Supplementary Information: Black, Cadogan and McNab

Formation of dibenzofurans by flash vacuum pyrolysis of aryl 2-(allyloxy)benzoates and related reactions.

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Aryl benzoates 3 and 4

Salicyclic acid or thiosalicyclic acid (0.127 mol) was melted with the appropriately substituted phenol (0.127 mol) at 135 °C. Phosphoryl chloride (7 g, 0.046 mol) was then added gradually and the temperature was moderated until the evolution of hydrogen chloride had ceased. The reaction mixture was cooled in ice, water (250 cm³) was added and the product was obtained by trituration of the organic precipitate. The reaction mixture was then washed with aqueous sodium carbonate (4 M, 50 cm³) to remove any unreacted acid.

If necessary, non-crystalline products were extracted with dichloromethane (3 × 50 cm³), the extracts washed with water (2 × 50 cm³), dried (MgSO₄), the solvent removed and the products purified by distillation.

The following compounds were prepared by this method, as outlined in the main paper:

4-Chlorophenyl (2-hydroxy)benzoate 3c (67%), mp 62-64 °C (from ethanol) (lit.,1 69.5-70.5 °C) δ₇ 10.41 (1H, br s) 8.05 (1H, m) and 7.58-6.93 (7H, m).

4-Methoxyphenyl (2-hydroxy)benzoate 3d (83%), mp 87-89 °C (from ethanol) (lit., 2) δ₇ 8.06 (1H, m), 7.63-6.84 (7H, m) and 3.81 (3H, s).

4-Nitrophenyl (2-hydroxy)benzoate 3e (80%), mp 149-151 °C (from 1,4-dioxan) (lit., 3) m/z 259 (M⁺, 10%), 212 (10), 121 (100) and 93 (10).

3-Methylphenyl (2-hydroxy)benzoate 3g (44%), mp 72-74 °C (from ethanol) (lit., 3) δ₇ 10.51 (1H, br s) 8.07 (1H, m), 7.64-6.80 (7H, m) and 2.39 (3H, s); m/z 228 (M⁺, 58%), 121 (100), 107 (28) and 93 (35).

2-Methylphenyl (2-hydroxy)benzoate 3h (82%), mp 32-33 °C (from methanol) δ₇ 10.59 (1H, br s) 8.13 (1H, m), 7.51-7.04 (7H, m) and 2.27 (3H, s); m/z 228 (M⁺, 33%), 121 (100), 108 (32) and 93 (25).

2-Chlorophenyl (2-hydroxy)benzoate 3i (80%), mp 53-54 °C (from ethanol) (lit., 1) δ₇ 10.25 (1H, br s) 8.09 (1H, m) and 7.66-6.87 (7H, m).

2-Methoxyphenyl (2-hydroxy)benzoate 3j (66%), mp 72-74 °C (from ethanol) (lit., 4) δ₇ 149-151 °C (from ethanol) (lit., 4) δ₇ 10.13 (1H, br s) 8.15 (1H, m), 7.65-6.80 (7H, m) and 3.80 (3H, s); m/z 228 (M⁺, 85%), 121 (100) and 93 (9).

4-Chlorophenyl (2-mercapto)benzoate 4c (37%), bp 166-168 °C (0.1 Torr) δ₇ 8.23 (1H, m), 7.45-7.08 (7H, m) and 4.67 (1H, s); m/z 244 (M⁺, 9%), 137 (100), 128 (18) and 109 (26).

3-Methylphenyl (2-mercapto)benzoate 4g (31%), mp 102-104 °C (from ethanol) δ₇ 7.31-7.00 (8H, m), 4.76 (1H, s) and 2.41 (3H, s); m/z 244 (M⁺, 100%), 137 (84) and 108 (31), characterised as its allyl derivative (see below).

2-Methylphenyl (2-mercapto)benzoate 4h (35%), mp 47-50 °C (from ethanol) δ₇ 7.41-7.11 (8H, m), 4.82 (1H, s) and 2.24 (3H, s); m/z 244 (M⁺, 100%), 137 (65) and 108 (22), characterised as its allyl derivative (see below).

Phenyl (2-hydroxy-4-methyl)benzoate (96%), mp 43-45 °C (from ethanol) (lit., 9) δ₇ 7.95 (1H, m), 7.49-7.23 (5H, m), 6.86-6.77 (2H, m) and 2.39 (3H, s).

Aryl 2-(allyloxy)benzoates 5 and aryl 2-(allylthio)benzoates 6

The following S- and O-allyl compounds were prepared by treatment of the appropriate aryl 2-mercaptopbenzoate or aryl 2-hydroxybenzoate with allyl bromide in DMF in the
The following compounds were prepared by this method, as outlined in the main paper:

**4-Methylphenyl 2-(allyloxy)benzoate** (83%), bp 163-165 °C (0.3 Torr) (Found: C, 76.2; H, 6.0. C_{17}H_{16}O_3 requires C, 76.1; H, 6.0%; δ_H 8.03 (1H, m), 7.55-7.01 (7H, m), 6.05 (1H, m), 5.60-5.25 (2H, m) and 2.37 (3H, s); δ_C 164.62 (quat), 158.56 (quat), 148.68 (quat), 135.11 (quat), 133.84, 132.44, 132.04, 129.76, 121.36, 120.33, 119.75 (quat), 117.34, 113.57, 69.36 and 28.73; m/z 268 (M^+, 1%), 228 (8), 121 (100) and 93 (10).

**4-Chlorophenyl 2-(allyloxy)benzoate** (86%), mp 43-45 °C (from ethanol) (Found: C, 66.0; H, 4.4. C_{16}H_{13}ClO_3 requires C, 66.6; H, 4.5%; δ_H 8.01 (2H, m), 7.56-6.81 (7H, m), 6.08 (1H, m), 5.58-5.25 (2H, m) and 4.65 (2H, m); δ_C 164.00 (quat), 158.70 (quat), 149.50 (quat), 134.05, 132.43, 132.01, 130.85 (quat), 129.23, 123.02, 120.38, 119.40 (quat), 117.40, 113.72 and 69.47; m/z 290 (M^+, <1%), 288 (M^+, <1%), 161 (100), 133 (10) and 92 (10).

**4-Methoxyphenyl 2-(allyloxy)benzoate** (94%), mp 136-140 °C (0.3 Torr) (Found: C, 76.3; H, 6.0. C_{17}H_{16}O_3 requires C, 76.1; H, 6.0%; δ_H 8.02 (1H, m), 7.99-7.01 (7H, m), 6.09 (1H, m), 5.59-5.24 (2H, m), 4.66 (2H, m) and 2.27 (3H, s); δ_C 164.52 (quat), 158.62 (quat), 150.96 (quat), 139.36 (quat), 128.95, 126.32, 120.84 (quat), 120.37, 119.91, 118.62, 69.16 and 55.33; m/z 284 (M^+, 12%), 161 (100), 132 (30) and 123 (15).

**3-Methylphenyl 2-(allyloxy)benzoate** (84%), bp 136-140 °C (0.3 Torr) (Found: C, 76.3; H, 6.0. C_{17}H_{16}O_3 requires C, 76.1; H, 6.0%; δ_H 8.02 (1H, m), 7.99-7.01 (7H, m), 6.09 (1H, m), 5.59-5.24 (2H, m), 4.66 (2H, m) and 2.27 (3H, s); δ_C 164.52 (quat), 158.62 (quat), 150.96 (quat), 139.36 (quat), 128.95, 126.32, 120.84 (quat), 120.37, 119.91, 118.62, 69.16 and 55.33; m/z 284 (M^+, 12%), 161 (100), 132 (30) and 123 (15).

**2-Methylphenyl 2-(allyloxy)benzoate** (80%), mp 39-41 °C (from ethanol) (Found: C, 76.3; H, 6.0. C_{17}H_{16}O_3 requires C, 76.1; H, 6.0%; δ_H 8.02 (1H, m), 7.99-7.01 (7H, m), 6.09 (1H, m), 5.59-5.24 (2H, m), 4.66 (2H, m) and 2.27 (3H, s); δ_C 164.52 (quat), 158.62 (quat), 150.96 (quat), 139.36 (quat), 128.95, 126.32, 120.84 (quat), 120.37, 119.91, 118.62, 69.16 and 55.33; m/z 284 (M^+, 1%), 161 (100) and 133 (12).

**2-Chlorophenyl 2-(allyloxy)benzoate** (84%), bp 193-198 °C (0.8 Torr) (Found: C, 66.9; H, 4.65. C_{17}H_{13}ClO_3 requires C, 66.6; H, 4.5%; δ_H 8.13 (1H, m), 7.57-7.45 (2H, m), 7.36-7.16 (3H, m), 7.10-6.94 (2H, m), 6.09 (1H, m), 5.59-5.24 (2H, m) and 4.65 (2H, m); δ_C 162.92 (quat), 158.91 (quat), 147.14 (quat), 134.30, 132.56, 132.35, 127.54, 126.99 (quat), 126.71, 123.95, 120.30, 118.59 (quat), 117.39, 113.53 and 69.32; m/z 322 (M^+, 4%), 161 (100) and 133 (12).

**2-Methoxyphenyl 2-(allyloxy)benzoate** (78%), mp 38-41 °C (from ethanol) (Found: C, 72.1; H, 5.8. C_{17}H_{16}O_4 requires C, 71.8; H, 5.65%; δ_H 8.23 (1H, m), 7.51-7.28 (2H, m), 7.26-7.10 (5H, m), 5.90 (1H, m), 5.45-5.18 (2H, m) and 3.70-3.63 (2H, m); δ_C 164.76 (quat), 148.45 (quat), 141.71 (quat), 135.19 (quat), 132.51, 132.36, 131.41,
129.68, 127.54 (quat), 126.47, 124.03, 121.20, 118.32, 35.34 and 20.62; m/z 284 (M⁺, 11%), 177 (100), 149 (26) and 108 (40).

4-Chlorophenyl 2-(allythio)benzoate 6c (75%), mp 45-47 °C (from ethanol) (Found: C, 62.6; H, 4.25. C₁₃H₁₉ClO₂S requires C, 63.05; H, 4.25%); δ H 8.16 (1H, m), 7.53-7.13 (7H, m), 5.92 (1H, m), 5.38-5.16 (2H, m) and 3.62 (2H, m); δ C 164.32 (quat), 149.05 (quat), 142.41 (quat), 132.82, 132.28, 131.66, 131.05 (quat), 129.29, 126.33 (quat), 126.10, 123.98, 123.02, 118.65 and 35.16; m/z 306 (M⁺, 1%), 304 (M⁺, 3), 177 (100), 149 (23) and 136 (39).

3-Methylphenyl 2-(allylthio)benzoate 6g (52%), mp 41-43 °C (from ethanol) (Found: C, 71.0; H, 5.6. C₁₇H₁₆O₂S.0.4H₂O requires C, 71.05; H, 5.75%); δ H 8.18 (1H, m), 7.55-7.01 (7H, m), 5.92 (1H, m), 5.38-5.16 (2H, m), 3.63 (2H, m) and 2.44 (3H, s); δ C 164.73 (quat), 150.51 (quat), 142.13 (quat), 139.40 (quat), 132.56, 132.40, 131.59, 128.95, 126.88 (quat), 126.49, 126.08, 123.93, 122.19, 118.51 (2C), 35.17 and 21.15; m/z 284 (M⁺, 14%), 177 (100), 149 (36) and 108 (35).

2-Methylphenyl 2-(allylthio)benzoate 6h (80%), mp 63-65 °C (from ethanol) (Found: C, 71.7; H, 5.65. C₁₇H₁₆O₂S requires C, 71.8; H, 5.6%); δ H 7.51-7.12 (8H, m), 5.90 (1H, m), 5.38-5.16 (2H, m), 3.63 (2H, m) and 2.25 (3H, s); δ C 164.80 (quat), 150.78 (quat), 141.80 (quat), 139.46 (quat), 132.66, 132.44, 131.52, 128.99, 127.82 (quat), 126.72, 126.51, 124.19, 122.23, 118.57, 118.39, 35.54 and 21.15; m/z 284 (M⁺, 14%), 177 (100), 149 (18) and 108 (20).

2-Chlorophenyl 2-(allylthio)benzoate 6i (64%), mp 34-36 °C (from ethanol) (Found: C, 62.8; H, 4.2. C₁₃H₁₉ClO₂S requires C, 63.0; H, 4.3%); δ H 8.30 (1H, m), 7.55-7.16 (7H, m), 5.92 (1H, m), 5.40-5.16 (2H, m) and 3.64 (2H, m); δ C 163.48 (quat), 157.08 (quat), 154.23 (quat), 135.47 (quat), 132.77, 132.46, 131.00 (quat), 130.80, 127.52, 126.92, 126.81, 126.48, 124.12, 123.91, 118.44 and 35.32; m/z 306 (M⁺, 2%), 304 (M⁺, 6), 177 (100), 149 (17) and 108 (26).

Phenyl 2-(allyloxy-4-methyl)benzoate 7 (90%), mp 51-53 °C (from ethanol) (Found: C, 76.2; H, 6.1. C₁₇H₁₆O₃ requires C, 76.0; H, 6.0%); δ H 7.95 (1H, m), 7.46-6.83 (7H, m), 6.04 (1H, m), 5.60-5.25 (2H, m) and 2.44 (3H, s); δ C 163.26 (quat), 154.42 (quat), 153.47 (quat), 132.77, 132.46, 131.00 (quat), 130.80, 127.52, 126.92, 126.81, 126.48, 124.12, 123.91, 118.44 and 35.32; m/z 268 (M⁺, 7%), 175 (100) 147 (26), 119 (32) and 91 (18).

Aryl 2-(allyloxy)benzoates 5 and aryl 2-(isopropylthio)benzoates 6′

2-Allyloxybenzoic acid 11 (3.56 g, 0.02 mol) and thionyl chloride (2.86 g, 0.024 mol) were heated under reflux for 30 min. Excess thionyl chloride was removed in vacuo (using a water pump). The acid chloride thus formed was dissolved in dichloromethane (25 cm³) and 4-dimethylaminopyridine (DMAP) (0.02 g, 0.0002 mol) was added, followed by the addition of the appropriate phenol (0.02 mol). Triethylamine (2.02 g, 0.02 mol) in dichloromethane (25 cm³) was added dropwise and the solution was stirred for 3 h. The dense white precipitate of triethylamine hydrochloride was removed by filtration and the filtrate was washed with water (3 × 15 cm³), dried (MgSO₄) and the solvent removed in vacuo.

The following compounds were prepared by this method as outlined in the main paper:

4-Cyanophenyl 2-(allyloxy)benzoate 5f (89%) mp 43-45 °C (from ethanol) (Found: C, 73.1; H, 4.6; N, 5.15. C₁₇H₁₃NO₃ requires C, 73.1; H, 4.7; N, 5.0%); δ H 7.99 (1H, m), 7.79-6.90 (7H, m), 6.04 (1H, m), 5.61-5.17 (2H, m) and 4.65 (2H, m); δ C 163.26 (quat), 158.89 (quat), 154.23 (quat), 134.63, 133.42, 132.17, 122.81, 120.34, 118.24 (quat), 118.12 (quat), 117.51, 113.52, 109.28 (quat) and 69.28; m/z 279 (M⁺, trace), 161 (100), 133 (35) and 92 (27).

3-Pyridyl 2-(allyloxy)benzoate 30 (87%) bp 173-178 °C (0.8 Torr) (Found: M⁺ 255.0901. C₁₅H₁₃NO₃ requires M 255.0895); δ H 8.53-8.45 (2H, m), 8.01 (1H, m), 7.62-
7.25 (3H, m), 7.06-6.97 (2H, m), 5.99 (1H, m), 5.54-5.22 (2H, m) and 4.62 (2H, m); δH: 167.98 (quat), 158.91 (quat), 156.97, 146.03 (quat), 143.04 (quat), 139.86, 137.90, 136.32, 133.68, 132.46, 124.87, 121.51, 119.18, 113.06 and 70.15; m/z: 255 (M⁺, < 1%), 161 (100), 133 (11) and 41 (19).

8-Quinolinyl 2-(allyloxy)benzoate 33 (91%) mp 124-126 °C (from ethanol) (Found: C, 74.9; H, 5.0; N, 4.5. C19H15NO3 requires C, 74.75; H, 4.9; N, 4.6%); δH: 8.89 (1H, m), 8.30-8.17 (2H, m), 7.73 (1H, m), 7.58-7.37 (4H, m), 7.13-7.01 (2H, m), 6.07 (1H, m), 5.56-5.20 (2H, m) and 4.68 (2H, m); δC: 164.23 (quat), 158.95 (quat), 150.31, 147.65 (quat), 141.43 (quat), 135.69, 133.95, 132.74, 132.59, 129.41 (quat), 126.05, 125.58, 121.59, 121.46, 120.40, 119.52 (quat), 117.20, 113.70 and 69.46; m/z: 305 (M⁺, 17 %), 161 (100), 133 (36) and 92 (41).

l-Naphthyl 2-(allyloxy)benzoate 34 (68%) mp 59-61°C (from ethanol) (Found: C, 78.6; H, 5.3. C20H16O3 requires C, 78.9; H, 5.25%); δH: 8.18-7.05 (11H, m), 6.10 (1H, m), 5.58-5.24 (2H, m) and 4.72 (2H, m); δC: 164.69 (quat), 158.66 (quat), 146.89 (quat), 134.57 (quat), 134.15, 132.39, 132.31, 127.79, 126.95 (quat), 126.23 (2C), 125.78, 125.36, 121.71, 120.45, 119.43 (quat), 118.20, 117.75, 113.47 and 69.47; m/z: 304 (M⁺, 22%), 161 (100), 133 (75) and 105 (56).

2-Naphthyl 2-(allyloxy)benzoate 37 (76%) mp 49-51 °C (from ethanol) (Found: C, 79.1; H, 5.2. C20H16O3 requires C, 78.9; H, 5.25%); δH: 8.11-7.01 (11H, m), 6.08 (1H, m), 5.60-5.25 (2H, m) and 4.68 (2H, m); δC: 164.52 (quat), 158.70 (quat), 148.60 (quat), 134.03, 133.72 (quat), 132.42, 132.15, 131.33 (quat), 129.19, 127.61, 127.54, 126.30, 125.44, 121.34, 120.37, 119.55 (quat), 118.62, 117.42, 113.60 and 69.38; m/z: 304 (M⁺, 15%), 161 (100) and 144 (30).

FVP reactions
The following FVP reactions were carried out by the method outlined in the main paper:

FVP of 4-methylphenyl 2-(allyloxy)benzoate 5b
FVP of 5b [0.821 g (3 mmol), Ti 160 °C, Tf 650 °C, P 0.001 Torr, t 30 min] gave, after the general work-up procedure, p-cresol (0.021 g, 6%) and 2-methyldibenzofuran 19b (0.38 g, 70%), mp 37-39 °C (from ethanol) (lit., 10 38-40°C); δH: 8.18-7.05 (11H, m), 6.10 (1H, m), 5.58-5.24 (2H, m) and 4.72 (2H, m); δC: 164.69 (quat), 158.66 (quat), 146.89 (quat), 134.57 (quat), 134.15, 132.39, 132.31, 127.79, 126.95 (quat), 126.23 (2C), 125.78, 125.36, 121.71, 120.45, 119.43 (quat), 118.20, 117.75, 113.47 and 69.47; m/z: 304 (M⁺, 15%), 161 (100), 133 (75) and 105 (56).

FVP of 4-chlorophenyl 2-(allyloxy)benzoate 5c
FVP of 5c [1.625 g (5.6 mmol), Ti 140 °C, Tf 650 °C, P 0.001 Torr, t 60 min] gave, after the general work-up procedure, 2-chlorodibenzofuran 19c (1.21 g, 87%) mp 94-96 °C (from n-hexane) (lit., 12 100 °C); δH: 7.97-7.80 (2H, m) and 7.54-7.28 (5H, m).

FVP of 4-methoxyphenyl 2-(allyloxy)benzoate 5d
FVP of 5d [0.55 g (2.3 mmol), Ti 170 °C, Tf 650 °C, P 0.001 Torr, t 120 min] followed by standard work-up afforded 2-methoxydibenzofuran 19d (0.37 g, 80%) mp 89-91 °C (from ethanol) (lit., 13 93-94 °C); δH: 7.97-7.80 (2H, m) and 7.54-7.28 (5H, m).

FVP of 4-nitrophenyl 2-(allyloxy)benzoate 5e
FVP of 5e [0.417 g (1.4 mmol), Ti 150 °C, Tf 650 °C, P 0.001 Torr, t 120 min] gave after general work-up 2-nitrodibenzofuran 19e (0.27 g, 90%), mp 50-51 °C (from ethanol) (lit., 14 50.5-51.5 °C); δH: 8.84 (1H, m), 8.37 (1H, m), 8.16-7.98 (2H, m) and 7.64-7.38 (3H, m).

FVP of 4-cyanophenyl 2-(allyloxy)benzoate 5f
FVP of 5f [0.286 g (1 mmol), Ti 160 °C, Tf 650 °C, P 0.001 Torr, t 40 min] gave, after
work-up 2-cyanodibenzofuran 19f (0.14 g, 73%), mp 132-135 °C (from n-hexane) (lit.,15 140 °C); δH 157.79 (quat), 156.58 (quat), 130.66, 128.57, 125.20, 125.08 (quat), 123.59, 122.38 (quat), 120.91, 119.00 (quat), 112.66, 111.91 and 106.42 (quat), m/z 193 (M+, 100%).

FVP of 3-methylphenyl 2-(allyloxy)benzoate 5g
GC/MS of the pyrolysate from FVP of 5g [0.077 g (0.28 mmol), T1 170 °C, Tf 650 °C, P 0.005 Torr, t 30 min] indicated the formation of a (1 : 1) mixture of 1-methyldibenzofuran 19ga and 3-methyldibenzofuran 19gb m/z 182 (M+, 100%) δH 8.09-7.05 (14H, m), 2.81 (3H, s) and 2.54 (3H, s) (c.f. ref. 11). On a preparative scale [0.202 g (0.75 mmol), T i 180 °C, T f 650 °C, P 0.001 Torr, t 30 min] after the general work-up procedure, the two isomers were obtained in a combined yield of 0.11 g (80%).

FVP of 2-methylphenyl 2-(allyloxy)benzoate 5h
GC/MS of the pyrolysate from FVP of 5h [0.048 g (0.18 mmol), T i 150 °C, T f 650 °C, P 0.001 Torr, t 30 min] indicated the presence of o-cresol (m/z 108), dibenzofuran (m/z 168) and 4-methyldibenzofuran 19h (m/z 182). The 1H NMR spectrum of the pyrolysate showed some 1-hydroxyfluorene 29 (ca. 2%) δH 3.84 (2H, s) whose methylene signal correlates with reported data.16 The major product is 4-methyldibenzofuran (ca. 30%); δH 8.00-7.30 (7H, m) and 2.61 (3H, s) (c.f. ref. 11).

FVP of 2-chlorophenyl 2-(allyloxy)benzoate 5i
The neural component from FVP of 5i [0.228 g (0.79 mmol), T i 140 °C, T f 650 °C, P 0.001 Torr, t 90 min], after general work-up, was chromatographed on a silica flash column, using ether/hexane as eluant, to provide 4-chlorodibenzofuran 19i (0.05 g, 22%) δC 156.01 (quat), 151.77 (quat), 127.66, 126.99, 125.83 (quat), 123.87 (quat), 123.40, 123.09, 120.81, 118.84, 116.98 (quat) and 111.89. Some dibenzofuran 19a (ca. 2%) was also detected.

FVP of 2-methoxyphenyl 2-(allyloxy)benzoate 5j
The 1H NMR spectrum of the total pyrolysate from the FVP of 5j [0.067 g (0.2 mmol), T i 160 °C, T f 650 °C, P 0.001 Torr, t 40 min] reveals a singlet at δH 4.06 due to 4-methoxydibenzofuran17 and singlets at δH 11.03 and 9.87, characteristic of salicylaldehyde.18 GC/MS confirms that 4-methoxydibenzofuran 19j (ca. 30%) is the major component [m/z 198 (M+)]. Minor components include salicylaldehyde 31 (ca.12%) [m/z 122 (M+) ] and dibenzofuran 19a m/z 168 (M+).

FVP of 2,6-dichlorophenyl 2-(allyloxy)benzoate 5k
FVP of 5k [0.259 g (0.8 mmol), T i 160 °C, T f 650 °C, P 0.001 Torr, t 90 min] gave a white crystalline solid and a green oil in the cold trap. After general work-up a yellow solid was obtained (0.064 g, 39%) which was identified by GC as 4-chlorodibenzofuran 19i (see above).

FVP of phenyl 2-(allyloxy-4-methyl)benzoate 7
The 1H NMR spectrum of the pyrolysate from 7 [0.050 g (0.19 mmol), T i 120 °C, T f 650 °C, P 0.001 Torr, t 30 min] showed the presence of two methyl signals δH 2.81 (3H, s) and 2.53 (3H, s) in a ratio of 1:3 respectively. These shifts are characteristic of 1- and 3-methyl dibenzofuran isomers 19ga and 19gb, respectively.11

FVP of 4-methylphenyl 2-(allylthio)benzoate 6b
FVP of 6b [3.21 g (11 mmol), T i 180 °C, T f 650 °C, P 0.001 Torr, t 120 min] gave 2-methylidibenzothiophene 20b (1.96 g, 90%) by using the general work-up procedure, mp 83-86 °C (from ethanol) (lit.,19 85-86 °C) δH 8.23-7.20 (7H, m) and 2.53 (3H, s); δC 139.78 (quat), 136.38 (quat), 135.63 (quat), 135.35 (quat), 133.91 (quat), 127.99, 126.28,
123.96, 122.61, 122.21, 121.55, 121.23 and 21.16; m/z 198 (M⁺, 100%) (spectra compatible with literature data¹¹).

**FVP of 4-chlorophenyl 2-(allylthio)benzoate 6c**
FVP of 6c [1.013 g (3.9 mmol), Tᵢ 160 °C, Tᵣ 650 °C, P 0.001 Torr, t 60 min] gave, after the general work-up removed a small trace of p-chlorophenol, 2-chlorodibenzo thiophene ²⁰c (0.81 g, 94%) mp 122-124 °C (from ethanol) (lit., ²⁰ 125-126 °C), δᵢ 8.09-7.37 (7H, m); δ₃ 140.13 (quat), 137.45 (quat), 136.83 (quat), 134.47 (quat), 130.59 (quat), 127.20, 126.79, 124.49, 123.60, 122.77, 121.63 and 121.35; m/z 220 (M⁺, 33%) and 218 (M⁺, 100) (spectra compatible with literature data¹¹).

**FVP of 3-methylphenyl 2-(allylthio)benzoate 6g**
The ¹H NMR spectrum of the pyrolysate from FVP of 6g [0.053 g (0.19 mmol), Tᵢ 120 °C, Tᵣ 650 °C, P 0.001 Torr, t 45 min] shows two methyl peaks suggesting the formation of 1-methyldibenzo thiophene ²⁰ga and 3-methyldibenzo thiophene ²⁰gb respectively δᵢ 8.41-8.36 (2H, m), 8.14-7.22 (12H, m), 2.93 (3H, s) and 2.52 (3H, s) in 58 : 42 ratio, (spectra consistent with literature data¹¹) m/z 198 (M⁺, 100%). Pyrolysis on a larger scale [0.14 g (0.5 mmol), Tᵢ 120 °C, Tᵣ 650 °C, P 0.005 Torr, t 50 min) followed by the general work-up, provided the two isomers in a combined yield of 0.07 g (58%).
Synthesis and FVP reactions of precursors related to 5 and 6

4-Methylphenyl 2-(allylamino)benzoate 40

Finely ground sodium hydroxide (0.004 g, 0.1 mmol) was added to a stirred mixture of N-allylisatoic anhydride (0.41 g, 2 mmol) and p-cresol (0.22 g, 2 mmol), in 1,4-dioxane (10 cm³) (c.f. ref 24). The mixture was then heated to 100 °C over 30 min. After a further 30 min at this temperature, the reaction mixture was cooled in ice and the volume was then increased threefold with ice-water. The solution was extracted with dichloromethane (2 × 10 cm³) and the combined organic extracts were washed with aqueous sodium hydroxide (2 M, 10 cm³), then washed with water (15 cm³), dried (MgSO₄) and the solvent removed in vacuo.

4-Methylphenyl 2-(allylamino)benzoate 40 was obtained as a brown oil (0.33 g, 63%) bp 150-158 °C (0.4 Torr) (Found: M + 267.1097. C₁₇H₁₇NO₂ requires M 267.1099); δH 8.20 (1H, m), 7.52-6.99 (7H, m), 5.98 (1H, m), 5.42-5.07 (2H, m), 3.86 (2H, m) and 2.37 (3H, s); δC 167.44 (quat), 151.47 (quat), 148.44 (quat), 135.21 (quat), 135.10, 134.12, 131.92, 129.83, 121.56, 116.17, 114.71, 111.54, 108.98 (quat), 45.13 and 20.75; m/z 267 (M+, 5%), 159 (89), 130 (100) and 77 (78).

FVP of 4-methylphenyl 2-(allylamino)benzoate 40

1H NMR spectroscopy and GC analysis of the pyrolysate from FVP of 40 at different furnace temperatures [0.054 g (0.2 mmol), Tᵣ 150 °C, Tᵢ 650 °C, P 0.005 Torr, t 60 min]; [0.053 g (0.2 mmol), Tᵣ 150 °C, Tᵢ 850 °C, P 0.005 Torr, t 50 min] indicate that p-cresol is the major product δH 7.10-6.60 (4H, m), 4.40 (1H, br s) and 2.20 (3H, s) and that a small quantity of quinoline is also formed; δH 8.64 (1H, m) and 8.05-7.00 (6H, m). No carbazoles were detected.

2-(Allyloxy)phenol

Catechol (6.61 g, 0.06 mol) was added to a solution of potassium carbonate (9.95 g, 0.072 mol) in dimethylformamide (60 cm³). Allyl bromide (8.71 g, 0.072 mol) was then added dropwise and the solution was stirred for 16 h. Water (80 cm³) was added and the mixture was washed with aqueous sodium hydroxide (2 M, 2 × 20 cm³), to remove the mono-alkylated product. The basic extracts were acidified with aqueous hydrochloric acid (2 M, 20 cm³) and extracted with ether (3 × 15 cm³). The combined organic extracts were washed with water (20 cm³), dried (MgSO₄) and the solvent removed in vacuo to give 2-(allyloxy)phenol as a yellow oil (1.81 g, 20%), bp 100-105 °C (1.5 Torr) [lit., 107.5-109 °C (15 Torr)]; δH 7.00-6.82 (4H, m), 5.90 (1H, m), 5.52-5.21 (2H, m) and 4.60 (2H, m); δC 145.75 (quat), 145.43 (quat), 132.76, 121.63, 119.99, 118.16, 114.65, 112.17 and 69.70; m/z 150 (M⁺, 37%) and 109 (66). This compound was used in the following reactions, without further purification.

2-(Allyloxy)phenyl benzoates

These compounds were prepared from the appropriate benzoyl chloride, 2-(allyloxy)phenol and a catalytic amount of 4-dimethylaminopyridine by the general procedure described above for the preparation of 5 and 6. The following compounds were prepared:

2-(Allyloxy)phenyl benzoate 41a (87%) mp 42-44 °C (from ethanol) (Found: C, 75.3; H, 5.5. C₁₆H₁₄O₃ requires C, 75.6; H, 5.5%); δH 8.26-8.22 (2H, m), 7.63 (1H, m), 7.53-7.48 (2H, m), 7.25-7.17 (2H, m), 7.03-6.98 (2H, m), 5.95 (1H, m), 5.33-5.14 (2H, m) and 4.56 (2H, m); δC 164.59 (quat), 164.59 (quat), 150.21 (quat), 140.35 (quat), 133.23, 132.74, 130.10, 129.45 (quat), 128.35, 126.63, 122.91, 120.99, 116.94, 114.07 and 69.26; m/z 254 (M⁺, 18%), 165 (100) and 77 (23).

2-(Allyloxy)phenyl 4-methylbenzoate 41b (90%) mp 40-42 °C (from ethanol) (Found: C, 76.1; H, 6.1. C₁₇H₁₆O₃ requires C, 76.1; H, 6.0%); δH 8.14-8.10 (2H, m), 7.32-7.15 (4H, m), 7.03-6.95 (2H, m), 5.90 (1H, m), 5.35-5.12 (2H, m), 4.54 (2H, m) and 2.44 (3H, s); δC 164.61 (quat), 150.21 (quat), 143.98 (quat), 140.37 (quat), 132.72, 130.11, 129.05, 126.62 (quat), 126.51, 122.93, 120.94, 116.85, 114.01, 69.19 and 21.53; m/z 268 (M⁺, 23).
FVP of 2-(allyloxy)phenyl benzoate 41a
FVP of 41a [0.123 g (0.48 mmol), T, 140 °C, Tf 650 °C, P 0.005 Torr, t 60 min] provided a brown deposit (0.011 g) and a dark polymeric material (0.034 g). GC/MS revealed that the brown fraction contained allylbenzene m/z 118 (M^+, 84%), 117 (100) and 91 (33); naphthalene m/z 128 (M^+, 100%), biphenyl m/z 154 (M^+, 100%) and 77 (13) and dibenzofuran m/z 168 (M^+, 100%), all identified by comparison with authentic samples.

FVP of 2-(allyloxy)4-methylbenzoate 41b
FVP of 41b [0.063 g (0.24 mmol), T i 100 °C, T f 650 °C, P 0.005 Torr, t 90 min] gave a white crystalline solid and a brown oil. The entire pyrolysate was analysed by 1H NMR spectroscopy and GC/MS which indicated that the major product was polymeric, however, a small quantity of 2-methylnaphthalene m/z 142 (M^+, 100%) and 2-methyldibenzofuran m/z 182 (M^+, 100%) were also detected.

2-(Allyloxy)-5-methylazobenzene 42
Aniline (5.0 g, 0.054 mol), was dissolved in concentrated hydrochloric acid (16 cm³). Water (16 cm³) was added carefully and the mixture was immersed in an ice bath, with stirring, until the temperature stabilised below 5 °C. A solution of sodium nitrite (4.0 g, 0.058 mol) in water (20 cm³) was chilled and added in small volumes (2-3 cm³), to the cold aniline hydrochloride solution. A solution of p-cresol (5.84 g, 0.054 mol) in aqueous sodium hydroxide (10%, 40 cm³) was stirred vigorously, chilled and added slowly to the cold diazonium salt solution. The product was filtered to provide 2-hydroxy-5-methylazobenzene as a brown solid (9.12 g, 80%) mp 104-107 °C (from glacial acetic acid) (lit., 26 108-109 °C) δH 9.60 (1H, br s), 7.92-6.87 (8H, m) and 2.38 (3H, s); m/z 212 (M^+, 96%), 135 (42) and 107 (100).

2-Hydroxy-5-methylazobenzene (2.0 g, 0.0094 mol) was added to a solution of potassium carbonate (2.60 g, 0.019 mol), in dimethylformamide (25 cm³). Allyl bromide (2.27 g, 0.019 mol) was added dropwise and the mixture was stirred at room temperature for 21 h. Water (30 cm³) was added and the mixture was extracted with ether (3 × 10 cm³). The combined organic extracts were washed with water (20 cm³), dried (MgSO₄) and the solvent removed in vacuo. 2-(Allyloxy)-5-methylazobenzene 42 was obtained as a red solid (2.20 g, 97%), mp 42-44 °C (from methanol) (Found: C, 76.3; H, 6.45; N, 11.2. C₁₆H₁₆N₂O requires C, 76.2; H, 6.45; N, 11.1%); δH 8.03-6.97 (8H, m), 6.15 (1H, m), 5.55-5.27 (2H, m), 4.75 (2H, m) and 2.34 (3H, m); δC 154.20 (quat), 153.10 (quat), 142.53 (quat), 133.28, 132.65, 130.64, 128.84, 123.01, 122.81, 119.65 (quat), 117.15, 115.47, 70.81 and 20.34; m/z 252 (M^+, 3%), 160 (26), 131 (24), 77 (75) and 41 (100).

FVP of 2-(allyloxy)-5-methylazobenzene 42
FVP of 42 [0.185 g (7.3 mmol), T, 160 °C, T f 650 °C, P 0.005 Torr, t 75 min] gave a significant black residue in the inlet (0.025 g). The mixture was chromatographed on a silica flash column, using n-hexane/ether as eluant. The major component was isolated as a yellow solid (0.036 g, 28%) m/z 182 (M^+, 100%), 152 (25) and 40 (71), consistent with authentic 2-methyl dibenzofuran 19b. There was no change in the proportion of products when the FVP was carried out at furnace temperatures of 750 °C and 850 °C.

2-(Allyloxy)biphenyl 43
2-Hydroxybiphenyl 45 (5.11 g, 0.03 mol) was reacted with allyl bromide in the presence of potassium carbonate in DMF, by the method described above, to give 2-(allyloxy)biphenyl 43 (5.66 g, 90%) bp 125-128 °C (1.0 Torr) [lit., 27 148-150 °C (7 Torr)] (Found: C, 86.2; H, 6.9. C₁₅H₁₄O requires C, 85.7%; H, 6.7%); δH 7.65-7.00 (9H, m), 6.02 (1H, m), 5.43-5.21 (2H, m) and 4.58 (2H, m); δC 155.41 (quat), 133.28, 132.65, 130.64, 128.84, 123.01, 122.81, 119.65 (quat), 117.15, 115.47, 70.81 and 20.34; m/z 210 (M^+, 89%), 169 (100), 141 (53) and 115 (59).
FVP of 2-allyloxybiphenyl 43
FVP of 43 [1.323 g (6.3 mmol), T, 100 °C, Tt 650 °C, P 0.001 Torr, 60 min] gave, after the general work-up procedure, dibenzofuran 19a (0.69 g, 65%), mp 79-81 °C (from ethanol) (lit.,29 83-84 °C) δH 7.96 (2H, m) and 7.61-7.30 (6H, m) and 2-hydroxybiphenyl 45 (0.18 g, 17%) mp 53-55 °C (from ethanol) (lit.,28 56 °C) δH 7.50 (5H, s), 7.30-7.26 (2H, m), 7.06-6.99 (2H, m) and 5.30 (1H, br s).
Selected NMR spectra of pyrolysis products 19, 20 and 39.

Figure S1. $^1$H NMR spectrum of 2-methoxydibenzofuran 19d

Figure S2. $^{13}$C NMR spectrum of 2-methyl dibenzofuran 19b
Figure S3. $^{13}$C NMR spectrum of 2-cyanodibenzofuran 19f

Figure S4. $^{13}$C NMR spectrum of dibenzothiophene 20a
Figure S5. $^{13}$C NMR spectrum of 2-methyldibenzothiophene 20b

Figure S6. $^{13}$C NMR spectrum of 2-chlorodibenzothiophene 20c
Figure S7. $^{13}$C NMR spectrum of benzo[b]naphtho[2,3-$d$]furan (β-brazan) 39.
References