

# A convenient one-pot synthesis of 4-methyl-3-phenyl-, 3-aryl- and 3-aryl-4-phenylcoumarins<sup>†</sup>

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Thermal condensation of 2'-hydroxyacetophenones **1a–e** with phenylacetic acid **2a** in refluxing diphenyl ether gives 4-methyl-3-phenylcoumarins **3a–e**. Similarly, reaction of 2-hydroxybenzaldehydes **1f–m** and 2-hydroxybenzophenones **1n–p** with phenylacetic acids **2a–d** gives the corresponding 3-arylcoumarins **3f–m** and 3-aryl-4-phenylcoumarins **3n–p** respectively. Formation of esters **4** and **5** and benzofuran **6** is also observed.

**Keywords:** coumarins, benzofurans, condensations

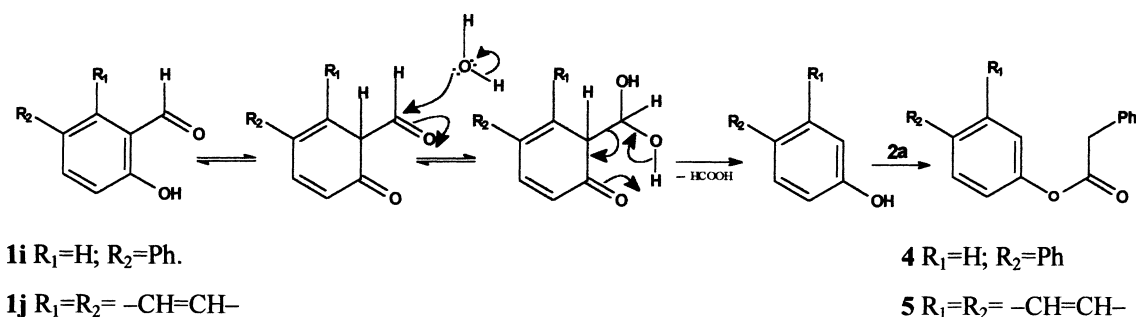
Base catalysed condensation of 2'-hydroxyacetophenones and 2-hydroxybenzaldehydes with phenylacetyl chloride in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> in dry acetone has been reported to give 4-methyl-3-phenylcoumarins and 3-phenylcoumarins respectively.<sup>1</sup> Wadia and co-workers<sup>2</sup> have used arylacetothiomorpholide (a phenylacetic acid equivalent) for condensation with 2-hydroxybenzaldehydes in the presence of POCl<sub>3</sub> to give 3-phenylcoumarins in 30–49% yield. In an improved version, 2'-hydroxyacetophenones or 2-hydroxybenzaldehydes are treated with substituted acetic acids in the presence of the Vilsmeier reagent (DMF-POCl<sub>3</sub>) to give substituted coumarins in 72–98% yield<sup>3</sup>. Reaction of 2-hydroxybenzaldehydes with phenylacetic anhydrides in the presence of dry benzene and triethylbenzylammonium chloride (TEBA) as a phase transfer catalyst has also been reported to give 3-phenylcoumarins in 50–95% yield.<sup>4</sup> A recent modification<sup>5</sup> of these procedures makes use of dicyclohexylcarbodiimide (DCC) in DMSO, perhaps with a view to activate the carbonyl group of phenylacetic acid to nucleophilic attack by the phenolic hydroxyl of 2-hydroxycarbonyl compounds. However, the average yield of coumarins obtained by these methods is less than 30%.

Thermal reactions often serve as one-pot synthetic routes to a number of compounds. Our interest in thermal reactions<sup>6–8</sup> prompted us to develop a simple and general procedure for the synthesis of 4-methyl-3-phenylcoumarins **3a–e**, 3-arylcoumarins **3f–m** and 3-aryl-4-phenylcoumarins **3n–p** in yield ranging from 41 to 89%.

Thermal condensation of 2'-hydroxyacetophenones **1a–e** with phenylacetic acid **2a** in refluxing diphenyl ether gave 4-methyl-3-phenylcoumarins **3a–e** (Reaction time, m.p., literature references, and yield are listed in Table 1). To our knowledge, except for **3a**,<sup>3,9</sup> all other coumarins (**3b–e**) are new and were identified by spectroscopy (IR, <sup>1</sup>H, and <sup>13</sup>C NMR, Table 2). 2'-Hydroxyacetophenones **1b–e** were prepared by Fries rearrangement of the acetates of the corresponding phenols followed by chromatographic separation. Interestingly, 2',4'-dihydroxyacetophenone, 2',5'-dihydroxyacetophenone and 5'-acetyl-2',4'-dihydroxyacetophenone failed to react with phenylacetic acid in refluxing diphenyl ether. Condensation of 2-hydroxybenzaldehydes **1f–m** with phenylacetic acids **2a–d** gave 3-phenyl- and 3-arylcoumarins **3f–m**. All the coumarins from **3f–m** are reported,<sup>2,5,10</sup> except **3i** and **3k**, which are new.

In the reactions of 2-hydroxybenzaldehydes **1i** and **1j** with phenyl acetic acid **2a**, two additional products **4** and **5** were obtained in about 8–10% yield. IR spectra of **4** and **5** showed the presence of an ester carbonyl at around 1765 cm<sup>–1</sup> which is distinctly different from that of a coumarin carbonyl (1710–1720 cm<sup>–1</sup>). In the <sup>1</sup>H NMR spectra, the presence of a sharp singlet at δ 3.9 ppm integrated for two protons clearly indicated that **4** and **5** are 4-biphenyl phenylacetate and 2-naphthyl phenylacetate respectively.

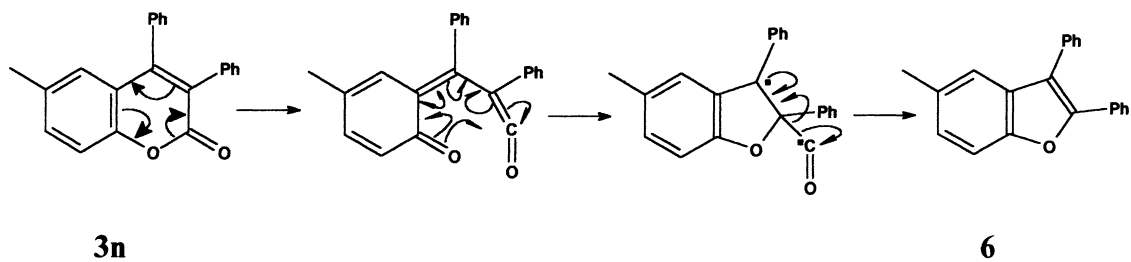
Mechanistically, 4-phenylphenol and 2-naphthol are formed *in situ* by thermal deformation of **1i** and **1j** as shown in



Scheme 1

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<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

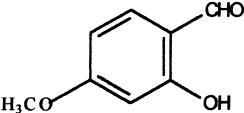
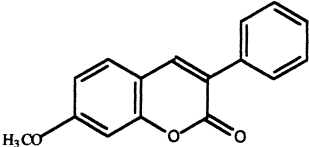
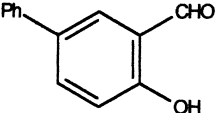
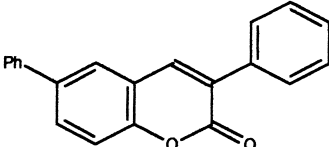
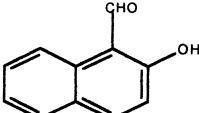
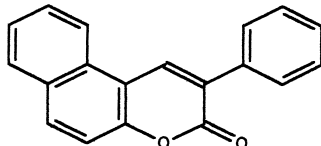
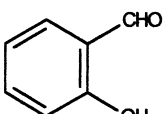
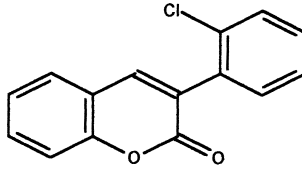
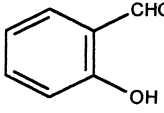
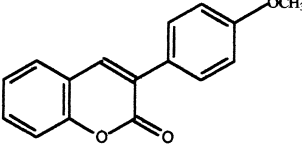
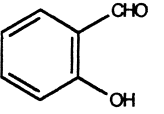
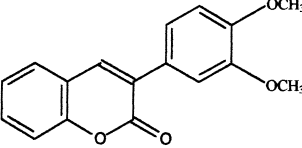
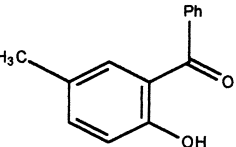
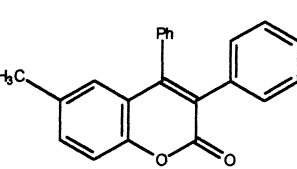
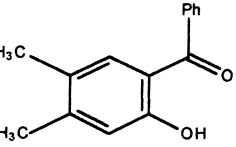
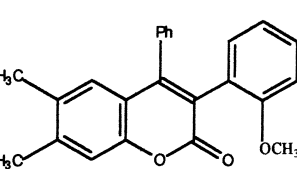
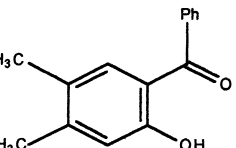
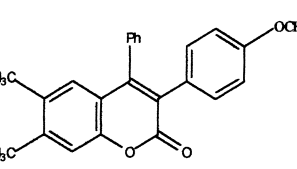


Scheme 2

**Table 1** Physical data of 3-aryl-, 4-methyl-3-phenyl- and 3-aryl-4-phenyl-coumarins

substrate 1	substrate 2 time/h	product 3	m.p./°C obsd # lit.	%/Yield
<b>a</b> 	<b>2a</b> 12.5		155 <sup>b</sup> 156–58 <sup>9</sup>	48
<b>b</b> 	<b>2a</b> 10		158 <sup>a</sup> ---	48
<b>c</b> 	<b>2a</b> 37		136 <sup>d</sup> ---	59
<b>d</b> 	<b>2a</b> 16		162 <sup>b</sup> ---	85
<b>e</b> 	<b>2a</b> 17		208 <sup>c</sup> ---	45
<b>f</b> 	<b>2a</b> 12		141 <sup>b</sup> 141–43 <sup>2</sup>	89
<b>g</b> 	<b>2a</b> 19		147 <sup>d</sup> 145 <sup>5</sup>	57

Table 1 continued

	substrate 1	substrate 2 time/h	product 3	m.p./°C obsd # lit.	%/Yield
h		<b>2a</b> 21		124 <sup>d</sup> 126 <sup>5</sup>	59
i		<b>2a</b> 19		118 <sup>b</sup> ---	51
j		<b>2a</b> 16		144 <sup>b</sup> 145–47 <sup>10</sup>	41
k		<b>2b</b> 21		138 <sup>b</sup> ---	50
l		<b>2c</b> 36		138 <sup>c</sup> 141 <sup>5</sup>	66
m		<b>2d</b> 36		130 <sup>b</sup> 133–4 <sup>5</sup>	55
n		<b>2a</b> 16		215 <sup>b</sup> 212 <sup>11,14</sup>	83
o		<b>2e</b> 31		182 <sup>c</sup> ---	75
p		<b>2c</b> 27.5		227 <sup>c</sup> ---	77

**2a** = phenylacetic acid, **2b** = 2-chlorophenylacetic acid, **2c** = 4-methoxy phenylacetic acid, **2d** = 3,4-dimethoxyphenylacetic acid, **2e** = 2-methoxyphenylacetic acid.

#Solvent for crystallisation: Products **3a–p**: (a) petroleum ether (b) petroleum ether and benzene (c) petroleum ether and dichloromethane (d) benzene and dichloromethane

**Eluents for column chromatography**: Petroleum ether:benzene (3:7) for **3f** and **3m** (7:3) for **3k** and **3i** (1:4) for **3h** (1:1) for **3a**, **3j** and **3n**. Petroleum ether:dichloromethane (9:1) for **3e** (7:3) for **3p** (3:2) for **3l** and **3o**. Benzene:dichloromethane (19:1) for **3g** (1:1) for **3c**.

**Table 2** IR and NMR spectral data of products **3a–p**

Product <b>3</b>	IR $\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR $\delta$ (p.p.m.)	$^{13}\text{C}$ NMR $\delta$ (p.p.m.)
<b>3a</b>	1710	2.28 (3H, s, $\text{C}_4\text{-CH}_3$ ), 7.2–7.66 (9H, m, Ar-H)	16.52 ( $\text{C}_4\text{-CH}_3$ ), 116.7 (C-8), 120.49 (C-4a), 124.19 (C-5), 125.06 (C-6), 127.25 (C-3), 128.12 (C-4'), 128.34 (C-2', C-6'), 129.95 (C-3', C-5'), 131.25 (C-7), 134.38 (C-1'), 147.57 (C-4), 152.6 (C-8a), 160.8 (C-2)
<b>3b</b>	1710	2.26 (3H, s, $\text{C}_4\text{-CH}_3$ ), 2.45 (3H, s, $\text{C}_7\text{-CH}_3$ ), 7.12–7.54 (8H, m, Ar-H)	16.58 ( $\text{C}_4\text{-CH}_3$ ), 21.59 ( $\text{C}_7\text{-CH}_3$ ), 116.9 (C-8), 118.1 (C-4a), 124.8 (C-5), 125.4 (C-6), 126.2 (C-3), 128.08 (C-4'), 128.38 (C-2', C-6'), 130.1 (C-3', C-5'), 134.6 (C-1'), 142.4 (C-7), 147.7 (C-4), 152.7 (C-8a), 161.24 (C-2).
<b>3c</b>	1710	2.25 (3H, s, $\text{C}_4\text{-CH}_3$ ), 3.86 (3H, s, $\text{C}_8\text{-OCH}_3$ ), 6.75–7.6 (8H, m, Ar-H)	16.52 ( $\text{C}_4\text{-CH}_3$ ), 58.69 ( $\text{C}_8\text{-OCH}_3$ ), 100.53 (C-5), 112.2 (C-8), 114.07 (C-4a), 124.16 (C-3), 126.05 (C-7), 127.9 (C-4'), 128.27 (C-2', C-6'), 130.12 (C-3', C-5'), 134.58 (C-1'), 147.8 (C-4), 154.24 (C-8a), 161.24 (C-6), 162.2 (C-2).
<b>3d</b>	1720	2.22 (3H, s, $\text{C}_4\text{-CH}_3$ ), 2.3 (6H, s, $\text{C}_6\text{-CH}_3$ , $\text{C}_7\text{-CH}_3$ ), 7.06 (1H, s, H-8), 7.27 (1H, s, H-5), 7.34 (5H, s, Ar-H)	–
<b>3e</b>	–	2.25 (3H, s, $\text{C}_4\text{-CH}_3$ ), 3.94 (3H, s, $\text{C}_7\text{-OCH}_3$ ), 6.83 (1H, s, H-8), 7.16–7.51 (5H, m, Ar-H), 7.8 (1H, s, H-5)	16.56 ( $\text{C}_4\text{-CH}_3$ ), 56.67 ( $\text{C}_7\text{-OCH}_3$ ), 99.94 (C-8), 107.38 (C-6), 115.039 (C-4a), 125.12 (C-3), 128.13 (C-5), 128.34 (C-2', C-6'), 129.06 (C-4'), 130.03 (C-3', C-5'), 134.1 (C-1'), 146.7 (C-4), 153.3 (C-8a), 158.03 (C-2), 160.69 (C-7).
<b>3f</b>	1720	See ref. 15	See ref. 15
<b>3g</b>	1720	2.42 (3H, s, $\text{C}_6\text{-CH}_3$ ), 7.26–7.7 (8H, m, Ar-H), 7.76 (1H, s, H-4)	20.78 ( $\text{C}_6\text{-CH}_3$ ), 116.17 (C-8), 119.47 (C-4a), 127.7 (C-5), 128.26, 128.46, 128.55 (5Ar-H), 128.77 (C-3), 132.4 (C-7), 134.16 (C-6), 134.93 (C-1'), 139.8 (C-4), 151.7 (C-8a), 160.73 (C-2).
<b>3h</b>	1720	3.88 (3H, s, $\text{C}_7\text{-OCH}_3$ ), 6.88 (2H, dd, $J = 8.1, 2.4$ Hz, H-6, H-8), 7.398 (1H, d, $J = 8.1$ Hz, H-5), 7.36–7.65 (5H, m, Ar-H), 7.76 (1H, s, H-4)	55.08 ( $\text{C}_7\text{-OCH}_3$ ), 100.49 (C-8), 112.7 (C-6), 113.4 (C-4a), 124.87 (C-3), 128.42 (C-2', C-3', C-4', C-5', C-6'), 128.86 (C-5), 135.07 (C-1'), 139.9 (C-4), 155.37 (C-8a), 160.83 (C-2), 162.6 (C-7).
<b>3i</b>	1720	7.29–7.70 (13H, m, Ar-H), 7.82 (1H, s, H-4)	116.7 (C-8), 119.71 (C-4a), 125.98, (C-5), 126.95 (2Ar-C), 127.69 (Ar-C), 128.42 (2Ar-C), 128.47 (2Ar-C), 128.53 (C-3), 128.84 (Ar-C), 128.95 (2Ar-C), 130.24 (C-7), 134.5 (C-1'), 137.7 (C-6), 139.4 (C-1''), 139.79 (C-4), 152.78 (C-8a), 160.43 (C-2).
<b>3j</b>	1720	7.42–8.21 (11H, m, Ar-H), 8.48 (1H, s, H-4)	113.6 (C-4a), 116.54 (C-10), 121.3 (Ar-C), 125.94 (C-9), 127.05 (C-3), 128.1 (Ar-C), 128.48 (4Ar-C), 128.78 (Ar-C), 128.98 (2Ar-C), 130.26 (C-5a, C-8a), 134.97 (C-1'), 135.5 (C-4), 153.01 (C-10a), 160.5 (C-2).
<b>3k</b>	1710	6.39–7.64 (8H, m, Ar-H), 7.78 (1H, s, H-4)	116.58 (C-8), 118.9 (C-4a), 124.5 (C-6), 126.7 (C-5'), 127 (C-3), 128 (C-5), 129.9 (C-6'), 129.8 (C-3'), 131.28 (C-4'), 131.79 (C-7), 133.54 (C-1'), 133.63 (C-2'), 142.6 (C-4), 153.84 (C-8a), 159.7 (C-2).
<b>3l</b>	1720	See ref. 15	See ref. 15
<b>3m</b>	1720	3.92 (3H, s, $\text{OCH}_3$ ), 3.94 (3H, s, $\text{OCH}_3$ ), 6.93 (1H, d, $J = 8.1$ Hz, H-5'), 7.27 (1H, d, $J = 2.4$ Hz, H-2'), 7.28–7.3 (2H, m, H-6, H-8), 7.35 (1H, d, $J = 8.1, 2.4$ Hz H-6'), 7.47–7.54 (2H, m, H-5, H-7), 7.79 (1H, s, H-4)	56.02 (2- $\text{OCH}_3$ ), 111.2 (C-5'), 112.06 (C-2'), 116.4 (C-8), 119.83 (C-4a), 121.3 (C-6'), 124.45 (C-6), 127.52 (C-3), 127.74 (C-5), 128 (C-1'), 131.09 (C-7), 138.66 (C-4), 148.86 (C-3'), 149.9 (C-4'), 153.38 (C-8a), 160.68 (C-2).
<b>3n</b>	1710	2.28 (3H, s, $\text{C}_6\text{-CH}_3$ ), 6.95 (1H, s, H-5), 7.04–7.43 (12H, m, Ar-H)	20.91 ( $\text{C}_6\text{-CH}_3$ ), 116.45 (C-8), 120.11 (C-4a), 126.86 (C-3), 127.48 (C-5), 127.4, 127.64, 128.18, 129.29, 130.48 (10 Ar-C), 132.4 (C-7), 133.9 (C-1''), 133.7 (C-1'), 134.53 (C-6), 151.32 (C-8a), 151.52 (C-4), 161.37 (C-2).
<b>3o</b>	1720	2.18 (3H, s, $\text{C}_7\text{-CH}_3$ ), 2.35 (3H, s, $\text{C}_6\text{-CH}_3$ ), 3.65 (3H, s, $\text{OCH}_3$ ), 6.9–6.94 (2H, m, H-8, H-3'), 7.208 (1H, s, H-5), 6.73–6.78 (3H, m, Ar-H), 7.13–7.29 (5H, m, Ar-H)	19.27 ( $\text{C}_7\text{-CH}_3$ ), 20.08 ( $\text{C}_6\text{-CH}_3$ ), 55.42 ( $\text{OCH}_3$ ), 110.79 (C-3'), 117.37 (C-8), 118.2 (C-4a), 120.2 (C-5'), 123.64 (C-1'), 123.96 (C-3), 127.57 (C-5), 127.67 (C-4''), 128.01, 128.11 (C-2'', C-6''), 128.88, 128.57 (C-3'', C-5''), 129.34 (C-6'), 131.52 (C-4'), 132.61 (C-7), 135.09 (C-6), 141.18 (C-1''), 151.9 (C-8a), 152.24 (C-4), 157.3 (C-2'), 161.13 (C-2).
<b>3p</b>	1710	2.18 (3H, s, $\text{C}_7\text{-CH}_3$ ), 2.35 (3H, s, $\text{C}_6\text{-CH}_3$ ), 3.72 (3H, s, $\text{OCH}_3$ ), 6.7 (2H, d, $J = 9.0, 1.8$ Hz, H-3', H-5'), 6.9 (1H, s, H-8), 7.04 (2H, d, $J = 9.0, 1.8$ Hz, H-2', H-6'), 7.19 (1H, s, H-5), 7.09–7.33 (5H, m, Ar-H)	19.3 ( $\text{C}_7\text{-CH}_3$ ), 20.1 ( $\text{C}_6\text{-CH}_3$ ), 55.1 ( $\text{OCH}_3$ ), 113.28 (C-3', C-5'), 117.3 (C-8), 118.3 (C-4a), 125.58 (C-1'), 126.5 (C-3), 127.7 (C-5), 128.3 (C-2'', C-6''), 129.47 (C-2', C-6'), 131.97 (C-3'', C-5''), 132.78 (C-7), 135.1 (C-6), 141.3 (C-1''), 151.1 (C-8a), 151.6 (C-4), 158.8 (C-4'), 161.94 (C-2).

Scheme 1. We propose that the aldehyde group is lost as formic acid.

Reaction of 2-hydroxybenzophenones with phenylacetic acid in the presence of triethylamine and acetic anhydride is known to give 3,4-diphenylcoumarins.<sup>11,12</sup> Our simple method of just refluxing 2-hydroxybenzophenones **1n–p** with phenylacetic acids **2a**, **2e** and **2c** in diphenyl ether could give 3-aryl-4-phenylcoumarins **3n–p** in more than 75% yield. In the reaction of 5-methyl-2-hydroxybenzophenone **1n** with phenylacetic acid **2a**, formation of 5-methyl-2,3-diphenylbenzofuran **6**<sup>13</sup> by thermal decarbonylation of 6-methyl-3,4-diphenylcoumarin **3n** (Scheme 2) was also observed.

On heating with alkali, 7-methoxy-4-(4'-hydroxyphenyl)-3-phenylcoumarin is reported<sup>11</sup> to give 2-phenyl-3-(4'-hydroxyphenyl)-6-methoxybenzofuran by decarbonylation. Neither the data on the benzofuran nor the mechanism of its formation is given. Assuming the participation of hydroxide ion, in all probability, the 2-pyrone carbonyl is lost as CO<sub>2</sub>. It is of interest to note that the base peak in the mass spectra of coumarins is due to loss of 2-pyrone carbonyl (M<sup>+</sup>-28) to give a positively charged benzofuran ion or its substitution product.<sup>16–18</sup>

## Experimental

Melting points are uncorrected. IR spectra (KBr) were recorded on FTIR-8101A Shimadzu spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Gemini 300 MHz and Bruker WT 300 MHz FT NMR spectrophotometers in CDCl<sub>3</sub> with TMS as an internal standard. Petroleum ether refers to hydrocarbon fractions boiling in the range 60–80°C. All yields refer to pure isolated products.

**4-Methyl-3-phenylcoumarins (3a–e), 3-arylcoumarin (3f–m) and 3-aryl-4-phenylcoumarins (3n–p): General procedure:** A mixture of 2-hydroxycarbonyl compounds **1a–p** (5.0 mmoles), phenylacetic acids **2a–e** (6.0 mmoles) and diphenylether (5.0 ml) was refluxed in an oil bath or a heating mantle for the time indicated in Table 1. The progress of the reaction was periodically monitored by TLC. After the reaction was complete, most of the diphenyl ether was removed by distillation. The residue on cooling was dissolved in diethyl ether (20 ml), washed with saturated aqueous NaHCO<sub>3</sub> (3 × 5.0 ml) and water until the organic phase is neutral. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, concentrated, and chromatographed over silica gel using eluents as indicated in Table 1, to give products **3a–p**, which were recrystallised using the solvent system indicated in Table 1.

**4-biphenyl phenylacetate 4 and 3,6-diphenylcoumarin 3i:** Reaction of 2-hydroxy-6-phenylbenzaldehyde **1i** and phenylacetic acid **2a**, after usual work-up and elution with petroleum ether gave **4** (0.12 g, 10%). Recrystallisation from aqueous ethanol afforded a pale yellow solid, m.p. 121°C; IR (KBr) 1760, 1490, 1340, 1225, 1190, 1170, 1130, 840, 755 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ ppm 7.11–7.58 (14H, m, Ar-H), 3.89 (2H, s, Ar-CH<sub>2</sub>-COO-). Compound **4** was found to be identical in all respects with an authentic sample prepared from phenylacetylchloride and 4-phenylphenol. Further elution with petroleum ether-benzene (7:3) gave **3i** (0.64 g, 51%) as a pale yellow solid.

**2-Naphthyl phenylacetate 5 and 3-phenyl-5,6-benzocoumarin 3j:** Reaction of 2-hydroxynaphthaldehyde **1j** and phenylacetic acid **2a**, after usual work-up and elution with petroleum ether gave **5** (0.1 g, 7%). Recrystallisation from petroleum ether afforded white solid, m.p. 84°C [lit.<sup>19</sup> 76–77°C from Et<sub>2</sub>O]; IR (KBr) 1760, 1355, 1240, 1220, 1130, 1110, 705 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ ppm 7.17–7.84 (12H, m, Ar-H), 3.92 (2H, s, Ar-CH<sub>2</sub>-COO-); <sup>13</sup>C NMR

(300 MHz, CDCl<sub>3</sub>) δ ppm 41.45, 118.40, 120.93, 125.67, 126.51, 127.35, 127.58, 127.70, 128.73, 129.31, 131.41, 133.41, 133.65, 148.31, 170.13. Further elution with petroleum ether-benzene (1:1) afforded **3j** (0.65 g, 41%).

**5-methyl-2,3-diphenylbenzofuran 6 and 6-methyl-3,4-diphenylcoumarin 3n:** Reaction of 2-hydroxy-6-methylbenzophenone **1n** and phenylacetic acid **2a** after usual work-up and elution with petroleum ether gave **6** (0.16 g, 11.0%) as a white solid. Recrystallisation from hexane gave white flakes, m.p. 113°C (lit.<sup>13</sup> 114°C); IR (KBr) 1600, 1460, 1375, 1210, 1055, 755, 685 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ ppm 7.22–7.44 (12H, m, Ar-H), 7.16 (1H, d, *J* = 8.4 Hz, H-7), 2.45 (3H, s, C<sub>5</sub>-CH<sub>3</sub>); <sup>13</sup>C NMR (200 MHz, CDCl<sub>3</sub>) δ ppm 21.3 (q, C<sub>5</sub>-CH<sub>3</sub>), 110.6 (d, C-7), 117.3 (s, C-3), 119.7 (d), 125.9 (d), 126.9 (2d), 127.5 (d), 128.2 (d), 128.4 (2d), 128.9 (2d), 129.8 (2d), 130.2 (s), 130.8 (s), 132.4 (s), 133.0 (s), 150.6 (s, C-7a), 152.4 (s, C-2); EIMS: *m/z* 284(M<sup>+</sup>), 268, 255, 239, 226, 178, 141, 120. Further elution with petroleum ether-benzene (1:1) gave **3n** (1.30 g, 83%).

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## References

- S. Neelakantan, P.V. Raman and A. Tinabaye, *Ind. J. Chem.*, 1982, **21B**, 256.
- M.S. Phansalkar, K.K. Deshmukh, S.L. Kelkar and M.S. Wadia, *Ind. J. Chem.*, 1987, **26B**, 562.
- A.K. Awasthi and R.S. Tewari, *Synthesis*, 1986, 1061.
- S. Mohanty, J.K. Makrandi, and S.K. Grover, *Ind. J. Chem.*, 1989, **28B**, 766.
- N. Hans, M. Singhi, V. Sharma and S.K. Grover, *Ind. J. Chem.*, 1996, **35B**, 1159.
- S.P. Kamat, L.G. Sardesai and S.K. Paknikar, *Ind. J. Chem.*, 1984, **23B**, 892.
- S.P. Kamat and S.K. Paknikar, *Ind. J. Chem.*, 1985, **24B**, 38.
- L.G. Sardesai, S.K. Paknikar, R.B. Bates, T.J. Siahann, V.V. Kane and P.K. Mishra, *Heterocycles*, 1987, **26**, 2941.
- N. Jain, N. Devi and H.G. Krishnamurthy, *Ind. J. Chem.*, 1994, **33B**, 1085.
- N.S. Narasimhan, R.S. Mali and M.V. Barve, *Synthesis*, 1979, 906.
- S. Ray, P.K. Grover, and N. Anand, *Ind. J. Chem.*, 1971, **9**, 619.
- I. Sharma and S. Ray, *Ind. J. Chem.*, 1988, **27B**, 374.
- B. Arventiev, M. Strul and H. Wexler, *Acad. Rep. Populare, Romine, Fidiaia, Isai, studii cecetari, stint. Chim.* 1960, **11**, 63; *Chem. Abstr.*, 1961, **55**, 15452a.
- N.P. Buu-Hoi, and B. Eckert, *J. Org. Chem.*, 1954, **19**, 1391.
- J. Mitra and A.K. Mitra, *Ind. J. Chem.*, 1996, **35B**, 588.
- N.S. Wulfson, V.I. Zaretskii and V.G. Zaikin, *Bull. Acad Sci, U.S.S.R. Chem. Div.*, 1963, 2046; *Chem. Abstr.*, 1964, **60**, 10040a.
- C.S. Barnes and J.L. Occolowitz, *Aust. J. Chem.*, 1964, **17**, 975.
- V.V.S. Murthy, P.S. Sampathkumar and T.R. Seshadri, *Ind. J. Chem.*, 1972, **10**, 19.
- F. Tanaka, M. Node, K. Tanaka, M. Mizuchi, S. Hosoi, M. Nakayama, T. Taga and K. Fuji, *J. Am. Chem. Soc.*, 1995, **117**, 12159.