aromatises (Scheme 6) by a mechanism that has been discussed by Padwa and co-workers.[6,7] In a similar manner, reaction with ethyl propynoate gave only a single product which was identified as the 5-hydroxybenzoate **28**. None of the isomeric 2-hydroxybenzoate was detected. Structure **28** was confirmed by ^{1}H, ^{13}C NMR using selective insensitive nuclei enhanced by polarization transfer (INEPT) and difference NOE techniques.[13] In the selective INEPT spectrum of compound **28** irradiation of the OH proton resulted in polarisation transfer to carbon atoms C-4 and C-6. Using difference NOE, saturating the resonance of the phenolic OH proton produced a 25% positive NOE for protons H-4 and H-6 showing their spatial proximity to the OH substituent. Similarly, saturation of the NH proton produced a 7% positive NOE for H-3. The observed regioselectivity is consistent with the results of an AM1 MO calculation on the furan **10a** (Table 1). In particular, the calculation shows that for this electron-rich diene ($IP_{calc.}$ 8.50 eV) the HOMO coefficient at C-2 is smaller than that at C-5. Since it is well known that for electron deficient alkynes such as ethyl propynoate the larger LUMO coefficient is on the alkyne C-2 atom, this frontier orbital analysis based on AM1 calculations is entirely consistent with the observed mode of reaction.

Table 1 Calculated charge distribution (*e*), frontier orbital energies (*E*) and orbital coefficients for *N*-(2-furyl)acetamide[a]



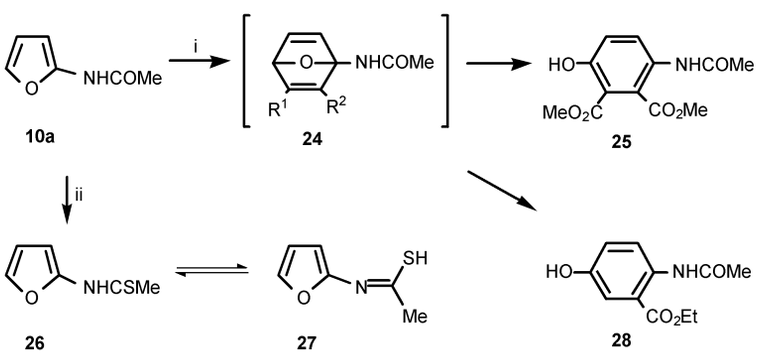
	Charge/*e*	HOMO	LUMO
E/eV	—	−8.50	−0.52
O1	−0.08	+0.04	−0.28
C2	+0.10	+0.45	+0.50
C3	−0.26	+0.48	−0.35
C4	−0.17	−0.27	−0.17
C5	−0.11	−0.52	+0.39
N6	−0.32	−0.41	0.00
C7	+0.31	−0.08	−0.47
O8	−0.31	+0.19	+0.35

[a] μ_{calcd} = 2.89 Debye.

Reaction of the amide **10a** with Lawesson's reagent gave the thioamide **26** (56%) as a stable crystalline compound. Although this reaction must proceed *via* a mechanism in which a tetrahedral intermediate removes the stabilising effect of the carbonyl group, the highly unstable 2-furylamine fragment remains intact and this transformation thus provides access to other derivatives. ^{1}H and ^{13}C NMR spectroscopy confirmed that compound **26** has the proposed thioamide structure in d_6-DMSO solution. A difference NOE spectrum showed the spatial proximity of the NH proton to the furyl C-3 proton and the methyl group. However, in $CDCl_3$ solution compound **28** is in equilibrium with the tautomer **27** (2 : 1).

Experimental

Melting points were determined using a Kofler hotplate apparatus and are uncorrected. Infrared spectra were recorded on a Philips FTIR PU 9802/25 spectrophotometer with only major absorbances being quoted. Unless otherwise stated IR spectra were measured using KBr pellets (0.5 mg/300 mg KBr). ^{1}H NMR (300 MHz) and ^{13}C NMR (75.43 MHz) spectra were recorded at ambient temperatures using a Varian VXR-300 NMR spectrometer with either TMS or HMDS as an internal



Scheme 6 *Reagents*: i, R^1CCR^2; ii, Lawesson's reagent.

reference, and were run in deuterated chloroform solution unless otherwise stated. The assignments of the carbon signals were based on the analysis of H,C-COSY spectra. Coupling constants are quoted to the nearest 0.1 Hz. Chemical shifts are quoted in parts per million and the following abbreviations are used: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. Elemental analyses were determined using either a Perkin-Elmer 240 CHN Elemental Analyser or a Carlo Erba CHNS-OEA 1108-Elemental Analyser. Low resolution mass spectra were recorded on an AEI MS 902-S Mass Spectrometer at 70 eV electron impact ionisation. Separations by column chromatography were carried out using silica gel S (Riedel-de Haen) 0.002–0.063 mm or silica gel (Janssen Chimica) 0.035–0.07 mm. All solvents were pre-distilled and dried appropriately prior to use. Concentration and evaporation refer to the removal of volatile materials under reduced pressure on a Büchi Rotovapor. Substances stated to be identical were so with respect to mps, mixed mps and IR spectra.

MO calculations were carried out using the AM1 semi-empirical method[14] and energy was minimised with respect to all geometrical variables.

Crystal data (15b) ‡

$C_{25}H_{17}N_3O_2$, $M_r = 391.42$, monoclinic, $a = 15.508(2)$, $b = 3.832(4)$, $c = 30.909(2)$ Å, $\beta = 92.30(3)°$, $V = 1835.60(2)$ Å^3, $Z = 4$, $\mu = 0.092$ mm^{-1}, space group $P2_1/n$ (alternative setting of $n°$. 14, $P2_1/c$), $T = 150$ K, crystal size $0.3 \times 0.02 \times 0.02$ mm^3.

Data collection and processing. Bruker AXS SMART CCD detector at a wavelength of 0.6875 Å on the single crystal diffraction station (N°. 9.8) at the Daresbury SRS.[15] 12000 reflections were collected, producing 5143 unique data ($R_{int} = 0.0446$) with $\theta_{min} = 2.25°$ and $\theta_{max} = 29.41°$.

Structure solution and refinement.[16] Direct methods, full-matrix least squares refinement based on F_o^2, weighting scheme $w = 1/[\sigma^2(F_o^2)]$, anisotropic displacement parameters and riding model H atoms. Final wR_2 and R_1 values = 0.1371 and 0.0624 respectively, for all data and 272 parameters (ρ_{max}, ρ_{min} 0.395, −0.263 eÅ^{-3}). The corresponding wR_2 and R_1 values for 4019 data with $F_o > 4\sigma(F_o)$ are 0.1316 and 0.0507 respectively.

Crystal data (23) ‡

$C_{20}H_{15}N_3$, $M_r = 297.35$, monoclinic, $a = 25.908(5)$, $b = 10.067(2)$, $c = 11.851(2)$ Å, $\beta = 102.36(3)°$, $V = 3007.3(10)$ Å^3, $Z = 8$, $\mu = 0.079$ mm^{-1}, space group $C2/c$, $T = 150$ K, crystal size $0.4 \times 0.2 \times 0.05$ mm^3.

Data collection and processing. Data were collected on a Nonius KappaCCD area detector diffractometer at the window of a rotating anode FR591 generator with a molybdenum target ($\lambda_{(Mo\text{-}K\alpha)} = 0.71069$ Å). 20181 reflections were collected producing 3426 unique data ($R_{int} = 0.0579$) with $\theta_{min} = 2.18°$ and $\theta_{max} = 27.52°$.

Structure solution and refinement.[16] Direct methods, full-matrix least squares refinement based on F_o^2, weighting scheme $w = 1/[\sigma^2(F_o^2)]$, anisotropic displacement parameters and riding model H atoms. Final wR_2 and R_1 values = 0.1500 and 0.0666 respectively, for all data and 209 parameters (ρ_{max}, ρ_{min} 0.370, −0.259 eÅ^{-3}). The corresponding wR_2 and R_1 values for 2720 data with $F_o > 4\sigma(F_o)$ are 0.1375 and 0.0515 respectively.

Preparation of 2-furonitriles (7)

The following derivatives were prepared using the literature method cited: 5-phenyl-2-furonitrile **7b**,[17] 5-(4-chlorophenyl)-2-furonitrile **7c**,[17] 5-(4-nitrophenyl)-2-furonitrile **7d**,[17] 5-(4-methylphenyl)-2-furonitrile **7e**,[17] 5-(4-methoxyphenyl)-2-furonitrile **7f**,[17] 5-(4-bromophenyl)-2-furonitrile **7g**.[17]

4,5-Dimethyl-2-furonitrile 7h. A stirred solution of 4,5-dimethylfuran-2-carbaldehyde[18] (2.48 g, 20 mmol) in toluene (70 cm^3) containing a catalytic amount of TsOH was treated with *N,N*-dimethylhydrazine (1.54 cm^3, 20 mmol) with cooling in an ice–salt bath. The solution was then heated under reflux (4 h) and the evolved water removed using a Dean–Stark trap. After evaporation the crude product was purified by column chromatography (silica gel: $CHCl_3$ as eluent) and identified as 4,5-dimethylfuran-2-carbaldehyde *N,N*-dimethylhydrazone (3.05 g, 92%), yellow oil; δ_H 1.92 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.91 (s, 6H, NCH_3), 6.16 (s, 1H, furyl 3-H), 7.06 (s, 1H, CH=N). Without further purification a solution of this hydrazone (1.66 g, 10 mmol) in CH_2Cl_2 (100 cm^3) was cooled in an ice-bath to −15 °C with vigorous stirring and 3-chloroperbenzoic acid (7.0 g, 22 mmol) in CH_2Cl_2 (300 cm^3) was added dropwise (4 h). Reaction was allowed to continue at room temperature (18 h) and anhydrous potassium carbonate (6.0 g) was then added. The mixture was stirred until gas evolution stopped. The solid material was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the crude product was distilled under vacuum and identified as 4,5-dimethyl-2-furonitrile **7h** (0.9 g, 41%), colourless oil, bp 50 °C at 0.27 kPa (lit.[19] bp 80 °C at 0.27 kPa) (Found: C, 69.22; H, 5.55; N, 11.40. Calc. for C_7H_7NO: C, 69.41; H, 5.82; N, 11.56%); ν_{max}/cm^{-1}(liquid film) 2959, 2930, 2226, 1618, 1528, 1477, 1445, 1264, 1255, 1165; δ_H 1.98 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 6.87 (s, 1H, furyl 3-H); *m/z* 121 ($M^{\bullet+}$).

Benzo[*b*]furan-2-carbonitrile

To a mixture of benzo[*b*]furan-2-carbaldehyde (5.0 g, 34 mmol), pyridine (26 cm^3) and hydroxylamine hydrochloride (4.75 g, 68 mmol) acetic anhydride (20 cm^3) was added with stirring at 95 °C. The reaction mixture was kept at 85–95 °C for 2 h, cooled and poured on ice. The separated precipitate was filtered off and identified as benzo[*b*]furan-2-carbonitrile (3.9 g, 80%), pale yellow crystals, mp 38 °C (lit.,[20] 36 °C). ν_{max}/cm^{-1} (KBr) 2226, 1444, 1180, 750; δ_H 7.25–7.74 (m, 5H, furyl 3-H and ArH); *m/z* 143 ($M^{\bullet+}$).

Preparation of amidines 8 and 12. Method A

***N*^{2}-Phenylfuran-2-carboximidamide 8a.** To a mixture of 2-furonitrile (4.65 g, 50 mmol) and aniline (4.65 g, 50 mmol) in dichloromethane (20 cm^3) was added powdered aluminium chloride (6.65 g, 50 mmol) in portions with constant swirling. A vigorous exothermic reaction occurred and the mixture turned orange. After evaporation of dichloromethane the thick mixture was added to warm water and basified (30% aqueous NaOH) to pH 14. The solid product was collected, air dried, recrystallized from toluene–isohexane and identified as compound **8a** (7.2 g, 77%), buff crystals, mp 107–109 °C (lit.,[4] 105–106 °C) (Found: C, 71.10; H, 5.30; N, 15.10. Calc. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04%); ν_{max}/cm^{-1} 3451, 3329, 3295, 3090, 3071, 1632, 1618, 1564, 1480, 1408, 1028; δ_H 4.80 (br s, 2H, 2NH), 6.47–6.54 (m, 1H, furyl 4-H), 6.87–7.75 (m, 7H, ArH, furyl 3-H, furyl 5-H); *m/z* 186 ($M^{\bullet+}$).

In a similar manner the following novel amidines were prepared from the appropriate 5-aryl-2-furonitriles.

***N*^{2}-Phenyl-5-phenylfuran-2-carboximidamide 8b.** Yield (90%), colourless crystals, mp 124–126 °C (Found: C, 77.62; H, 5.25; N, 10.52. $C_{17}H_{14}N_2O$ requires C, 77.84; H, 5.38; N, 10.68%); ν_{max}/cm^{-1} 3453, 3310, 3167, 3115, 3073, 1618, 1581, 1566, 1480, 1385, 1024; δ_H 5.00 (br s, 2H, 2NH), 6.72 (d, 1H,

‡ CCDC reference number(s) 155638 and 155639. See http://www.rsc.org/suppdata/p1/b0/b010010m/ for crystallographic files in CIF and other electronic format.

J 3.6 Hz, furyl 3-H), 6.81–7.88 (m, 11H, ArH, furyl 4-H); *m*/*z* 262 ($M^{\bullet+}$).

***N*²-Phenyl-5-(4-chlorophenyl)furan-2-carboximidamide 8c.** Yield (85%), light yellow crystals, mp 167–168 °C (Found: C, 68.50; H, 4.20; N, 9.35; Cl, 11.75. $C_{17}H_{13}ClN_2O$ requires C, 68.81; H, 4.42; N, 9.44; Cl, 11.95%); ν_{max}/cm^{-1} 3482, 3359, 3069, 3058, 1622, 1593, 1587, 1480, 1410, 1017; δ_H 4.50 (br s, 2H, 2NH), 6.75 (d, 1H, *J* 3.5 Hz, furyl 3-H), 6.88–7.50 (m, 6H, ArH, furyl 4-H), 7.37 (d, 2H, *J* 8.9 Hz, ArH), 7.65 (d, 2H, *J* 8.9 Hz, ArH); *m*/*z* 296 ($M^{\bullet+}$).

***N*²-Phenyl-5-(4-nitrophenyl)furan-2-carboximidamide 8d.** Yield (75%), yellow crystals, mp 184–186 °C (Found: C, 66.31; H, 4.08; N, 13.55. $C_{17}H_{13}N_3O_3$ requires C, 66.44; H, 4.26; N, 13.67%); ν_{max}/cm^{-1} 3490, 3372, 3125, 3075, 3029, 1622, 1599, 1541, 1506, 1480, 1356, 1337, 1109, 1022; δ_H 5.00 (br s, 2H, 2NH), 6.93–7.69 (m, 7H, ArH, furyl 3-H, furyl 4-H), 7.82 (d, 2H, *J* 9.1 Hz, ArH), 8.26 (d, 2H, *J* 9.1 Hz, ArH); *m*/*z* 307 ($M^{\bullet+}$).

***N*²-Phenyl-5-(4-methylphenyl)furan-2-carboximidamide 8e.** Yield (80%), light yellow crystals, mp 167–168 °C (Found: C, 78.00; H, 5.62; N, 9.98. $C_{18}H_{16}N_2O$ requires C, 78.24; H, 5.84; N, 10.14%); ν_{max}/cm^{-1} 3480, 3357, 3121, 3069, 3056, 3038, 3020, 1624, 1613, 1592, 1572, 1483, 1369, 1016; δ_H 2.37 (s, 3H, CH_3), 4.96 (br s, 2H, 2NH), 6.69 (d, 1H, *J* 3.6 Hz, furyl 3-H), 6.84–7.50 (m, 6H, ArH and furyl 4-H), 7.19 (d, 2H, *J* 8.5 Hz, ArH), 7.60 (d, 2H, *J* 8.5 Hz, ArH); *m*/*z* 276 ($M^{\bullet+}$).

***N*²-Phenyl-5-(4-methoxyphenyl)furan-2-carboximidamide 8f.** Yield (72%), light yellow crystals, mp 142–143 °C (Found: C, 73.75; H, 5.40; N, 9.40. $C_{18}H_{16}N_2O_2$ requires C, 73.95; H, 5.52; N, 9.58%); ν_{max}/cm^{-1} 3455, 3237, 3127, 3075, 3061, 3024, 1628, 1603, 1588, 1549, 1497, 1485, 1460, 1375, 1248, 1020; δ_H 3.84 (s, 3H, OCH_3), 4.91 (br s, 2H, 2NH), 6.61 (d, 1H, *J* 3.5 Hz, furyl 3-H), 6.93 (d, 2H, *J* 8.7 Hz, ArH), 6.85–7.54 (m, 6H, ArH and furyl 4-H), 7.64 (d, 2H, *J* 8.7 Hz, ArH); *m*/*z* 292 ($M^{\bullet+}$).

***N*²-Phenyl-5-(4-bromophenyl)furan-2-carboximidamide 8g.** Yield (76%), light yellow crystals, mp 182–184 °C (Found: C, 59.65; H, 3.68; N, 8.05; Br, 23.30. $C_{17}H_{13}BrN_2O$ requires C, 59.84; H, 3.84; N, 8.21; Br, 23.42%); ν_{max}/cm^{-1} 3482, 3359, 3127, 3069, 3053, 3023, 1622, 1593, 1508, 1478, 1404, 1368, 1019; δ_H 4.74 (br s, 2H, 2NH), 6.75 (d, 1H, *J* 3.7 Hz, furyl 3-H), 6.88–7.65 (m, 6H, ArH and furyl 4-H), 7.54 (s, 4H, ArH); *m*/*z* 341 ($M^{\bullet+}$).

***N*²-Phenyl-4,5-dimethylfuran-2-carboximidamide 8h.** Yield (79%), colourless crystals, mp 114–115 °C (Found: C, 72.58; H, 6.40; N, 12.85. $C_{13}H_{14}N_2O$ requires C, 72.87; H, 6.59; N, 13.07%); ν_{max}/cm^{-1} 3474, 3285, 3154, 1640, 1624, 1587, 1537, 1482, 1400, 1235, 1161; δ_H 1.97 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 4.58 (br s, 2H, 2NH), 6.60–7.50 (m, 6H, ArH and furyl 3-H); *m*/*z* 214 ($M^{\bullet+}$).

***N*²-Phenylbenzo[*b*]furan-2-carboximidamide 12a.** Yield (93%), colourless needles, mp 181–183 °C (Found: C, 76.19; H, 5.09; N, 11.99. $C_{15}H_{12}N_2O$ requires C, 76.25; H, 5.12; N, 11.86%); ν_{max}/cm^{-1} 3495, 3271, 3112, 1635, 1618, 1589, 1559, 1483, 1449, 1400, 1260, 1250, 1238, 1234, 1186, 1113, 1067, 1007; δ_H 5.01 (br s, 2H, NH), 6.98–7.7 (m, 10H, H-3 and aromatic H); *m*/*z* 236 ($M^{\bullet+}$).

Method B

***N*²-(4-Methylphenyl)furan-2-carboximidamide 8l.** To a mixture of 2-furonitrile (1.86 g, 20 mmol) and 4-methylaniline (2.25 g, 20 mmol) in dichloromethane (10 cm³) was added powdered aluminium chloride (2.80 g, 20 mmol) in portions with constant swirling. A vigorous exothermic reaction occurred and the mixture turned yellow. After evaporation of dichloromethane the thick reaction mixture was added to warm water and basified (30% aqueous NaOH) to pH 14. After cooling with ice the solid product was filtered off, air dried, crystallized from toluene–isohexane and identified as *compound* **8l** (2.8 g, 70%), colourless crystals, mp 80–82 °C (Found: C, 71.78; H, 5.85; N, 13.77. $C_{12}H_{12}N_2O$ requires C, 71.98; H, 6.04; N, 13.99%); ν_{max}/cm^{-1} 3455, 3295, 3137, 1618, 1597, 1566, 1505, 1485, 1363, 1231; δ_H 2.32 (s, 3H, CH_3), 4.58 (br s, 2H, 2NH), 6.50 (dd, 1H, *J* 3.4 and 1.7 Hz, furyl 3-H), 6.70–7.35 (m, 5H, ArH and furyl 4-H), 7.46 (m, 1H, furyl 5-H); *m*/*z* 200 ($M^{\bullet+}$).

In a similar manner the following novel amidine was prepared.

***N*²-(4-Methylphenyl)benzo[*b*]furan-2-carboximidamide 12b.** Yield (90%), colourless needles (from toluene), mp 188–190 °C (Found: C, 76.74; H, 5.60; N, 11.18. $C_{16}H_{14}N_2O$ requires C, 76.78; H, 5.64; N, 11.19%); ν_{max}/cm^{-1} 3495, 3271, 3112, 1635, 1618, 1589, 1559, 1483, 1449, 1400, 1260, 1234, 1113, 1067; δ_H (d_6-DMSO) 2.26 (s, 3H, CH_3), 6.42 (br s, 2H, NH_2), 6.83 (br d, 2H, *J* 8.1 Hz, H-2', H-6′), 7.13 (d, 2H, *J* 8.1 Hz, H-3′, H-5′), 7.30 (dd, 1H, H-5), 7.41 (dd, 1H, H-6), 7.55 (s, 1H, H-3), 7.64 (d, 1H, *J* 8.2 Hz, H-4), 7.73 (d, 1H, *J* 7.9 Hz, H-7); δ_C (d_6-DMSO) 20.62 (CH_3), 106.99 (C-3), 111.65, (C-7), 121.49 (C-2′, C-6′), 122.22 (C-4), 123.55 (C-5), 125.98 (C-6), 127.76 (C-3a), 129.85 (C-3′, C-5′), 131.13 (C-4′), 146.62 (C-1′), 146.64 (C-8), 151.23 (C-2), 154.27 (C-7a); *m*/*z* 250 ($M^{\bullet+}$).

Reactions of furan-2-carboximidamides 8 with (dicarboxyiodo)-benzenes [PhI(O_2CR^3)$_2$]

(i) At 80 °C. *N*²-Phenylfuran-2-carboximidamide 8a. A solution of amidine **8a** (0.93 g, 5 mmol) in toluene (25 cm³) was added dropwise to a suspension of DAIB (1.61 g, 5 mmol) in distilled toluene (25 cm³) heated in an oil bath maintained at 80 °C. After evaporation the residue was purified by column chromatography (silica gel: $CHCl_3$ as eluent). In addition to iodobenzene, one major product was obtained. The material was crystallized from isohexane and identified as *N*¹-acetyl-*N*¹-(2-furyl)-*N*²-phenylurea **9a** (0.35 g, 25%), colourless crystals, mp 102–104 °C (lit.,[4] 107–109 °C) (Found: C, 63.70; H, 4.70; N, 11.30. $C_{13}H_{12}N_2O_3$ requires C, 63.93; H, 4.95; N, 11.47%); ν_{max}/cm^{-1} 3206, 3135, 1721, 1688, 1597, 1553, 1505, 1491, 1449, 1426, 1372, 1271, 1221, 1181; δ_H 2.08 (s, 3H, $COCH_3$), 6.19–6.75 (m, 2H, furyl 3-H and 4-H), 6.94–7.88 (m, 6H, ArH and furyl 5-H), 11.02 (br s, 1H, NH); *m*/*z* 244 ($M^{\bullet+}$).

The reaction was repeated with one equivalent of triethylamine added to the amidine solution before addition. This procedure gave compound **9a** in 37% yield.

In a similar manner the following compounds were prepared. Unless otherwise stated the quoted yield is for the procedure without addition of triethylamine.

*N*¹-*Propanoyl*-*N*¹-*(2-furyl)*-*N*²-*phenylurea* ***9i.*** Yield (23%; 30% with Et_3N), colourless crystals, mp 119–121 °C (Found: C, 65.00; H, 5.30; N, 10.58. $C_{14}H_{14}N_2O_3$ requires C, 65.11; H, 5.46; N, 10.85%); ν_{max}/cm^{-1} 3196, 3144, 1728, 1686, 1599, 1556, 1497, 1449, 1420, 1410, 1267, 1221, 1176, 1156; δ_H 1.11 (t, 3H, CH_3), 2.30 (q, 2H, CH_2), 6.38 (dd, 1H, *J* 3.35 and 0.85 Hz, furyl 3-H), 6.52 (dd, 1H, *J* 3.35 and 2.17 Hz, furyl 4-H), 6.88–7.75 (m, 6H, ArH and furyl 5-H), 11.14 (br s, 1H, NH); *m*/*z* 258 ($M^{\bullet+}$).

*N*¹-*Benzoyl*-*N*¹-*(2-furyl)*-*N*²-*phenylurea* ***9j.*** Yield (26%; 30% with Et_3N), colourless crystals, mp 121–122 °C (Found: C, 70.44; H, 4.45; N, 8.98. $C_{18}H_{14}N_2O_3$ requires C, 70.58; H, 4.61; N, 9.15%); ν_{max}/cm^{-1} 3225, 3173, 3119, 1725, 1667, 1597, 1593, 1579, 1549, 1496, 1446, 1318, 1306, 1277, 1231, 1181, 1115; δ_H 6.02 (d, 1H, *J* 3.35 Hz, furyl 3-H), 6.24 (dd, 1H, *J* 3.35 and 2.17 Hz, furyl 4-H), 6.90–7.90 (m, 11H, ArH and furyl 5-H), 11.06 (br s, 1H, NH); *m*/*z* 306 ($M^{\bullet+}$).

N^1-*Furoyl*-*N*^{1}-*(2-furyl)*-*N*^{2}-*phenylurea* ***9k.*** Yield (10%; 20% with Et_3N), colourless crystals, mp 119–121 °C (Found: C, 64.58; H, 3.89; N, 9.18. $C_{16}H_{12}N_2O_4$ requires C, 64.86; H, 4.08; N, 9.45%); ν_{max}/cm^{-1} 3235, 3138, 1730, 1659, 1597, 1557, 1464, 1279, 1173, 1129; δ_H (d_6-DMSO) 5.85 (d, 1H, *J* 3.5 Hz, furyl 3-H), 6.25–6.50 (m, 2H, furyl 3′-H and 4-H), 6.55 (dd, 1H, *J* 3.35 and 2.0 Hz, furyl 4′-H), 6.87–7.75 (m, 5H, ArH, furyl 5-H and 5′-H), 11.16 (br s, 1H, NH); *m*/*z* 296 ($M^{\bullet+}$).

N^1-*Acetyl*-*N*^{1}-*(2-furyl)*-*N*^{2}-*(4-methylphenyl)urea* ***9l.*** Yield (16%), colourless crystals, mp 109–112 °C (Found: C, 64.95; H, 5.28; N, 10.62. $C_{14}H_{14}N_2O_3$ requires C, 65.11; H, 5.46; N, 10.85%); ν_{max}/cm^{-1} 3179, 3129, 3079, 3032, 1730, 1682, 1593, 1549, 1516, 1499, 1321, 1271, 1175, 1072, 1049; δ_H 2.07 (s, 3H, $COCH_3$), 2.30 (s, 3H, CH_3), 6.36 (dd, 1H, *J* 3.15 and 0.8 Hz, furyl 3-H), 6.49 (dd, 1H, *J* 3.15 and 2.2 Hz, furyl 4-H), 7.11 (d, 2H, *J* 8.5 Hz, ArH), 7.41 (d, 2H, *J* 8.5 Hz, ArH), 7.42 (dd, 1H, *J* 2.2 and 0.8 Hz, furyl 5-H), 10.96 (br s, 1H, NH); δ_C 20.77 (Ar-*C*H$_3$), 24.74 (CO-*C*H$_3$), 108.12 (C-3), 111.61 (C-4), 120.18 (C-2′, C-6′), 129.15 (C-3′, C-5′), 133.92 (C-4′), 134.64 (C-1′), 141.35 (C-5), 143.92 (C-2), 150.61 (NH-*C*O), 175.30 (*C*O-CH$_3$); *m*/*z* 258 ($M^{\bullet+}$).

(ii) At 60 °C. Using a procedure identical to that described above using DAIB (without addition of Et_3N), except that the reaction flask was maintained at 60 °C, *N*^{2}-phenyl-5-phenylfuran-2-carboximidamide **8b** gave *N*^{1}-*acetyl*-*N*^{1}-*(5-phenyl-2-furyl)*-*N*^{2}-*phenylurea* **9b** (19%), colourless crystals, mp 128–130 °C (Found: C, 71.00; H, 4.85; N, 8.50. $C_{19}H_{16}N_2O_3$ requires C, 71.24; H, 5.03; N, 8.74%); ν_{max}/cm^{-1} 3185, 3148, 3127, 3085, 3067, 3042, 1725, 1686, 1599, 1559, 1541, 1447, 1368, 1262, 1229, 1175, 1015; δ_H 2.17 (s, 3H, $COCH_3$), 6.45 (d, 1H, *J* 3.5 Hz, furyl 3-H), 6.73 (d, 1H, *J* 3.5 Hz, furyl 4-H), 6.88–7.75 (m, 10H, ArH), 11.04 (br s, 1H, NH); *m*/*z* 320 ($M^{\bullet+}$).

In a similar manner the following compounds were prepared from amidines **8c**–**g** respectively.

N^1-*Acetyl*-*N*^{1}-*[5-(4-chlorophenyl)-2-furyl]*-*N*^{2}-*phenylurea* ***9c.*** Yield (17%), colourless crystals, mp 190–193 °C (Found: C, 64.15; H, 4.05; N, 7.68; Cl, 9.70. $C_{19}H_{15}ClN_2O_3$ requires C, 64.32; H, 4.26; N, 7.90; Cl, 9.99%); ν_{max}/cm^{-1} 3202, 3137, 1725, 1597, 1557, 1537, 1482, 1446, 1368, 1267, 1174, 1092; δ_H 2.17 (s, 3H, $COCH_3$), 6.46 (d, 1H, *J* 3.4 Hz, furyl 3-H), 6.73 (d, 1H, *J* 3.4 Hz, furyl 4-H), 6.88–7.88 (m, 9H, ArH), 11.03 (br s, 1H, NH); *m*/*z* 354 ($M^{\bullet+}$).

N^1-*Acetyl*-*N*^{1}-*[5-(4-nitrophenyl)-2-furyl]*-*N*^{2}-*phenylurea* ***9d.*** Yield (21%), light yellow crystals, mp 240–242 °C (Found: C, 62.30; H, 3.98; N, 11.25. $C_{19}H_{15}N_3O_5$ requires C, 62.46; H, 4.14; N, 11.50%); ν_{max}/cm^{-1} 3256, 3196, 3133, 3111, 1725, 1690, 1593, 1561, 1541, 1508, 1448, 1369, 1267, 1174; δ_H 2.20 (s, 3H, $COCH_3$), 6.56 (d, 1H, *J* 3.5 Hz, furyl 3-H), 6.97 (d, 1H, *J* 3.5 Hz, furyl 4-H), 7.00–8.13 (m, 5H, ArH), 7.79 (d, 2H, *J* 8.7 Hz, ArH), 8.26 (d, 2H, *J* 8.7 Hz, ArH), 11.01 (br s, 1H, NH); *m*/*z* 365 ($M^{\bullet+}$).

N^1-*Acetyl*-*N*^{1}-*[5-(4-methylphenyl)-2-furyl]*-*N*^{2}-*phenylurea* ***9e.*** Yield (15%), colourless crystals, mp 125–128 °C (Found: C, 71.68; H, 5.28; N, 8.25. $C_{20}H_{18}N_2O_3$ requires C, 71.84; H, 5.43; N, 8.38%); ν_{max}/cm^{-1} 3181, 3137, 3077, 3034, 1725, 1686, 1601, 1560, 1552, 1498, 1446, 1372, 1269, 1173, 1019; δ_H 2.17 (s, 3H, $COCH_3$), 2.36 (s, 3H, CH_3), 6.43 (d, 1H, *J* 3.4 Hz, furyl 3-H), 6.67 (d, 1H, *J* 3.4 Hz, furyl 4-H), 7.04–7.70 (m, 9H, ArH), 11.18 (br s, 1H, NH); *m*/*z* 334 ($M^{\bullet+}$).

N^1-*Acetyl*-*N*^{1}-*[5-(4-methoxyphenyl)-2-furyl]*-*N*^{2}-*phenylurea* ***9f.*** Yield (15%), colourless crystals, mp 142–144 °C (Found: C, 68.35; H, 4.98; N, 7.88. $C_{20}H_{18}N_2O_4$ requires C, 68.56; H, 5.18; N, 8.00%); ν_{max}/cm^{-1} 3202, 3131, 3061, 3015, 1730, 1686, 1618, 1601, 1543, 1498, 1446, 1365, 1267, 1250, 1179, 1022; δ_H 2.18 (s, 3H, $COCH_3$), 3.83 (s, 3H, OCH_3), 6.42 (d, H, *J* 3.4 Hz, furyl 3-H), 6.60 (d, 1H, *J* 3.4 Hz, furyl 4-H), 6.91 (d, 2H, *J* 8.9 Hz, ArH), 7.04–7.70 (m, 5H, ArH), 7.59 (d, 2H, *J* 8.9 Hz, ArH), 11.06 (br s, 1H, NH); *m*/*z* 350 ($M^{\bullet+}$).

N^1-*Acetyl*-*N*^{1}-*[5-(4-bromophenyl)-2-furyl]*-*N*^{2}-*phenylurea* ***9g.*** Yield (12%; 35% with Et_3N), colourless crystals, mp 142–144 °C (Found: C, 56.95; H, 3.65; N, 6.85; Br, 19.83. $C_{19}H_{15}BrN_2O_3$ requires C, 57.16; H, 3.79; N, 7.02; Br, 20.01%); ν_{max}/cm^{-1} 3204, 3142, 3111, 3065, 3044, 1728, 1686, 1601, 1528, 1480, 1448, 1370, 1271, 1173; δ_H 2.18 (s, 3H, $COCH_3$), 6.47 (d, 1H, *J* 3.4 Hz, furyl 3-H), 6.75 (d, 1H, *J* 3.4 Hz, furyl 4-H), 6.94–7.75 (m, 5H, ArH), 7.52 (s, 4H, ArH), 11.03 (br s, 1H, NH); *m*/*z* 399 ($M^{\bullet+}$).

N^1-*Acetyl*-*N*^{1}-*(4,5-dimethyl-2-furyl)*-*N*^{2}-*phenylurea* ***9h.*** Yield (16%; 27% with Et_3N), colourless crystals, mp 71–74 °C (Found: C, 66.00; H, 5.78; N, 12.98. $C_{15}H_{16}N_2O_3$ requires C, 66.16; H, 5.92; N, 10.29%); ν_{max}/cm^{-1} 3245, 3189, 1732, 1686, 1599, 1595, 1547, 1447, 1372, 1316, 1306, 1271, 1235, 1217, 1190; δ_H 1.97 (s, 3H, CH_3), 2.11 (s, 3H, $COCH_3$), 2.23 (s, 3H, CH_3), 6.12 (s, 1H, furyl 3-H), 7.09 (t, 1H, ArH-4′), 7.30 (t, 2H, ArH-3′,5′), 7.53 (d, 2H, ArH-2′,6′), 11.04 (br s, 1H, NH); δ_C 9.92 (CH_3), 11.26 (CH_3), 24.82 (CO*C*H$_3$), 110.86 (C-3), 115.92 (C-4), 120.09 (C-2′,6′), 124.17 (C-4′), 128.85 (C-3′,5′), 137.31 (C-1′), 140.48 (C-5), 146.52 (C-2), 150.82 (NH*C*O), 175.68 (CH$_3$*C*O); *m*/*z* 272 ($M^{\bullet+}$).

(iii) At 110 °C. ***N*^{2}-Phenyl-5-phenylfuran-2-carboximidamide 8b.** A solution of amidine **8b** (0.33 g, 1.25 mmol) in toluene (5 cm^3) was added dropwise to a suspension of DAIB (0.4 g, 1.25 mmol) in toluene (5 cm^3) and heated under reflux. After evaporation, the residue was purified by column chromatography (silica gel: $CHCl_3$ as eluent). The major product was crystallised from toluene and identified as *N*^{1}-*(phenylcarbamoyl)*-*N*^{2}-*phenyl-5-phenylfuran-2-carboximidamide* **11b** (0.1 g, 42%), colourless crystals, mp 210–213 °C (Found: C, 75.40; H, 4.82; N, 10.88. $C_{24}H_{19}N_3O_2$ requires C, 75.57; H, 5.02; N, 11.02%); ν_{max}/cm^{-1} 3243, 3134, 1684, 1641, 1599, 1562, 1514, 1487, 1449, 1302, 1277; δ_H (d_6-DMSO) 6.60–8.00 (m, 17H, ArH, furyl 3-H, furyl 4-H), 9.45 (br s, 1H, NH), 9.52 (br s, 1H, NH); *m*/*z* 381 ($M^{\bullet+}$).

In a similar manner the following compounds were prepared from amidines **8c**–**g** respectively.

N^1-*(Phenylcarbamoyl)*-*N*^{2}-*phenyl-5-(4-chlorophenyl)furan-2-carboximidamide* ***11c.*** Yield (43%), light yellow crystals, mp 216–218 °C (Found: C, 69.15; H, 4.10; N, 10.00. $C_{24}H_{18}ClN_3O_2$ requires C, 69.31; H, 4.36; N, 10.10%); ν_{max}/cm^{-1} 3262, 3130, 1682, 1640, 1597, 1556, 1512, 1485, 1448, 1298, 1281; δ_H (d_6-DMSO) 6.60–8.00 (m, 16H, ArH), 9.48 (br s, 1H, NH), 9.53 (br s, 1H, NH); *m*/*z* 415 ($M^{\bullet+}$).

N^1-*(Phenylcarbamoyl)*-*N*^{2}-*phenyl-5-(4-nitrophenyl)furan-2-carboximidamide* ***11d.*** Yield (40%), yellow needles, mp 205–208 °C (Found: C, 67.40; H, 4.10; N, 12.98. $C_{24}H_{18}N_4O_4$ requires C, 67.60; H, 4.25; N, 13.14%); ν_{max}/cm^{-1} 3245, 3133, 1684, 1638, 1599, 1559, 1516, 1485, 1447, 1337, 1279; δ_H (d_6-DMSO) 6.70–8.25 (m, 16H, ArH), 9.58 (br s, 2H, 2NH); *m*/*z* 426 ($M^{\bullet+}$).

N^1-*(Phenylcarbamoyl)*-*N*^{2}-*phenyl-5-(4-methylphenyl)furan-2-carboximidamide* ***11e.*** Yield (45%), beige crystals, mp 205–208 °C (Found: C, 75.70; H, 5.15; N, 10.40. $C_{25}H_{21}N_3O_2$ requires C, 75.93; H, 5.35; N, 10.63%); ν_{max}/cm^{-1} 3268, 3129, 1680, 1638, 1595, 1559, 1522, 1489, 1447, 1308, 1298, 1279, 1230, 1136; δ_H (d_6-DMSO) 2.21 (s, 3H, CH_3), 6.60–8.00 (m, 16H, ArH), 9.43 (br s, 1H, NH), 9.51 (br s, 1H, NH); *m*/*z* 395 ($M^{\bullet+}$).

N^1-*(Phenylcarbamoyl)*-*N*^{2}-*phenyl-5-(4-methoxyphenyl)-furan-2-carboximidamide* ***11f.*** Yield (38%), light yellow crystals, mp 204–206 °C (Found: C, 72.70; H, 5.00; N, 10.00. $C_{25}H_{21}N_3O_3$ requires C, 72.98; H, 5.14; N, 10.21%); ν_{max}/cm^{-1} 3237, 3135, 1682, 1638, 1597, 1557, 1487, 1449, 1298, 1277, 1256; δ_H (d_6-DMSO) 3.68 (s, 3H, OCH_3), 6.50–8.00 (m, 16H, ArH), 9.41 (br s, 1H, NH), 9.48 (br s, 1H, NH); *m*/*z* 411 ($M^{\bullet+}$).

N^1-*(Phenylcarbamoyl)*-*N*^{2}-*phenyl-5-(4-bromophenyl)furan-2-carboximidamide* ***11g.*** Yield (40%), light yellow crystals, mp 215–218 °C (Found: C, 62.40; H, 3.80; N, 9.00. $C_{24}H_{18}BrN_3O_2$ requires C, 62.62; H, 3.94; N, 9.13%); ν_{max}/cm^{-1} 3264, 3131,

1682, 1638, 1595, 1557, 1509, 1482, 1449, 1296, 1281; δ_H (d_6-DMSO) 6.50–8.00 (m, 16H, ArH), 9.49 (br s, 1H, NH), 9.52 (br s, 1H, NH); *m*/*z* 460 ($M^{\bullet+}$).

Thermolysis of *N*-acyl-*N*-(2-furyl)ureas 9

***N*-(2-Furyl)acetamide 10a.** A mixture of compound **9a** (2.7 g, 11 mmol) and freshly distilled aniline (1.05 g, 11 mmol) in toluene (100 cm^3) was stirred in an oil bath at 110 °C and maintained under reflux (1 h). The mixture was allowed to cool to room temperature and the *N*,*N*′-diphenylurea that separated was collected. Evaporation of the yellow filtrate gave a solid that was purified by column chromatography (silica gel: isohexane–ethyl acetate 2 : 1 as eluent) and identified as *N*-(2-furyl)acetamide **10a** (0.90 g, 65%), buff needles, mp 115–117 °C (lit.,[4] mp 111–113 °C) (Found: C, 57.38; H, 5.35; N, 10.95. $C_6H_7NO_2$ requires C, 57.59; H, 5.64; N, 11.19%); ν_{max}/cm^{-1} 3200, 3042, 2836, 1656, 1566, 1366, 1280, 1232, 1216, 1148, 1068; δ_H (d_6-DMSO) 1.95 (s, 3H, $COCH_3$), 6.06 (d, 1H, *J* 3.15 Hz, furyl 3-H), 6.33 (m, 1H, furyl 4-H), 7.19 (d, 1H, *J* 0.9 Hz, furyl 5-H), 10.62 (br s, 1H, NH); *m*/*z* 125 ($M^{\bullet+}$).

In a similar manner the following compounds were prepared from the ureas **9b**–**k**.

***N*-(5-Phenyl-2-furyl)acetamide 10b.** Yield (45%), colourless crystals, mp 170–172 °C (Found: C, 71.48; H, 5.35; N, 6.72. $C_{12}H_{11}NO_2$ requires C, 71.63; H, 5.51; N, 6.96%); ν_{max}/cm^{-1} 3193, 1667, 1570, 1375, 1290, 1205, 1154, 1061, 1017; δ_H (d_6-DMSO) 2.04 (s, 3H, $COCH_3$), 6.25 (d, 1H, *J* 3.4 Hz, furyl 3-H), 6.88 (d, 1H, *J* 3.4 Hz, furyl 4-H), 7.05–7.80 (m, 5H, ArH); *m*/*z* 201 ($M^{\bullet+}$).

***N*-[5-(4-Chlorophenyl)-2-furyl]acetamide 10c.** Yield (48%), colourless crystals, mp 170–172 °C (Found: C, 61.00; H, 4.05; N, 5.71; Cl, 14.88. $C_{12}H_{10}ClNO_2$ requires C, 61.16; H, 4.28; N, 5.94; Cl, 15.04%); ν_{max}/cm^{-1} 3195, 1647, 1584, 1574, 1553, 1485, 1428, 1406, 1381; δ_H (d_6-DMSO) 2.04 (s, 3H, $COCH_3$), 6.25 (d, 1H, *J* 3.4 Hz, furyl 3-H), 6.94 (d, 1H, *J* 3.4 Hz, furyl 4-H), 7.42 (d, 2H, *J* 8.9 Hz, ArH), 7.61 (d, 2H, *J* 8.9 Hz, ArH), 10.96 (br s, 1H, NH); *m*/*z* 235 ($M^{\bullet+}$).

***N*-[5-(4-Nitrophenyl)-2-furyl]acetamide 10d.** Yield (40%), yellow crystals, mp 240–245 °C (Found: C, 58.25; H, 3.88; N, 11.15. $C_{12}H_{10}N_2O_4$ requires C, 58.54; H, 4.09; N, 11.38%); ν_{max}/cm^{-1} 3187, 3114, 3029, 1665, 1587, 1564, 1537, 1506, 1329, 1290, 1207, 1177, 1055, 1020; δ_H (d_6-DMSO) 2.07 (s, 3H, $COCH_3$), 6.37 (d, 1H, *J* 3.5 Hz, furyl 3-H), 7.28 (d, 1H, *J* 3.5 Hz, furyl 4-H), 7.79 (d, 2H, *J* 9.1 Hz, ArH), 8.25 (d, 2H, *J* 9.1 Hz, ArH), 11.21 (br s, 1H, NH); *m*/*z* 246 ($M^{\bullet+}$).

***N*-[5-(4-Methylphenyl)-2-furyl]acetamide 10e.** Yield (49%), beige crystals, mp 162–164 °C (Found: C, 72.31; H, 5.95; N, 6.45. $C_{13}H_{13}NO_2$ requires C, 72.54; H, 6.09; N, 6.51%); ν_{max}/cm^{-1} 3198, 3042, 1647, 1586, 1580, 1512, 1502, 1428, 1379, 1348, 1308, 1287; δ_H (d_6-DMSO) 2.03 (s, 3H, $COCH_3$), 2.29 (s, 3H, CH_3), 6.21 (d, 1H, *J* 3.3 Hz, furyl 3-H), 6.79 (d, 1H, *J* 3.3 Hz, furyl 4-H), 7.19 (d, 2H, *J* 8.1 Hz, ArH), 7.48 (d, 2H, *J* 8.1 Hz, ArH), 10.87 (br s, 1H, NH); *m*/*z* 231 ($M^{\bullet+}$).

***N*-[5-(4-Methoxyphenyl)-2-furyl]acetamide 10f.** Yield (45%), colourless crystals, mp 153–155 °C (Found: C, 67.35; H, 5.42; N, 5.88. $C_{13}H_{13}NO_3$ requires C, 67.52; H, 5.67; N, 6.06%); ν_{max}/cm^{-1} 3195, 3013, 1665, 1559, 1501, 1373, 1294, 1246, 1022; δ_H (d_6-DMSO) 2.03 (s, 3H, $COCH_3$), 3.76 (s, 3H, OCH_3), 6.19 (d, 1H, *J* 3.0 Hz, furyl 3-H), 6.69 (d, 1H, *J* 3.0 Hz, furyl 4-H), 6.96 (d, 2H, *J* 8.7 Hz, ArH), 7.52 (d, 2H, *J* 8.7 Hz, ArH); *m*/*z* 231 ($M^{\bullet+}$).

***N*-[5-(4-Bromophenyl)-2-furyl]acetamide 10g.** Yield (43%), colourless crystals, mp 219–221 °C (Found: C, 51.25; H, 3.35; N, 4.80; Br, 28.35. $C_{12}H_{10}BrNO_2$ requires C, 51.45; H, 3.60; N, 5.00; Br, 28.53%); ν_{max}/cm^{-1} 3193, 1647, 1550, 1576, 1480, 1427, 1280; δ_H (d_6-DMSO) 2.04 (s, 3H, $COCH_3$), 6.25 (d, 1H, *J* 3.5 Hz, furyl 3-H), 6.95 (d, 1H, *J* 3.5 Hz, furyl 4-H), 7.55 (s, 4H, ArH), 10.97 (br s, 1H, NH); *m*/*z* 280 ($M^{\bullet+}$).

***N*-(4,5-Dimethyl-2-furyl)acetamide 10h.** Yield (78%), colourless crystals, mp 42–45 °C (Found: C, 62.53; H, 7.05; N, 8.99. $C_8H_{11}NO_2$ requires C, 62.73; H, 7.24; N, 9.14%); ν_{max}/cm^{-1} 3429, 3094, 2993, 2940, 1678, 1433, 1372, 1313, 1236, 1171, 1141; δ_H (d_6-DMSO) 1.65 (s, 3H, CH_3), 1.97 (d, 3H, *J* 1.6 Hz, CH_3), 2.36 (s, 3H, $COCH_3$), 5.86 (d, 1H, *J* 1.6 Hz, furyl 3-H), 6.54 (s, 1H, NH); δ_C (d_6-DMSO) 11.74 (CH_3), 22.59 (CH_3), 25.80 ($COCH_3$), 91.11 (C-4), 119.39 (C-3), 166.75, 168.64, 168.66 (C-2, C-5, C=O); *m*/*z* 153 ($M^{\bullet+}$).

***N*-(2-Furyl)propanamide 10i.** Yield (55%), colourless crystals, mp 62–64 °C (Found: C, 60.25; H, 6.30; N, 9.88. $C_7H_9NO_2$ requires C, 60.42; H, 6.52; N, 10.07%); ν_{max}/cm^{-1} 3425, 3215, 3058, 2979, 1668, 1608, 1561, 1518, 1244, 1213, 1002; δ_H (d_6-DMSO) 0.99 (t, 3H, CH_3), 2.23 (q, 2H, CH_2), 6.07 (d, 1H, *J* 2.95 Hz, furyl 3-H), 6.34 (dd, 1H, *J* 2.95 and 2.16 Hz, furyl 4-H), 7.20 (d, 1H, *J* 2.16 Hz, furyl 5-H), 10.55 (br s, 1H, NH).

***N*-(2-Furyl)benzamide 10j.** Yield (65%), beige crystals, mp 88–90 °C (Found: C, 70.38; H, 4.60; N, 7.35. $C_{11}H_9NO_2$ requires C, 70.58; H, 4.85; N, 7.48%); ν_{max}/cm^{-1} 3239, 3154, 3081, 1655, 1601, 1580, 1557, 1292, 1211, 1009; δ_H 6.45 (m, 2H, furyl 3-H, furyl 4-H), 7.09 (br s, 1H, furyl 5-H), 7.10–8.10 (m, 5H, ArH), 8.34 (br s, 1H, NH); *m*/*z* 187 ($M^{\bullet+}$).

***N*-(2-Furyl)furan-2-carboxamide 10k.** Yield (60%), light yellow crystals, mp 100–101 °C (Found: C, 60.95; H, 3.70; N, 7.75. $C_9H_7NO_3$ requires C, 61.02; H, 3.98; N, 7.91%); ν_{max}/cm^{-1} 3257, 3130, 3068, 1650, 1581, 1545, 1473, 1448, 1395, 1371, 1300, 1214, 1178, 1119, 1011; δ_H (d_6-DMSO) 6.23 (dd, 1H, *J* 3.15 and 0.79 Hz, furyl 3-H), 6.42 (dd, 1H, *J* 3.15 and 1.97 Hz, furyl 4-H), 6.63 (dd, 1H, *J* 3.35 and 1.58 Hz, furyl 4′-H), 7.25–7.35 (m, 2H, furyl 3′-H, furyl 5-H), 7.87 (d, 1H, *J* 0.98 Hz, furyl 5′-H), 11.03 (br s, 1H, NH); *m*/*z* 177 ($M^{\bullet+}$).

Reactions of benzo[*b*]furan-2-carboximidamides 12 with (diacetoxyiodo)benzene (DAIB)

***N*²-Phenylbenzo[*b*]furan-2-carboximidamide 12a.** The reaction was carried out as described for furan-2-carboximidamides **8** at 60 °C and after evaporation the reaction mixture was separated by column chromatography (silica gel: $CHCl_3$ as eluent) to give the following products.

*N*¹-*Acetyl*-*N*¹-*(benzo[b]furan-2-yl)*-*N*²-*phenylurea* ***14a*.** Yield (14%), pale beige needles (from isohexane), mp 102–105 °C (Found: C, 69.26; H, 4.66; N, 9.62. $C_{17}H_{14}N_2O_3$ requires C, 69.38; H, 4.79; N, 9.52%); ν_{max}/cm^{-1} 3243, 3200, 3121, 3061, 1736, 1732, 1686, 1593, 1545, 1541, 1493, 1447, 1373, 1316, 1306, 1275, 1030, 1010; δ_H 2.17 (s, 3H, CH_3), 6.79 (s, 1H, H-3), 7.09–7.67 (m, 9H, ArH), 11.02 (br s, 1H, NH); *m*/*z* 294 ($M^{\bullet+}$).

2-Phenylamino-4-(benzo[b]furan-2-yl)benzo[4,5]furo[2,3-d]-pyrimidine ***15a*.** Yield (4%), yellow needles (from DMF), mp 277–279 °C (Found: C, 76.42; H, 4.08; N, 11.06. $C_{24}H_{15}N_3O_2$ requires C, 76.38; H, 4.01; N, 11.13%); ν_{max}/cm^{-1} 3345, 3056, 1632, 1605, 1586, 1541, 1526, 1501, 1458, 1447, 1427, 1360, 1262, 1194, 1188, 1113; δ_H (d_6-DMSO) 6.98–7.89 (m, 13H, ArH), 8.60–8.71 (m, 1H, H-5), 10.03 (s, 1H, NH); *m*/*z* 377 ($M^{\bullet+}$).

*N*¹-*(N*-Phenylcarbamoyl)-*N*²-*(phenyl)benzo[b]furan-2-carboximidamide* ***13a*.** Yield (8%), colourless needles (from toluene–isohexane), mp 171–175 °C (Found: C, 74.22; H, 4.74; N, 11.88. $C_{22}H_{17}N_3O_2$ requires C, 74.35; H, 4.82; N, 11.82%); ν_{max}/cm^{-1} 3432, 1694, 1642, 1620, 1599, 1561, 1545, 1499, 1269, 1260, 1181, 1115; δ_H (d_6-DMSO) 6.87–7.76 (m, 15H,

H-3,4,5,6,7 and ArH), 9.51 (s, 1H, NH), 9.80 (s, 1H, NH); *m/z* 355 ($M^{\bullet+}$).

***N*²-(4-Methylphenyl)benzo[*b*]furan-2-carboximidamide 12b.** In a similar manner *N*²-(4-methylphenyl)benzo[*b*]furan-2-carboximidamide **12b** gave the following products.

N-Acetyl-N-(benzo[b]furan-2-yl)-N′-(4-methylphenyl)urea ***14b*.** Yield (16%), pale beige needles (from isohexane), mp 101–103 °C (Found: C, 69.98; H, 5.12; N, 9.09. $C_{18}H_{16}N_2O_3$ requires C, 70.12; H, 5.23; N, 9.09%); ν_{max}/cm^{-1} 3212, 1730, 1686, 1595, 1541, 1454, 1410, 1366, 1314, 1277, 1258, 1238, 1204, 1175, 1109, 1057, 1008; δ_H 2.18 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 6.08 (s, 1H, H-3), 7.12 (d, 2H, *J* 8.4 Hz, H-3′, H-5′), 7.29 (t, 1H, *J* 8.1 Hz, H-5), 7.37 (t, 1H, *J* 7.8 Hz, H-6), 7.42 (d, 2H, *J* 8.4 Hz, H-2′, H-6′), 7.51 (d, 1H, *J* 7.8 Hz, H-7), 7.61 (d, 1H, *J* 8.1 Hz, H-4), 10.97 (br s, 1H, NH); δ_C 20.84 (Ph-*C*H$_3$), 24.99 (*C*OCH$_3$), 105.45 (C-3), 111.71 (C-7), 120.30 (C-2′, C-6′), 121.69 (C-4), 123.46 (C-5), 125.51 (C-6), 127.55 (C-3a), 129.54 (C-3′, C-5′), 134.15 (C-1′), 134.53 (C-4′), 146.25 (C-2), 150.42 (NH-*C*O), 153.05 (C-7a), 174.85 (CH$_3$*C*O); *m/z* 308 ($M^{\bullet+}$).

2-(4-Methylphenylamino)-4-(benzo[b]furan-2-yl)benzo[4,5]-furo[2,3-d]pyrimidine ***15b*.** Yield (5%), yellow needles (from toluene), mp 257–258 °C (Found: C, 76.64; H, 4.18; N, 10.74. $C_{25}H_{17}N_3O_2$ requires C, 76.71; H, 4.38; N, 10.74%); ν_{max}/cm^{-1} 3432, 3272, 1664, 1611, 1584, 1556, 1522, 1458, 1261, 1196, 1111; δ_H (d$_6$-DMSO) 2.30 (s, 3H, CH_3), 7.19 (d, 2H, *J* 8.1 Hz, H-3″, H-5″), 7.41 (dd, 1H, H-5′), 7.46–7.58 (m, 3H, H-6, H-7, H-6′), 7.68 (m, 1H, H-8), 7.76 (d, 2H, *J* 8.1 Hz, H-2″, H-6″), 7.85 (s, 1H, H-3′), 7.88 (d, 1H, *J* 7.7 Hz, H-4′), 7.95 (d, 1H *J* 8.1 Hz, H-7′), 8.07 (m, 1H, H-5), 9.98 (br s, 1H, NH); δ_C (d$_6$-DMSO) 20.01 (CH_3), 101.88 (C-4a), 109.46 (C-3′), 111.02 (C-8), 111.41 (C-7′), 119.38 (C-2″, C-6″), 120.57 (C-4b), 122.30 (C-4′), 123.16 (C-5), 123.66 (C-5′), 124.14 (C-6), 126.44 (C-6′), 127.02 (C-7), 127.16 (C-3′a), 128.62 (C-3″, C-5″), 130.77 (C-4″), 137.17 (C-1″), 149.69 (C-4), 152.59 (C-8a), 153.15 (C-2′), 155.01 (C-7′a), 157.76 (C-9a), 170.46 (C-2); *m/z* 391 ($M^{\bullet+}$).

N¹-[N-(4-Methylphenyl)carbamoyl]-N²-(4-methylphenyl)-benzo[b]furan-2-carboximidamide ***13b*.** Yield (3%) (from toluene–isohexane 9 : 1), mp 197–199 °C (Found: C, 75.06; H, 5.38; N, 10.94. $C_{24}H_{21}N_3O_2$ requires C, 75.18; H, 5.52; N, 10.96%); ν_{max}/cm^{-1} 3438, 3027, 2919, 1698, 1647, 1630, 1613, 1597, 1541, 1505, 1264, 1234, 1183, 1107; δ_H 2.31 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 6.17 (s, 1H, H-3), 6.70–7.60 (m, 12H, H-4,5,6,7 and ArH), 8.00 (br s, 1H, NH), 11.60 (br s, 1H, NH); *m/z* 383 ($M^{\bullet+}$).

2-(Benzo[b]furan-2-yl)-5-methyl-1H-benzimidazole ***17*** *(R = Me).* Yield (6%) (from toluene–isohexane 9 : 1), mp 207–210 °C (Found: C, 77.48; H, 4.87; N, 11.28. $C_{16}H_{12}N_2O$ requires C, 77.40; H, 4.87; N, 11.28%); ν_{max}/cm^{-1} 3407, 3110, 3038, 2957, 2922, 2855, 2768, 2712, 1633, 1591, 1447, 1416, 1343, 1314, 1277, 1258, 1179; δ_H (d$_6$-DMSO) 2.43 (s, 3H, CH_3), 7.07 (d, 1H, $J_{6,7}$ 8.1 Hz, H-6), 7.34 (t, 1H, H-5′), 7.42 (t, 1H, H-6′), 7.47–7.58 (br s, 2H, H-4 and H-7′), 7.62 (s, 1H, H-3′), 7.70 (d, 1H, $J_{6,7}$ 8.1 Hz, H-7), 7.78 (d, 1H, $J_{4',5'}$ 8.1 Hz, H-4′), 13.04 (br s, 1H, NH); δ_C (d$_6$-DMSO) 21.31 (CH_3), 105.87 (C-3′), 111.39 (C-7′), 121.98 (C-4′), 123.71 (C-5′), 125.73 (C-6′), 128.01 (C-3′a), 147.42 (C-2′), 154.43 (C-7′a), 118.71, 124.74, 131.30, 132.70, 134.73, 142.00, 142.82 (C-2, C-3a, C-4, C-5, C-6, C-7, C-7a); *m/z* 248 ($M^{\bullet+}$).

Thermolysis of *N*¹-acetyl-*N*¹-(benzo[*b*]furan-2-yl)-*N*²-phenylurea 14a

The reaction was carried out as described for *N*-acyl-*N*-(2-furyl)ureas **9**. Evaporation of the yellow filtrate gave a solid that was purified by column chromatography (silica gel: isohexane–ethyl acetate 2 : 1 as eluent) and identified as 2-acetylaminobenzo[*b*]furan **16** (89%) (from toluene–isohexane 9 : 1), mp 129–130 °C (lit.[3] 129–130 °C) (Found: C, 68.40; H, 5.10; N, 7.80. $C_{10}H_9NO_2$ requires C, 68.56; H, 5.18; N, 8.00%); ν_{max}/cm^{-1} 3272, 3216, 1684, 1674, 1607, 1551, 1456, 1248, 1190; δ_H 2.23 (s, 3H, CH_3), 6.75 (s, 1H, H-3), 7.00–7.60 (m, 4H, ArH), 8.41 (br s, 1H, NH).

2-Phenyl-4-phenylaminoquinazoline 23

*N*¹,*N*²-Diphenyl[phenyl(phenylimino)methylamino]formamidin-*N*³-ium toluene-*p*-sulfonate (0.40 g)[4] was treated with 2 M NaOH and extracted into $CHCl_3$ to give the free base **21** (0.27 g) as a pale yellow solid. Compound **21** (0.25 g) in xylene solution (50 cm³) was heated under reflux (48 h). After evaporation, the residue was separated by chromatotron chromatography (silica gel: petroleum ether–ethyl acetate (3 : 1) as eluent). In addition to unchanged starting material, a faster running fraction was collected, recrystallised from cyclohexane–ethyl acetate and identified as *2-phenyl-4-phenylaminoquinazoline* **23** (0.15 g, 78%), pale yellow needles, mp 155–156 °C (lit.[21] 152 °C) (Found: C, 80.54; H, 5.01; N, 13.78. $C_{20}H_{15}N_3$ requires C, 80.78; H, 5.08; N, 14.13%); ν_{max}/cm^{-1} 1621, 1599, 1573, 1558, 1520, 1490, 1447, 1437, 1412, 1364, 1328, 1237, 948, 767, 747, 706, 694, 594; δ_H 7.1–8.6 (m, 14H, ArH); δ_C (+ DEPT) 160.2 (q), 157.1 (q), 150.8 (q), 138.5 (q), 138.4 (q), 132.7 (CH), 130.2 (CH), 129.0 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 125.9 (CH), 123.9 (CH), 121.1 (CH), 120.1 (CH), 113.6 (q); *m/z* 297 ($M^{\cdot+}$).

Reactions of *N*-(2-furyl)acetamide 10a

(i) With Lawesson's reagent. To a stirred solution of *N*-(2-furyl)acetamide **10a** (0.13 g, 1 mmol) in dry tetrahydrofuran (3 cm³) was added Lawesson's reagent (0.20 g, 1 mmol) at room temperature and stirring was maintained (21 h). After evaporation the crude product was purified by column chromatography (silica gel: isohexane–ethyl acetate 6 : 1 as eluent) and identified as *N-(2-furyl)thioacetamide* **26** (80 mg, 56%), beige crystals, mp 75–77 °C (Found: C, 49.88; H, 4.90; N, 9.80; S, 22.48. C_6H_7NOS requires C, 51.04; H, 5.00; N, 9.92; S, 22.71%); ν_{max}/cm^{-1} 3200, 3050, 1568, 1358, 1237, 1223, 1159, 1152; δ_H (d$_6$-DMSO) 2.67 (s, 3H, CH_3), 6.60 (dd, 1H, *J* 3.4 and 2.0 Hz, furyl 4-H), 7.10 (d, 1H, *J* 3.3 Hz, furyl 3-H), 7.50 (dd, 1H, *J* 2.0 and 1.0 Hz, furyl 5-H), 12.58 (s, 1H, NH); δ_C (d$_6$-DMSO) 34.36 (CH_3), 97.97 (C-3), 111.37 (C-4), 136.77 (C-5), 147.76 (C-2), 196.57 (C=S); δ_H ($CDCl_3$) (major isomer) 2.71 (s, 3H, CH_3), 6.42 (m, 1H, furyl 4-H), 7.08 (d, 1H, *J* 3.3 Hz, furyl 3-H), 7.27 (s, 1H, furyl 5-H), 9.36 (br s, 1H, NH); δ_C ($CDCl_3$) (major isomer) 35.31 (CH_3), 98.20 (C-3), 111.38 (C-4), 135.96 (C-5), 146.45 (C-2), 195.87 (C=S); δ_H ($CDCl_3$) (minor isomer) 2.54 (s, 3H, CH_3), 6.09 (d, 1H, *J* 3.0 Hz, furyl 3-H), 6.42 (m, 1H, furyl 4-H), 7.11 (s, 1H, furyl 5-H), 9.36 (br s, 1H, SH); δ_C ($CDCl_3$) (minor isomer) 30.55 (CH_3), 102.00 (C-3), 111.38 (C-4), 139.56 (C-5), 144.24 (C-2), 206.65 (C=N).

(ii) With dimethyl butynedioate. To a stirred solution of *N*-(2-furyl)acetamide **10a** (0.3 g, 2.4 mmol) in acetonitrile (4 cm³) was added dimethyl butynedioate (0.38 g, 2.7 mmol) at room temperature. After 20 h a solid separated and was crystallized from toluene–isohexane and identified as *dimethyl 3-acetamino-6-hydroxyphthalate* **25** (0.32 g, 50%), colourless needles, mp 164–167 °C (Found: C, 53.68; H, 4.80; N, 5.04. $C_{12}H_{13}NO_6$ requires C, 53.93; H, 4.90; N, 5.24%); ν_{max}/cm^{-3} 3328, 3204, 1711, 1692, 1522, 1474, 1452, 1439, 1345, 1329, 1267, 1207; δ_H (d$_6$-DMSO) 1.97 (s, 3H, $COCH_3$), 3.71 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 7.05 (d, 1H, *J* 8.1 Hz, H-4), 7.35 (d, 1H, *J* 8.1 Hz, H-5), 9.64 (br s, 1H, OH), 10.22 (br s, 1H, NH); δ_C (d$_6$-DMSO) 23.20 (CO*C*H$_3$), 52.38 (OCH_3), 119.22 (C-4), 120.22 (C-2), 126.13 (C-1), 127.72 (C-6), 128.61 (C-5), 152.16 (C-3), 166.09 (*C*O$_2$CH$_3$), 166.81 (*C*O$_2$CH$_3$), 168.70 (*C*OCH$_3$); *m/z* 267 ($M^{\bullet+}$).

(iii) With ethyl propynoate. *N*-(2-Furyl)acetamide **10a** (0.4 g, 3.2 mmol) was heated under reflux (7 h) in ethyl propynoate

(1.5 g, 15.3 mmol). After evaporation, ethanol (1.5 cm^3) was added to the residue. Refrigeration gave a solid product that was recrystallized from toluene–isohexane and identified as *ethyl 2-acetamido-5-hydroxybenzoate* **28** (0.35 g, 49%), beige crystals, mp 165–167 °C (Found: C, 58.95; H, 5.67; N, 6.15. $C_{11}H_{13}NO_4$ requires C, 59.19; H, 5.87; N, 6.27%); ν_{max}/cm^{-1} 3152, 1692, 1655, 1607, 1557, 1369, 1316, 1246, 1231; δ_H (d_6-DMSO) 1.30 (t, 3H, CH_3), 2.04 (s, 3H, $COCH_3$), 4.27 (q, 2H, OCH_2), 6.98 (dd, 1H, *J* 8.7 and 2.7 Hz, H-4), 7.27 (d, 1H, *J* 2.7 Hz, H-6), 7.86 (d, 1H, *J* 8.7 Hz, H-3), 9.63 (s, 1H, OH), 10.12 (br s, 1H, NH); δ_C (d_6-DMSO) 14.03 (CH_3), 24.18 ($COCH_3$), 61.00 (CH_2), 115.90 (C-6), 120.47 (C-1), 120.56 (C-4), 123.86 (C-3), 131.19 (C-2), 153.05 (C-5), 166.75 ($CO_2CH_2CH_3$), 167.96 ($COCH_3$); *m*/*z* 223 ($M^{\bullet+}$).

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