A novel method for the synthesis of substituted naphthalenes and phenanthrenes

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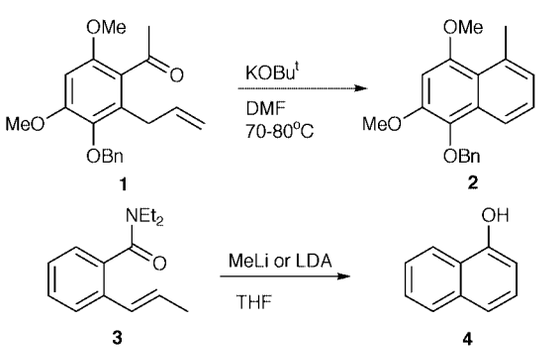
Heating of *o*-allyl-substituted acylbenzenes with potassium *tert*-butoxide in DMF with simultaneous irradiation from a high-pressure mercury lamp afforded substituted naphthalenes, including arylnaphthalenes. 2-(*o*-Tolyl)-substituted aromatic aldehydes were converted into phenanthrenes under the same conditions. A formal synthesis of tanshinone I has also been achieved.

Introduction

Natural products that contain a naphthalene or phenanthrene nucleus often exhibit biological activity, which makes them attractive targets in organic synthesis.[1–3] However, the regioselective synthesis of multi-substituted compounds of these types is often difficult.[4] Thus there is a need for more efficient and general methods for the regiospecific preparation of highly substituted naphthalene and phenanthrene systems.

In attempting to bring the double bond of 2-allyl-3-benzyloxy-4,6-dimethoxyacetophenone[5] **1** into conjugation by isomerization with potassium *tert*-butoxide in DMF at 70 °C according to a reported procedure,[6] an unexpected product, the 5-methylnaphthalene **2**, was isolated in a moderate yield of 48% (Scheme 1). Examination of the literature showed that this



Scheme 1

cyclization reaction is related to a reaction published by Snieckus and co-workers[7] in which base-induced cyclization of similarly substituted benzamides (*e.g.*, **3**) resulted in the formation of naphthols (*e.g.*, **4**). Our method, by contrast, leads to substituted *naphthalenes* rather than *naphthols*.

In this paper we report the results and full experimental details on the use and generalization of this unusual reaction in the synthesis of substituted naphthalenes and phenanthrenes. Two communications on this work have already been published.[8,9]

Results and discussion

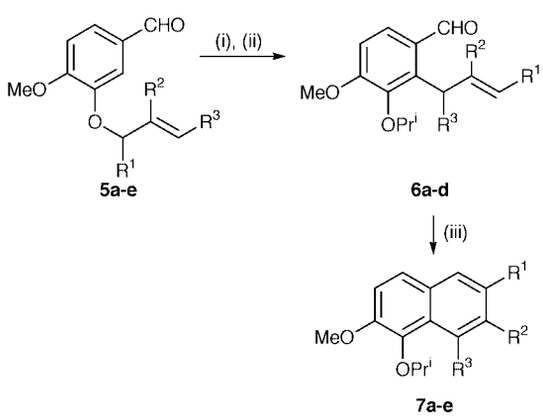
Synthesis of naphthalenes

Allylation of isovanillin with allyl bromide or various substituted allylic halides afforded the corresponding allyl ethers **5a**–**e** (Table 1). Claisen rearrangement gave the corresponding phenols, which were immediately protected as the isopropyl ethers **6a**–**d** (Scheme 2). In the case of the cinnamyl ether **5e**, the isolated product was the styrene **6e**.

Table 1 Yields (%) for the reaction sequence **5** ⟶ **6** ⟶ **7**

Substituents	Allyl ethers **5**	Protected Claisen products **6**	Naphthalenes **7**
a $R^1 = R^2 = R^3 = H$	99	93	81[a]
b $R^1 = R^2 = H$, $R^3 = Me$	98	68	61
c $R^1 = R^3 = H$, $R^2 = Me$	97	62	82
d $R^1 = Me$, $R^2 = R^3 = H$	90	87	69
e $R^1 = R^2 = H$, $R^3 = Ph$	85	51[b]	82

[a] Bubbling oxygen through the solution prior to irradiation gave **7a** (61%), naphthol **12** (2%) and phthalide **22** (4%). [b] Isolated as the styrene **6e**.



Scheme 2 *Reagents and conditions*: (i) DMF or neat, 190 °C; (ii) Pr^iBr, K_2CO_3, 60 °C; (iii) KOBu^t, DMF, 80 °C, *hν*.

Precursor **6a** was selected as a model on which to test our new reaction for the synthesis of naphthalenes. Treatment of **6a** with four mole equivalents of potassium *tert*-butoxide in DMF at 80 °C, as for the formation of **2**, again resulted in a moderate yield (48%) of the desired product **7a**. Evidence for the formation of the product was obtained from the ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum showed signals from the two *ortho*-coupled protons (3-H and 4-H) on the more electron-rich ring at δ 7.24 and 7.53 ($J = 8.9$ Hz) respectively. Signals from another two aromatic protons (5-H and 8-H) appeared as double doublets at δ 7.72 ($J = 8.2$ and 1.3 Hz) and 8.15 ($J = 8.5$

Table 2 Yields (%) for the reaction sequence **6a** ⟶ **9** ⟶ **10**

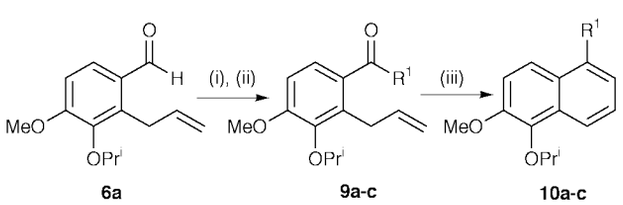
Entry	Ketones **9**	Naphthalenes **10**
a R^1 = Ph	80	79
b R^1 = 1-Naphthyl	77	71
c R^1 = 3,4-$(MeO)_2C_6H_3$	68	31

and 1.3 Hz). Signals from the remaining two aromatic protons (6-H and 7-H) appeared as double double doublets at δ 7.31 (J = 8.2, 6.7 and 1.3 Hz) and 7.42 (J = 8.5, 6.7 and 1.3 Hz). Finally, the methoxy and isopropoxy groups gave rise to signals in their characteristic regions of δ 3.91, and 4.64 and 1.35, respectively. The ^{13}C NMR spectrum also confirmed the assignment, as two characteristic signals for C-4a and C-8a of the naphthalene ring were visible at δ_C 130.4 and 129.7. In addition, high-resolution mass spectroscopy showed the expected molecular ion at *m/z* 216.1151 ($C_{14}H_{16}O_2$ requires *M*, 216.1150).

Conditions were varied in attempts to improve the yield of this reaction. It was found that when **6a** was treated under the same conditions but with simultaneous irradiation from a 400 W high-pressure mercury lamp through a quartz filter, the desired product **7a** was formed in an improved yield of 81%. Attempts at varying the solvent did not seem to facilitate this novel, photochemically mediated reaction. The use of THF under the same conditions yielded only 29% of product **7a**, while using DMSO afforded 33% of **7a**, along with a number of uncharacterized by-products. Owing to the difficulties in removing DMSO from the reaction mixture, this procedure was not pursued. DMF was therefore used exclusively for the formation of the desired naphthalenes.

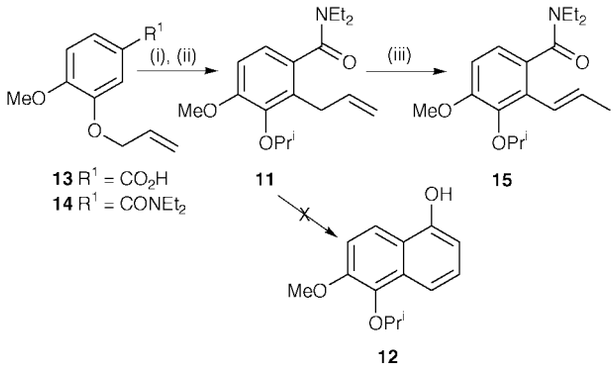
In order to establish the generality of this novel aromatization reaction, the remaining 2-allyl substituted substrates **6b–d** and the styrene **6e** were treated under the same conditions (DMF; 2–4 equiv. potassium *tert*-butoxide; 80 °C; 400 W Hg lamp) and in general gave good to excellent yields of the desired naphthalenes **7b–e** as shown in Table 1. The results demonstrate that introduction of alkyl substituents into positions 6, 7 or 8 of the newly formed aromatic ring of the naphthalene is possible. The last example (**6e** ⟶ **7e**) illustrates the formation of a biaryl compound, a potentially useful transformation in view of the extensive occurrence of such compounds in Nature.[10]

The introduction of substituents at C-5 of the naphthalene requires ketones rather than aldehydes as substrates. Three ketones **9a–c** were made in high yield by treatment of **6a** with the three aryllithiums **8a–c**, followed by oxidation with manganese(IV) oxide in benzene (Scheme 3). The base-induced photochemical cyclization of these compounds gave 5-arylnaphthalenes **10a–c** in moderate to good yields (Table 2).



Scheme 3 *Reagents and conditions*: (i) PhLi **8a**, 1-naphthyllithium **8b**, 3,4-$(MeO)_2C_6H_3Li$ **8c**, THF, −78 °C; (ii) MnO_2, benzene, 25 °C; (iii) KOBu^t, DMF, 80 °C, *hv*.

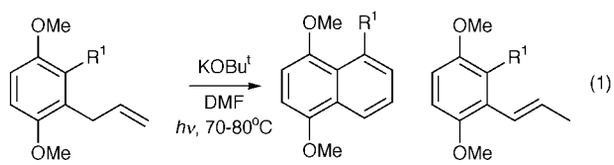
Snieckus and co-workers[7] have shown that aromatic tertiary amides with *ortho*-allyl substituents undergo cyclization in the presence of methyllithium or lithium diisopropylamide (LDA) to afford naphthols (*e.g.*, **3** ⟶ **4**). It therefore seemed logical to subject the amide **11**, which is related to our most studied precursor **6a**, to our cyclization conditions in order to ascertain if the naphthol **12** could be formed. The synthesis of **11**, involving oxidation of aldehyde **6a** to acid **13** followed by conversion



Scheme 4 *Reagents and conditions*: (i) DMF, 190 °C; (ii) Pr^{i}Br, K_2CO_3, 60 °C, 38% (two steps); (iii) KOBu^t, DMF, 80 °C, *hv*, 83%.

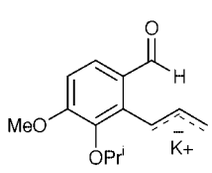
into amide **14**, proceeded smoothly in an overall yield of 79%. Claisen rearrangement of **14** followed by protection of the resulting phenol afforded the desired precursor **11** (Scheme 4). However, exposure of **11** to potassium *tert*-butoxide in DMF at 80 °C with simultaneous irradiation by a 400 W high-pressure mercury lamp yielded only the styrene **15** (83%). Conversely, subjection of our most studied precursor **6a** to the conditions developed by Snieckus (LDA; THF, −78 °C) produced none of the desired naphthalene **7a**. However, treatment of **6a** under Snieckus' conditions with concomitant irradiation by the mercury lamp afforded a low yield of **7a** (12%).

Additionally it was postulated that the corresponding esters might undergo an analogous reaction to afford the related naphthols. This was tested by comparing the potassium *tert*-butoxide-mediated reaction of the aldehyde **16**[11a] with that of the ester **17**.[11b] We found that aldehyde **16** afforded the desired 1,4-dimethoxynaphthalene **18**, but ester **17**, under identical conditions, did not yield the related naphthol **19**. Instead only the styrene **20** was recovered (99%) [reaction (1)].



Mechanism of the reaction

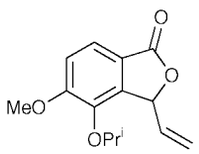
The preceding results suggest that the mechanism for the potassium *tert*-butoxide-mediated reaction might be different from the naphthol-forming reaction described by Snieckus and co-workers.[7] As mentioned previously our reactions proceed poorly (48%) in the presence of base alone, so a conventional anionic mechanism involving an allyl anion intermediate **21**,



while perfectly feasible, is unlikely to be the only reaction pathway. Because our reaction proceeds faster, more cleanly, and in a higher yield when irradiated with UV light, photochemically generated intermediates are almost certainly involved.

To test the feasibility of radical photochemical intermediates in this reaction, we chose to conduct the experiment in the presence of oxygen, as this is known to quench radical

formation.[12a] Using our most studied reaction (**6a** ⟶ **7a**), oxygen was bubbled through the mixture for 5 min before addition of base or irradiation. On performing the cyclization reaction, a lower yield (61%) of **7a** was obtained. Two additional, minor, by-products were also produced in this reaction. The 1-naphthol **12** was isolated in 2% yield. The ^{1}H NMR spectrum showed four *ortho*-coupled protons at δ 7.97, 7.72, 7.28 and 6.67 corresponding to 8-H, 4-H, 7-H and 2-H respectively. The remaining aromatic proton appeared as an overlapping double doublet at δ 7.23. The second by-product (formed in 4% yield) was shown to be the phthalide **22**. It was clear from the ^{1}H



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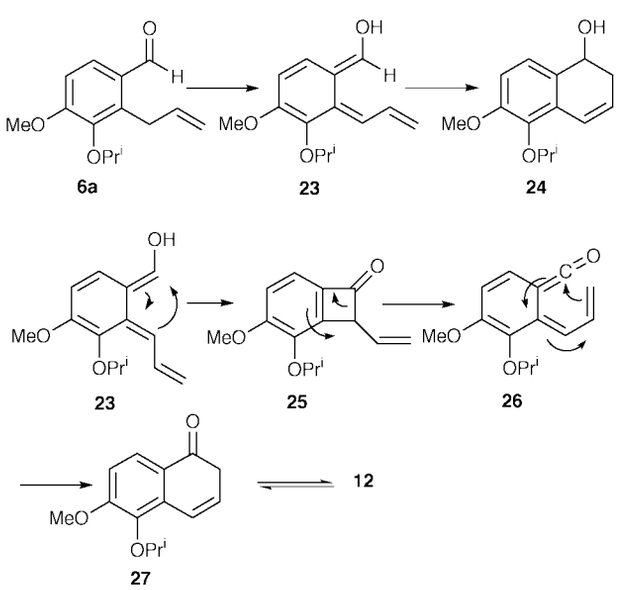
NMR spectrum that the aldehyde proton of the starting material **6a** was absent. However, the ^{13}C NMR spectrum showed a carbonyl carbon at δ_C 169.9, and the IR spectrum showed a carbonyl stretching band at 1760 cm^{-1}, reminiscent of a lactone. It was also evident from the ^{1}H NMR spectrum that the vinyl group from the starting material was still intact, but the benzylic methylene protons from the allyl side-chain of **6a** were replaced by a new peak at δ 5.83, which appeared as a broad doublet (J = 6.1 Hz) and integrated for one proton. This information seemed to suggest that a bond had now been formed between the aldehyde substituent and the benzylic methylene group of the starting material **6a**. High-resolution mass spectrometry indicated a molecular ion at *m*/*z* 248.1035 ($C_{14}H_{16}O_4$ requires *M*, 248.1048), thereby supporting the case for identifying the product as **22**.

We speculate that the *o*-allylbenzaldehydes (or their corresponding anions) may undergo photoenolization[13] to yield the corresponding diene, *e.g.*, **6a** ⟶ **23**. A 6π electrocyclic process to afford the alcohol **24** then follows. Dehydration of this product in the presence of potassium *tert*-butoxide would yield the desired naphthalene **7a**. The formation of both by-products **12** and **22** would appear to substantiate this proposed mechanism as the photoenol intermediate **23** may also undergo an alternative 4π electrocyclic reaction, as shown in Scheme 5, to afford (after oxidation)[12b] the cyclobutanone **25**.[14] This product could then undergo a well known oxygen-insertion reaction[15] to afford the first by-product, lactone **22**. Alternatively, the



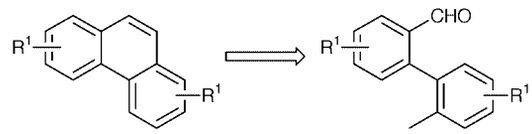
Scheme 5

cyclobutanone **25** could rearrange to the ketene intermediate **26**, ultimately resulting in the formation of the second by-product **12** *via* the ketone **27**.

In conclusion, these results suggest that the reaction could be proceeding through at least two different pathways. However, as this reaction does *not* proceed in the absence of potassium *tert*-butoxide, other mechanisms involving radical intermediates cannot be ruled out at this stage, especially since precedents exist for single-electron transfer from alkoxide bases.[16]

Synthesis of phenanthrenes

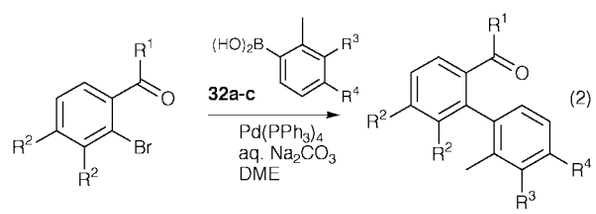
Extending this methodology to the synthesis of other condensed aromatic systems was a logical step in the utilization of this novel methodology. Retrosynthesis of the phenanthrene nucleus **28** would lead to a biaryl precursor of the type **29**.



28 **29**

Biaryl compounds such as **29** could be synthesized using the now well developed Suzuki coupling methodology.[17] If this proposal were successful and resulted in the synthesis of substituted phenanthrenes it would be related to that documented by Snieckus and co-workers, who cyclized biphenyl-2-carboxylates with LDA to produce phenanthrols.[18]

Suzuki coupling of acylbenzenes containing a bromine *ortho* to a carbonyl group (**30** and **31**)[19] with *o*-tolylboronic acids[20–22]

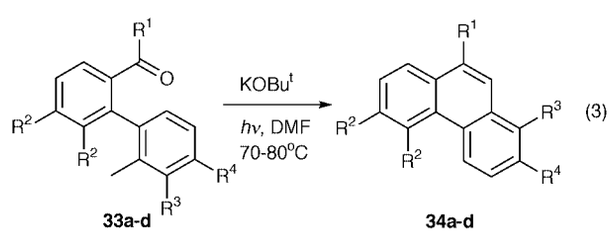


30 R^1 = Me, R^2 = H
31 R^1 = H, R^2 = OMe

33a-d

32a–**c** in DME–ethanol in the presence of a palladium(0) catalyst and aq. sodium carbonate afforded the desired phenanthrene precursors **33a**–**d** in generally high yields as shown in Table 3 [reaction (2)]. Evidence for the formation of the biaryl products **33a**–**d** was obtained from ^{1}H and ^{13}C NMR spectroscopy. For example, **33b** showed two *ortho*-coupled protons at δ 7.83 and δ 7.06 (J = 8.7 Hz) as well as a characteristic aromatic methyl singlet at δ 2.10 in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum exhibited, *inter alia*, signals at δ_C 191.1 and δ_C 20.1 for the aldehyde and aromatic methyl carbons, respectively. High-resolution mass spectroscopy also showed the correct molecular ion at *m*/*z* 256.1107 ($C_{16}H_{16}O_3$ requires *M*, 256.1099).

Reaction of each of the biphenyls **33a**–**d** with potassium



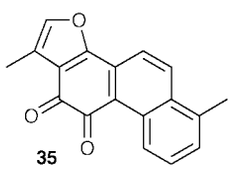
33a-d **34a-d**

tert-butoxide in DMF with simultaneous irradiation from a high-pressure mercury lamp gave the desired substituted phenanthrenes **34a**–**d** in yields of 31–70% (Table 3) [reaction (3)]. It

Table 3 Yields (%) for the reaction sequence **32** ⟶ **33** ⟶ **34**

ArBr	Boronic acid **32**	Biphenyl **33**	Phenanthrene **34**
30	**32a** ($R^3 = R^4 = H$)	**33a** ($R^1 = Me$, $R^2 = R^3 = R^4 = H$); 98	**34a** ($R^1 = Me$, $R^2 = R^3 = R^4 = H$); 31
31	**32a** ($R^3 = R^4 = H$)	**33b** ($R^1 = R^3 = R^4 = H$, $R^2 = OMe$); 86	**34b** ($R^1 = R^3 = R^4 = H$, $R^2 = OMe$); 62
31	**32b** ($R^3 = Me$, $R^4 = H$)	**33c** ($R^1 = R^4 = H$, $R^2 = OMe$, $R^3 = Me$); 96	**34c** ($R^1 = R^4 = H$, $R^2 = OMe$, $R^3 = Me$); 70
31	**32c** ($R^3 = H$, $R^4 = OMe$)	**33d** ($R^1 = R^3 = H$, $R^2 = R^4 = OMe$); 72	**34d** ($R^1 = R^3 = H$, $R^2 = R^4 = OMe$); 61

was clear from spectroscopic evidence, and the absence of aldehyde signals (both ^1H and ^{13}C NMR spectra), that the desired products had been formed. It appears that oxygen substituents on the aromatic rings facilitate phenanthrene formation, as the yield of **34a** is substantially lower than that of **34b–d**. By using this methodology we are now able to synthesize phenanthrenes containing oxygen substituents in positions 2, 5 and 6, as well as alkyl groups in positions 1 and 9 of the phenanthrene nucleus. It should also be noted that the synthesis of **34c** represents a formal synthesis of a naturally occurring biologically active phenanthrene, tanshinone I **35**,[23,24] since Hout and Brassard have demonstrated the conversion of **34c** into **35** in 6 steps.[23]



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Experimental

^1H and ^{13}C NMR spectra were recorded either on a Bruker AC-200 or Bruker DRX 400 spectrometer at the frequency indicated. DEPT, CH-correlated and HMBC spectra were run on some samples to enable complete assignments of all the signals. NMR spectroscopic assignments with the same superscript may be interchanged. *J*-Values are given in Hz. IR spectra were recorded either on a Bruker IFS 25 Fourier Transform spectrometer, or on a Bruker Vector 22 Fourier Transform spectrometer. Mass spectra were recorded on a Kratos MS 9/50, VG 70E MS or a VG 70 SEQ mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyser. Macherey-Nagel Kieselgel 60 (particle size 0.063–0.200 mm) was used for conventional silica gel chromatography, and Macherey-Nagel Kieselgel 60 (particle size 0.040–0.063 mm) was used for preparative flash chromatography. All solvents used for reactions and chromatography were distilled prior to use.

1-Benzyloxy-2,4-dimethoxy-5-methylnaphthalene 2

Potassium *tert*-butoxide (1.23 g, 11.0 mmol) was added to a solution of compound **1**[4] (300 mg, 0.92 mmol) in dry DMF (20 cm^3). The reaction mixture was stirred at 70 °C for 2 h and then at room temperature for a further 18 h. The reaction mixture was diluted with water and made acidic with conc. hydrochloric acid. The organic material was extracted into diethyl ether and separated from the aqueous layer. The organic layer was dried with magnesium sulfate and filtered. The organic solvent was then evaporated under reduced pressure to afford a pale residue, which was subjected to chromatography (10% ethyl acetate–hexane) to afford the *product* **2** as a clear oil (134 mg, 48%) (Found: M^+, 308.1397. $C_{20}H_{20}O_3$ requires *M*, 308.1412); ν_{max}(film)/cm^{-1} 1618, 1597 and 1588 (ArC=C); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.83 (3H, s, $ArCH_3$), 3.84 and 3.94 (each 3H, s, OCH_3), 5.02 (2H, s, OCH_2), 6.59 (1H, s, 3-H), 7.07–7.03 (1H, m, 6-H[a]), 7.58–7.23 (6H, m, Ph and 7-H[a]) and 7.97 (1H, dd, *J* 0.5 and 9.0, 8-H); δ_C (50.32 MHz; $CDCl_3$) 24.5 ($ArCH_3$), 55.5 and 57.1 (each OCH_3), 75.1 (OCH_2), 96.2 (3-C), 119.3 (6-C), 121.0 (ArC), 126.2 (7-C[b]), 126.6 (8-C[b]), 127.7 (ArC), 128.2 (ArC), 128.4 (ArC), 131.2 (ArC), 135.3 (ArC), 135.8 (ArC), 138.0 (ArC), 147.9 (ArC) and 155.3 (ArC); *m*/*z* 308 (M^+, 9%), 217 (100), 189 (51), 174 (14) and 91 (11).

General procedure for preparing substituted 3-allyloxybenzaldehydes 5

Typically, isovanillin (6.00 g, 0.039 mol) and the appropriate allylic halide (0.098 mol) were dissolved in dry DMF (75 cm^3) containing a suspension of potassium carbonate (13.63 g, 0.098 mol). The reaction mixture was stirred at 60 °C for 3–12 h. Once the reaction mixture had cooled, the inorganic solids were filtered off and the solvent was removed under reduced pressure to yield a yellow oil, which was purified by chromatography (10–20% ethyl acetate–hexane). The following compounds were prepared by this method. (Yields are reported in Table 1.)

3-Allyloxy-4-methoxybenzaldehyde 5a. *Pale yellow oil* (Found: M^+, 192.0797. $C_{11}H_{12}O_3$ requires *M*, 192.0786); ν_{max}(film)/cm^{-1} 2840 (OCH_3), 1690 (C=O), 1649 and 1597 (ArC=C), 1438 (CH_2C=C), 1279 (C–O) and 811 (Ar–H oop†); δ_H (200 MHz; $CDCl_3$; Me_4Si) 3.95 (3H, s, OCH_3), 4.63–4.68 (2H, m, OCH_2CH=CH_2), 5.28–5.50 (2H, m, OCH_2CH=CH_2), 6.00–6.16 (1H, m, OCH_2CH=CH_2), 6.99 (1H, d, *J* 8.2, 5-H), 7.40 (1H, d, *J* 1.9, 2-H), 7.46 (1H, dd, *J* 1.9 and 8.2, 6-H) and 9.83 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 55.9 (OCH_3), 69.4 (OCH_2CH=CH_2), 110.5 (5-C), 110.6 (2-C), 118.2 (OCH_2-CH=CH_2), 126.5 (6-C), 129.7 (1-C), 132.3 (OCH_2CH=CH_2), 148.2 (4-C[a]), 154.6 (3-C[a]) and 190.5 (CHO); *m*/*z* 192 (M^+, 88%), 177 (13), 151 (100), 95 (74), 77 (39) and 41 (44).

3-(But-2-enyloxy)-4-methoxybenzaldehyde 5b. A mixture of *Z* and *E* isomers (ratio 1 : 4); *pale yellow oil* (Found: M^+, 206.0931. $C_{12}H_{14}O_3$ requires *M*, 206.0943); ν_{max}(film)/cm^{-1} 2840 (OCH_3), 1687 (C=O), 1594 and 1511 (ArC=C), 1436 (CH_2C=C), 1272 (C–O) and 810 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) (*E* product) 1.74–1.77 (3H, m, OCH_2CH=$CHCH_3$), 3.95 (3H, s, OCH_3), 4.58 (2H, dd, *J* 1.8 and 6.1, OCH_2CH=$CHCH_3$), 5.74–5.81 and 5.87–5.92 (2H, each m, OCH_2CH=$CHCH_3$), 6.98 (1H, d, *J* 8.2, 5-H), 7.41 (1H, d, *J* 1.8, 2-H), 7.45 (1H, dd, *J* 1.8 and 8.2, 6-H) and 9.83 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 17.7 (OCH_2CH=$CHCH_3$), 56.0 (OCH_3), 69.4 (OCH_2CH=$CHCH_3$), 110.4 (5-C), 110.5 (2-C), 125.2 (OCH_2CH=$CHCH_3$), 126.5 (6-C), 129.85 (1-C), 131.3 (OCH_2CH=$CHCH_3$), 148.5 (4-C[a]), 154.7 (3-C[a]) and 190.7 (CHO); δ_H (400 MHz; $CDCl_3$; Me_4Si) (*Z* product) 1.74–1.77 (3H, m, OCH_2CH=$CHCH_3$), 3.95 (3H, s, OCH_3), 4.72 (2H, dd, *J* 0.9 and 5.6, OCH_2CH=$CHCH_3$), 5.73–5.81 (2H, m, OCH_2CH=$CHCH_3$), 6.99 (1H, d, *J* 8.2, 5-H), 7.42 (1H, d, *J* 1.9, 2-H), 7.46 (1H, dd, *J* 1.9 and 8.2, 6-H) and 9.84 (1H, s, CHO); δ_C (100.625 MHz) 13.2 (OCH_2CH=$CHCH_3$), 56.0 (OCH_3), 64.5 (OCH_2CH=$CHCH_3$), 110.4 (5-C), 110.5 (2-C), 124.8 (OCH_2CH=$CHCH_3$), 126.6 (6-C), 129.1 (OCH_2-CH=$CHCH_3$), 129.9 (1-C), 148.5 (4-C[a]), 154.7 (3-C[a]) and 190.7 (CHO); *m*/*z* 206 (M^+, 16%), 153 (16), 149 (5) and 55 (100).

4-Methoxy-3-(2-methylprop-2-enyloxy)benzaldehyde 5c. *Pale yellow oil* (Found: M^+, 206.0945); ν_{max}(film)/cm^{-1} 2840 (OCH_3), 1686 (C=O), 1586 and 1510 (ArC=C), 1437 [$CH_2C(CH_3)$=C], 1286 (C–O) and 811 (Ar–H, oop); δ_H (400 MHz; $CDCl_3$; Me_4Si)

† oop = out-of-plane deformation.

1.84 [3H, s, $OCH_2C(CH_3)=CH_2$], 3.96 (3H, s, OCH_3), 4.57 [2H, s, $OCH_2C(CH_3)=CH_2$], 5.01 and 5.13 [each 1H, s, one of $OCH_2C(CH_3)=CH_2$], 6.98 (1H, d, *J* 8.2, 5-H), 7.40 (1H, d, *J* 1.9, 2-H), 7.45 (1H, dd, *J* 1.9 and 8.2, 6-H) and 9.83 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 19.2 [$OCH_2C(CH_3)=CH_2$], 56.1 (OCH_3), 72.4 [$OCH_2C(CH_3)=CH_2$], 110.7 (5-C), 111.1 (2-C), 113.1 [$OCH_2C(CH_3)=CH_2$], 126.6 (6-C), 129.9 (1-C), 134.0 [$OCH_2C(CH_3)=CH_2$], 148.6 (4-C[a]), 154.9 (3-C[a]) and 190.8 (CHO); *m*/*z* 206 (M^+, 44%), 191 (8), 177 (10), 163 (5), 151 (46), 95 (29), 91 (3), 77 (18) and 55 (100).

4-Methoxy-3-(1-methylprop-2-enyloxy)benzaldehyde 5d. *Pale yellow oil* (Found: M^+, 206.0930); ν_{max}(film)/cm^{-1} 2840 (OCH_3), 1687 (C=O), 1594 and 1509 (ArC=C), 1435 ($CH(CH_3)$-$CH=CH_2$), 1266 (C–O) and 811 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.51 [3H, d, *J* 6.4, $OCH(CH_3)CH=CH_2$], 3.95 (3H, s, OCH_3), 4.89 [1H, dq, *J* 6.3 and 6.4, $OCH(CH_3)CH=CH_2$], 5.19 [1H, dd, *J* 1.1 and 10.6, (*E*)-$OCH(CH_3)CH=CH_2$], 5.30 [1H, dd *J* 1.1 and 17.3, (*Z*)-$OCH(CH_3)CH=CH_2$], 5.94 [1H, ddd, *J* 6.3, 10.6 and 17.3, $OCH(CH_3)CH=CH_2$], 6.98 (1H, d, *J* 8.2, 5-H), 7.42 (1H, d, *J* 1.8, 2-H), 7.45 (1H, dd, *J* 1.8 and 8.2, 6-H) and 9.82 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 21.1 [$OCH(CH_3)CH=CH_2$], 56.1 (OCH_3), 76.1 [$OCH(CH_3)CH=CH_2$], 110.9 (5-C), 113.8 [$OCH(CH_3)CH=CH_2$[a]], 116.3 (2-C[a]), 126.5 (6-C), 129.9 (1-C), 138.4 [$OCH(CH_3)CH=CH_2$], 147.8 (4-C[b]), 155.5 (3-C[b]) and 190.8 (CHO); *m*/*z* 206 (M^+, 13%), 191 (1), 152 (100) and 55 (71).

4-Methoxy-3-[(*E*)-3-phenylprop-2-enyloxy]benzaldehyde 5e. *Waxy solid* (Found: M^+, 268.1090. $C_{17}H_{16}O_3$ requires *M*, 268.1100); ν_{max}(film)/cm^{-1} 2839 (OCH_3), 1686, (C=O), 1587 and 1517 (ArC=C), 1436 ($CH_2C=C$) and 1212 (C–O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.96 (3H, s, OCH_3), 4.81 (2H, dd, *J* 1.3 and 6.0, $OCH_2CH=CHPh$), 6.45 (1H, td, *J* 6.0 and 15.9, $OCH_2CH=CHPh$), 6.75 (1H, d, *J* 15.9, $OCH_2CH=CHPh$), 6.99 (1H, d, *J* 8.7, 5-H), 7.25–7.48 (7H, m, Ph, 2- and 6-H) and 9.84 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 56.1 (OCH_3), 69.6 (OCH_2-$CH=CHPh$), 110.7 (5-C), 110.9 (2-C), 123.5 (ArCH), 126.6 (2 × ArCH), 126.8 (6-C), 128.0 ($OCH_2CH=CHPh$), 128.5 (2 × ArCH), 130.0 (1-C), 134.0 ($OCH_2CH=CHPh$), 136.2 (ArC), 148.5 (4-C[a]), 154.8 (3-C[a]) and 190.8 (CHO); *m*/*z* 268 (M^+, 7%), 177 (2), 151 (10), 131 (3), 122 (2), 118 (72), 116 (32), 115 (100) and 91 (53).

General procedure for preparing substituted 2-allyl-3-isopropoxybenzaldehydes 6

Typically, Claisen rearrangement was effected by heating an aldehyde **5** (9.53 mmol) in dry DMF (20 cm^3) at 190 °C with stirring under nitrogen for 40 h. Once the reaction mixture had cooled to 60 °C, potassium carbonate (3.29 g, 23.83 mmol) and isopropyl bromide (1.17 g, 23.83 mmol) were added, and the reaction mixture was stirred for 18 h. Once the reaction mixture had cooled, the inorganic solids were filtered off and the solvent was removed under reduced pressure to yield a yellow oil, which was subjected to chromatography (5–10% ethyl acetate–hexane). The following compounds were prepared by this method. (Yields are reported in Table 1.)

2-Allyl-3-isopropoxy-4-methoxybenzaldehyde 6a. *Colourless oil* (Found: M^+, 234.1251. $C_{14}H_{18}O_3$ requires *M*, 234.1256); ν_{max}(film)/cm^{-1} 2842 (OCH_3), 1684 (C=O), 1637 and 1589 (ArC=C), 1440 ($CH_2C=C$) and 1286 (C–O); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.26 [6H, d, *J* 6.2, $CH(CH_3)_2$], 3.84–3.88 (2H, m, $ArCH_2CH=CH_2$), 3.89 (3H, s, OCH_3), 4.49 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 4.84–5.02 (2H, m, $ArCH_2CH=CH_2$), 5.91–6.05 (1H, m, $ArCH_2CH=CH_2$), 6.88 (1H, d, *J* 8.6, 5-H), 7.61 (1H, d, *J* 8.6, 6-H) and 10.04 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 22.4 [$CH(CH_3)_2$], 28.9 ($ArCH_2CH=CH_2$), 55.6 (OCH_3), 74.9 [$CH(CH_3)_2$], 109.6 (5-C), 115.8 ($ArCH_2CH=CH_2$), 128.0 (6- and 1-C), 136.3 (2-C), 137.1 ($ArCH_2CH=CH_2$), 144.8 (4-C[a]), 157.5 (3-C[a]) and 191.0 (CHO); *m*/*z* 234 (M^+, 27%), 219 (6), 192 (34), 191 (19) and 177 (100).

3-Isopropoxy-4-methoxy-2-(1-methylprop-2-en-yl)benzaldehyde 6b. *Pale yellow oil* (Found: M^+, 248.1403. $C_{15}H_{20}O_3$ requires *M*, 248.1412); ν_{max}(film)/cm^{-1} 2936 (ArC–H), 2883s (CHO), 2833 (OCH_3), 1682 (C=O), 1620 and 1584 (ArC=C), 1439 ($CH_2C=C$), 1243 and 1218 [$CH(CH_3)_2$] and 1288 (C–O); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.26 and 1.32 [each 3H, d, *J* 6.2, $CH(CH_3)_2$], 1.50 [3H, d, *J* 7.2, $ArCH(CH_3)CH=CH_2$], 3.91 (3H, s, OCH_3), 4.51 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 4.48–4.59 [1H, m, $ArCH(CH_3)CH=CH_2$], 5.01 [1H, ddd, *J* 1.2, 2.7 and 10.6, (*E*)-$ArCH(CH_3)CH=CH_2$], 5.11 [1H, ddd, *J* 1.2, 2.7 and 17.5, (*Z*)-$ArCH(CH_3)CH=CH_2$], 6.23 [1H, ddd, *J* 3.9, 10.6 and 17.5, $ArCH(CH_3)CH=CH_2$], 6.91 (1H, d, *J* 8.7, 5-H), 7.75 (1H, d, *J* 8.3, 6-H) and 10.33 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 21.2 [$ArCH(CH_3)CH=CH_2$], 22.4 and 22.5 [$CH(CH_3)_2$], 33.1 [$ArCH(CH_3)CH=CH_2$], 55.7 (OCH_3), 74.8 [$CH(CH_3)_2$], 109.8 (5-C), 113.7 [$ArCH(CH_3)CH=CH_2$], 125.9 (6-C), 128.4 (1-C), 142.2 (4-C[a]), 143.4 [$ArCH(CH_3)CH=CH_2$], 144.1 (2-C[a]), 157.3 (3-C[a]) and 191.2 (CHO); *m*/*z* 248 (M^+, 14%), 233 (9), 219 (2), 206 (31), 191 (100), 178 (9) and 177 (21).

3-Isopropoxy-4-methoxy-2-(2-methylprop-2-enyl)benzaldehyde 6c. *Colourless oil* (Found: M^+, 248.1415); ν_{max}(film)/cm^{-1} 2842 (OCH_3), 1686 (C=O), 1597 and 1586 (ArC=C), 1442 [$CH_2C(CH_3)=CH$], 1269 (C–O) and 811 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.27 [6H, d, *J* 6.2, $CH(CH_3)_2$], 1.83 [3H, s, $ArCH_2C(CH_3)=CH_2$], 3.77 [2H, s, $ArCH_2C(CH_3)=CH_2$], 3.91 (3H, s, OCH_3), 4.29 and 4.77 [each 1H, m, one of $ArCH_2C(CH_3)=CH_2$], 4.46 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 6.91 (1H, d, *J* 8.6, H-5), 7.66 (1H, d, *J* 8.6, H-6) and 10.01 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 22.4 [$CH(CH_3)_2$], 23.3 [$ArCH_2C(CH_3)=CH_2$], 32.5 [$ArCH_2C(CH_3)=CH_2$], 55.7 (OCH_3), 75.0 [$CH(CH_3)_2$], 109.6 (5-C), 111.2 [$ArCH_2C(CH_3)=CH_2$], 126.8 (6-C), 128.3 (1-C), 136.3 (2-C[a]), 145.1 [$ArCH_2C(CH_3)=CH_2$[a]], 145.5 (4-C[a]), 157.5 (3-C[a]) and 190.8 (CHO); *m*/*z* 248 (M^+, 68%), 233 (20), 206 (63), 192 (40), 191 (100), 188 (21), 173 (29), 164 (20), 157 (35), 149 (59) and 91 (20).

2-[(*E*)-But-2-enyl]-3-isopropoxy-4-methoxybenzaldehyde 6d. *Pale yellow oil* (Found: M^+, 248.1411); ν_{max}(film)/cm^{-1} 2852 (OCH_3), 1686 (C=O), 1586 (ArC=C), 1439 [$CH_2CH=CH(CH_3)$], 1280 (C–O) and 810 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.28 [6H, d, *J* 6.2, $CH(CH_3)_2$], 1.60 (3H, tdd, *J* 1.5, 1.6 and 6.4, $ArCH_2CH=CHCH_3$), 3.81 (2H, dqd, *J* 1.5, 1.6 and 5.9, $ArCH_2CH=CHCH_3$), 3.90 (3H, s, OCH_3), 4.50 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 5.37 (1H, tqd, *J* 1.6, 6.4 and 15.3, $ArCH_2CH=CHCH_3$), 5.59 (1H, dtq, *J* 1.6, 5.9 and 15.3, $ArCH_2CH=CHCH_3$), 6.88 (1H, d, *J* 8.6, 5-H), 7.62 (1H, d, *J* 8.6, 6-H) and 10.10 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 17.7 ($ArCH_2CH=CHCH_3$), 22.4 [$CH(CH_3)_2$], 27.8 ($ArCH_2CH=CHCH_3$), 55.9 (OCH_3), 74.8 [$CH(CH_3)_2$], 109.4 (5-C), 126.2 (6-C), 127.5 ($ArCH_2CH=CHCH_3$), 127.9 (1-C), 129.7 ($ArCH_2CH=CHCH_3$), 137.6 (2-C), 144.6 (4-C[a]), 157.6 (3-C[a]) and 191.2 (CHO); *m*/*z* 248 (M^+, 24%), 219 (8), 206 (53), 191 (36), 177 (100), 164 (56), 149 (19) and 91 (12).

3-Isopropoxy-4-methoxy-2-[(*E*)-1-phenylprop-2-enyl]benzaldehyde 6e. *Pale yellow oil* (Found: M^+, 310.1568. $C_{20}H_{22}O_3$ requires *M*, 310.1569); ν_{max}(film)/cm^{-1} 2826 (OCH_3), 1682 (C=O), 1580 (ArC=C), 1439 ($CH_3C=C$), 1277 and 1252 [$(CH_3)_2$-CH] and 1208 (C–O); δ_H (200 MHz; $CDCl_3$; Me_4Si) 0.99 and 1.12 [each 3H, d, *J* 6.2, $CH(CH_3)_2$], 1.63 [3H, d, *J* 7.0, $ArC(Ph)=CHCH_3$], 3.91 (3H, s, OCH_3), 4.37 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 6.51 [1H, q, *J* 7.0, $ArC(Ph)=CHCH_3$], 7.02 (1H, d, *J* 8.6, 5-H), 7.17–7.26 (5H, m, Ph), 7.83 (1H, d, *J* 8.6, 6-H) and 9.84 (1H, s, CHO); δ_C (50.32 MHz; $CDCl_3$) 16.0 [$ArC(Ph)=CHCH_3$], 22.3 [$CH(CH_3)_2$], 55.7 (OCH_3), 74.9 [$CH(CH_3)_2$], 111.0 (5-C), 123.8

(ArCH), 125.9 (2 × ArCH), 126.9 (6-C[a]), 127.2 [ArC(Ph)=*C*HCH$_3$[a]], 128.3 (2 × ArCH[a]), 129.0 (1-C), 134.4 [Ar*C*(Ph)=CHCH$_3$], 138.0 (ArC[b]), 141.6 (2-C[b]), 144.3 (4-C[c]), 158.4 (3-C[c]) and 191.7 (CHO); *m*/*z* 310 (M^+, 43%), 295 (20), 281 (10), 267 (33), 253 (100), 239 (59) and 149 (22).

General procedure for preparing diaryl ketones 9

(a) Preparation of diarylmethanols. Typically, lithium metal (2.0 mmol) was added to dry diethyl ether (20 cm^3) in a Schlenk tube. The bromoarene (2.0 mmol) was added and the reaction mixture was stirred under nitrogen for 18 h. The aryllithium **8** generated in this way was added dropwise through a cannula to a stirred solution of aldehyde **6a** (1.32 mmol) in dry diethyl ether (10 cm^3), and the reaction mixture was stirred at 0 °C for the specified time. The mixture was allowed to warm to room temperature and stirred for a further period under nitrogen. The reaction mixture was diluted with water, the solution was extracted into diethyl ether, and the organic layer was dried with magnesium sulfate. Filtration, and evaporation of the solvent under reduced pressure, afforded a brown residue, which was subjected to chromatography (5–10% ethyl acetate–hexane) to afford the intermediate methanols. The following compounds were prepared by this method. (Yields are reported in Table 2.)

(2-Allyl-3-isopropoxy-4-methoxyphenyl)(phenyl)methanol. (82%) From phenyllithium **8a** and aldehyde **6a** (reaction time 30 min at 0 °C, 3 h at rt), as a *clear oil* (Found: M^+, 312.1718. $C_{20}H_{24}O_3$ requires *M*, 312.1725); ν_{max}(film)/cm^{-1} 3422 (OH), 2836 (OCH$_3$), 1636, 1598 and 1579 (ArC=C), 1437 (CH$_2$CH=CH$_2$), 1272 (C–O) and 700 (Ar–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.24 and 1.27 [each 3H, d, *J* 6.2, CH(C*H*$_3$)$_2$], 2.21 [1H, br s, ArC*H*(OH)], 3.40 (1H, tdd, *J* 1.7, 6.0 and 15.8, ArC*H*$_2$CH=CH$_2$), 3.65 (1H, tdd, *J* 1.9, 5.4 and 15.8, ArC*H*$_2$CH=CH$_2$), 3.80 (3H, s, OCH$_3$), 4.52 [1H, sept, *J* 6.2, C*H*(CH$_3$)$_2$], 4.94 [1H, tdd, *J* 1.7, 3.4 and 17.2, (*Z*)-ArCH$_2$CH=C*H*$_2$], 5.02 [1H, tdd, *J* 1.7, 3.4 and 10.2, (*E*)-ArCH$_2$CH=C*H*$_2$], 5.95 (1H, m, ArCH$_2$C*H*=CH$_2$), 6.01 (1H, br s, OH), 6.75 (1H, d, *J* 8.6, 5-H), 6.98 (1H, d, *J* 8.6, 6-H) and 7.22–7.31 (5H, m, ArH); δ_C (50.32 MHz; $CDCl_3$) 22.5 and 22.6 [CH(*C*H$_3$)$_2$], 30.4 (Ar*C*H$_2$CH=CH$_2$), 55.5 (OCH$_3$), 72.2 [Ar*C*H(OH)Ar], 74.5 [*C*H(CH$_3$)$_2$], 110.2 (5-C), 115.1 (ArCH$_2$-CH=*C*H$_2$), 122.6 (6′-C[a]), 126.7 (2 × ArCH), 127.1 (ArCH[a]), 128.2 (2 × ArCH), 131.9 (1′-C), 135.2 (ArC), 137.5 (ArCH$_2$-*C*H=CH$_2$), 143.6 (2′-C[b]), 144.9 (4′-C[b]) and 152.1 (3′-C[b]); *m*/*z* 312 (M^+, 47%), 294 (9), 270 (16), 252 (34), 237 (14), 193 (100), 105 (28), 91 (21) and 77 (32).

(2′-Allyl-3′-isopropoxy-4′-methoxyphenyl)(1″-naphthyl)-methanol. (77%) From 1-naphthyllithium **8b** (30 min for preparation) and aldehyde **6a** (reaction time 2 h at rt), as a *clear oil* (Found: M^+, 362.1891. $C_{24}H_{26}O_3$ requires *M*, 362.1882); ν_{max}($CHCl_3$)/cm^{-1} 3596 (OH), 2838 (OCH$_3$), 1636, 1598 and 1579 (ArC=C), 1432 (CH$_2$CH=CH$_2$) and 1211 (C–O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.85 and 0.86 [each 3H, d, *J* 6.2, CH(C*H*$_3$)$_2$], 1.96 [1H, br s, ArCH(O*H*)Ar], 3.01 (1H, tdd, *J* 1.6, 6.1 and 15.5, one of ArC*H*$_2$CH=CH$_2$), 3.32 (3H, s, OCH$_3$), 3.38 (1H, tdd, *J* 1.7, 5.7 and 15.5, one of ArC*H*$_2$CH=CH$_2$), 4.14 [1H, sept, *J* 6.2, C*H*(CH$_3$)$_2$], 4.58 [1H, tdd, *J* 1.7, 3.3 and 17.3, (*Z*)-ArCH$_2$CH=C*H*$_2$], 4.62 [1H, tdd, *J* 1.6, 3.3 and 10.3, (*E*)-ArCH$_2$CH=C*H*$_2$], 5.55–5.67 (1H, m, ArCH$_2$C*H*=CH$_2$), 6.19 (1H, d, *J* 8.6, 5′-H), 6.26 [1H, br s, ArC*H*(OH)Ar], 6.36 (1H, d, *J* 8.6, 6′-H), 6.92–6.97 (2H, m, 6″- and 7″-H), 6.99 (1H, dd, *J* 7.1 and 7.6, 3″-H), 7.10 (1H, d, *J* 7.1, 2″-H), 7.34 (1H, d, *J* 8.2, 5″-H[a]), 7.40 (1H, br d, *J* 7.6, 4″-H) and 7.41 (1H, br d, *J* 8.1, 8″-H[a]); δ_C (100.625 MHz; $CDCl_3$) 22.6 and 22.5 [CH(*C*H$_3$)$_2$], 30.7 (Ar*C*H$_2$CH=CH$_2$), 55.3 (OCH$_3$), 69.2 [Ar*C*H(OH)Ar], 74.4 [*C*H(CH$_3$)$_2$], 109.9 (5-C), 115.2 (CH$_2$CH=*C*H$_2$), 122.6 (ArCH), 123.9 (ArCH), 124.1 (ArCH), 125.2 (ArCH), 125.4 (ArCH), 125.9 (ArCH), 128.0 (ArCH), 128.5 (ArCH), 130.8 (ArC), 132.0 (ArC), 133.6 (ArC), 134.4 (ArC), 137.5 (CH$_2$*C*H=CH$_2$), 138.8 (2′-C), 144.9 (4′-C[a]) and 152.2 (3′-C[a]); *m*/*z* 362 (M^+, 72%), 320 (17), 302 (50), 291 (100), 287 (13), 193 (62), 127 (30) and 91 (7).

(2′-Allyl-3′-isopropoxy-4′-methoxyphenyl)(3″,4″-dimethoxyphenyl)methanol. (72%) From 3,4-dimethoxyphenyllithium **8c** (made in THF from bromoveratrole, *n*-butyllithium and TMEDA) and aldehyde **6a** (reaction time 15 min at −78 °C, 30 min at rt), as a *clear oil* (Found: M^+, 372.1935. $C_{22}H_{28}O_5$ requires *M*, 372.1937); ν_{max}(film)/cm^{-1} 3598 (OH), 2838 (OCH$_3$), 1514 (ArC=C), 1439 (CH$_2$CH=CH$_2$), 1267 and 1216 (C–O) and 774 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.25 and 1.27 [each 3H, d, *J* 6.3, CH(C*H*$_3$)$_2$], 2.13 (1H, br s, OH), 3.38 (1H, br dd, *J* 6.1 and 15.8, one of ArC*H*$_2$CH=CH$_2$), 3.65 (1H, br dd, *J* 5.3 and 15.8, one of ArC*H*$_2$CH=CH$_2$), 3.81, 3.82 and 3.86 (each 3H, s, OCH$_3$), 4.54 [1H, sept, *J* 6.3, C*H*(CH$_3$)$_2$], 4.94 [1H, dd, *J* 1.5 and 17.2, (*Z*)-ArCH$_2$CH=C*H*$_2$], 5.01 [1H, dd, *J* 1.5 and 10.2, (*E*)-ArCH$_2$CH=C*H*$_2$], 5.91–6.01 [2H, m, ArCH$_2$C*H*=CH$_2$ and ArC*H*(OH)Ar], 6.78–6.83 (2H, m, 5″- and 6″-H), 6.78 (1H, d, *J* 8.5, 5′-H), 6.87 (1H, s, 2″-H) and 7.04 (1H, d, *J* 8.5, 6′-H); δ_C (100.625 MHz; $CDCl_3$) 22.5 and 22.7 [CH(*C*H$_3$)$_2$], 30.4 (Ar*C*H$_2$CH=CH$_2$), 55.5, 55.8 and 55.9 (each OCH$_3$), 72.1 [Ar*C*H(OH)Ar], 74.5 [*C*H(CH$_3$)$_2$], 110.2 (2″-C[a]), 110.8 (5″-C[a]), 115.1 (5′-C[a] and ArCH$_2$CH=*C*H$_2$), 119.0 (6″-C[b]), 122.4 (6′-C[b]), 131.8 (2′-C[b]), 135.2 (1′-C[b]), 136.3 (1″-C[b]), 137.5 (ArCH$_2$*C*H=CH$_2$[b]), 144.9 (4″-C[c]), 148.2 (4′-C[c]), 148.8 (3″-C[c]) and 152.2 (3′-C[c]); *m*/*z* 372 (M^+, 100%), 355 (24), 330 (45), 313 (59), 312 (60), 301 (70), 271 (88), 193 (63), 192 (35), 165 (68), 151 (56) and 91 (14).

(b) Oxidation of diarylmethanols to diaryl ketones. Typically, a solution of the intermediate alcohol (0.48 mmol) in dry benzene (5 cm^3) was added to a suspension of manganese(IV) oxide (10 mass equiv.) in dry benzene (5 cm^3), and the mixture was stirred at room temperature for 90 min. The reaction mixture was filtered through Celite, the solvent evaporated under reduced pressure, and the residue purified by column chromatography (20% ethyl acetate–hexane) to afford the desired *ketones* **9**. The following compounds were prepared by this method. (Overall yields in two steps from aldehydes **6** are reported in Table 2.)

2′-Allyl-3′-isopropoxy-4′-methoxybenzophenone ***9a***. (97%) *Clear oil* (Found: M^+, 310.1561. $C_{20}H_{22}O_3$ requires *M*, 310.1569); ν_{max}(film)/cm^{-1} 2840 (OCH$_3$), 1657 (C=O), 1589 (ArC=C), 1428 (CH$_2$CH=CH$_2$), 1274 (C–O) and 919 (Ar–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 0.91 [6H, d, *J* 6.2, CH(C*H*$_3$)$_2$], 3.23–3.26 (2H, m, ArC*H*$_2$CH=CH$_2$), 3.48 (3H, s, OCH$_3$), 4.16 [1H, sept, *J* 6.2, C*H*(CH$_3$)$_2$], 4.40–4.45 (2H, m, ArCH$_2$CH=C*H*$_2$), 5.39–5.46 (1H, m, ArCH$_2$C*H*=CH$_2$), 6.37 (1H, d, *J* 8.5, 5′-H), 6.63 (1H, d, *J* 8.5, 6′-H), 7.00–7.04 (2H, m, Ph), 7.12–7.16 (1H, m, Ph) and 7.34–7.36 (2H, m, Ph); δ_C (50.32 MHz; $CDCl_3$) 22.6 [CH(*C*H$_3$)$_2$], 30.7 (Ar*C*H$_2$CH=CH$_2$), 55.6 (OCH$_3$), 74.9 [*C*H(CH$_3$)$_2$], 108.6 (5′-C), 115.4 (ArCH$_2$CH=*C*H$_2$), 125.7 (ArCH[a]), 128.1 (2 × ArCH), 130.2 (2 × ArCH), 132.0 (2′-C), 132.6 (6′-C[a]), 134.6 (ArC[b]), 136.8 (ArCH$_2$-*C*H=CH$_2$), 138.5 (1′-C[b]), 145.3 (4′-C[c]), 154.8 (3′-C[c]) and 197.7 (CO); *m*/*z* 310 (M^+, 25%), 295 (4), 268 (33), 267 (18), 253 (100), 191 (17), 105 (32), 91 (5) and 77 (29).

2′-Allyl-3′-isopropoxy-4′-methoxyphenyl 1″-naphthyl ketone ***9b***. (100%) *Clear oil* (Found: M^+, 360.1720. $C_{24}H_{24}O_3$ requires *M*, 360.1725); ν_{max}(film)/cm^{-1} 2840 (OCH$_3$), 1652 (C=O), 1588 and 1568 (ArC=C), 1428 (CH$_2$CH=CH$_2$), 1212 (C–O) and 786 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 [6H, d, *J* 6.2, CH(C*H*$_3$)$_2$], 3.39 (3H, s, OCH$_3$), 3.39–3.41 (2H, m, ArC*H*$_2$-CH=CH$_2$), 4.13 [1H, sept, *J* 6.2, C*H*(CH$_3$)$_2$], 4.46–4.51 (2H, m, ArCH$_2$CH=C*H*$_2$), 5.51 (1H, tdd, *J* 6.3, 10.4 and 16.9, ArCH$_2$-C*H*=CH$_2$), 6.20 (1H, d, *J* 8.5, 5′-H), 6.60 (1H, d, *J* 8.5, 6′-H), 6.95 (1H, dd, *J* 7.1 and 8.2, 3″-H), 7.05–7.09 (2H, m, 6″- and 7″-H), 7.05 (1H, d, *J* 7.1, 2″-H), 7.43 (1H, m, 5″-H[a]), 7.49 (1H, d, *J* 8.2, 4″-H) and 7.95 (1H, m, 8″-H[a]); δ_C (100.625 MHz; $CDCl_3$) 22.5 [CH(*C*H$_3$)$_2$], 30.7 (Ar*C*H$_2$CH=CH$_2$), 55.5 (OCH$_3$), 74.8 [*C*H(CH$_3$)$_2$], 108.5 (5′-C), 115.3 (ArCH$_2$CH= *C*H$_2$), 124.2

(3″-C), 125.9 (8″-C), 126.2 (7″-C[a]), 127.3 (6″-C[a]), 128.0 (6′-C), 128.2 (5″-C), 129.4 (2″-C[a]), 131.1 (8a″-C[b]), 131.8 (4″-C), 132.9 (4a″-C[b]), 133.7 (1″-C[b]), 135.6 (1′-C[b]), 137.0 ($ArCH_2CH=CH_2$), 137.4 (2′-C), 145.3 (4′-C[c]), 155.5 (3′-C[c]) and 199.0 (CO); *m*/*z* 360 (M^+, 38%), 345 (4), 318 (40), 303 (62), 177 (12), 155 (30), 127 (55), 91 (7) and 45 (100).

(2′-Allyl-3′-isopropoxy-3″,4′,4″-trimethoxybenzophenone ***9c***. (94%) *Clear oil* (Found: M^+, 370.1770. $C_{22}H_{26}O_5$ requires *M*, 370.1780); $\nu_{max}(CHCl_3)/cm^{-1}$ 2840 (OCH_3), 1650 (C=O), 1593 and 1512 (ArC=C), 1418 ($CH_2CH=CH_2$), 1212 (C–O) and 774 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.31 [6H, d, *J* 6.2, $CH(CH_3)_2$], 3.59 (2H, td, *J* 1.5 and 6.2, $ArCH_2CH=CH_2$), 3.88, 3.92 and 3.94 (each 3H, s, OCH_3), 4.57 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 4.81–4.84 (2H, m, $ArCH_2CH=CH_2$), 5.77–5.85 (1H, m, $ArCH_2CH=CH_2$), 6.78 (1H, d, *J* 8.4, 5′-H), 6.85 (1H, d, *J* 8.3, 6″-H), 7.01 (1H, d, *J* 8.4, 6′-H), 7.24 (1H, dd, *J* 1.8 and 8.3, 5″-H) and 7.49 (1H, d, *J* 1.8, 2″-H); δ_C (100.625 MHz; $CDCl_3$) 22.6 and 22.5 [$CH(CH_3)_2$], 31.0 ($ArCH_2CH=CH_2$), 55.6, 55.9 and 56.0 (each OCH_3), 74.8 [$CH(CH_3)_2$], 108.7 (2″-C), 109.6 (5″-C[a]), 111.6 (5′-C[a]), 115.3 ($ArCH_2CH=CH_2$), 124.8 (6″-C[b]), 125.7 (6′-C[b]), 131.3 (2′-C[c]), 132.4 (1″-C[c]), 133.9 (1′-C[c]), 136.7 ($ArCH_2CH=CH_2$), 145.2 (4″-C[d]), 148.8 (4′-C[d]), 153.1 (3″-C[e]), 154.3 (3′-C[e]) and 196.5 (CO); *m*/*z* 370 (M^+, 87%), 355 (11), 339 (5), 339 (5), 328 (57), 313 (100), 297 (56), 190 (16), 175 (17), 165 (46), 149 (17), 138 (28) and 91 (8).

1-Isopropoxy-2-methoxynaphthalene 7a, 5-isopropoxy-6-methoxy-1-naphthol 12 and 4-isopropoxy-5-methoxy-3-vinylisobenzofuran-1(3*H*)-one 22

The aldehyde **6a** (302 mg, 1.28 mmol) was dissolved in dry DMF (20 cm^3) and oxygen was bubbled through the mixture for 5 min. Potassium *tert*-butoxide (288 mg, 2.56 mmol) was added to the reaction mixture, which was heated under nitrogen at 80 °C and irradiated with a high-pressure mercury lamp through a quartz filter for 1.5 h. The reaction mixture was diluted with water and acidified with conc. hydrochloric acid. The organic material was extracted into diethyl ether, and the organic layer was dried with magnesium sulfate. Filtration, and evaporation of the solvent under reduced pressure, afforded a brown residue, which was subjected to chromatography (5% ethyl acetate–hexane) to afford, firstly, the desired *naphthalene* **7a** (164 mg, 61%) as a clear oil. This was spectroscopically identical in all respects with the product obtained as described in the general procedure detailed below.

Starting material **6a** (23 mg) was isolated as the second (recovered) product.

The third product isolated from the column was the *phthalide* **22** (10 mg, 4%) as a pale oil (Found: M^+, 248.1035. $C_{14}H_{16}O_4$ requires *M*, 248.1048); $\nu_{max}(CHCl_3)/cm^{-1}$ 2929 (OCH_3), 1760 (C=O), 1643, 1610 and 1597 (ArC=C), 1278 [$(CH_3)_2CH$], 1218 (C–O) and 768 (Ar–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.26 and 1.31 [each 3H, d, *J* 6.1, $CH(CH_3)_2$], 3.94 (3H, s, OCH_3), 4.68 [1H, sept, *J* 6.1, $CH(CH_3)_2$], 5.34 [1H, ddd, *J* 1.1, 1.2 and 10.3, (*E*)-$CH=CH_2$], 5.57 [1H, ddd, *J* 1.1, 1.2 and 17.1, (*Z*)-$CH=CH_2$], 5.83 (1H, br d, *J* 6.1, 3-H), 6.01 (1H, ddd, *J* 6.1, 10.3 and 17.1, $CH=CH_2$), 7.06 (1H, d, *J* 8.3, 6-H) and 7.60 (1H, d, *J* 8.3, 7-H); δ_C (50.32 MHz; $CDCl_3$) 22.6 and 22.7 [$CH(CH_3)_2$], 56.3 (OCH_3), 74.8 [$CH(CH_3)_2$], 80.0 (3-C), 114.0 (6-C), 118.5 ($CH=CH_2$), 118.8 (7a-C), 121.5 (7-C), 132.5 ($CH=CH_2$), 141.1 (4-C), 141.8 (3a-C), 157.4 (5-C) and 169.9 (1-C); *m*/*z* 248 (M^+, 20%), 206 (100), 205 (12), 179 (32), 151 (73) and 27 (29).

The fourth product was the *1-naphthol* **12** (5.5 mg, 2%), also isolated as a pale oil (Found: M^+, 232.1113. $C_{14}H_{16}O_3$ requires *M*, 232.1099); $\nu_{max}(CHCl_3)/cm^{-1}$ 3690 (OH), 1621 and 1595 (ArC=C), 1211 (C–O) and 750 (Ar–H oop); δ_H (200 MHz; $CHCl_3$; Me_4Si) 1.35 [6H, d, *J* 6.1, $CH(CH_3)_2$], 3.97 (3H, s, OCH_3), 4.63 [1H, sept, *J* 6.1, $CH(CH_3)_2$], 5.34 (1H, br s, OH), 6.67 (1H, d, *J* 7.2, 2-H), 7.23 (1H, dd, *J* 8.6 and 7.2, 3-H), 7.28 (1H, d, *J* 9.2, 7-H), 7.72 (1H, d, *J* 8.6, 4-H) and 7.97 (1H, d, *J* 9.2, 8-H); δ_C (50.32 MHz; $CDCl_3$) 23.0 [$CH(CH_3)_2$], 57.1 (OCH_3), 75.3 [$CH(CH_3)_2$], 106.9 (2-C), 114.2 (3-C[a]), 114.9 (7-C[a]), 118.9 (4-C), 122.2 (8a-C), 127.0 (8-C), 133.0 (4a-C), 141.5 (1-C[b]), 149.9 (5-C[b]) and 154.0 (6-C[b]); *m*/*z* 232 (M^+, 3%), 190 (9), 175 (7) and 149 (100).

General procedure for the cyclization of substituted 2-allylated acylbenzenes 6 and 9 to naphthalenes 7 and 10

Typically, the aldehyde **6** or ketone **9** (0.63 mmol) was dissolved in dry DMF (20 cm^3). Potassium *tert*-butoxide (282 mg, 2.52 mmol) was added, and the reaction mixture was heated under nitrogen at 80 °C for 10 min with simultaneous irradiation with a high-pressure mercury lamp through a quartz filter. The reaction mixture was diluted with water and acidified with conc. hydrochloric acid. The organic material was extracted into diethyl ether, and the organic layer was dried with magnesium sulfate. Filtration, and evaporation of the solvent under reduced pressure, afforded a pale residue, which was subjected to chromatography (5–10% ethyl acetate–hexane) to afford the desired *naphthalenes* **7** and **10**. The following compounds were prepared by this method. (Yields are reported in Tables 1 and 2.)

1-Isopropoxy-2-methoxynaphthalene 7a. *Clear oil* (Found: M^+, 216.1151. $C_{14}H_{16}O_2$ requires *M*, 216.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 2853 (OCH_3), 1626, 1596 and 1573 (C=C), 1270 (C–O) and 802 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.35 [6H, d, *J* 6.1, $CH(CH_3)_2$], 3.91 (3H, s, OCH_3), 4.64 [1H, sept, *J* 6.1, $CH(CH_3)_2$], 7.24 (1H, d, *J* 8.9, 3-H), 7.31 (1H, ddd, *J* 1.3, 6.7 and 8.2, 6-H), 7.42 (1H, ddd, *J* 1.3, 6.7 and 8.5, 7-H), 7.53 (1H, d, *J* 8.9, 4-H), 7.72 (1H, dd, *J* 1.3 and 8.2, 5-H) and 8.15 (1H, dd, *J* 1.3 and 8.5, 8-H); δ_C (50.32 MHz; $CDCl_3$) 22.7 [$CH(CH_3)_2$], 56.8 (OCH_3), 75.3 [$CH(CH_3)_2$], 115.3 (3-C), 122.1 (8-C), 123.6 (4-C), 123.9 (6-C), 125.6 (7-C), 127.4 (5-C), 129.7 (4a-C), 130.4 (8a-C), 140.9 (1-C) and 148.5 (2-C); *m*/*z* 216 (M^+, 38%), 174 (100), 169 (91), 131 (29) and 77 (12).

1-Isopropoxy-2-methoxy-8-methylnaphthalene 7b. *Clear oil* (Found: M^+, 230.1319. $C_{15}H_{18}O_2$ requires *M*, 230.1307); ν_{max}(film)/cm^{-1} 2839 (OCH_3), 1618, 1599 and 1573 (ArC=C), 1269 (C–O) and 815 (Ar–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.27 [6H, d, *J* 6.2, $CH(CH_3)_2$], 2.91 (3H, s, $ArCH_3$), 3.94 (3H, s, OCH_3), 4.77 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 7.15–7.23 (2H, m, 6- and 7-H), 7.23 (1H, d, *J* 8.8, 3-H), 7.51 (1H, d, *J* 8.8, 4-H) and 7.56–7.59 (1H, m, 5-H); δ_C (50.32 MHz; $CDCl_3$) 22.2 [$CH(CH_3)_2$], 25.0 ($ArCH_3$), 56.8 (OCH_3), 74.3 [$CH(CH_3)_2$], 114.8 (3-C), 123.5 (4-C), 124.3 (6-C), 126.3 (7-C), 129.1 (5-C), 129.8 (8-C), 131.0 (4a-C), 133.8 (8a-C), 142.6 (1-C) and 149.7 (2-C); *m*/*z* 230 (M^+, 28%), 188 (89), 173 (68), 149 (100) and 43 (36).

1-Isopropoxy-2-methoxy-7-methylnaphthalene 7c. *Clear oil* (Found: M^+, 230.1304); ν_{max}(film)/cm^{-1} 2938 (OCH_3), 1639, 1601 and 1515 (ArC=C), 1211 (C–O) and 776 (Ar–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.36 [6H, d, *J* 6.2, $CH(CH_3)_2$], 2.50 (3H, d, *J* 0.8, $ArCH_3$), 3.93 (3H, s, OCH_3), 4.63 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 7.16 (1H, dd, *J* 1.9 and 8.4, 6-H), 7.18 (1H, d, *J* 8.9, 3-H), 7.50 (1H, d, *J* 8.9, 4-H), 7.63 (1H, d, *J* 8.4, 5-H) and 7.90 (1H, qd, *J* 0.8 and 1.9, 8-H); δ_C (50.32 MHz; $CDCl_3$) 22.0 ($ArCH_3$), 22.7 [$CH(CH_3)_2$], 56.7 (OCH_3), 75.1 [$CH(CH_3)_2$], 114.3 (3-C), 120.9 (8-C), 123.4 (4-C), 126.2 (6-C), 127.3 (5-C), 128.0 (7-C), 130.5 (4a-C), 135.3 (8a-C), 140.4 (1-C) and 148.6 (2-C); *m*/*z* 230 (M^+, 24%), 188 (82), 173 (56) and 149 (100).

1-Isopropoxy-2-methoxy-6-methylnaphthalene 7d. (Reaction time 15 min); *clear oil* (Found: M^+, 230.1313); ν_{max}(film)/cm^{-1} 2837 (OCH_3), 1603, 1571 and 1503 (ArC=C), 1270 (C–O), 1192 and 1177 [$CH(CH_3)_2$] and 820 (Ar–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.34 [6H, d, *J* 6.2, $CH(CH_3)_2$], 2.45 (3H, s, $ArCH_3$), 3.91 (3H, s, OCH_3), 4.63 [1H, sept, *J* 6.2, $CH(CH_3)_2$],

7.20 (1H, d, *J* 8.9, 3-H), 7.26 (1H, dd, *J* 1.7 and 8.7, 7-H), 7.44 (1H, d, *J* 8.9, 4-H), 7.49 (1H, br s, 5-H) and 8.05 (1H, d, *J* 8.7, 8-H); δ_C (50.32 MHz; $CDCl_3$) 21.4 (Ar*C*H_3), 22.7 [CH(*C*H_3)$_2$], 56.9 (OCH_3), 75.2 [*C*H(CH_3)$_2$], 115.5 (7-C), 122.1 (8-C), 122.9 (4-C), 126.3 (7-C), 128.0 (5-C), 128.6 (6-C), 130.0 (4a-C), 133.3 (8a-C), 141.1 (1-C) and 147.9 (2-C); *m*/*z* 230 (M^+, 28%), 188 (78), 173 (69), 149 (100), 91 (13), 55 (59) and 43 (79).

1-Isopropoxy-2-methoxy-8-phenylnaphthalene 7e. (Reaction time 30 min); *white crystalline solid*, mp 68–69 °C (from ethyl acetate–hexane) (Found: C, 82.02; H, 7.08; M^+, 292.1464. $C_{20}H_{20}O_2$ requires C, 82.02; H, 7.08%; *M*, 292.1463); ν_{max}($CHCl_3$)/cm^{-1} 2935 (OCH_3), 1629, 1597 and 1520 (ArC=C), 1212 (C–O) and 786 (Ar–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 0.58 [6H, d, *J* 6.1, CH(C*H*$_3$)$_2$], 3.91 (3H, s, OCH_3), 4.06 [1H, sept, *J* 6.1, C*H*(CH_3)$_2$], 7.25–7.45 (8H, m, 3-, 6-, 7-H and Ph), 7.64 (1H, d, *J* 9.0, 4-H) and 7.74 (1H, dd, *J* 2.1 and 7.3, 5-H); δ_C (50.32 MHz; $CDCl_3$) 20.9 [CH(*C*H_3)$_2$], 56.3 (OCH_3), 74.3 [*C*H(CH_3)$_2$], 114.2 (3-C), 123.0 (4′-C[a]), 124.5 (6-C[a]), 125.8 (4-C[a]), 126.8 (3′- and 5′-C[b]), 127.5 (4a-C[c]), 127.9 (7-C[d]), 129.8 (2′- and 6′-C[b]), 130.6 (5-C[d]), 130.8 (8a-C[d]), 137.7 (8-C[c]), 141.0 (1′-C[c]), 144.3 (1-C) and 150.4 (2-C); *m*/*z* 292 (M^+, 33%), 250 (100), 235 (34), 218 (31), 202 (2) and 189 (15).

1-Isopropoxy-2-methoxy-5-phenylnaphthalene 10a. (Reaction time 30 min); *clear oil* (Found: M^+, 292.1477); ν_{max}(film)/cm^{-1} 2836 (OCH_3), 1615, 1592 and 1512 (ArC=C), 1213 (C–O) and 786 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.30 [6H, d, *J* 6.2, CH(C*H*$_3$)$_2$], 3.84 (3H, s, OCH_3), 4.59 [1H, sept, *J* 6.2, C*H*(CH_3)$_2$], 7.10 (1H, d, *J* 9.3, 3-H), 7.17 (1H, dd, *J* 1.1 and 6.9, 6-H), 7.28–7.34 (2H, m, *m*′- or *o*′-Hs), 7.34–7.40 (4H, m, *o*′- or *m*′-Hs, *p*′-H, 7-H), 7.51 (1H, d, *J* 9.3, 4-H) and 8.11 (1H, dd, *J* 1.1 and 8.6, 8-H); δ_C (50.32 MHz; $CDCl_3$) 22.8 [CH(C*H*$_3$)$_2$], 56.7 (OCH_3), 75.4 [OC*H*(CH_3)$_2$], 115.0 (3-C), 121.8 (4′-C[a]), 122.1 (8-C[a]), 125.1 (6-C[b]), 125.3 (4-C[b]), 127.1 (7-C), 127.9 (4a-C[c]), 128.1 (3′- and 5′-C[d]), 130.0 (2′- and 6′-C[d]), 130.9 (8a-C[c]), 139.9 (5-C[c]), 140.9 (1′-C[c]), 141.0 (1-C) and 148.3 (2-C); *m*/*z* 292 (M^+, 100%), 277 (1), 251 (65), 249 (20), 235 (54), 202 (8), 189 (31) and 178 (42).

1-Isopropoxy-2-methoxy-5-(1′-naphthyl)naphthalene 10b. (Reaction time 15 min); *clear oil* (Found: M^+, 342.1612. $C_{24}H_{22}O_2$ requires *M*, 342.1620); ν_{max}($CHCl_3$)/cm^{-1} 2943 (OCH_3), 1629, 1590 and 1511 (ArC=C), 1212 (C–O) and 786 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.32 and 1.34 [each 3H, d, *J* 6.2, each one of CH(C*H*$_3$)$_2$], 3.78 (3H, s, OCH_3), 4.61 [1H, sept, *J* 6.2, C*H*(CH_3)$_2$], 6.93 (1H, d, *J* 9.3, 3-H), 6.99 (1H, d, *J* 9.3, 4-H), 7.12–7.19 (1H, m, ArH), 7.23 (1H, dd, *J* 1.2 and 6.9, ArH), 7.30–7.37 (3H, m, ArH), 7.41 (1H, d, *J* 6.9, ArH), 7.43–7.47 (2H, m, ArH), 7.81 (1H, d, *J* 8.4, ArH) and 8.18 (1H, d, *J* 8.5, ArH); δ_C (100.625 MHz; $CDCl_3$) 22.8 and 22.9 [CH(*C*H_3)$_2$], 56.6 (OCH_3), 75.5 [*C*H(CH_3)$_2$], 115.0 (3-C), 122.1 (ArCH), 122.5 (ArCH), 125.3 (2 × ArCH), 125.7 (ArCH), 125.9 (2 × ArCH), 126.6 (ArCH), 127.7 (2 × ArCH), 128.1 (ArCH), 129.1 (4a-C[a]), 130.6 (8a-C[a]), 132.9 (8a′-C[a]), 133.5 (4a′-C[a]), 138.1 (1′-C[b]), 138.7 (5-C[b]), 140.9 (1-C) and 148.3 (2-C); *m*/*z* 342 (M^+, 100%), 301 (67), 299 (13), 267 (36), 255 (29), 239 (53), 226 (32), 215 (9), 149 (36) and 43 (37).

5-(3′,4′-Dimethoxyphenyl)-1-isopropoxy-2-methoxynaphthalene 10c. *Clear oil* (Found: M^+, 352.1661. $C_{22}H_{24}O_4$ requires *M*, 352.1675); ν_{max}($CHCl_3$)/cm^{-1} 2978 and 2935 (OCH_3), 1586 and 1519 (ArC=C), 1213 (C–O), 1094 and 1107 [CH(CH_3)$_2$] and 776 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.39 [6H, d, *J* 6.1, CH(C*H*$_3$)$_2$], 3.89, 3.95 and 3.96 (each 3H, s, OCH_3), 4.68 [1H, sept, *J* 6.1, C*H*(CH_3)$_2$], 6.98 (1H, d, *J* 7.9, 5′-H), 7.02 (1H, d, *J* 1.2, 2′-H), 7.02–7.04 (1H, m, 6′-H), 7.21 (1H, d, *J* 9.3, 3-H), 7.26–7.28 (1H, m, 6-H), 7.46 (1H, dd, *J* 7.0 and 8.5, 7-H), 7.65 (1H, d, *J* 9.3, 4-H) and 8.18 (1H, d, *J* 8.5, 8-H); δ_C (100.625 MHz; $CDCl_3$) 22.8 [CH(*C*H_3)$_2$], 56.0, 56.0 and 56.8 (each OCH_3), 75.5 [*C*H(CH_3)$_2$], 111.0 (5′-C[a]), 113.5 (2′-C[a]), 115.0 (3-C[a]), 121.7 (6′-C[b]), 122.1 (7-C[b]), 122.2 (8-C[b]), 125.0 (6-C[c]), 125.3 (4-C[c]), 128.2 (4a-C[d]), 130.9 (8a-C[d]), 133.8 (1′-C), 139.7 (5-C), 141.0 (1-C), 148.2 (4′-C[e]), 148.3 (2-C[e]) and 148.6 (3′-C[e]); *m*/*z* 352 (M^+, 54%), 311 (34), 310 (100) and 309 (10).

3-Allyloxy-4-methoxybenzoic acid 13

The aldehyde **5a** (563 mg, 2.93 mmol) as a solution in acetone (30 cm^3) was cooled to 0 °C. Jones' reagent (CrO_3; 6.15 mmol, 615 mg and H_2SO_4; 9.84 mmol, 0.52 cm^3 in 1 cm^3 H_2O) was added dropwise. The mixture was stirred at 0 °C for 30 min under nitrogen and then for a further 3 h at rt. The acetone was removed under reduced pressure. To the residue were added water (50 cm^3) and dichloromethane (50 cm^3). The organic layer was removed and the aqueous layer washed with more dichloromethane. The organic layers were combined, dried with magnesium sulfate, and filtered. The dichloromethane was then evaporated under reduced pressure to afford a brown residue, which was subjected to chromatography (50% ethyl acetate–hexane) to afford the *acid* **13** (538 mg, 88%), mp 146–147 °C (from ethyl acetate–hexane) (Found: C, 63.21; H, 5.70. $C_{11}H_{12}O_4$ requires C, 63.44; H, 5.81%); ν_{max}($CHCl_3$)/cm^{-1} 3025br (OH), 2843 (OCH_3), 1686 (C=O), 1601 and 1587 (ArC=C), 1517 (C=C) and 1268 (C–O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.95 (3H, s, OCH_3), 4.68 (2H, td, *J* 1.4 and 5.4, CH_2CH=CH_2), 5.33 [1H, dtd, *J* 1.3, 1.4 and 10.4, (*E*)-CH_2CH=C*H*$_2$], 5.45 [1H, dtd, *J* 1.3, 1.4 and 17.3, (*Z*)-CH_2CH=C*H*$_2$], 6.11 (1H, tdd, *J* 5.4, 10.4 and 17.3, CH_2C*H*=CH_2), 6.93 (1H, d, *J* 8.5, 5-H), 7.61 (1H, d, *J* 2.0, 2-H) and 7.78 (1H, dd, *J* 2.0 and 8.5, 6-H); δ_C (100.625 MHz; $CDCl_3$) 56.0 (OCH_3), 71.5 (*C*H_2CH=CH_2), 110.6 (5-C[a]), 114.3 (2-C[a]), 118.5 (CH_2CH=*C*H_2), 121.6 (1-C), 124.8 (6-C), 132.7 (CH_2*C*H=CH_2), 147.6 (4-C[b]), 154.1 (3-C[b]) and 171.9 (CO).

3-Allyloxy-*N*,*N*-diethyl-4-methoxybenzamide 14

The acid **13** (487 mg, 2.34 mmol) was dissolved in benzene (30 cm^3). Thionyl dichloride (0.21 cm^3, 334 mg, 2.81 mmol) was added dropwise, followed by one drop of DMF. The reaction mixture was heated to reflux for 2 h. The mixture was allowed to cool and diethylamine (0.97 cm^3, 684 mg, 9.36 mmol) was added by syringe. The mixture was stirred at rt for 30 min. To the mixture were added water (50 cm^3) and diethyl ether (100 cm^3). The organic layer was washed with 10% aq. sodium hydroxide. The organic layer was dried with magnesium sulfate and filtered. The solvents were then evaporated under reduced pressure and the residue was subjected to chromatography (50% ethyl acetate–hexane) to afford the *amide* **14** (552 mg, 90%) (Found: M^+, 263.1520. $C_{15}H_{21}NO_3$ requires *M*, 263.1521); ν_{max}(film)/cm^{-1} 2868 (OCH_3), 1630 (C=O), 1587, 1561 and 1518 (ArC=C), 1430 (CH_2C=CH_2), 1259 (C–O) and 755 (Ar–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.18 [6H, br s, CON(CH_2CH_3)$_2$], 3.41 [4H, br s, CON(CH_2CH_3)$_2$], 3.89 (3H, s, OCH_3), 4.61–4.63 (2H, m, CH_2CH=CH_2), 5.27–5.43 (2H, m, CH_2CH=C*H*$_2$), 6.05–6.11 (1H, m, CH_2C*H*=CH_2), 6.86 (1H, d, *J* 8.1, 5-H), 6.94 (1H, d, *J* 1.8, 2-H) and 6.96 (1H, dd, *J* 1.8 and 8.1, 6-H); δ_C (100.625 MHz; $CDCl_3$) 13 [br, CON(CH_2*C*H_3)$_2$], 39 and 44 [br, CON(*C*H_2CH$_3$)$_2$], 55.9 (OCH_3), 69.8 (*C*H_2CH=CH_2), 111.0 (5-C[a]), 112.1 (2-C[a]), 118.0 (CH_2CH=*C*H_2[b]), 119.5 (6-C[b]), 129.4 (1-C), 132.9 (CH_2*C*H=CH_2), 147.6 (4-C[c]), 150.1 (3-C[c]) and 170.9 (CO); *m*/*z* 263 (M^+, 39%), 222 (72), 191 (84), 163 (4), 151 (87), 149 (100), 122 (24) and 57 (30).

2-Allyl-*N*,*N*-diethyl-3-isopropoxy-4-methoxybenzamide 11

The amide **14** (273 mg, 1.04 mmol) was dissolved in DMF (10 cm^3). The mixture was heated under reflux for 20 h. The reaction mixture was cooled to 60 °C, isopropyl bromide (319 mg,

2.59 mmol) and potassium carbonate (358 mg, 2.59 mmol) were added, and the reaction mixture was stirred at 60 °C under nitrogen for a further 20 h. The inorganic salts were removed by filtration and the DMF removed under reduced pressure. The residue was subjected to chromatography (30% ethyl acetate–hexane) to afford the *amide* **11** (120 mg, 38%) (Found: M^+, 305.1988. $C_{18}H_{27}NO_3$ requires *M*, 305.1991); ν_{max}(film)/cm^{-1} 2843 (OCH_3), 1630 (C=O), 1593 and 1575 (ArC=C), 1430 ($CH_2CH=CH_2$), 1288 and 1271 [$(CH_3)_2CH$] and 1219 (C–O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.03 [3H, t, *J* 7.1, $CON(CH_2CH_3)_2$], 1.23 [3H, t, *J* 7.1, $CON(CH_2CH_3)_2$], 1.27 [6H, br s, $CH(CH_3)_2$], 3.02–3.10 [2H, br m, $CON(CH_2CH_3)_2$], 3.20–3.39 [1H, br m, one of $CON(CH_2CH_3)_2$], 3.45 (2H, md, *J* 6.7, $ArCH_2CH=CH_2$), 3.57–3.90 [1H, br m, one of $CON(CH_2CH_3)_2$], 3.83 (3H, s, OCH_3), 4.57 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 4.95 [1H, mdd, *J* 1.8 and 10.0, (*E*)-$ArCH_2CH=CH_2$], 5.04 [1H, mdd, *J* 1.8 and 17.0, (*Z*)-$ArCH_2CH=CH_2$], 5.90 (1H, tdd, *J* 6.7, 10.0 and 17.0, $ArCH_2CH=CH_2$), 6.76 (1H, d, *J* 8.3, 5-H) and 6.86 (1H, d, *J* 8.3, 6-H); δ_C (100.625 MHz; $CDCl_3$) 12.5 and 13.7 [$CON(CH_2CH_3)_2$], 22.6 [$CH(CH_3)_2$], 32.0 ($ArCH_2CH=CH_2$), 38.5 and 43.0 [$CON(CH_2CH_3)_2$], 55.5 (OCH_3), 74.5 [$CH(CH_3)_2$], 109.9 (5-C), 115.2 ($ArCH_2CH=CH_2$), 120.7 (6-C), 130.4 (1-C[a]), 131.2 (2-C[a]), 136.3 ($ArCH_2CH=CH_2$), 145.1 (4-C[b]), 152.8 (3-C[b]) and 170.5 (CO); *m*/*z* 305 (M^+, 15%), 290 (5), 262 (14), 246 (9), 233 (13), 219 (7), 191 (54), 190 (100), 149 (41) and 91 (19).

N,*N*-Diethyl-3-isopropoxy-4-methoxy-2-[(*E*)-prop-1-enyl]-benzamide 15

The amide **11** (58 mg, 0.19 mmol) was dissolved in dry DMF (15 cm^3), and potassium *tert*-butoxide (85 mg, 0.76 mmol) was added under nitrogen while the solution was heated to 80 °C. The reaction mixture was irradiated using a high-pressure mercury lamp through a quartz filter for 6 h. The reaction mixture was then treated as described previously for **7a** to afford a brown residue, which was subjected to chromatography (50% ethyl acetate–hexane) to afford the *styrene* **15** (48 mg, 83%) (Found: M^+, 305.1985. $C_{18}H_{27}NO_3$ requires *M*, 305.1991); ν_{max}(film)/cm^{-1} 1630 (C=O), 1593 and 1570 (ArC=C) and 1290 (C–O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.94 [3H, t, *J* 7.1, one of $CON(CH_2CH_3)_2$], 1.18 [3H, t, *J* 7.1, one of $CON(CH_2CH_3)_2$], 1.25 [6H, br s, $CH(CH_3)_2$], 1.82 (3H, dd, *J* 1.7 and 6.6, $ArCH=CHCH_3$), 2.88–3.01 [2H, br m, $CON(CH_2CH_3)_2$], 3.08–3.22 [1H, br m, one of $CON(CH_2CH_3)_2$], 3.83 (3H, s, OCH_3), 3.85–3.87 [1H, br m, one of $CON(CH_2CH_3)_2$], 4.36 [1H, sept, *J* 6.2, $CH(CH_3)_2$], 6.18 (1H, qd, *J* 6.6 and 16.1, $ArCH=CHCH_3$), 6.49 (1H, qd, *J* 1.7 and 16.1, $ArCH=CHCH_3$), 6.78 (1H, d, *J* 8.4, 5-H) and 6.90 (1H, d, *J* 8.4, 6-H); δ_C (100.625 MHz; $CDCl_3$) 12.3 and 13.5 [$CON(CH_2CH_3)_2$], 19.0 ($ArCH=CHCH_3$), 22.4 [$CH(CH_3)_2$], 38.6 and 42.4 [$CON(CH_2CH_3)_2$], 55.6 (OCH_3), 75.4 [$CH(CH_3)_2$], 110.4 (5-C), 121.9 (6-C), 124.5 ($CH=CHCH_3$[a]), 129.1 (1-C[b]), 130.0 (2-C[b]), 131.3 ($CH=CH-CH_3$[a]), 144.3 (4-C[c]), 153.1 (3-C[c]) and 170.9 (CO); *m*/*z* 305 (M^+, 22%), 262 (35), 219 (36), 191 (100), 131 (20), 103 (29), 72 (14) and 41 (8).

1,4-Dimethoxynaphthalene 18

The aldehyde **17**[11a] (217 mg, 1.05 mmol) was dissolved in dry DMF (10 cm^3). Potassium *tert*-butoxide (177 mg, 1.58 mmol) was added and the reaction mixture heated at 80 °C under nitrogen for 2 h. The reaction mixture was diluted with water and acidified with conc. hydrochloric acid. The organic material was extracted into diethyl ether and then separated from the aqueous layer. The diethyl ether layer was dried with magnesium sulfate and filtered. The diethyl ether was then evaporated under reduced pressure to afford a brown residue which was subjected to chromatography (5% ethyl acetate–hexane) to afford the *naphthalene* **18** (92 mg, 46%) as a white solid, mp 86–87 °C (from methanol), identical in all respects with that reported in the literature (mp 87–88 °C).[25]

Prop-2-enyl 3,6-dimethoxy-2-[(*E*)-prop-1-enyl]benzoate 20

Prop-2-enyl 3,6-dimethoxy-2-(prop-2-enyl)benzoate **17**[11b] (1.223 g, 4.68 mmol) was dissolved in dry DMF (45 cm^3). Potassium *tert*-butoxide (1.05 g, 9.36 mmol) was added to the stirred solution. The reaction mixture was heated under nitrogen at 80 °C and irradiated with a high-pressure mercury lamp through a quartz filter for 15 min under nitrogen. The reaction mixture was quenched with water (100 cm^3), acidified with conc. hydrochloric acid, and the aqueous phase was thoroughly extracted with diethyl ether (5 × 40 cm^3). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated under reduced pressure. Column chromatography (10% ethyl acetate–hexane) afforded the *E-product* **20** (with traces of the *Z*-product) as a yellow oil (1.211 g, 99%) (Found: M^+, 262.1208. $C_{15}H_{18}O_4$ requires *M*, 262.1205); ν_{max}(film)/cm^{-1} 1734 (C=O), 1648 and 1591 (ArC=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.84 [3H, dd, *J* 1.7 and 6.6, $CH=CH(CH_3)$], 3.77 and 3.77 (each 3H, s, OCH_3), 4.79 (2H, ddd, *J* 1.4, 1.4 and 5.8, $CO_2CH_2CH=CH$), 5.26 [1H, ddd, *J* 1.4, 2.8 and 10.4, (*E*)-$OCH_2CH=CH_2$], 5.40 [1H, ddd, *J* 1.4, 2.8 and 17.2, (*Z*)-$OCH_2CH=CH_2$], 5.99 (1H, tdd, *J* 5.8, 10.4 and 17.2, $CO_2CH_2CH=CH$), 6.16 [1H, qd, *J* 6.6 and 16.0, $CH=CH(CH_3)$], 6.40 (1H, qd, *J* 1.7 and 16.0, $ArCH=CH$), 6.73 (1H, d, *J* 9.0, 5-H[a]) and 6.84 (1H, d, *J* 9.0, 4-H[a]); δ_C (100.625 MHz; $CDCl_3$) 19.2 [$CH=CH(CH_3)$], 56.0 (OCH_3), 56.3 (OCH_3), 65.7 ($CO_2CH_2CH=CH$), 109.9 ($CH=CH_2$[a]), 112.1 (5-C[a]), 118.5 (4-C[a]), 123.9 (2-C[b]), 124.1 [$CH=CH(CH_3)$], 125.9 (1-C[b]), 131.5 ($ArCH=CH$[c]), 131.9 ($CO_2CH_2CH=CH_2$[c]), 150.1 (6-C[d]), 151.5 (3-C[d]) and 167.7 (CO); *m*/*z* 262 (M^+, 82%), 221 (100), 205 (40), 193 (54) and 178 (20).

General method for the preparation of boronic acids 32a–c[26]

The appropriate aromatic bromide (25–30 mmol) was dissolved in THF (100 cm^3) and the solution cooled to −78 °C under nitrogen. *n*-Butyllithium (1.1 mol equiv.) was added dropwise, and the mixture stirred at −78 °C for 15 min. Freshly distilled trimethyl borate or triisopropyl borate (3 mol equiv.) was added, and the mixture stirred at −78 °C for 30 min before being warmed to rt and stirred for a further 20 min, after which it was cooled to 0 °C and acidified with 10% aq. hydrochloric acid. The resulting mixture was added to dichloromethane (100 cm^3) and the organic material extracted with dichloromethane (2 × 60 cm^3). The combined organic phases were dried with magnesium sulfate before the solvent was evaporated under reduced pressure to afford off-white crystalline materials (in quantitative yields) that were used without further purification or characterization.

General procedure for the preparation of biaryls 33

Typically, a solution of 2-bromoacetophenone or 2-bromo-3,4-dimethoxybenzaldehyde **31**[19] (1.35 mmol) in DME (5 cm^3) was deoxygenated by passing nitrogen through the mixture for 5 min. The solution was added to $Pd(PPh_3)_4$ (10%; 0.13 mmol) and stirred under nitrogen for 10 min. A solution of 2-methylphenylboronic acid **32a**,[20] 2,3-dimethylphenylboronic acid **32b**[21] or 4-methoxy-2-methylphenylboronic acid **32c**[21] (2.02 mmol) in ethanol (2 cm^3) was deoxygenated and added to the mixture. The mixture was stirred for a further 10 min. 2 M Aq. sodium carbonate (11.46 mmol; 5.7 cm^3) was also deoxygenated and added to the reaction mixture, which was then stirred for 5 min at rt before being heated at reflux for 18 h. The mixture was cooled to rt and then water (20 cm^3) was added. The organic material was extracted by washing this mixture with dichloromethane (3 × 30 cm^3). The combined organic extracts were dried with magnesium sulfate before the solvent was evaporated under reduced pressure to afford a pale residue, which was subjected to chromatography (hexane to 20% ethyl acetate–hexane) to afford the desired biaryls **33**. The following compounds were prepared by this method. (Yields are reported in Table 3.)

1-(2′-Methylbiphenyl-2-yl)ethanone 33a. *Colourless oil* (Found: M^+, 210.1043. $C_{15}H_{14}O$ requires *M*, 210.1045); ν_{max}(film)/cm^{-1} 3059 (ArC–H), 1689 (C=O), 1595 (ArC=C) and 764 (ArC–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.96 (3H, s, ArCH_3), 2.12 (3H, s, COCH_3), 7.10 (1H, d, *J* 7.2, 3′-H), 7.19–7.28 (4H, m, ArH), 7.38–7.43 (1H, m, 5-H[a]), 7.47–7.51 (1H, m, 4-H[a]) and 7.67 (1H, dd, *J* 1.4 and 7.7, 3-H); δ_C (50.32 MHz; $CDCl_3$) 20.1 (Ar*C*H$_3$), 29.7 (CO*C*H$_3$), 125.8 (ArCH), 127.3 (ArCH), 127.9 (ArCH), 128.1 (ArCH), 129.4 (ArCH), 130.2 (ArCH), 130.6 (ArCH), 130.8 (ArCH), 135.5 (2-C), 140.1 (1-C[a]), 140.4 (1′-C[a]), 140.7 (2′-C[a]) and 203.0 (*C*OCH$_3$); *m*/*z* 210 (M^+, 13%), 196 (16), 195 (100), 167 (25), 165 (30), 152 (17), 149 (36) and 43 (20).

5,6-Dimethoxy-2′-methylbiphenyl-2-carbaldehyde 33b. *Colourless oil* (Found: M^+, 256.1107. $C_{16}H_{16}O_3$ requires *M*, 256.1099); ν_{max}(film)/cm^{-1} 2838 (OCH$_3$), 1686 (C=O), 1584 (ArC=C), 1256 (C–O) and 758 (ArC–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.10 (3H, s, ArCH$_3$), 3.54 and 3.98 (each 3H, s, OCH$_3$), 7.06 (1H, d, *J* 8.7, 4-H), 7.17 (1H, dd, *J* 1.0 and 7.3, ArH), 7.23–7.33 (3H, m, ArH), 7.83 (1H, d, *J* 8.7, 3-H) and 9.46 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 20.1 (Ar*C*H$_3$), 55.9 and 60.6 (each OCH$_3$), 111.3 (4-C), 124.5 (ArCH), 125.3 (ArCH), 128.0 (2-C), 128.2 (3-C), 129.8 (ArCH), 130.3 (ArCH), 132.9 (1′-C), 137.0 (1-C), 134.0 (2′-C[a]), 146.0 (5-C[a]), 157.8 (6-C[a]) and 191.1 (CHO); *m*/*z* 256 (M^+, 100%), 241 (30), 224 (15) and 115 (18).

5,6-Dimethoxy-2′,3′-dimethylbiphenyl-2-carbaldehyde 33c. *Colourless oil* (Found: M^+, 270.1248. $C_{17}H_{18}O_3$ requires *M*, 270.1256); ν_{max}(film)/cm^{-1} 2841 (OCH$_3$), 1686 (C=O), 1583 (ArC=C), 1256 (C–O) and 815 (ArC–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.99 (3H, s, ArCH$_3$), 2.34 (3H, s, ArCH$_3$), 3.54 and 3.99 (each 3H, s, OCH$_3$), 7.01 (1H, d, *J* 7.5, 4′-H[a]), 7.04 (1H, d, *J* 8.7, 4-H), 7.13–7.16 (1H, m, 5′-H), 7.21 (1H, d, *J* 7.4, 6′-H[a]), 7.83 (1H, d, *J* 8.7, 3-H) and 9.45 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 16.8 (Ar*C*H$_3$), 20.5 (Ar*C*H$_3$), 55.9 and 60.6 (each OCH$_3$), 111.1 (4-C), 124.3 (4′-C[a]), 124.9 (5′-C[a]), 128.1 (3- and 2-C), 129.7 (6′-C[a]), 132.9 (1′-C[b]), 135.5 (3′-C[b]), 136.9 (1-C), 140.7 (2′-C[b]), 146.1 (5-C[c]), 157.7 (6-C[c]) and 191.1 (CHO); *m*/*z* 270 (M^+, 100%), 255 (45), 240 (23), 239 (36), 211 (15) and 165 (9).

4′,5,6-Trimethoxy-2′-methylbiphenyl-2-carbaldehyde 33d. *Colourless oil* (Found: M^+, 286.1198. $C_{17}H_{18}O_4$ requires *M*, 286.1205); ν_{max}(film)/cm^{-1} 2840 (OCH$_3$), 1682 (C=O), 1608 and 1584 (ArC=C), 1256 and 1239 (C–O) and 813 (ArC–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 2.08 (3H, s, ArCH$_3$), 3.53, 3.85 and 3.99 (each 3H, s, OCH$_3$), 6.80 (1H, dd, *J* 2.7 and 8.2, 5′-H), 6.85 (1H, d, *J* 2.7, 3′-H), 7.04 (1H, d, *J* 8.6, 4-H), 7.08 (1H, d, *J* 8.2, 6′-H), 7.82 (1H, d, *J* 8.6, 3-H) and 9.49 (1H, s, CHO); δ_C (100.625 MHz; $CDCl_3$) 20.4 (Ar*C*H$_3$), 55.2, 56.0 and 60.6 (each OCH$_3$), 110.8 (5′-C[a]), 111.2 (3′-C[a]), 115.3 (4-C[a]), 124.4 (6′-C), 125.1 (1′-C[b]), 128.4 (2-C[b]), 131.4 (3-C), 138.5 (1-C[b]), 139.8 (2′-C), 146.4 (5-C[c]), 157.7 (4′-C[c]), 159.4 (6-C[c]) and 191.2 (CHO); *m*/*z* 286 (M^+, 100%), 271 (20), 255 (24), 227 (14) and 128 (18).

General procedure for the cyclization of substituted 2-aryl acylbenzenes 33 to phenanthrenes 34

Typically, an aldehyde or ketone **33** (0.71 mmol) was dissolved in dry DMF (15 cm^3). Potassium *tert*-butoxide (317 mg, 2.82 mmol) was added, and the reaction mixture was heated under nitrogen at 80 °C for 10 min with simultaneous irradiation with a high-pressure mercury lamp through a quartz filter. The reaction mixture was diluted with water and acidified with conc. hydrochloric acid. The organic material was extracted into diethyl ether, and the organic layer was dried with magnesium sulfate. Filtration, and evaporation of the solvent under reduced pressure, afforded a pale residue, which was subjected to chromatography (5–10% ethyl acetate–hexane) to afford the desired *phenanthrenes* **34**. The following compounds were prepared by this method. (Yields are reported in Table 3.)

9-Methylphenanthrene 34a. *Pale yellow solid*, mp 90–91 °C (lit.,[27] 92 °C) (Found: M^+, 192.0932. $C_{15}H_{12}$ requires *M*, 192.0939); ν_{max}($CHCl_3$)/cm^{-1} 3079 (ArC–H), 1627 and 1604 (ArC=C) and 884 (ArC–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.72 (3H, d, *J* 0.8, ArCH$_3$), 7.54 (1H, dd, *J* 1.6 and 7.0, 4-H), 7.55–7.57 (1H, m, ArH), 7.59 (1H, dd, *J* 1.8 and 7.0, 5-H), 7.61–7.68 (2H, m, ArH), 7.78–7.80 (1H, m, ArH), 8.02–8.06 (1H, m, ArH), 8.63–8.65 (1H, m, ArH) and 8.69–8.73 (1H, m, ArH); δ_C (100.625 MHz; $CDCl_3$) 20.0 (Ar*C*H$_3$), 122.4 (ArCH), 123.0 (ArCH), 124.6 (ArCH), 125.8 (ArCH), 126.2 (ArCH), 126.5 (ArCH), 126.6 (ArCH), 126.7 (ArCH), 127.8 (ArCH), 129.7 (ArC), 130.4 (ArC), 132.0 (ArC), 132.1 (ArC) and 132.5 (ArC); *m*/*z* 192 (M^+, 100%), 191 (32), 176 (3) and 149 (42).

3,4-Dimethoxyphenanthrene 34b.[28] *Clear oil* (Found: M^+, 238.0983. $C_{16}H_{14}O_2$ requires *M*, 238.0994); ν_{max}(film)/cm^{-1} 2835 (OCH$_3$), 1610 and 1597 (ArC=C), 1278 (C–O) and 829 (ArC–H oop); δ_H (200 MHz; $CDCl_3$; Me_4Si) 3.95 and 3.98 (each 3H, s, OCH$_3$), 7.27 (1H, d, *J* 8.7, 10-H), 7.51–7.66 (5H, m, ArH), 7.80–7.84 (1H, m, ArH) and 9.60–9.65 (1H, m, 5-H); δ_C (50.32 MHz; $CDCl_3$) 56.5 and 59.7 (each OCH$_3$), 113.1 (10-C), 124.7 (ArC), 124.8 (ArCH), 125.6 (ArCH), 126.5 (2 × ArCH), 126.9 (ArCH), 127.9 (ArCH), 128.3 (ArCH), 128.4 (ArC), 129.6 (ArC), 133.1 (ArC), 147.2 (3-C[a]) and 151.5 (4-C[a]); *m*/*z* 238 (M^+, 100%), 223 (58), 195 (31), 180 (37), 152 (34), 126 (9), 76 (14) and 41 (10).

5,6-Dimethoxy-1-methylphenanthrene 34c.[23] *Pale yellow oil* (Found: M^+, 252.1151. $C_{17}H_{16}O_2$ requires *M*, 252.1150); ν_{max}(film)/cm^{-1} 3131 (ArC–H str), 2836 (OCH$_3$), 1607 and 1595 (ArC=C), 1277 (C–O) and 828 (ArC–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.74 (3H, s, ArCH$_3$), 3.93 and 4.03 (each 3H, s, OCH$_3$), 7.33 (1H, d, *J* 8.7, 9-H), 7.44 (1H, dd, *J* 0.4 and 7.1, 2-H), 7.52 (1H, dd, *J* 7.1 and 8.5, 3-H), 7.67 (1H, d, *J* 8.7, 10-H), 7.70 (1H, d, *J* 9.1, 7-H), 7.80 (1H, d, *J* 9.1, 8-H) and 9.56 (1H, dd, *J* 0.4 and 8.5, 4-H); δ_C (100.625 MHz; $CDCl_3$) 20.5 (Ar*C*H$_3$), 56.6 and 59.8 (each OCH$_3$), 113.2 (9-C), 121.2 (8-C), 124.8 (10-C), 125.1 (4b-C[a]), 126.0 (3- and 4-C), 126.8 (7-C), 127.9 (2-C), 128.1 (8a-C[a]), 129.7 (10a-C[a]), 131.7 (4a-C[a]), 134.0 (1-C[a]), 147.2 (6-C[b]) and 151.6 (5-C[b]); *m*/*z* 252 (M^+, 100%), 237 (57), 209 (23), 194 (25), 165 (18), 111 (7) and 83 (5).

2,5,6-Trimethoxyphenanthrene 34d. *Pale oil* which crystallized over time, mp 88.5–90 °C (colourless needles from ethanol) (Found: M^+, 268.1105. $C_{17}H_{16}O_3$ requires *M*, 268.1099); ν_{max}($CHCl_3$)/cm^{-1} 2839 (OCH$_3$), 1616 and 1600 (ArC=C), 1279 (C–O) and 856 (ArC–H oop); δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.92, 3.93 and 3.98 (each 3H, s, OCH$_3$), 7.20 (1H, d, *J* 2.7, 1-H), 7.22 (1H, d, *J* 8.6, 9-H), 7.25 (1H, dd, *J* 2.7 and 9.3, 3-H), 7.47 (1H, d, *J* 8.8, 7-H), 7.56 (1H, d, *J* 8.6, 10-H), 7.57 (1H, d, *J* 8.8, 8-H) and 9.53 (1H, d, *J* 9.3, 4-H); δ_C (100.625 MHz; $CDCl_3$) 55.2, 56.5 and 59.6 (each OCH$_3$), 108.8 (1-C), 112.2 (9-C), 116.1 (3-C), 123.7 (8a-C[a]), 124.8 (4a-C[a] and 10-C), 125.1 (7-C), 127.5 (10a-C[a] and 8-C), 129.5 (4-C), 134.8 (4b-C[a]), 146.4 (2-C[b]), 151.5 (6-C[b] and 5-C[b]); *m*/*z* 268 (M^+, 100%), 254 (13), 253 (74), 225 (21), 210 (48) and 167 (24).

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References and notes

1 Naphthalenes: R. H. Thomson, *Naturally Occurring Quinones III*: *Recent Advances,* Chapman and Hall, London and New York, 1987, pp. 125–343.

2 Phenanthrenes: (*a*) H. M. G. Al-Hazimi and H. Z. Al-Khathlan, *J. Saudi Chem. Soc.*, 1997, **1**, 47; (*b*) ref. 1, pp. 567–572.

3 General reviews on the synthesis of naphthalenes and phenanthrenes: (*a*) R. H. Thomson, in *The Total Synthesis of Natural Products*, ed. J. ApSimon, John Wiley & Sons, Inc., New York, 1992, vol. 8, pp. 311–531; (*b*) T. J. Simpson, in *The Chemistry of Natural Products*, ed. R. H. Thomson, Blackie, Glasgow and London, 1985, pp. 107–153; M. Gill, in *The Chemistry of Natural Products*, ed. R. H. Thomson, Blackie Academic and Professional, London, 2nd edn., 1993, pp. 60–105; (*c*) N. Campbell, in *Rodd's Chemistry of Carbon Compounds*, *Volume III – Aromatic Compounds – Part G*, ed. S. Coffey, Elsevier, Amsterdam, 2nd edn., 1977, ch. 27, pp. 99–286; (*d*) N. H. Wilson, in *Supplements to the 2nd Edition of Rodd's Chemistry of Carbon Compounds*, *Volume III – Aromatic Compounds – Part F* (*partial*) *and Part G*, ed. M. F. Ansell, Elsevier Science Publishers B.V., Amsterdam, 1984, ch. 27, pp. 175–236; (*e*) N. H. Wilson, in *Second Supplements to the 2nd Edition of Rodd's Chemistry of Carbon Compounds*, *Volume III – Aromatic Compounds – Part F* (*partial*) *Part G and H*, ed. M. Sainsbury, Elsevier Science Publishers B.V., Amsterdam, 1995, ch. 27, pp. 147–192; (*f*) M. Sainsbury, in *Rodd's Chemistry of Carbon Compounds*, *Volume III – Aromatic Compounds – Part H*, ed. S. Coffey, Elsevier, Amsterdam, 2nd edn., 1979, ch. 28, pp. 104–136; (*g*) R. Bolton, in *Supplements to the 2nd Edition of Rodd's Chemistry of Carbon Compounds*, *Volume III – Aromatic Compounds – Part H*, ed. M. F. Ansell, Elsevier Science Publishers B.V., Amsterdam, 1988, ch. 28, pp. 17–26.

4 See for example: (*a*) N. G. Andersen, S. P. Maddaford and B. A. Keay, *J. Org. Chem.*, 1996, **61**, 2885; (*b*) R. H. Thomson, in *The Total Synthesis of Natural Products*, ed. J. ApSimon, John Wiley & Sons Inc., New York, 1992, vol. 8, p. 330; (*c*) S. J. Teague and G. P. Roth, *Synthesis*, 1986, 427.

5 C. B. de Koning, J. P. Michael and W. A. L. van Otterlo, *Tetrahedron Lett.*, 1999, **40**, 3037.

6 (*a*) G. H. Whitham, in *Comprehensive Organic Chemistry*, ed. J. F. Stoddart, Pergamon Press Ltd., Oxford, 1979, vol. 1, p. 166; (*b*) D. E. Pearson and C. A. Buehler, *Chem. Rev.*, 1974, **74**, 45.

7 M. P. Sibi, J. W. Dankwardt and V. Snieckus, *J. Org. Chem.*, 1986, **51**, 271.

8 C. B. de Koning, J. P. Michael and A. L. Rousseau, *Tetrahedron Lett.*, 1997, **38**, 893.

9 C. B. de Koning, J. P. Michael and A. L. Rousseau, *Tetrahedron Lett.*, 1998, **39**, 8725.

10 General reviews: (*a*) S. P. Stanforth, *Tetrahedron*, 1998, **54**, 263; (*b*) G. Bringmann, R. Walter and R. Weirich, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 977.

11 (*a*) J. R. Oliveira, unpublished results, University of the Witwatersrand, South Africa. Compound **16** was prepared from **17** by reduction of the ester with $LiAlH_4$ followed by oxidation with MnO_2; (*b*) I. R. Green, V. I. Hugo, F. J. Oosthuisen, N. van Eeden and R. G. F. Giles, *S. Afr. J. Chem.*, 1995, **48**, 15.

12 J. Fossey, D. Lefort and J. Sorba, *Free Radicals in Organic Chemistry*, John Wiley & Sons, Chichester, 1995, (*a*) p. 208; (*b*) p. 218.

13 P. G. Sammes, *Tetrahedron*, 1976, **32**, 405.

14 V. Snieckus[7] has suggested that cyclobutanols may be possible intermediates in the course of their reaction resulting in the formation of naphthols, but we did not isolate this type of intermediate.

15 (*a*) D. R. Morton, E. Lee-Ruff, R. M. Southam and N. J. Turro, *J. Am. Chem. Soc.*, 1970, **92**, 4349; (*b*) N. M. Crossland, S. M. Roberts and R. F. Newton, *J. Chem. Soc., Chem. Commun.*, 1978, 661.

16 G. A. Russell, E. G. Janzen and E. T. Strom, *J. Am. Chem. Soc.*, 1964, **86**, 1807.

17 (*a*) A. Suzuki, *Acc. Chem. Res.*, 1982, **15**, 178; (*b*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*c*) A. Suzuki, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. F. Diederich and P. J. Stang, Wiley-VCH, Weinheim, 1998, pp. 49–97; (*d*) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.

18 (*a*) J.-m. Fu, M. J. Sharp and V. Snieckus, *Tetrahedron Lett.*, 1988, **29**, 5459; (*b*) X. Wang and V. Snieckus, *Tetrahedron Lett.*, 1991, **32**, 4879; (*c*) S. Chowdhury, B. Zhao and V. Snieckus, *Polycyclic Aromat. Comp.*, 1994, **5**, 27.

19 The aromatic bromide **30** is commercially available. Compound **31** was prepared by treatment of isovanillin with bromine in acetic acid followed by methylation with dimethyl sulfate in the presence of potassium carbonate and DMF.

20 (*a*) *Organometallic Compounds of Boron*, ed. K. Smith, Chapman & Hall, London and New York, 1985, p. 93; (*b*) N. P. Bullen, K. S. Chiheru and F. G. Thorpe, *J. Organomet. Chem.*, 1980, **195**, 147.

21 (*a*) *Eur. Pat. Appl.* EP 733 365, 1996 (*Chem. Abstr.*, 1997, **126**, 8006x); (*b*) *PCT Int. Appl.* WO 9 840 331, 1998 (*Chem. Abstr.*, 1999, **129**, 260575v).

22 T. Eicher, S. Fey, W. Puhl, E. Büchel and A. Speicher, *Eur. J. Org. Chem.*, 1998, 877.

23 R. Hout and P. Brassard, *Can. J. Chem.*, 1974, **52**, 88.

24 Other syntheses of Tanshinone I: (*a*) R. L. Danheiser, D. S. Casebier and J. L. Loebach, *Tetrahedron Lett.*, 1992, **33**, 1149; (*b*) A. C. Baillie and R. H. Thomson, *J. Chem. Soc. C*, 1968, 48.

25 (*a*) B. R. Baker and G. H. Carlson, *J. Am. Chem. Soc.*, 1942, **64**, 2657; (*b*) L. F. Fieser, *J. Am. Chem. Soc.*, 1948, **70**, 3165.

26 Slight modification of a procedure used by Snieckus: B. I. Alo, A. Kandil, P. A. Patil, M. J. Sharp, M. A. Siddiqui and V. Snieckus, *J. Org. Chem.*, 1991, **56**, 3763.

27 O. Kruber and A. Marx, *Ber. Dtsch. Chem. Ges., Abt. B*, 1938, **71**, 2478.

28 R. Pschorr and C. Sumuleanu, *Ber. Dtsch. Chem.*, 1900, **33**, 1810.

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