Synthesis of fused furans by gas-phase pyrolysis of 2-allyloxyarylpropenoic esters[1]

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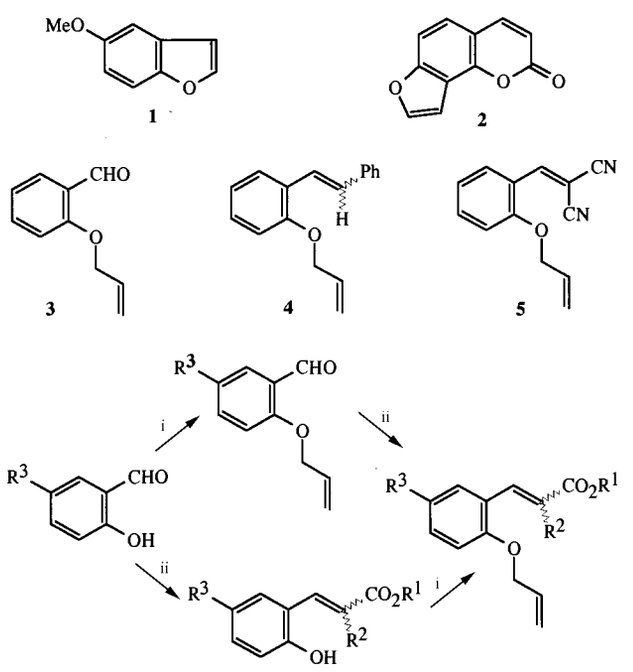
Flash vacuum pyrolysis of 2-allyloxypropenoic esters (*e.g.* 7) gives benzo[*b*]furans (*e.g.* 32) in synthetically useful yields by sequential generation of a phenoxyl radical, cyclisation and ejection of the carboxylic ester function as a free radical leaving group. The method is compatible with a range of substituents on either the benzene ring or the propenoate chain, and is particularly effective for 2-substituted benzo[*b*]furans. The natural products 5-methoxybenzo[*b*]furan 1 and angelicin 2 have been synthesised in three and four steps respectively from commercially available starting materials by this route. Related cyclisations to give naphtho[2,1-*b*]furan 40 were complicated by competitive formation of naphtho-[2,1-*b*]pyran-3-ones (*e.g.* 41 and 42), but the yield of the required product could be optimised by the choice of the radical precursor. Annelation of a furan ring onto a thiophene is also possible by this method, but lower yields are obtained in such pyrolyses.

In earlier papers we have reported application of the technique of flash vacuum pyrolysis (FVP) to the gas-phase generation of aryloxyl radicals, and their reactions with adjacent aromatic systems.[2,3] These processes are often dominated by hydrogen abstractions, and relatively small amounts of useful cyclisation products are formed. In extending this work to the properties of aryloxyls with adjacent alkene systems, it became apparent at an early stage that the carboxylic ester function behaves as a specific and highly efficient radical leaving group under these conditions, leading to a useful synthetic route to benzo[*b*]-furans.[1] We now present full details of this work, and its extensions, which have led to concise syntheses of the natural products 5-methoxybenzo[*b*]furan **1** and angelicin **2**. The results of preliminary attempts to annelate a furan ring onto five-membered heterocyclic systems are also reported.

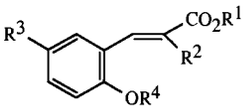
As in our previous work,[2,3] we have employed *O*-allyl or *O*-benzyl ethers as radical generators, made in high yield from the corresponding phenol by treatment with the appropriate bromoalkane in dimethylformamide containing anhydrous potassium carbonate. The alkene function was made from an appropriate carbonyl compound by Wittig or Knoevenagel methodology (Scheme 1). In many cases, the order of the allylation and Wittig steps was unimportant, though in practice 2-allyloxybenzaldehyde **3** was used to make the Wittig products **4** and **14** (obtained in low, but unoptimised yields) and the Knoevenagel products **5**, **19** and **20** (61–97%). Compounds **5** and **20** were made from the appropriate active methylene compound using piperidinium acetate catalyst, but it proved necessary to use more vigorous conditions (titanium tetrachloride–pyridine) for the synthesis of the diester **19**. The precursors **7**, **9**, **11**, **13**, **16** and **18** were made by allylation of the phenols **6**, **8**, **10, 12, 15** and **17** (80–100%) respectively, which were themselves made by Wittig reactions with salicylaldehydes, to give predominantly—often exclusively—the *E*-isomers (75–90%).[4] The alkoxynaphthols **22–24** and **26** were made from the naphthols **21** and **25** in similar yields, though significant amounts of the *Z*-isomer were present in these cases. Because of the possibility of thermal elimination of ethene from ethyl esters,[5] the methyl esters were generally employed. However, it was more convenient to make the ethyl esters of the side chain methylated derivatives **16**, **18** and **26** owing to the commercial availability of the Wittig reagent, and this proved to have no effect on the pyrolysis.



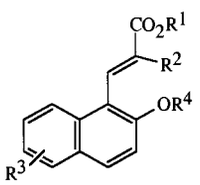
Scheme 1 *Reagents and conditions:* i, CH_2=$CHCH_2Br$, K_2CO_3, DMF; ii, Ph_3P=$CR^2CO_2R^1$ or $R^2CH_2CO_2Me$

Because of the low reactivity of acetophenones with stabilised Wittig reagents, a Wittig–Horner reaction was employed to make the ester **28**; a 3:1 mixture of *E*:*Z* isomers was obtained. To avoid possible problems owing to the basic conditions, the phenol was first protected as its benzyl ether **27**, and in addition this substituent ultimately served as the radical leaving group.

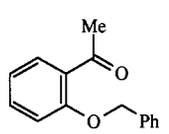
The mass spectra of the majority of these acrylates show the results of initial ionisation at the carbonyl group followed by



6 R^1 = Me, R^2 = H, R^3 = H, R^4 = H
7 R^1 = Me, R^2 = H, R^3 = H, R^4 = allyl
8 R^1 = Me, R^2 = H, R^3 = Cl, R^4 = H
9 R^1 = Me, R^2 = H, R^3 = Cl, R^4 = allyl
10 R^1 = Me, R^2 = H, R^3 = NO_2, R^4 = H
11 R^1 = Me, R^2 = H, R^3 = NO_2, R^4 = allyl
12 R^1 = Me, R^2 = H, R^3 = OMe, R^4 = H
13 R^1 = Me, R^2 = H, R^3 = OMe, R^4 = allyl
14 R^1 = Me, R^2 = Me, R^3 = H, R^4 = allyl
15 R^1 = Et, R^2 = Me, R^3 = H, R^4 = H
16 R^1 = Et, R^2 = Me, R^3 = H, R^4 = allyl
17 R^1 = Et, R^2 = Me, R^3 = Cl, R^4 = H
18 R^1 = Et, R^2 = Me, R^3 = Cl, R^4 = allyl
19 R^1 = Me, R^2 = CO_2Me, R^3 = H, R^4 = allyl
20 R^1 = Me, R^2 = CN, R^3 = H, R^4 = allyl



21 R^1 = Me, R^2 = H, R^3 = H, R^4 = H
22 R^1 = Me, R^2 = H, R^3 = H, R^4 = allyl
23 R^1 = Me, R^2 = H, R^3 = H, R^4 = Pr^i
24 R^1 = Me, R^2 = H, R^3 = H, R^4 = CH_2Ph
25 R^1 = Et, R^2 = Me, R^3 = H, R^4 = H
26 R^1 = Et, R^2 = Me, R^3 = H, R^4 = allyl



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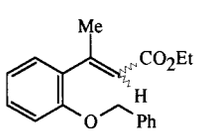

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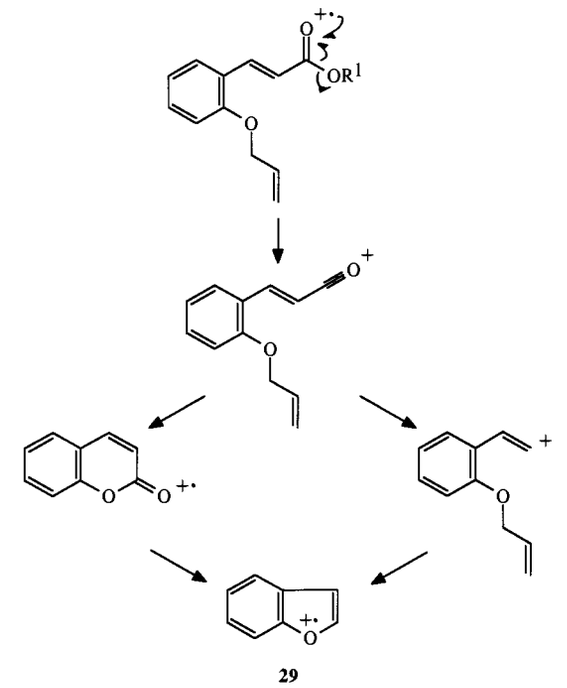
standard α-cleavage of the alkoxy group to give initial breakdown peaks at M − 31 (methyl esters) and M − 45 (ethyl esters) which may be of low intensity (Scheme 2). There follow two competing pathways involving either sequential loss of CO and the allyl group or *vice versa*. Both routes converge at the benzo[*b*]furan radical cation **29** which forms the base peak in many cases. For example the parent compound of the series **7** (M^+ 218, 35%) shows an initial minor breakdown peak at *m/z* 187 (M − 31, 8%) followed by competitive loss of the allyl function (*m/z* 146, 12%) and of CO (cluster centred at *m/z* 158, 27%), and then by generation of the radical cation **29** (*m/z* 118, 95%). Minor variants of this general pathway include initial loss of the phenolic *O*-alkyl group (from the stilbene **4** and the isopropyl compound **23**)—a route which is analogous to the anticipated thermal breakdown. In addition, both alkoxy groups and the allyl group are lost from the diester **19** to give the base peak at *m/z* 173 which can then undergo two further decarbonylations [*m/z* 145 (50%) and 117 (45%)]. It is worth pointing out that the mass spectrometric breakdowns are controlled by the site of lowest ionisation potential (generally the ester function) whereas the thermal behaviour is initiated at the weakest bond in the molecule (generally the *O*-allyl or benzyl linkage). It is therefore not possible in general to predict the pyrolytic behaviour of a molecule from its electron impact mass spectrometric cleavage pattern.

The initial pyrolysis of the stilbene **4** at 650 °C (0.001 Torr) showed that the phenoxyl radicals generated by homolysis of the *O*-allyl bond under these conditions can indeed interact



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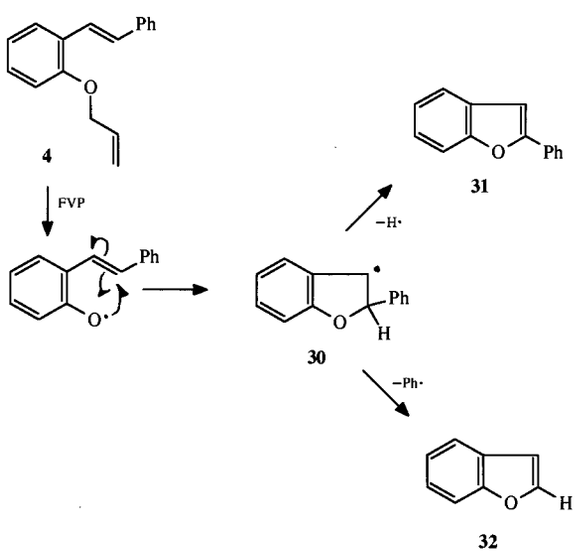
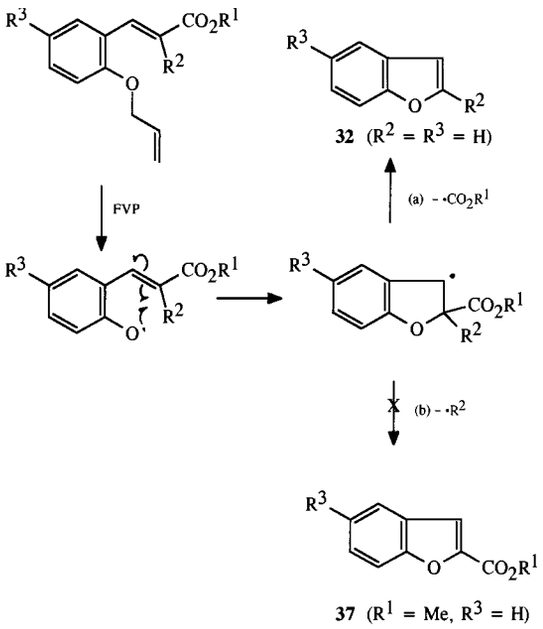
Scheme 2



Scheme 3

with the alkene function to give benzo[*b*]furans (Scheme 3). The mechanism presumably involves attack of the phenoxyl radical at the terminal position of the alkene to give the resonance stabilised intermediate **30** which can then aromatise either by loss of a phenyl radical or a hydrogen atom. In practice, the latter route predominates and 2-phenylbenzo[*b*]furan **31** was obtained in 55% yield. Traces of benzo[*b*]furan **32** (together with the co-formed biphenyl) were detected by GC–MS. In contrast to the reaction of phenoxyl radicals with aromatic systems, there were apparently no complications caused by hydrogen-transfer processes. However, the method is not useful in its present form as a general synthetic route to benzo[*b*]-furans, because of the incomplete control over the radical leaving group.

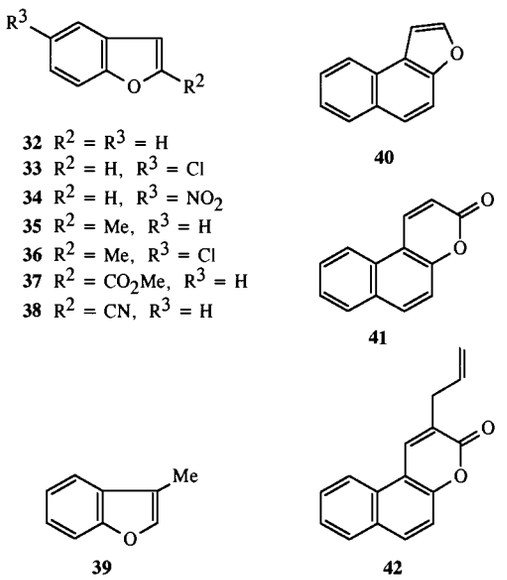
This problem was unexpectedly solved by pyrolysis of alkenes containing terminal esters, since it was found that initial cyclisation was followed by loss of the entire ester function with total specificity [Scheme 4, route (a)]. For example, FVP of the allyl ether **7** at 650 °C (0.01 Torr) gave benzo[*b*]furan **32** in 65% isolated yield without the formation of significant quantities of any by-products (Scheme 4, R^1 = Me, R^2 = R^3 = H); in particu-



Scheme 4

lar, no methyl benzo[*b*]furan-2-carboxylate **37** could be detected [Scheme 4, route (b)]. The crude product was satisfactorily purified by bulb-to-bulb distillation; chromatography was not required. The reaction is therefore a pyrolytic homolytic substitution in which $\cdot CO_2R$ acts as the leaving group. This group presumably splits further into CO_2 and an alkyl radical, though in practice no products from these fragments were detected. The alternative aromatisation by loss of a hydrogen atom [Scheme 4, route (b), $R^2 = H$] is not observed, though this is not entirely unexpected owing to its relatively high heat of formation (*cf.* previous paragraph). It was therefore important to establish that the ester function could behave as a leaving group in competition with other well-known radical leaving groups, such as alkyl groups.[3,6] The pyrolysis of the methyl ester **14** and the corresponding ethyl ester **16** at 650 °C were therefore studied, and 2-methylbenzo[*b*]furan **35** (75% from **16**) was formed exclusively in both cases, *i.e.* the ester moiety behaved as the leaving group even in the presence of a competitive alkyl substituent (Scheme 4, R^1 = Me or Et, R^2 = Me, R^3 = H). Indeed the yield for the 2-substituted product is greater than that for its unsubstituted analogue, and this trend appears to be general (see below). We were therefore confident that 2-allyloxycinnamate esters fulfilled our criteria as useful benzo[*b*]furan precursors and embarked on a systematic investigation of the synthetic scope of this novel pyrolytic process.

The reaction proceeds well with mildly electron withdrawing or electron donating substituents in the benzene ring. Thus the 5-chloro compound **33** (60%), the 5-chloro-2-methyl compound **36** (85%) and the 5-methoxy compound **1** (90%) were obtained from the cinnamate precursors **9**, **18** and **13** respectively. Compound **1** is a fungal metabolite produced from—amongst others—*Stereum subpileatum* species,[7–9] and the present route is a convenient three-step synthesis from commercially available starting materials. Although the 5-nitro compound **11** gave the benzo[*b*]furan **34** as the major product (55%), this pyrolysis also gave rise to significant by-products (see below). However, the pyrolysis proceeds well with electron withdrawing groups in the side chain of the precursor, and the 2-methoxycarbonyl compound **37** (95%) and 2-cyano compound **38** (52%) were obtained from the malonate and cyanoacetate derivatives **19** and **20** respectively. As expected in the absence of a good radical leaving group, the malononitrile **5** gave no useful products under FVP conditions. The butenoate **28** gave a good yield of 3-methylbenzo[*b*]furan **39** (67%), though this had to be purified by chromatography to remove the co-formed bibenzyl, originating from dimerisation of the benzyl radical. No hydrogen abstraction reactions involving interaction of the phenoxyl radical with a methyl group in either position of the propenoate side-chain were observed (*cf.* ref. 2).

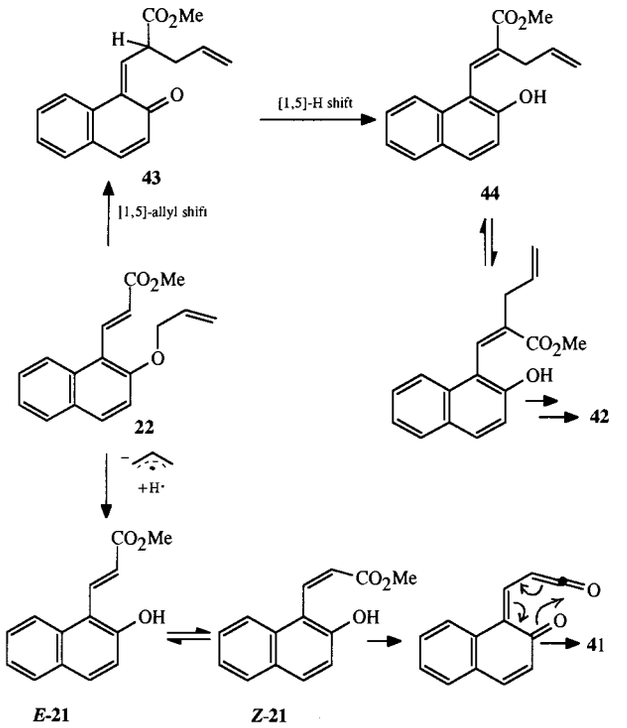


Extension of these results into a bicyclic series by pyrolysis of the 1-naphthylpropenoate **22** again gave the expected cyclisation to naphtho[2,1-*b*]furan **40**, though the yield was much lower than expected (39%) and two significant by-products were isolated. These were identified as naphtho[2,1-*b*]pyran-3-one **41** (13%), by comparison with an authentic sample[4] and its 2-allyl derivative **42** (*m/z* 236) (21%). The presence of a *C*-allyl group in **42** was clear from the characteristic five proton resonances in the ^{1}H NMR spectrum, and in particular the chemical shift of the alkyl CH_2 group was at much lower frequency (δ_H 3.40) than would be expected of an *O*-allyl function (*e.g.* δ_H 4.72 in the precursor **22**). The position of the substitution follows from the absence of a signal at *ca.* δ_H 6.5 corresponding to the pyranone 2-position, and the consequent appearance of the 1-proton resonance as a singlet at δ_H 8.24 [*cf.* δ_H 8.48 (d) in **41**].

It is known that FVP of the naphthol **21** gives the naphthopyranone **41** in high yield[4] by *E*–*Z* isomerisation, ketene formation and cyclisation (Scheme 5) and that hydrogen atom capture by phenoxyl-type radicals to give phenols can be a common process.[2] This sequence is the most likely route to **41** from the *O*-allyl precursor **22**, though it is surprising that the route is found for the naphthyl propenoates and not for the corresponding benzene derivatives.

The occurrence of the 2-allyl product **42** is unprecedented in reactions of this type. Its formation may be rationalised by either a [1,5] or a [3,5] sigmatropic shift of the allyl group to generate the *o*-quinomethane intermediate **43** (Scheme 5) followed by a [1,5] hydrogen shift in the reverse direction to generate the naphthol **44** which can then cyclise to a pyranone in the same way as **21**. The observation of this pathway in the naphthalene series but not in the corresponding benzene series was again unexpected. It is possible that the initial sigmatropic shift is relatively favoured by the increased localisation of the formal double bonds in the naphthalene system compared with the situation in the benzene ring. Alternatively, less aromatic character is destroyed in the initial migration product **43** than is the case with the corresponding benzenoid compounds.

The proposed mechanisms were tested in two ways. In the past, we have attempted to minimise the hydrogen atom flux in such experiments by the use of benzyl rather than allyl groups as radical generators.[2] However in this case pyrolysis of the benzyl ether **24** gave only slightly reduced levels of the pyranone **41** (11%), though the yield of naphthofuran **40** had increased to 55%. This increase was due instead to a much

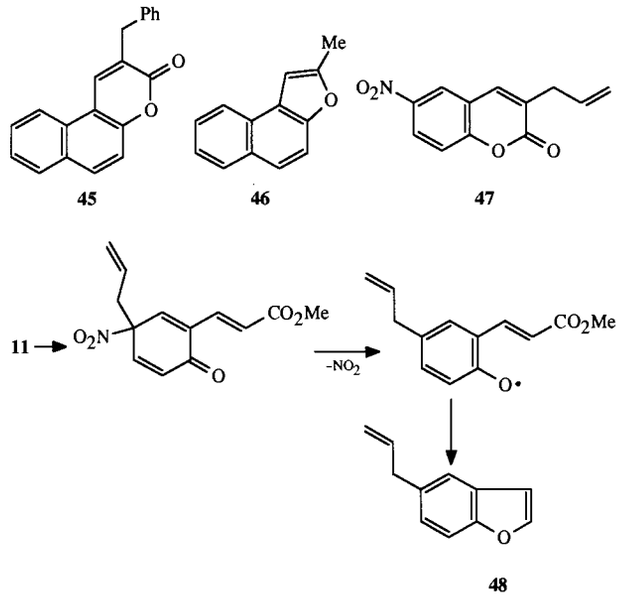


Scheme 5

lower yield of the 2-substituted product **45** (structure established as above), so clearly the benzyl group has a poorer migrating aptitude than the allyl group under these conditions. Nevertheless, the isolation of **45** demonstrates that a [3,5] sigmatropic shift is not a required mechanism for the formation of the 2-substituted naphthopyranones. Since minimisation of the formation of the parent naphthopyranone was unsuccessful, an attempt was made to reduce the yield of the 2-substituted naphthopyranone by employing a radical leaving group with a very poor migratory aptitude[10] in sigmatropic shifts. The isopropyl ether **23** was therefore synthesised and pyrolysed, though a higher temperature (750 °C) was required for complete cleavage of the isopropyl group. As expected, only the naphthofuran **40** (59%) and the parent naphthopyranone **41** (32%) were obtained, and these were readily separated by chromatography. It is noteworthy that by control of the radical leaving group the yield of the required naphthofuran **40** can be increased to an acceptable level.

In contrast to these results, FVP of the *C*-methyl derivative **26** proceeded smoothly to give 2-methylnaphtho[2,1-*b*]furan **46** in 88% yield with no trace of pyranone products. This again serves to emphasise the efficiency of the cyclisation for such 2-substituted derivatives.

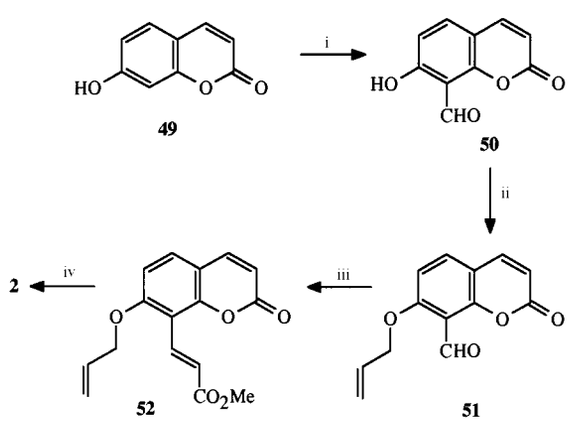
As mentioned above, pyrolysis of the nitro-compound **11** also led to anomalous products. On the basis of the work on the naphthalene derivatives, one of these was readily identified as 3-allyl-6-nitrocoumarin **47** (4%). It is possible that electron withdrawal from the nitro function may weaken the *O*-allyl bond and facilitate the key [1,5] allyl shift in this particular example. A second product (*ca.* 20%) showed no signals in its ^{1}H NMR spectrum above δ_H 8.0, and therefore is likely to have lost its nitro group, though signals due to a *C*-allyl group and a benzofuran ring [δ_H 7.59 (^3J 2.1 Hz) and 6.71 (^3J 2.1 and ^5J 0.8 Hz)] are present in its ^{1}H NMR spectrum. The presence of the characteristic ^5J coupling indicates that position 7 is also unsubstituted but it was not possible to define the position of substitution further because two of the proton signals in the ^{1}H NMR spectrum overlapped. The product may be 5-allylbenzo[*b*]furan **48**, and its ^{13}C NMR spectrum is consistent with this interpretation. A rationalisation of the formation of this compound is shown in Scheme 6. Thus the key quinonoid



Scheme 6

intermediate may be created by two sequential [3,3] sigmatropic shifts of the allyl group, whence cleavage of the nitro-substituent generates the phenoxyl radical which can cyclise in the usual way. However, it is not clear why a remote nitro-group should influence the course of the reaction in this way.

In view of the general success of these model reactions, the route shown in Scheme 7 was devised as a synthesis of the



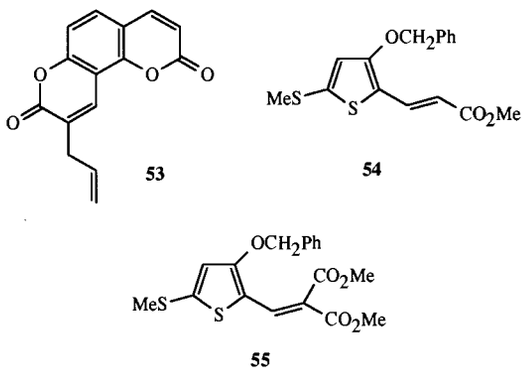
Scheme 7 *Reagents and conditions:* i, hexamethylenetetramine, acetic acid, 95 °C, 5.5 h; ii, CH_2=$CHCH_2Br$, K_2CO_3, DMF; iii, Ph_3P=CH-CO_2Me; iv, FVP (650 °C, 0.001 Torr)

furocoumarin natural product angelicin **2**.[11] This compound has been isolated from a number of plant sources and has been the subject of some recent syntheses.[12,13] Thus the commercially available 7-hydroxycoumarin **49** was formylated with complete regioselectivity, though in low yield, by the Duff reaction to give the 8-formyl compound **50**.[14] Allylation under standard conditions gave **51**, which was subjected to a Wittig reaction to give the propenoate precursor **52** which was purified by chromatography on silica. FVP of **52** gave angelicin **2** in 45% yield after recrystallisation. The ^{1}H and ^{13}C NMR spectra of the final product are in full agreement with those reported in the literature[15–17] (see Experimental section). A small amount of a compound which is probably the allylpyrone **53** was also isolated from this pyrolysis, presumably formed by a mechanism similar to that in Scheme 5.

It is clear that the cyclisation of oxygen centred radicals onto adjacent acrylate functions is an efficient process under FVP conditions if these groups are present on a six-membered ring framework. We have also studied the pyrolysis of the thiophene

precursors **54** and **55** in which the cyclisation—if successful—would give a more strained thieno[3,2-*b*]furan system. Very little is known of the synthesis of this system.[18–20] In the event, a viable (though low yielding) pyrolytic synthesis of thieno-[3,2-*b*]furans was developed, but it was unclear whether these low yields were due to an inefficient cyclisation step or to decomposition of the (rather unstable) products during isolation and work-up. The problem was exacerbated by some poor yields *en route* to the pyrolysis precursors.

3-Hydroxy-5-(methylthio)thiophene **56** was chosen as the starting material for the syntheses since it is readily available as its thiophen-3(2*H*)-one tautomer in two steps from Meldrum's acid (Scheme 8).[21] Benzylation of this compound under conditions optimised for the *O*-alkylation of analogous pyrrol-3-(2*H*)-ones[22] gave instead a mixture of 3-benzyloxy-5-(methylthio)thiophene **57** and a product of *C*,*O*-dialkylation **58**, from which the required product **57** could be isolated in 39% yield after careful bulb-to-bulb distillation. Vilsmeier formylation of this product was unsuccessful, but it was nevertheless reactive enough to condense with methoxymethylene Meldrum's acid **59** over two days at room temperature in acetonitrile solution to give the 'Meldrumsated' product **60** in 42% yield after recrystallisation. Similar reactions have also been carried out in the 3-alkoxypyrrole series.[23] Cleavage of the Meldrum's acid ring was effected with sodium methoxide in methanol solution (1 h at room temperature) which gave the malonate mono ester **61**, which could either be decarboxylated under bulb-to-bulb distillation conditions or alkylated (MeI, K_2CO_3, DMF) to give the acrylate **54** (67%) and the malonate **55** (82%) respectively (*cf.* ref. 24).



53 **54** **55**

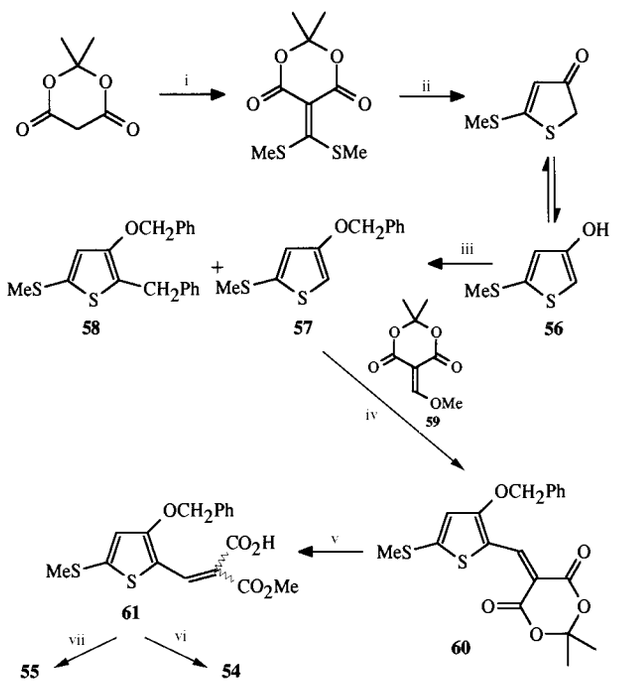
FVP of the acrylate **54** at 650 °C gave the expected bibenzyl together with a single unstable heterocyclic product, which were separated by dry-flash chromatography on silica. This was identified as 5-(methylthio)thieno[3,2-*b*]furan **62** by comparison of its ^{1}H NMR spectrum with that of the parent thieno[3,2-*b*]-furan previously reported (Table 1).[20] The chemical shifts and coupling constants are closely similar, though the value of $^5J_{2,6}$ was negligible in our example; the very small effect of the methylthio substituent on the chemical shift of the adjacent site is also evident in a comparison of the spectra of 3-methoxythiophene **63** [δ_H(4-H) 6.79] and 5-(methylthio)-3-methoxythiophene **64** [δ_H(4-H) 6.71].[25] Due to its low stability —particularly in [^{2}H]chloroform solution—we were unable to characterise the product **62** further, and this may also account in part for the low yield of the pyrolysis product (21%).

Similarly, FVP of the malonate **55** gave the thieno[3,2-*b*]-furan-2-carboxylate **65** (22%). Its ^{1}H NMR spectrum is also summarised in Table 1 together with that of a known 2-carboxylic acid,[20] but again our material proved to be too unstable for complete characterisation.

To conclude, it is clear that FVP of 2-*O*-allylcinnamate esters and related compounds is a useful synthetic route to the benzo[*b*]furan ring system which can be directly applied to modest synthetic targets. The reaction is compatible with a wide range of substituents, yields are generally in the range 60–90%,

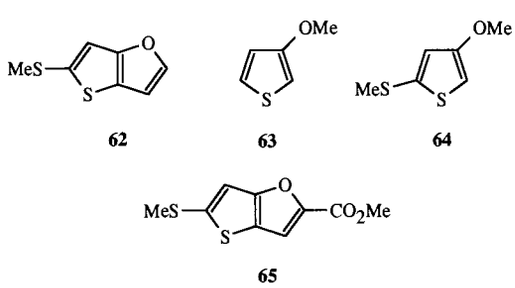
Table 1 ^{1}H NMR spectra of thieno[3,2-*b*]furans

Compound	δ_H 2-H	3-H	6-H	J/Hz
Thieno[3,2-*b*]furan[20]	7.51	6.69	7.02	$^3J_{2,3}$ 2.0 $^5J_{2,6}$ *ca.* 1 $^5J_{3,6}$ 0.5
62	7.55	6.67	7.15	$^3J_{2,3}$ 2.0 $^5J_{3,6}$ 0.8
Thieno[3,2-*b*]furan-2-carboxylic acid[20]	—	7.71	7.33	$^5J_{3,6}$ 0.5
65	—	7.41	7.09	$^5J_{3,6}$ 0.6



58 **57** **56** **59** **61** **60** **55** **54**

Scheme 8 *Reagents and conditions:* i, CS_2, Et_3N, DMSO; ii, FVP (600 °C, 0.001 Torr); iii, $PhCH_2OTs$, NaH, DMI; iv, acetonitrile, room temperature, 2 days; v, NaOMe, 1 h; vi, heat (Kugelrohr); vii, MeI, K_2CO_3, DMF



62 **63** **64** **65**

and in favourable cases the product can be isolated without chromatography. We have also shown that a furan ring can be fused onto a thiophene system using this methodology, though in much lower yield. More work will be required to establish whether this reduced yield is due to an inefficient cyclisation step or to the relative instability of the products.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz respectively for solutions in deuteriochloroform unless otherwise stated. Coupling constants (*J*) are quoted in Hz. Light petroleum refers to the fraction boiling between 40–60 °C.

2-Allyloxybenzaldehyde 3

Benzaldehyde (20.8 g, 0.17 mol) was added to a suspension of

potassium carbonate (47.0 g, 0.34 mol) in dimethylformamide (250 cm^3). Allyl bromide (20.6 g, 0.17 mol) was added dropwise and the mixture was stirred for 21 h. Water (300 cm^3) was then added and the mixture was extracted with diethyl ether (3 × 50 cm^3). The combined organic extracts were washed with water (100 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to give 2-*allyloxybenzaldehyde* **3** (23.3 g, 84%) as a colourless viscous liquid, bp 115–118 °C (0.4 Torr) (Found: M^+, 162.0678. $C_{10}H_{10}O_2$ requires *M*, 162.0680); δ_H 10.40 (1H, s), 7.72 (1H, m), 7.40 (1H, m) 6.93–6.84 (2H, m), 5.97 (1H, m), 5.39–5.18 (2H, m) and 4.52 (2H, m); δ_C 189.37, 160.68 (q), 135.63, 132.17, 128.06, 124.81 (q), 120.56, 117.72, 112.67 and 68.87; *m/z* 162 (M^+, 56%) 133 (32), 121 (90), 92 (37) and 41 (100).

2-Allyloxystilbene 4 (*cf.* ref. 26)

Benzyltriphenylphosphonium bromide (6.94 g, 0.016 mol) was added to a solution of sodium ethoxide [from sodium (0.46 g, 0.02 mol) in 'super-dry' ethanol (50 cm^3)], under an atmosphere of nitrogen, to form an orange-coloured suspension. A solution of 2-allyloxybenzaldehyde (2.58 g, 0.016 mol) in dry ethanol (10 cm^3) was then added dropwise, thus forming a clear solution which was stirred at room temperature for 50 h. The solution was then poured into a solution of hydrobromic acid in acetic acid (33%, 50 cm^3) and cooled in ice. The resulting pink precipitate was filtered to yield recovered phosphonium salt (2.22 g). The filtrate was extracted with diethyl ether (3 × 30 cm^3) and the combined organic extracts were washed with aqueous sodium bisulfite (5%; 40 cm^3). Triphenylphosphine oxide (1.57 g, 35%) deposited as a white solid and was filtered off. The filtrate was evaporated to dryness under vacuum and the resulting viscous brown oil (3.42 g) was purified by distillation to give 2-*allyloxystilbene* **4** (1.40 g, 37%) as a clear oil, bp 184–187 °C (0.6 Torr), which slowly crystallised, mp 46–48 °C (from ethanol) (Found: C, 85.5; H, 6.8. $C_{17}H_{16}O{\cdot}0.1H_2O$ requires C, 85.8; H, 6.8%); δ_H 7.80–6.87 (11H, m), 6.15 (1H, m), 5.56–5.28 (2H, m) and 4.66 (2H, m); δ_C 155.87 (q), 137.89 (q), 133.31, 129.02, 128.51, 128.46, 127.27, 126.71 (q), 126.46, 126.42, 123.47, 120.91, 117.19, 112.45 and 69.13; *m/z* 236 (M^+, 33%) 195 (26), 167 (100), 152 (57) and 41 (63).

General method[27] for preparation of methyl 3-(2-hydroxyphenyl)propenoate derivatives

The appropriate aldehyde was dissolved in dry dichloromethane. Methyl triphenylphosphoranylideneacetate was added with stirring. Reaction was continued until TLC showed complete disappearance of the aldehyde (*ca*. 2 h). The mixture was then pre-adsorbed onto silica (5 × weight of mixture), and subjected to dry flash chromatography on silica.

The following compounds were prepared by this method. Salicylaldehyde gave methyl 3-(2-hydroxyphenyl)propenoate **6**,[4] 2-hydroxy-5-chlorobenzaldehyde gave methyl 3-(2-hydroxy-5-chlorophenyl)propenoate **8**,[4] 2-hydroxy-5-nitrobenzaldehyde gave methyl 3-(2-hydroxy-5-nitrophenyl)propenoate **10**,[4] 2-hydroxy-5-methoxybenzaldehyde gave methyl 3-(2-hydroxy-5-methoxyphenyl)propenoate **12**;[28] δ_H 8.00 (1H, d), 6.94 (2H, d), 6.80 (1H, d), 6.56 (1H, d), 3.80 (3H, s) and 3.76 (3H, s); *m/z* 208 (M^+, 20%), 176 (100), 145 (44), 133 (48), 77 (49) and 52 (40) and 2-hydroxy-1-naphthaldehyde gave methyl 3-(2-hydroxy-1-naphthyl)propenoate **21**.[4]

General method[4] for preparation of ethyl 2-methyl-3-(2-hydroxyphenyl)propenoate derivatives

The appropriate aldehyde was dissolved in dry dichloromethane. Ethyl 2-triphenylphosphoranylidenepropionate was added with stirring. Reaction was continued until TLC showed complete disappearance of the aldehyde. The mixture was then pre-adsorbed on to silica (5 × weight of mixture), and subjected to dry flash chromatography on silica.

The following compounds were prepared by this method. Salicylaldehyde gave ethyl 2-methyl-3-(2-hydroxyphenyl)-propenoate **15**,[4] 2-hydroxy-5-chlorobenzaldehyde gave ethyl 2-methyl-3-(2-hydroxy-5-chlorophenyl)propenoate **17**,[4] 2-hydroxy-1-naphthaldehyde (0.52 g, 3 mmol) gave ethyl 2-methyl-3-(2-hydroxy-1-naphthyl)propenoate **25** as a mixture of *E* and *Z* isomers (0.62 g, 81%), mp 93–96 °C (lit.,[29] 97–99 °C) (Found: M^+, 256.1101. $C_{16}H_{16}O_3$ requires *M*, 256.1099); δ_H 8.20 (1H, m), 7.90–7.19 (6H, m), 6.23 (1H, br s), 4.33 (2H, q, ^3J 7.1), 1.86 (3H, d, ^4J 1.0) and 1.39 (3H, t, ^3J 7.1); δ_C 167.82 (q), 150.28 (q), 133.07, 130.01, 128.18, 126.62, 123.81, 123.43, 117.69, 61.12, 14.57 and 14.15 (four quaternary signals not assigned because of the presence of *ca*. 25% of minor diastereomer); *m/z* 256 (M^+, 31%), 211 (31), 210 (96), 183 (38), 182 (100), 181 (57), 153 (17), 152 (31), 139 (12), 91 (14) and 76 (18).

In addition, methyl 2-methyl-3-(2-allyloxyphenyl)propenoate **14** was prepared from 2-allyloxybenzaldehyde **3** (0.3 g, 1.7 mmol) and methyl 2-triphenylphosphoranylidenepropionate[30] (0.49 g, 1.4 mmol) by a similar method. After reaction, the solution was concentrated to half its volume and the majority of the triphenylphosphine oxide was precipitated by the addition of light petroleum. The filtrate was concentrated to give a brown oil (0.42 g) which contained the product and some unreacted aldehyde which was removed as a water-soluble hydrazone by treatment with Girard's reagent 'T'. Pure *methyl 2-methyl-3-(2-allyloxyphenyl)propenoate* **14** (0.16 g, 50%) was obtained as a clear oil by distillation, bp 162–166 °C (1.5 Torr) (Found: M^+, 232.1097. $C_{14}H_{16}O_3$ requires *M*, 232.1099); δ_H 7.87 (1H, m), 7.31–7.23 (2H, m), 6.99–6.87 (2H, m), 6.00 (1H, m), 5.45–5.24 (2H, m), 4.57 (2H, m), 3.80 (3H, s) and 2.05 (3H, s); δ_C 168.97 (q), 156.43 (q), 134.82, 132.96, 130.07, 129.49, 128.11 (q), 125.05 (q), 120.13, 117.17, 111.86, 68.87, 51.76 and 14.10; *m/z* 232 (M^+, 49%), 131 (76) and 41 (100).

2-Benzyloxyacetophenone 27

Potassium carbonate (0.76 g, 5.5 mmol) was added to DMF (25 cm^3). After stirring for 5 min, 2-hydroxyacetophenone (0.68 g, 5 mmol) was added and the mixture was stirred for 5 min. Benzyl bromide (0.94 g, 5.5 mmol) was then added dropwise and the mixture was stirred overnight. TLC confirmed that all the starting materials had been consumed and water (25 cm^3) was added. The mixture was then extracted with diethyl ether (3 × 25 cm^3). The combined extracts were washed with water (3 × 50 cm^3) and dried ($MgSO_4$). The solvent was then removed on the rotary evaporator to yield 2-*benzyloxyacetophenone* **27**, bp 165–170 °C (12 Torr) (Found: M^+, 226.0990. $C_{15}H_{14}O_2$ requires *M*, 226.0994); δ_H 7.75 (1H, dd, ^3J 8.2, ^4J 2.0), 7.48–7.34 (6H, m), 7.02 (2H, d, ^3J 7.9), 5.16 (2H, s) and 2.60 (3H, s); δ_C 199.77 (q), 157.87 (q), 136.05 (q), 133.46, 130.60 (q), 130.30, 128.55, 128.09, 127.42, 120.72, 112.66, 70.49 and 31.96; *m/z* 226 (M^+, 8%), 92 (11), 91 (100) and 65 (17).

Ethyl 3-(2-benzyloxyphenyl)but-2-enoate 28 (*cf.* ref 31)

To a solution of sodium ethoxide [from sodium (0.25 g, 11 mmol) in ethanol (50 cm^3)] was added methyl diethyl phosphonoacetate (2.10 g, 10 mmol). After stirring for 30 min the mixture was cooled in ice and 2-benzyloxyacetophenone **27** (0.73 g, 3 mmol) was added dropwise. The mixture was then heated under reflux for 48 h. (During reflux the methyl ester transesterified to the ethyl ester.) Water (100 cm^3) was added and the mixture was extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed with water (1 × 50 cm^3) and dried ($MgSO_4$). The crude product was pre-adsorbed onto silica (5 g) and separated by dry flash chromatography (5% ethyl acetate–hexane; 5% gradient). This gave two products which were the *E* and *Z* isomers of *ethyl* 3-(2-*benzyloxyphenyl*)*but*-2-*enoate* **28**. *E*-isomer (0.714 g, 73%) bp 134–138 °C (2 Torr) (Found: M^+, 296.1417. $C_{19}H_{20}O_3$ requires *M*, 296.1412); δ_H 7.44–7.17 (7H, m), 7.00–6.93 (2H, m), 5.96 (1H, q, ^4J 1.3), 5.11 (2H, s), 4.22 (2H, q, ^3J 7.1), 2.56 (3H, d, ^4J 1.3) and 1.32 (3H, t, ^3J 7.1); δ_C 166.66 (q), 156.52 (q), 155.33 (q), 136.69 (q), 133.40

(q), 129.36, 128.90, 128.44, 127.75, 127.02, 120.79, 119.22, 112.43, 70.15, 59.58, 19.94 and 14.25; *m/z* 296 (M^+, 2%), 205 (8), 131 (8) and 91 (100). *Z*-isomer (0.240 g, 25%), bp 120–124 °C (2 Torr) (Found: M^+, 296.1403. $C_{19}H_{20}O_3$ requires *M*, 296.1412); δ_H 7.41–7.22 (6H, m), 7.10–6.94 (3H, m), 5.99 (1H, q, ^4J 1.4), 5.09 (2H, s), 3.98 (2H, q, ^3J 7.1), 2.20 (3H, d, ^4J 1.3) and 1.04 (3H, t, ^3J 7.1); δ_C 165.39 (q), 154.17 (q), 153.28 (q), 137.04 (q), 130.65 (q), 128.39, 128.17, 127.87, 127.38, 126.66, 120.40, 118.65, 112.12, 69.82, 59.25, 26.02 and 13.70; *m/z* 296 (M^+, 3%), 204 (8), 132 (7), 131 (9), 92 (8), 91 (100) and 65 (9).

General method for *O*-alkylation of 3-(2-hydroxyaryl)propenoates

Potassium carbonate (0.152 g, 1.1 mmol) was added to DMF (5 cm^3). After stirring for 5 min the appropriate methyl 3-(2-hydroxyaryl)propenoates or ethyl 3-(2-hydroxyaryl)-2-methylpropenoates (1 mmol) were added and the mixture was stirred for 5 min. Allyl bromide (0.133 g, 1.1 mmol) was then added dropwise and the mixture was stirred overnight. TLC confirmed that all the substrates had been consumed and water (10 cm^3) was added. The mixture was then extracted with diethyl ether (3 × 10 cm^3). The combined extracts were washed with water (3 × 25 cm^3) and dried ($MgSO_4$). The solvent was then removed on the rotary evaporator to yield the following methyl 3-(2-allyloxyaryl)propenoates or ethyl 3-(2-allyloxyaryl)-2-methylpropenoates.

Methyl 3-(2-hydroxyphenyl)propenoate **6** gave *methyl* 3-(2-*allyloxyphenyl*)*propenoate* **7** (90%), bp 100–105 °C (8 Torr) (Found: M^+, 218.0946. $C_{13}H_{14}O_2$ requires *M*, 218.0943); δ_H 8.03 (1H, d, ^3J 16.2), 7.48 (1H, dd, ^3J 7.7, ^4J 1.4), 7.30 (1H, m), 6.97–6.85 (2H, m), 6.52 (1H, d, ^3J 16.2), 6.05 (1H, m), 5.45–5.26 (2H, m), 4.58 (2H, m) and 3.78 (3H, s); δ_C 167.73 (q), 157.10 (q), 140.05, 132.67, 131.21, 128.68, 120.68, 118.11, 117.63, 112.27, 68.96 and 51.39 (one quaternary carbon not apparent); *m/z* 218 (M^+, 35%), 158 (27), 131 (20), 118 (95), 105 (46), 90 (34), 89 (37), 59 (32) and 41 (100).

Methyl 3-(2-hydroxy-5-chlorophenyl)propenoate **8** gave *methyl* 3-(2-*allyloxy*-5-*chlorophenyl*)*propenoate* **9** (94%), bp 82–87 °C (0.12 Torr) (Found: M^+, 254.0517 and 252.0554. $C_{13}H_{13}{}^{37}ClO_3$ and $C_{13}H_{13}{}^{35}ClO_3$ require *M*, 254.0524 and 252.0553 respectively); δ_H 7.92 (1H, d, ^3J 16.2), 7.44 (1H, d, ^4J 2.6), 7.22 (1H, dd, ^3J 8.9, ^4J 2.6), 6.79 (1H, d, ^3J 8.9), 6.74 (1H, d, ^3J 16.2), 6.03 (1H, m), 5.43–5.26 (2H, m), 4.58–4.54 (2H, m) and 3.78 (3H, m); δ_C 167.26 (q), 155.53 (q), 138.51, 132.27, 130.61, 127.98, 125.47 (q), 124.94 (q), 119.32, 117.98, 113.62, 69.35 and 51.52; *m/z* 254 (M^+, 33%), 252 (M^+, 100), 195 (13), 194 (14), 193 (15), 192 (35), 180 (30), 152 (31), 113 (19), 89 (11) and 59 (39).

Methyl 3-(2-hydroxy-5-nitrophenyl)propenoate **10** gave *methyl* 3-(2-*allyloxy*-5-*nitrophenyl*)*propenoate* **11** (81%), unpurified mp 88–91 °C (Found: M^+, 263.0799. $C_{13}H_{13}NO_5$ requires *M*, 263.0794); δ_H 8.37 (1H, d, ^4J 2.7), 8.18 (1H, dd, ^3J 9.1, ^4J 2.7), 7.93 (1H, d, ^3J 16.2), 6.96 (1H, d, ^3J 9.1), 6.58 (1H, d, ^3J 16.2), 6.04 (1H, m), 5.47–5.32 (2H, m), 4.72–4.70 (2H, m) and 3.79 (3H, s); δ_C 166.88 (q), 161.30 (q), 141.21 (q), 137.49, 131.28, 126.48, 124.11 (q), 123.95, 120.91, 118.94, 112.04, 69.85 and 51.72; *m/z* 263 (M^+, 13%), 59 (11), 44 (21), 41 (100) and 40 (90).

Methyl 3-(2-hydroxy-5-methoxyphenyl)propenoate **12** gave *methyl* 3-(2-*allyloxy*-5-*methoxyphenyl*)*propenoate* **13** (74%), bp 142–145 °C (0.3 Torr) (Found: M^+, 248.1057. $C_{14}H_{16}O_4$ requires *M*, 248.1049); δ_H 8.00 (1H, d), 7.03 (1H, d), 6.85 (2H, d), 6.49 (1H, d), 6.05 (1H, m), 5.44–5.24 (2H, m), 4.56–4.51 (2H, m), 3.79 (3H, s) and 3.77 (3H, s); δ_C 167.62 (q), 153.53 (q), 151.61 (q), 139.86 (q), 133.02, 124.23, 118.38, 117.52, 116.94, 114.04, 112.95, 69.88, 55.58 and 51.43; *m/z* 248 (M^+, 75%), 207 (36), 176 (28), 148 (100), 135 (63), 105 (59), 77 (38) and 59 (62).

Ethyl 2-methyl-3-(2-hydroxyphenyl)propenoate **15** gave *ethyl* 2-*methyl*-3-(2-*allyloxyphenyl*)*propenoate* **16** (100%), bp 65–70 °C (0.08 Torr) (Found: M^+, 246.1250. $C_{15}H_{18}O_3$ requires *M*, 246.1256); δ_H 7.88 (1H, s), 7.30–7.22 (2H, m), 6.99–6.86 (2H, m), 6.04 (1H, m), 5.47–5.23 (2H, m), 4.58–4.54 (2H, m), 4.26 (2H, q, ^3J 7.1), 2.04 (3H, d, ^4J 1.4) and 1.33 (3H, t, ^3J 7.1); δ_C 168.55 (q), 156.41 (q), 134.53, 132.93, 130.09, 129.47, 128.36 (q), 125.08 (q), 120.12, 117.02, 111.81, 68.77, 60.55, 14.14 and 14.07; *m/z* 246 (M^+, 73%), 201 (32), 189 (42), 173 (40), 161 (44), 160 (31), 159 (30), 145 (26), 133 (60), 132 (80), 131 (100), 105 (67), 103 (28) and 77 (37).

Ethyl 2-methyl-3-(2-hydroxy-5-chlorophenyl)propenoate **17** gave *ethyl* 2-*methyl*-3-(2-*allyloxy*-5-*chlorophenyl*)*propenoate* **18** (93%), bp 110–115 °C (0.08 Torr) (Found: M, 282.0841 and 280.0864. $C_{15}H_{17}{}^{37}ClO_3$ and $C_{15}H_{17}{}^{35}ClO_3$ require M^+, 282.0837 and 280.0866 respectively); δ_H 7.75 (1H, d, ^4J 0.5), 7.25–7.16 (2H, m), 6.79 (1H, d, ^3J 8.5), 5.99 (1H, m), 5.43–5.22 (2H, m), 4.54–4.50 (2H, m), 4.25 (2H, q, ^3J 7.1), 2.02 (3H, d, ^4J 1.4) and 1.32 (3H, t, ^3J 7.1); δ_C 168.19 (q), 154.94 (q), 133.13, 132.49, 129.60, 128.96, 126.60 (q), 125.07 (q), 117.32, 113.03, 69.10, 60.73, 14.11 and 14.03 (one quaternary carbon not apparent); *m/z* 282 (M^+, 12%), 280 (M^+, 41), 235 (16), 223 (32), 207 (21), 195 (21), 169 (16), 168 (19), 167 (60), 166 (28), 165 (100), 139 (27), 131 (24) and 103 (26).

Methyl 3-(2-hydroxy-1-naphthyl)propenoate **21** gave *methyl* 3-(2-*allyloxy*-1-*naphthyl*)*propenoate* **22** (94%), bp 100–105 °C (0.07 Torr) (Found: M^+, 268.1098. $C_{17}H_{16}O_3$ requires *M*, 268.1099); δ_H 8.35 (1H, d, ^3J 16.2), 8.16 (1H, d, ^3J 8.3), 7.77 (2H, m), 7.53–7.32 (2H, m), 7.22 (1H, d, ^3J 9.1), 6.78 (1H, d, ^3J 16.2), 6.08 (1H, m), 5.47–5.27 (2H, m), 4.74–4.70 (2H, m) and 3.84 (3H, s); δ_C 168.12 (q), 155.51 (q), 137.78, 132.80, 131.25, 128.40, 127.22, 123.84, 123.13, 122.91, 117.74, 113.97, 69.75 and 51.48 (three quaternary carbons not assigned); *m/z* 268 (M^+, 61%), 237 (10), 196 (22), 195 (19), 168 (100), 155 (36), 140 (22), 139 (45) and 59 (24).

Ethyl 2-methyl-3-(2-hydroxy-1-naphthyl)propenoate **25** gave *ethyl* 2-*methyl*-3-(2-*allyloxy*-1-*naphthyl*)*propenoate* **26** (91%), bp 95–100 °C (0.1 Torr) (Found: M^+, 296.1411. $C_{19}H_{20}O_3$ requires *M*, 296.1412) δ_H 7.95 (1H, s), 7.84–7.71 (3H, m), 7.51–7.24 (3H, m), 6.06 (1H, m), 5.47–5.24 (2H, m), 4.69–4.65 (2H, m), 4.34 (2H, q, ^3J 7.2), 1.77 (3H, d, ^4J 1.3) and 1.40 (3H, t, ^3J 7.2); δ_C 167.99 (q), 152.93 (q), 133.99, 133.23, 132.03 (q), 131.92 (q), 129.58, 128.74 (q), 128.09, 126.53, 124.45, 123.71, 119.10 (q), 117.15, 114.44, 69.74, 60.63, 14.92 and 14.23; *m/z* 296 (M^+, 39%), 210 (12), 183 (34), 182 (100), 181 (40), 153 (12) and 152 (19).

Methyl 3-(2-isopropoxy-1-naphthyl)propenoate 23 and methyl 3-(2-benzyloxy-1-naphthyl)propenoate 24

Preparation and work-up were performed as described in the previous section but with replacement of allyl bromide with isopropyl bromide. Methyl 3-(2-hydroxy-1-naphthyl)propenoate **21** gave *methyl* 3-(2-*isopropoxy*-1-*naphthyl*)*propenoate* **23** (0.204 g, 76%), bp 107–111 °C (2 Torr) (Found: M^+, 270.1243. $C_{17}H_{18}O_3$ requires *M*, 270.1256); δ_H 8.37 (1H, d, ^3J 16.1), 8.19 (1H, d, ^3J 8.1), 7.82–7.75 (2H, m), 7.56–7.24 (3H, m), 6.82 (1H, d, ^3J 16.1), 6.35 (1H, septet, ^3J 6.1), 3.86 (3H, s) and 1.41 (6H, d, ^3J 6.1); δ_C 168.28 (q), 155.16 (q), 138.12, 132.80 (q), 131.17, 129.46 (q), 128.37, 127.12, 123.78, 123.15, 122.61, 117.84 (q), 115.45, 71.81, 51.46 and 22.27; *m/z* 270 (M^+, 28%), 228 (19), 197 (25), 196 (75), 169 (28), 168 (100), 141 (16), 140 (18) and 139 (26).

Similarly, preparation and work-up were performed as above, but with replacement of allyl bromide with benzyl bromide. Methyl 3-(2-hydroxy-1-naphthyl)propenoate **21** gave *methyl* 3-(2-*benzyloxy*-1-*naphthyl*)*propenoate* **24** (0.267 g, 85%), bp 135–140 °C (3 Torr) (Found: M^+, 318.1246. $C_{21}H_{18}O_3$ requires *M*, 318.1256); δ_H 8.43 (1H, d, ^3J 16.2), 8.21 (1H, d, ^3J 8.6), 7.77 (2H, d, ^3J 8.8), 7.47–7.33 (7H, m), 7.26 (1H, d, ^3J 9.2), 6.85 (1H, d, ^3J 16.2), 5.27 (2H, s) and 3.86 (3H, d, ^4J 0.6); δ_C 168.14 (q), 155.52 (q), 137.83, 131.33, 128.55, 128.47, 127.93, 127.29, 127.02, 123.95, 123.22, 123.13, 114.25, 70.96 and 51.53 (four

quaternary carbons not assigned); *m/z* 318 (M^+, 13%), 286 (11), 196 (27), 168 (36), 140 (10), 139 (22), 92 (10) and 91 (100).

Dimethyl (2-allyloxyphenyl)methylenemalonate 19 (*cf.* ref. 32)
A solution of titanium tetrachloride (2.2 cm^3, 0.02 mol) in carbon tetrachloride (5 cm^3) was added dropwise to ice-cold dry tetrahydrofuran (40 cm^3) under an atmosphere of nitrogen. A solution of dimethyl malonate (1.32 g, 0.01 mol) and 2-allyloxybenzaldehyde (1.62 g, 0.01 mol) in dry tetrahydrofuran (10 cm^3) was added slowly, followed by the addition of a solution of pyridine (3.2 cm^3, 0.04 mol) in dry tetrahydrofuran (5 cm^3), and the resulting suspension was stirred at 0 °C for 1 h. At the end of this period, water (50 cm^3) was added and the mixture was extracted with methylene dichloride (2 × 25 cm^3). The combined organic extracts were washed, first with brine (20 cm^3), then with saturated aqueous sodium hydrogen carbonate (20 cm^3) and finally with water (30 cm^3). The extracts were then dried ($MgSO_4$) and the solvent was removed *in vacuo* to give *dimethyl* (2-*allyloxyphenyl*)*methylenemalonate* **19** (1.69 g, 61%) as a yellow oil, bp 187–190 °C (1.0 Torr) (Found: C, 64.9; H, 5.9. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.8%); δ_H 8.14 (1H, s), 7.29 (2H, m), 6.87 (2H, m), 6.01 (1H, m), 5.41–5.22 (2H, m), 4.54 (2H, m), 3.80 (3H, s) and 3.74 (3H, s); δ_C 166.98 (q), 164.52 (q), 156.96 (q), 138.73, 132.56, 131.86, 128.74, 125.22 (q), 122.34 (q), 120.57, 117.48, 112.18, 69.04, 52.27 and 52.19; *m/z* 276 (M^+, 35%), 217 (12), 173 (100), 145 (50) and 117 (45).

(2-Allyloxyphenyl)methylenemalononitrile 5 (*cf.* ref. 32)
Piperidine (5 drops) and acetic acid (5 drops) were added to a solution of malononitrile (0.198 g, 3 mmol) and 2-allyloxybenzaldehyde (0.49 g, 3 mmol) in toluene (15 cm^3) and the mixture was stirred at room temperature for 21 h. Water (20 cm^3) was added and the solution was extracted with methylene dichloride (2 × 10 cm^3). The combined organic extracts were dried ($MgSO_4$) and concentrated to give (2-*allyloxyphenyl*)-*methylenemalononitrile* **5** (0.52 g, 83%) as a brown oil which slowly crystallised, mp 50–52 °C (from ethanol) (Found: C, 74.2; H, 4.75; N, 13.3. $C_{13}H_{10}N_2O$ requires C, 74.3; H, 4.75; N, 13.3%); δ_H 8.30 (1H, s), 8.16 (1H, m), 7.55 (1H, m), 7.08–6.94 (2H, m), 6.02 (1H, m), 5.46–5.32 (2H, m) and 4.63 (2H, m); δ_C 157.87 (q), 154.31, 136.33, 131.75, 128.65, 121.17, 120.19 (q), 118.76, 114.23 (q), 112.90 (q), 112.64, 81.16 (q) and 69.54; *m/z* 210 (M^+, 35%), 183 (91), 143 (20), 41 (100) and 39 (70).

Methyl (2-allyloxyphenyl)methylene(cyano)acetate 20
(*cf.* ref. 32)
Prepared from methyl cyanoacetate (0.30 g, 3 mmol) and 2-allyloxybenzaldehyde (0.49 g, 3 mmol) by a similar procedure to that described above for **5**, *methyl* 3-(2-*allyloxyphenyl*)-*methylene*(*cyano*)*acetate* **20** (0.71 g, 97%) was obtained as a yellow solid, mp 63–65 °C (from ethanol) (Found: C, 67.6; H, 5.2; N, 5.4. $C_{14}H_{13}NO_3 \cdot 0.3H_2O$ requires C, 67.6; H, 5.5; N, 5.6%); δ_H 8.81 (1H, s), 8.29 (1H, m), 7.48 (1H, m), 7.09–6.90 (2H, m), 6.01 (1H, m), 5.45–5.28 (2H, m), 4.64 (2H, m) and 3.91 (3H, s); δ_C 163.13 (q), 158.12 (q), 149.88, 134.77, 132.10, 129.23, 120.96, 120.75 (q), 118.00, 115.68 (q), 112.30, 101.83 (q), 69.21 and 53.03; *m/z* 243 (M^+, 29%), 201 (15), 182 (51), 143 (34) and 41 (100).

Flash vacuum pyrolysis reactions

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 and pyrolysis time are indicated in parenthesis.

FVP of 2-allyloxystilbene 4
2-Allyloxystilbene **4** (0.387 g, 1.6 mmol, T_f 650 °C, T_i 110 °C, 0.001 Torr, 90 min) gave a colourless solid (0.21 g) which was recrystallised from ethanol to constant melting point affording 2-phenylbenzo[*b*]furan **31** (0.17 g, 55%), mp 113–115 °C (lit.,[33] 121 °C); *m/z* 194 (M^+, 100%), 165 (47) and 77 (11).

Analysis of the crude pyrolysate by GLC showed two minor products in addition to the 2-phenylbenzo[*b*]furan, which were identified as benzo[*b*]furan **32** and biphenyl by comparison with authentic samples.

Preparation of benzo[*b*]furans by FVP of 2-allyloxycinnamate esters and related compounds
Methyl 3-(2-allyloxyphenyl)propenoate **7** (0.103 g, 0.5 mmol, T_f 650 °C, T_i 80–100 °C, 0.01 Torr, 15 min) gave benzo[*b*]furan **32** (0.038 g, 68%), bp 97–99 °C (80 Torr) [lit.,[34] 173–175 °C (760 Torr)]; δ_H 7.69–7.22 (5H, m) and 6.79 (1H, dd, ^3J 2.2, ^5J 0.9); *m/z* 118 (M^+, 100%), 90 (48), 89 (43), 63 (30), 62 (12) and 39 (15).

Methyl 3-(2-allyloxy-5-chlorophenyl)propenoate **9** (0.110 g, 0.4 mmol, T_f 650 °C, T_i 120–140 °C, 0.01 Torr, 20 min) gave 5-chlorobenzo[*b*]furan **33** (0.040 g, 60%), bp 65–70 °C (20 Torr) (lit.,[35] bp 215–217 °C) (Found: M^+, 154.0004 and 152.0031. $C_8H_5{}^{37}ClO$ and $C_8H_5{}^{35}ClO$ require *M*, 153.9999 and 152.0029 respectively); δ_H 7.63 (1H, d, ^3J 2.2), 7.57 (1H, d, ^4J 2.0), 7.42 (1H, dd, ^3J 8.8, ^5J 0.9), 7.25 (1H, dd, ^3J 8.8 and ^4J 2.0) and 6.71 (1H, dd, ^3J 2.2, ^5J 0.9); δ_C 153.19 (q), 146.17, 128.64 (q), 128.18 (q), 124.34, 120.64, 112.21 and 106.14; *m/z* 154 (M^+, 39%), 152 (M^+, 100), 89 (32) and 63 (13).

Methyl 3-(2-allyloxy-5-nitrophenyl)propenoate **11** (0.102 g, 0.4 mmol, T_f 650 °C, T_i 140–460 °C, 0.01 Torr, 20 min) gave three products. These were separated by dry-flash chromatography to give, first, a compound which was tentatively identified as 5-allylbenzo[*b*]furan **48** (0.010 g, 21%); δ_H 7.59 (1H, d, ^3J 2.1), 7.44–7.39 (2H, m), 7.11 (1H, m), 6.71 (1H, dd, ^3J 2.1, ^5J 0.8), 6.00 (1H, m), 5.06 (2H, m) and 3.46 (2H, d, ^3J 6.7); δ_C(CH's only) 144.99, 137.88, 124.92, 120.55, 115.38, 110.94, 106.26 and 39.96. The second was 5-nitrobenzo[*b*]furan **34** (0.034 g, 55%) mp 107–109 °C (from ethanol) (lit.,[36] 116 °C) (Found: M^+, 163.0269. $C_8H_5NO_3$ requires *M*, 163.0269); δ_H 8.54 (1H, d, ^4J 2.2), 8.23 (1H, dd, ^3J 9.0, ^4J 2.2), 7.78 (1H, d, ^3J 2.3), 7.58 (1H, apparent d, ^3J 9.0) and 6.92 (1H, dd, ^3J 2.3, ^5J 0.9); δ_C 157.55 (q), 147.86, 144.04 (q), 127.66 (q), 120.06, 117.72, 111.63 and 107.45; *m/z* 163 (M^+, 77%), 117 (45), 89 (100), 77 (16), 63 (75) and 62 (28). The third was 3-*allyl*-6-*nitrobenzopyran*-2-*one* **47** (0.004 g, 4%) (not purified further) (Found: M^+, 231.0529. $C_{12}H_9NO_4$ requires *M*, 231.0532); δ_H 8.39–8.30 (2H, m), 7.58 (1H, s), 7.43 (1H, d, ^3J 8.9), 5.93 (1H, m), 5.28–5.20 (2H, m) and 3.35 (2H, m); δ_C(DEPT 3π/4) 137.36, 132.54, 125.42, 123.01, 119.10, 117.44 and 34.38; *m/z* 231 (M^+, 100%), 203 (36), 157 (45), 128 (77), 127 (40), 102 (27), 77 (28) and 63 (25).

Methyl 3-(2-allyloxy-5-methoxyphenyl)propenoate **13** (0.16 g, 0.65 mmol, T_f 650 °C, T_i 160 °C, 0.01 Torr, 30 min) gave 5-methoxybenzo[*b*]furan **1** (0.087 g, 90%), mp 30 °C (from ethanol) (lit.,[7] 34 °C), NMR spectra identical with literature values.[37]

Ethyl 3-(2-allyloxyphenyl)-2-methylpropenoate **16** (0.123 g, 0.5 mmol, T_f 650 °C, T_i 100–120 °C, 0.01 Torr, 20 min) gave 2-methylbenzo[*b*]furan **35** (0.049 g, 75%), bp 115–118 °C (41 Torr) [lit.,[38] 192 °C (744 Torr)] (Found: M^+, 132.0581. C_9H_8O requires *M*, 132.0575); δ_H 7.53–7.43 (2H, m), 7.27–7.19 (2H, m), 6.39 (1H, apparent quintet, ^4J and ^5J 1.0) and 2.48 (3H, d, ^4J 1.0); δ_C 155.27 (q), 154.61 (q), 129.05 (q), 122.90, 122.27, 119.92, 110.48, 102.43 and 13.91; *m/z* 132 (M^+, 87%), 131 (100), 77 (11), 51 (14), 44 (16) and 43 (13). Pyrolysis of the corresponding methyl ester **14** (0.036 g, 0.16 mmol, T_f 650 °C, T_i 100 °C, 0.001 Torr, 45 min) also gave 2-methylbenzo[*b*]furan **35** (identical spectra with those described above) as the major product.

Ethyl 3-(2-allyloxy-5-chlorophenyl)-2-methylpropenoate **18** (0.130 g, 0.5 mmol, T_f 650 °C, T_i 100–120 °C, 0.01 Torr, 20 min) gave 5-chloro-2-methylbenzo[*b*]furan **36** (0.066 g, 85%), bp 75–80 °C (20 Torr) [lit.,[39] 128–130 °C (25 Torr)] (Found: M^+, 168.0178 and 166.0177. $C_9H_7{}^{37}Cl$ and $C_9H_7{}^{35}Cl$ require *M*, 168.0156 and 166.0185 respectively); δ_H 7.42 (1H, m), 7.30 (1H, m), 7.14 (1H, m), 6.31 (1H, q, ^4J 0.9) and 2.44 (3H, d, ^4J 0.9); δ_C 156.96 (q), 152.95 (q), 130.41 (q), 127.77 (q), 123.00, 119.55, 111.38, 102.20 and 13.98; *m/z* 168 (M^+, 30%), 166 (M^+, 100), 165 (67), 131 (21), 103 (13) and 51 (19).

Dimethyl (2-allyloxyphenyl)methylenemalonate **19** (0.335 g, 1.2 mmol, T_f 650 °C, T_i 130 °C, 0.001 Torr, 90 min) gave methyl benzo[*b*]furan-2-carboxylate **37** (0.20 g, 95%), mp 51–52 °C (from hexane) (lit.,[40] 54–55 °C); δ_H 7.68–7.24 (5H, m) and 3.95 (3H, s); *m/z* 176 (M^+, 78%), 145 (100) and 117 (8). No other products were detected.

Methyl (2-allyloxyphenyl)methylene(cyano)acetate **20** (0.134 g, 0.55 mmol, T_f 650 °C, T_i 150 °C, 0.001 Torr, 90 min) gave a colourless solid pyrolysate which was purified by column chromatography on silica (hexane–diethyl ether eluent) and identified by ^{1}H NMR spectroscopy and GC–MS as 2-cyanobenzo[*b*]-furan **38**[41] (0.041 g, 52%); δ_H 7.67 (1H, m) and 7.58–7.31 (4H, m); *m/z* 143 (M^+, 100%). Thermal decomposition prior to sublimation gave rise to a substantial inlet residue (0.029 g).

(2-Allyloxyphenyl)methylenemalononitrile **5** (0.035 g, 0.16 mmol, T_f 650 °C, T_i 110 °C, 0.005 Torr, 30 min) gave a yellow solid (0.011 g, *ca.* 30%) which was not identified, together with some polymeric material.

Ethyl 3-(2-benzyloxyphenyl)but-2-enoate **28** (0.125 g, 0.4 mmol, T_f 650 °C, T_i 140–160 °C, 0.003 Torr, 15 min) gave the crude product which was purified by dry-flash chromatography to give 3-methylbenzo[*b*]furan **39** (0.042 g, 67%), bp 70–80 °C (12 Torr) [lit.,[38] 86 °C (20 Torr)] (Found: M^+, 132.0566. C_9H_8O requires *M*, 132.0609); δ_H 7.60–7.46 (2H, m), 7.44 (1H, t, ^4J 1.3), 7.37–7.28 (2H, m) and 2.29 (3H, d, ^3J 1.3); δ_C 155.13 (q), 141.24, 128.90 (q), 123.93, 122.08, 119.28, 115.48 (q), 111.18 and 7.76; *m/z* 132 (M^+, 98%), 131 (100), 121 (67), 103 (35), 91 (71), 78 (16), 77 (45), 65 (22), 63 (22), 51 (27) and 39 (27).

Methyl 3-(2-allyloxy-1-naphthyl)propenoate **22** (0.102 g, 0.4 mmol, T_f 650 °C, T_i 140–160 °C, 0.002 Torr, 20 min) gave three products which were separated by dry flash chromatography (4% ethyl acetate–hexane; 10% gradient); naphtho[2,1-*b*]furan **40** (0.025 g, 39%), mp 53–55 °C (from light petroleum, bp 80–100 °C) (lit.,[42] 60–61 °C) (Found: M^+, 168.0583. $C_{12}H_8O$ requires *M*, 168.0575); δ_H 8.17 (1H, m), 7.98 (1H, m), 7.79–7.47 (5H, m) and 7.28 (1H, m); δ_C 152.38 (q), 144.05, 130.18 (q), 128.58, 127.68 (q), 126.15, 125.03, 124.34, 123.28, 122.49 (q), 112.37 and 105.44; *m/z* 168 (M^+, 100%), 148 (11), 139 (35), 84 (11) and 39 (53), 2-*allyl*-3H-*naphtho*[2,1-b]*pyran*-3-*one* **42** (0.020 g, 21%) (not purified further) (Found: M^+, 236.0836. $C_{16}H_{12}O_2$ requires *M*, 236.0837); δ_H 8.24 (1H, s), 8.21 (1H, d, ^3J 10.0), 7.92–7.85 (2H, m), 7.70–7.49 (2H, m), 7.42 (1H, d, ^3J 9.0), 6.05 (1H, m), 5.34–5.23 (2H, m) and 3.44–3.40 (2H, m); δ_C 161.50 (q), 152.36 (q), 134.60, 133.79, 131.81, 130.14 (q), 128.81, 127.79, 126.96 (q), 125.72, 121.34, 118.15, 116.61, 113.25 (q) and 34.75 (one quaternary carbon not apparent); *m/z* 236 (M^+, 100%), 235 (22), 221 (11), 208 (19), 207 (25), 181 (40), 178 (13), 165 (12), 152 (27), 139 (13) and 89 (12) and 3*H*-naphtho[2,1-*b*]pyran-3-one **41** (0.010 g, 13%), mp 104–106 °C (from ethanol) (lit.,[43] 117–118 °C) (Found: M^+, 196.0531. $C_{13}H_8O_2$ requires *M*, 196.0524); δ_H 8.48 (1H, d, ^3J 9.8), 8.22 (1H, d, ^3J 8.3), 8.00–7.82 (2H, m), 7.72–7.42 (3H, m) and 6.75 (1H, d, ^3J 9.8); δ_C 160.82 (q), 153.77 (q), 139.00, 133.02, 130.16 (q), 128.90, 128.18, 125.95, 121.24, 116.96, 115.53 and 112.87 (q) (one quaternary carbon not apparent); *m/z* 196 (M^+, 100%), 195 (11), 168 (69), 139 (42), 84 (15), 70 (12), 69 (13) and 63 (12).

Methyl 3-(2-benzyloxy-1-naphthyl)propenoate **24** (0.130 g, 0.4 mmol, T_f 650 °C, T_i 140–160 °C, 0.001 Torr, 20 min) gave three products which were separated by dry flash chromatography (4% ethyl acetate–hexane; 10% gradient); naphtho-[2,1-*b*]furan **40** (0.038 g, 55%), mp 54–56 °C (from light petroleum, bp 80–100 °C) (lit.,[42] 60–61 °C) (Found: M^+, 168.0576. $C_{12}H_8O$ requires *M*, 168.0575); ^{1}H NMR and mass spectra as above, 2-*benzyl*-3H-*naphtho*[2,1-b]*pyran*-3-*one* **45** (0.008 g, 7%) (Found: M^+, 286.1000. $C_{20}H_{14}O_2$ requires *M*, 286.0993); δ_H 8.09 (1H, s), 8.04 (1H, d, ^3J 8.2), 7.93–7.85 (2H, t), 7.61–7.29 (8H, m) and 4.00 (2H, s); δ_C 161.62 (q), 152.38 (q), 137.67 (q), 135.02, 131.89, 130.12 (q), 129.20, 128.79, 128.67, 128.34 (q), 127.75, 126.74, 125.70, 121.26, 116.61, 113.25 (q) and 36.77 (one quaternary carbon not apparent); *m/z* 286 (M^+, 100%), 258 (12), 257 (29) and 181 (21) and 3*H*-naphtho[2,1-*b*]pyran-3-one **41** (0.009 g, 11%), mp 106–108 °C (from ethanol) (lit.,[43] 117–118 °C) (Found: M^+, 196.0524. $C_{13}H_8O_2$ requires *M*, 196.0524); ^{1}H NMR and mass spectra as above.

Methyl 3-(2-isopropoxy-1-naphthyl)propenoate **23** (0.148 g, 0.5 mmol, T_f 750 °C, T_i 160–180 °C, 0.001 Torr, 20 min) gave two products which were separated by dry flash chromatography (4% ethyl acetate–hexane; 10% gradient). Naphtho-[2,1-*b*]furan **40** (0.054 g, 59%) mp 52–55 °C (lit.,[42] 60–61 °C) (Found: M^+, 168.0574. $C_{12}H_8O$ requires *M*, 168.0575); ^{1}H and ^{13}C NMR and mass spectra as above and 3*H*-naphtho[2,1-*b*]-pyran-3-one **41** (0.034 g, 32%), mp 107–109 °C (from ethanol) (lit.,[43] 117–118 °C) (Found: M^+, 196.0516. $C_{13}H_8O_2$ requires *M*, 196.0524); ^{1}H and ^{13}C NMR and mass spectra as above.

Ethyl 3-(2-allyloxy-1-naphthyl)-2-methylpropenoate **26** (0.133 g, 0.4 mmol, T_f 650 °C, T_i 120–140 °C, 0.01 Torr, 20 min) gave one major product after purification by dry-flash chromatography (4% ethyl acetate–hexane; 10% gradient) which was identified as 2-methylnaphtho[2,1-*b*]furan **46** (0.071 g, 88%), mp 46–50 °C (from water–ethanol) (lit.,[44] mp 57–58 °C) (Found: M^+, 182.0731. $C_{13}H_{10}O$ requires *M*, 182.0732); δ_H 8.11 (1H, m), 7.98 (1H, m), 7.68–7.47 (4H, m), 6.88 (1H, m) and 2.60 (3H, s); δ_C 154.49 (q), 151.77 (q), 130.11 (q), 128.52, 127.25 (q), 125.75, 124.01, 123.63, 123.29, 111.91, 101.59 and 14.03 (one quaternary carbon not apparent); *m/z* 182 (M^+, 100%), 181 (96), 153 (11), 152 (30), 76 (20) and 63 (12).

Preparation of angelicin

8-Formyl-7-hydroxycoumarin 50.[14] 7-Hydroxycoumarin **49** (20.0 g, 0.123 mol) and hexamethylenetetramine (40.0 g, 0.285 mol) were added to glacial acetic acid (150 cm^3) and stirred at 95 °C for 5.5 h. Aqueous hydrochloric acid [HCl–water = 84:100 (v/v), 300 cm^3] was added and the solution was heated under reflux for 30 min. After cooling, the mixture was added to water (1500 cm^3) and extracted with diethyl ether (1 × 1000 cm^3, 2 × 500 cm^3), the combined organic layers were washed with brine (500 cm^3), dried ($MgSO_4$) and the solvent was removed under reduced pressure. The 8-formyl-7-hydroxy-coumarin **50** (1.58 g, 7%) so obtained had mp 178–180 °C (from ethanol) (lit.,[14] 189–191 °C); δ_H 12.18 (1H, s), 10.57 (1H, d, ^nJ 0.6), 7.64 (1H, d, ^3J 9.6), 7.58 (1H, d, ^3J 8.8), 6.86 (1H, dd, ^3J 8.8 and ^nJ 0.6) and 6.30 (1H, d, ^3J 9.6); δ_C 192.78, 165.36 (q), 158.96 (q), 156.62 (q), 143.23, 135.87, 114.56, 113.27, 110.74 (q) and 108.54 (q); *m/z* 190 (M^+, 100%), 162 (40) and 134 (58).

7-Allyloxy-8-formylcoumarin 51. 8-Formyl-7-hydroxy-coumarin **50** (0.5 g, 2.6 mmol) was allylated as above using allyl bromide (0.34 g, 2.8 mmol) in dimethylformamide (15 cm^3) containing potassium carbonate (0.59 g, 4.3 mmol), and worked up in the usual way to give 7-*allyloxy*-8-*formylcoumarin* **51** (0.48 g, 81%), mp 156–158 °C (from toluene–hexane) (Found: C, 67.3; H, 4.3. $C_{13}H_{10}O_4$ requires C, 67.85; H, 4.35%); δ_H 10.64 (1H, s), 7.63 (1H, d, ^3J 9.6), 7.60 (1H, d, ^3J 8.8), 6.91 (1H, d, ^3J 8.8), 6.30 (1H, d, ^3J 9.6), 6.04 (1H, m), 5.35–5.51 (2H, m) and 4.73 (2H, m); δ_C 186.64, 162.24 (q), 159.40 (q), 155.64 (q), 142.91, 133.87, 131.24, 118.53, 113.93, 112.84 (q) 112.51 (q), 109.20 and 69.87; *m/z* 230 (M^+, 5%), 189 (100) and 41 (88).

Methyl 3-(7-allyloxycoumarin-8-yl)propenoate 52. 7-Allyl-oxy-8-formylcoumarin **51** (0.46 g, 2.0 mmol) was reacted overnight with methyl (triphenylphosphoranylidene)acetate in dichloromethane as described above, and the product was

purified by dry flash chromatography on silica to give *methyl* 3-(7-*allyloxycoumarin*-8-*yl*)*propenoate* **52** (0.27 g, 47%), mp 142–144 °C (from ethanol) (Found: C, 66.6; H, 4.4. $C_{16}H_{14}O_5$ requires C, 67.15; H, 4.9%); δ_H 8.11 (1H, d, ^3J 16.4), 7.60 (1H, d, ^3J 9.6), 7.38 (1H, d, ^3J 8.7), 7.06 (1H, d, ^3J 16.4), 6.85 (1H, d, ^3J 8.7), 6.25 (1H, d, ^3J 9.6), 6.05 (1H, m), 5.37 (2H, m), 4.71 (2H, m) and 3.79 (3H, s); δ_C 167.94 (q), 160.29 (q), 159.98 (q), 153.65 (q), 143.40, 132.50, 131.70, 129.65, 123.44, 118.59, 113.33, 112.73 (q), 111.57 (q), 108.69, 69.83 and 51.52; *m/z* 286 (M^+, 54%), 227 (99), 226 (64), 214 (34), 201 (54), 186 (59), 158 (61) and 41 (100).

2*H*-Furo[2,3-*h*]-1-benzopyran-2-one (angelicin) 2. Methyl 3-(7-allyloxycoumarin-8-yl)propenoate **52** was pyrolysed under FVP conditions (0.048 g, 0.16 mmol, T_f 650 °C, T_i 180 °C, 0.001 Torr, 40 min) to give angelicin **2** (0.014 g, 45%) mp 139–141 °C (from methanol) (lit.,[7] 140 °C); δ_H 7.80 (1H, d, ^3J 9.6), 7.68 (1H, d, ^3J 2.2), 7.42 (1H, dd, ^3J 8.5 and ^5J 0.8), 7.37 (1H, d, ^3J 8.5), 7.11 (1H, dd, ^3J 2.2 and ^5J 0.8) and 6.38 (1H, d, ^3J 9.6); δ_C 160.71 (q), 157.22 (q), 148.36 (q), 145.75, 144.39, 123.69, 116.79 (q), 113.98, 113.38 (q), 108.68 and 103.97. A minor non-volatile product of this pyrolysis was identified as 9-*allyl*-2H,8H-*benzo*[1,2-b;3,4-b′]*dipyran*-2,8-*dione* **53** (Found: M^+, 254.0584. $C_{15}H_{10}O_4$ requires *M*, 254.0579); δ_H 8.09 (1H, m), 7.74 (1H, d, ^3J 9.6), 7.55 (1H, d, ^3J 8.7), 7.24 (1H, dd, ^3J 8.7 and ^nJ 0.6), 6.44 (1H, d, ^3J 9.6), 5.95 (1H, m), 5.24 (2H, m) and 3.36 (2H, m); *m/z* 254 (M^+, 45%), 226 (24), 186 (100) and 158 (93).

3-Benzyloxy-5-(methylthio)thiophene 57 (*cf.* ref. 22)

A stirred suspension of sodium hydride (0.72 g, 0.03 mol) in *N*,*N*-dimethylimidazolidinone (DMI) (25 cm^3) was prepared under nitrogen. A solution of 3-hydroxy-5-(methylthio)-thiophene[21] **56** (1.46 g, 0.01 mol) in DMI (20 cm^3) and a solution of benzyl toluene-*p*-sulfonate (2.62 g, 0.01 mol) in DMI (20 cm^3) were then added dropwise and the mixture was stirred for 6 h. Water (50 cm^3) was added and the mixture was extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed with water (3 × 50 cm^3) and dried ($MgSO_4$). Removal of the solvent gave a mixture of two products, in which *O*-alkylation and *O*,*C*-dialkylation respectively had taken place. These products were separated by careful bulb to bulb distillation to yield the pure 3-*benzyloxy*-5-(*methylthio*)*thiophene* **57** (0.92 g, 39%), bp 120–125 °C (0.05 Torr) (Found: M^+, 236.0326. $C_{12}H_{12}OS_2$ requires *M*, 236.0330); δ_H 7.50–7.35 (5H, m), 6.89 (1H, d, ^4J 1.8), 6.31 (1H, d, ^4J 1.8), 5.02 (2H, s) and 2.53 (3H, s); δ_C 156.25 (q), 136.38 (q), 128.32, 127.87, 127.35, 122.24, 99.79, 71.58 and 21.05 (one quaternary carbon not apparent); *m/z* 236 (M^+, 10%), 123 (17), 117 (11), 92 (100), 91 (100), 89 (15), 85 (19), 60 (13), 51 (15), 45 (44), 41 (10) and 39 (24).

5-[(3-Benzyloxy-5-methylthio-2-thienyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 60

A solution of freshly prepared 2,2-dimethyl-5-methoxymethylene-1,3-dioxane-4,6-dione **59** (0.65 g, 3.5 mmol) in acetonitrile (20 cm^3) was added to a stirred solution of 3-benzyloxy-5-(methylthio)thiophene **57** (0.80 g, 3.4 mmol) in acetonitrile (10 cm^3). The mixture was then stirred for 2 days. TLC showed that reaction was complete and the solid was filtered to give the crude product (0.87 g, 64%). This was then recrystallised from ethanol to give 5-[(3-*benzyloxy*-5-*methylthio*-2-*thienyl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **60** (0.62 g, 42%), mp 206–208 °C (from ethanol) (Found: C, 58.45; H, 4.70%; M^+, 390.0608. $C_{19}H_{18}O_5S_2$ requires C, 58.45; H, 4.70%; *M*, 390.0595); δ_H 8.77 (1H, s), 7.36 (5H, s), 6.63 (1H, s), 5.22 (2H, s), 2.63 (3H, s) and 1.70 (6H, s); δ_C 168.05 (q), 164.28 (q), 163.44 (q), 162.79 (q), 141.78, 134.76 (q), 128.75, 128.55, 127.18, 115.69 (q), 110.74, 103.70 (q), 98.37 (q), 73.77, 27.10 and 16.60; *m/z* 390 (M^+, 7%), 332 (22), 226 (15), 225 (15), 198 (31), 92 (12), 91 (100) and 65 (12).

Methyl 3-(3-benzyloxy-5-methylthio-2-thienyl)propenoate 54 (*cf.* ref. 24)

5-[(3-Benzyloxy-5-methylthio-2-thienyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione **60** (0.20 g, 5 mmol) was dissolved in methanol (5 cm^3) and a solution of sodium methoxide [from sodium (0.023 g, 1 mmol) in methanol (5 cm^3)] was added. The reaction mixture was then stirred at room temperature for 1 h and was poured into water (20 cm^3) and acidified with hydrochloric acid. The acid solution was extracted with dichloromethane (3 × 20 cm^3), the combined extracts were dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give crude 3-(3-benzyloxy-5-methylthio-2-thienyl)-2-methoxycarbonylpropenoic acid **61** (0.160 g, 88%), mp 115–120 °C (decomp.); δ_H 8.72 (1H, s), 7.39 (5H, s), 6.63 (1H, s), 5.22 (2H, s), 3.86 (3H, s) and 2.63 (3H, s), OH not apparent; δ_C 171.83 (q), 166.65 (q), 166.25 (q), 161.13 (q), 140.97, 135.33 (q), 128.65, 128.38, 126.93 (q), 115.39 (q), 110.81, 101.88 (q), 73.43, 52.85 and 16.60. This compound was used directly in the next stage. Bulb to bulb distillation gave the decarboxylated product, *methyl* 3-(3-*benzyloxy*-5-*methylthio*-2-*thienyl*)*propenoate* **54** (0.121 g, 76%), bp 120–125 °C (0.05 Torr) (Found: M^+, 320.0523. $C_{16}H_{16}O_3S_2$ requires *M*, 320.0541); δ_H 7.82 (1H, d, ^3J 15.7), 7.38 (5H, s), 6.70 (1H, s), 5.99 (1H, d, ^3J 15.7), 5.09 (2H, s), 3.74 (3H, s) and 2.50 (3H, s); δ_C 167.65 (q), 157.37 (q), 141.44 (q), 135.98 (q), 133.42, 128.52, 128.15, 127.20, 118.00 (q), 117.23, 112.37, 73.22, 51.26 and 19.42; *m/z* 320 (M^+, 42%), 288 (10), 261 (15), 170 (10) and 91 (100).

Methyl 2-methoxycarbonyl-3-(3-benzyloxy-5-methylthio-2-thienyl)propenoate 55 (*cf.* ref. 24)

5-[(3-Benzyloxy-5-methylthio-2-thienyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione **60** (0.200 g, 0.5 mmol) was dissolved in methanol (5 cm^3) and a solution of sodium methoxide [from sodium (0.023 g, 1 mmol) in methanol (5 cm^3)] was added. The reaction mixture was then stirred at room temperature for 1 h. The methanol was then removed on a rotary evaporator and the residual anion was dissolved in dimethylformamide (10 cm^3). Potassium carbonate (0.069 g, 0.5 mmol) and methyl iodide (0.07 g, 0.031 cm^3, 0.5 mmol) were added and the mixture was stirred overnight. Water (20 cm^3) was added, and the mixture was extracted with diethyl ether (3 × 20 cm^3). The combined extracts were washed with water (3 × 40 cm^3) and dried ($MgSO_4$). The solvent was then removed on a rotary evaporator to yield *methyl* 2-*methoxycarbonyl*-3-(3-*benzyloxy*-5-*methylthio*-2-*thienyl*)*propenoate* **55** (0.155 g, 82%), bp 130–135 °C (0.05 Torr) (Found: M^+, 378.0594. $C_{18}H_{18}O_5S_2$ requires *M*, 378.0596); δ_H 8.15 (1H, s), 7.37 (5H, s), 6.64 (1H, s), 5.13 (2H, s), 3.88 (3H, s), 3.78 (3H, s) and 2.53 (3H, s); δ_C 166.97 (q), 165.59 (q), 161.29 (q), 148.15 (q), 135.65 (q), 133.12, 128.57, 128.22, 127.08, 114.63 (q), 114.28, 73.32, 52.20, 52.07 and 18.35 (one quaternary carbon not apparent); *m/z* 378 (M^+, 30%), 302 (15), 271 (10), 256 (10), 228 (10), 111 (20) and 91 (100).

Pyrolysis of methyl 3-(3-benzyloxy-5-methylthio-2-thienyl)-propenoate 54 and methyl 2-methoxycarbonyl-3-(3-benzyloxy-5-methylthio-2-thienyl)propenoate 55

Methyl 3-(3-benzyloxy-5-methylthio-2-thienyl)propenoate **54** (0.054 g, 0.17 mmol, T_f 650 °C, T_i 160–180 °C, 0.002 Torr, 10 min) gave the crude product which was purified by dry-flash chromatography (4% ethyl acetate–hexane; 5% gradient) to remove bibenzyl and give 5-methylthiothieno[3,2-*b*]furan **62** (0.006 g, 21%); δ_H 7.55 (1H, d, ^3J 2.0), 7.15 (1H, d, ^5J 0.8), 6.67 (1H, dd, ^3J 2.0, ^5J 0.8) and 2.60 (3H, s). This compound decomposed after 2 days in chloroform solution, so could not be further characterised.

Methyl 2-methoxycarbonyl-3-(3-benzyloxy-5-methylthio-2-thienyl)propenoate **55** (0.060 g, 0.16 mmol, T_f 650 °C, T_i 160–180 °C, 0.002 Torr, 10 min) gave the crude product which was purified by dry-flash chromatography (4% ethyl acetate–

hexane; 5% gradient) to remove bibenzyl and give 2-methoxycarbonyl-5-methylthiothieno[3,2-*b*]furan **65** (0.008 g, 22%); δ_H 7.41 (1H, d, ^5J 0.6), 7.09 (1H, d, ^5J 0.6), 3.23 (3H, s) and 2.56 (3H, s). This compound decomposed after 2 days in chloroform solution, so could not be further characterised.

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