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Synthesis of 6-substituted-3,4-dihydro-2*H*-1-benzopyran-2-ones(dihydrocoumarins) via palladium catalysed coupling reactions

Stephen G. Davies *, Dirk Pyatt,

The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY (U.K.)

and Colin Thomson

Fisons, Pharmaceutical Division, Bakewell Road, Loughborough, LE11 0RH (U.K.)

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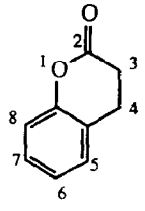
Abstract

6-Alkenyl, alkynyl, and aryl-3,4-dihydrocoumarins have been prepared from 6-bromo-3,4-dihydrocoumarin via palladium catalysed coupling reactions. 6-Carboalkoxy- and 6-keto-3,4-dihydrocoumarins have been obtained via palladium-catalysed carbonylations of 6-bromo- and 6-iodo-3,4-dihydrocoumarins respectively.

Introduction

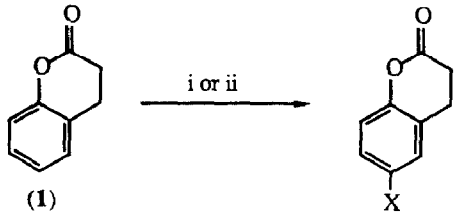
The benzopyrans are ubiquitous in nature and are of pharmacological interest [1]. In particular the coumarins have received considerable attention owing to the important physiological properties of many of their derivatives [2]. Derivatives of 3,4-dihyrocoumarin (**1**) are of particular interest. In the past decade exploration of the potential of organometallic chemistry has resulted in many novel synthetically useful transformations [3]. Activation of aromatic halogens via insertion of palladium(0) is a well known process, and provides access to intermediates which can undergo a number of coupling reactions [4]. In this case the methodology provides a convenient route for the systematic introduction of a wide range of functional groups into the 6 position of 3,4-dihydrocoumarin starting from the simple and readily available precursors, 6-bromo and 6-iodo-3,4-dihydrocoumarin.



(1)

Results and discussion

The parent compound 3,4-dihydrocoumarin (**1**) is cheap and commercially available and is halogenated selectively in good yield upon treatment with bromine or iodine monochloride to afford 6-bromo-3,4-dihydrocoumarin (**2**) and 6-iodo-3,4-dihydrocoumarin (**3**), respectively.



(**1**)

(**2**) X= Br
(**3**) X= I

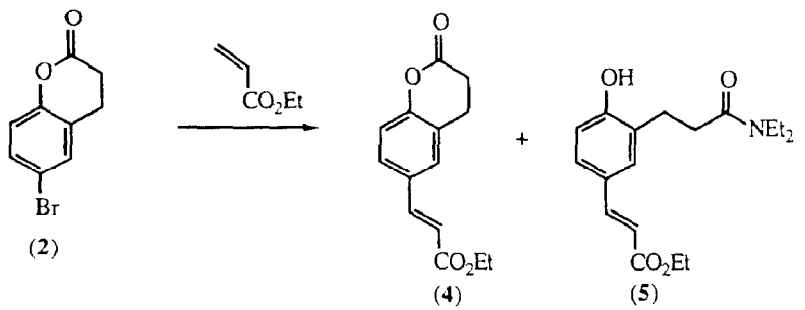
Reagents: i) Br_2, CH_2Cl_2; ii) ICl, CH_2Cl_2.

The Heck olefination is perhaps the best known of palladium-catalysed coupling reactions in which vinyl, benzyl, and aryl halides are coupled with olefins [5]. In the present work 6-bromo-3,4-dihydrocoumarin (**2**) was coupled successfully with ethylacrylate in the presence of catalytic amounts of palladium acetate and tri-*o*-tolylphosphine in triethylamine to yield 61% of ethyl 6-(3,4-dihydrocoumarin)propenoate (**4**) and 30% of the corresponding ring opened diethylamide (**5**) (Scheme 1). Both compounds **4** and **5** were formed completely stereoselectively, and the *E* geometry was assigned on the basis of the 16 Hz coupling constants between the olefinic protons. Compound **5** is probably formed by attack of triethylamine on the phenolic lactone, the resulting intermediate being de-ethylated by a bromide ion produced in the Heck reaction.

A related coupling of **2** with trimethylsilylacetylene [6] afforded 6-(trimethylsilylethynyl)-3,4-dihydrocoumarin (**6**) in 80% yield. The silyl protecting group was removed using cesium fluoride in acetonitrile to yield 79% of 6-ethynyl-3,4-dihydrocoumarin (**7**) (Scheme 2).

The lability of the lactone ring of **6** is illustrated by the formation of the ring-opened methyl ester **8** in 71% yield on treatment with potassium carbonate in methanol at 18 °C (Scheme 3).

Cross coupling of aryl halides with organostannanes catalysed by palladium(0), as developed principally by Stille, facilitates the transfer of many organic groups

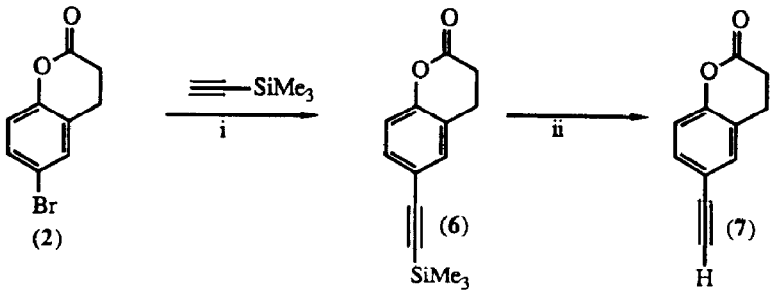


(**2**)

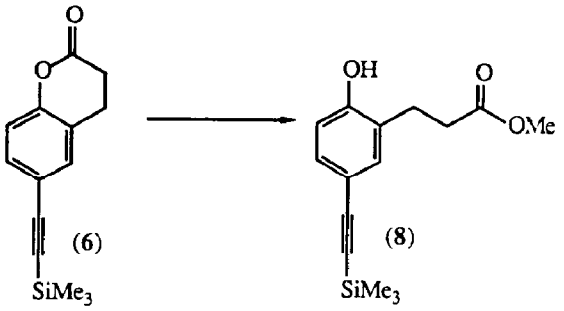
(**4**)

(**5**)

Scheme 1. Reagents: $Pd(OAc)_2$ (2%), P(*o*-tolyl)$_3$ (8%), Et_3N, 100 °C, 24 h.



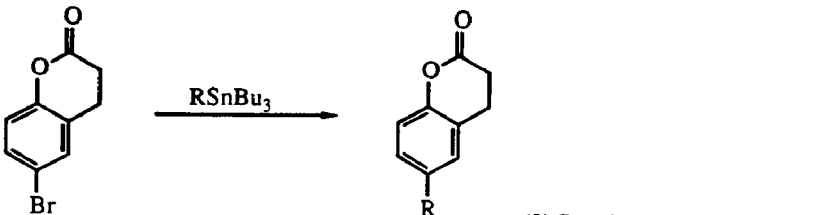
Scheme 2. Reagents: (i) $Pd(OAc)_2$ (2%), PPh_3 (8%), Et_3N, 100 °C, 24 h; (ii) CsF, MeCN.



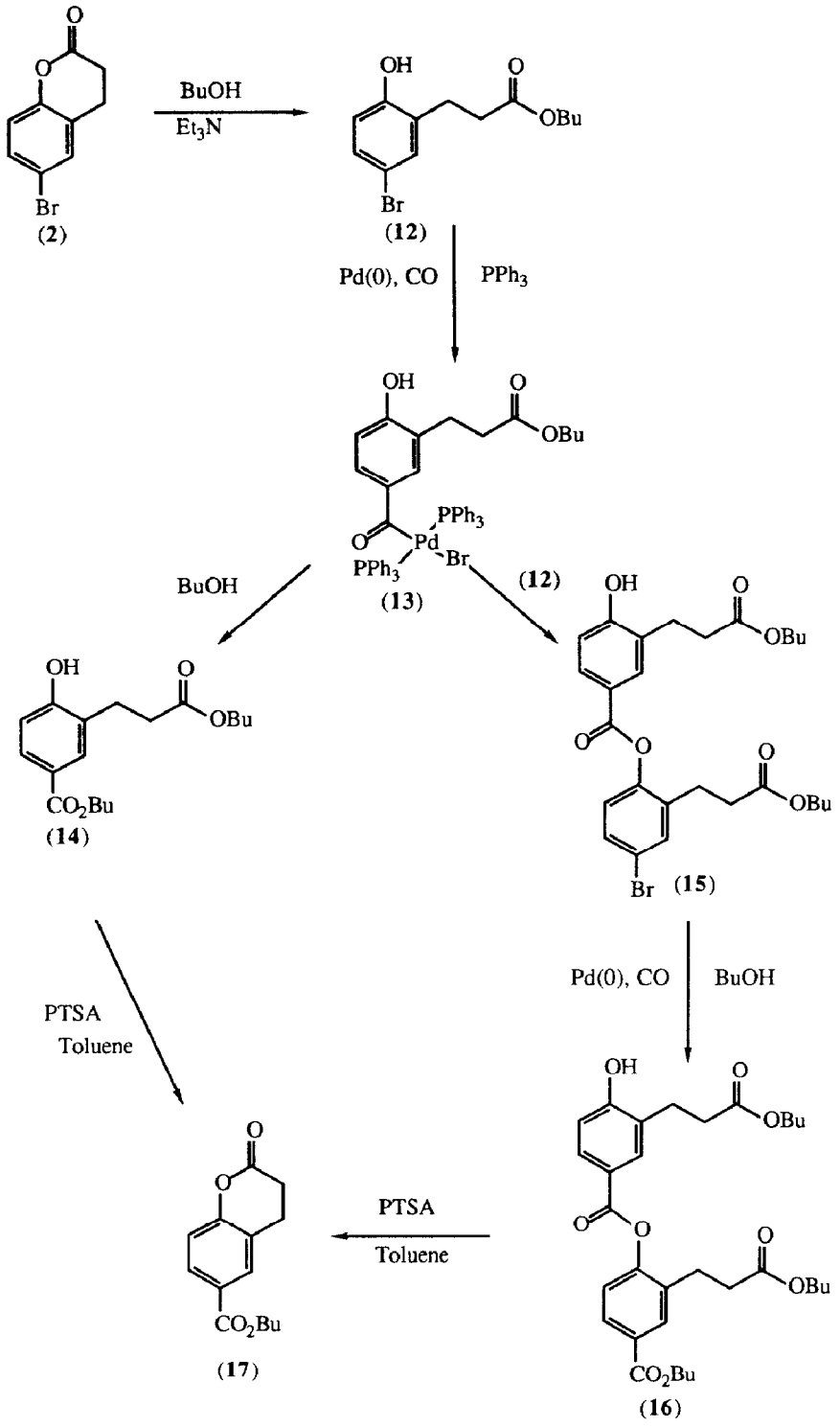
Scheme 3. Reagents: K_2CO_3, MeOH.

[7,8]. The use of unsymmetrical organostannanes ($RSnBu_3$) results in the selective transfer of the R group as transmetallation of a butyl group from tin to palladium is sluggish relative to that of most other organic groups [7]. The synthesis of unsymmetrical organostannanes is readily achieved, and the possible range of R groups is extensive [8]. Compound **2** was successfully coupled with vinyl-, phenyl-, and phenylethynyl-tributylstannanes as shown in Scheme 4. The transfer of alkyl groups was not investigated as the resulting 6-alkyl-3,4-dihydrocoumarins are accessible by other methods [9].

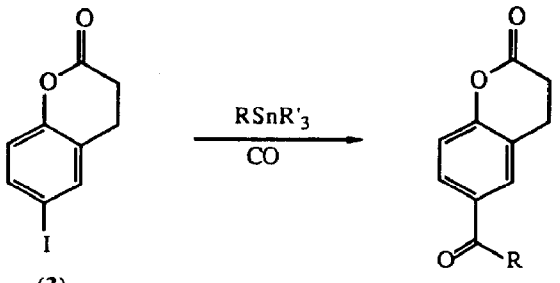
Carbonylation of η^1-arylpalladium complexes generally leads to the formation of the corresponding acylpalladium complexes, which can be trapped nucleophilically by alcohols and amines to yield esters and amides respectively [10]. A recent mechanistic study on the stoichiometric version of this reaction [11] showed that carbonylation of the intermediate aryl-palladium complex is rapid at room tempera-



Scheme 4. Reagents: $Pd(OAc)_2$ (2%), PPh_3 (8%), Et_3N, 100 °C, 24 h.


BuOH
Et3N
(2)
(12)
Pd(0), CO
PPh3
(13)
BuOH
(12)
(14)
(15)
Pd(0), CO
BuOH
PTSA
Toluene
PTSA
Toluene
(17)
(16)

Scheme 5



(3) (18)-(22)

Scheme 6. Reagents: $Pd(OAc)_2$ (2%), PPh_3 (4%), THF.

R	R'	Product	Reaction temperature (°C)	Yield (%)
Phenylethynyl	butyl	**18**	40–45	81
Vinyl	butyl	**19**	50–55	64
Phenyl	butyl	**20**	65–70	62
Methyl	methyl	**21**	65	74
Butyl	butyl	**22**	85	74

ture and is irreversible. Furthermore in the case of methanol as the nucleophile the presence of a base is required for attack on the acylpalladium complex. A base is essential in the catalytic reaction to remove the acid by-product and regenerate the catalyst. Carbonylation of **2** in butanol in the presence of catalytic amounts of palladium chloride and triphenylphosphine resulted in two products, **14** and **16**. It was found that both of the products **14** and **16**, either independently or in the crude reaction mixture, could be converted to butyl 3,4-dihydrocoumarin-6-carboxylate (**17**) by treatment with a catalytic amount of *p*-toluenesulphonic acid in toluene at reflux, and in this manner **2** was converted to **17** in 68% overall yield (Scheme 5). The first step probably involves formation of the ester **12**, and products **14** and **15** presumably arise from trapping of the intermediate acylpalladium (**13**) with butanol or **12**, respectively.

Carbonylation of aryl iodides (aryl bromides are not suitable substrates) in the presence of organostannanes gives ketones. This reaction was first reported by Tanaka [12], who used severe conditions (120 °C, HMPA, 30 atm CO). Subsequently milder conditions involving use of a ligand-free palladium catalyst were employed (20 °C, 1 atm CO, HMTA) [13]. The main drawbacks of this procedure are the use of a toxic solvent and that large amounts of non-carbonylated cross-coupled products are formed in the reactions involving vinyl and ethynyl stannanes. We found that this reaction can be performed in THF as a solvent, with palladium acetate and triphenylphosphine as catalyst, under an atmosphere of carbon monoxide at temperatures between 40–85 °C depending on the organostannane. In this fashion a variety of ketones were prepared in good yield to the exclusion of non-carbonylated cross coupling (Scheme 6).

Experimental

The palladium-catalysed coupling reactions were carried out in a glass Fischer-Porter pressure bottle, except in the case of the tin cross couplings of 6-bromo-3,4-

dihydrocoumarin (**2**), which were performed in Schlenk tubes under nitrogen. THF was distilled from sodium benzophenone ketyl, and triethylamine was stored over potassium hydroxide pellets. Petroleum of boiling point 40–60 °C was used. Butanol was distilled prior to use and stored over 4A molecular sieves. Other solvents were used as supplied. Palladium chloride and palladium acetate were supplied by Johnson–Matthey. Ethyl acrylate, trimethylsilylacetylene, tetramethyltin and tetrabutyltin (Aldrich) were used as supplied. Vinyltributyltin [14], phenyltributyltin [15], and phenylethynyltributyltin [16] were prepared by published procedures. Chromatography was performed on silica gel (Merck Kieselgel 60 H). ^{1}H NMR spectra were recorded in deuteriochloroform on a Bruker WH 300 (300 MHz) instrument, ^{13}C NMR spectra were recorded on a Bruker AM 250 (62.89 MHz) instrument for solutions in deuteriochloroform. Quoted chemical shifts are from the broad band decoupled spectrum, while assignments are from the off resonance spectrum. Mass spectra were obtained with a V.G. Micromass VG ZAB IF and TRIO-1 GC-MS instruments by both electron impact and chemical ionisation techniques. Melting points were determined with a Gallenkamp apparatus and are uncorrected.

6-Bromo-3,4-dihydro-2H-1-benzopyran-2-one (2). A solution of bromine (15.5 ml) in dichloromethane (50 ml) was added during 30 min to a solution of 3,4-dihydrocoumarin (**1**) (45 g, 0.3 mol) in dichloromethane (200 ml). The mixture was stirred overnight at 15 °C, (after which the colour had been discharged) then diluted with dichloromethane (200 ml), and washed with aqueous sodium bicarbonate (sat. 2 × 100 ml) followed by water (100 ml). The solution was dried over magnesium sulphate, filtered, and concentrated under reduced pressure. The residue was washed with petroleum ether (2 × 50 ml), the filtrate concentrated to precipitate the residual starting material (4 g, 9%), and the remaining solid was recrystallised from dichloromethane/petroleum ether to give the title compound **2** as thick white crystals (50.3 g, 74%), m.p. 104–105 °C (Lit. 106–106.5 °C [17]), δ 7.36 (2H, m, H7, H5); 6.93 (1H, d, J 8 Hz, H8); 2.99 (2H, m, CH_2 pyrone); 2.78 (2H, m, CH_2 pyrone).

6-Iodo-3,4-dihydro-2H-1-benzopyran-2-one (3). Iodine monochloride (60 ml, 1 M solution in CH_2Cl_2) was added to 3,4-dihydrocoumarin (**1**) (8.8 g, 0.6 mol) in dichloromethane (60 ml) under nitrogen, and the mixture was stirred at 18 °C for 60 h. The solution was then washed with aqueous sodium thiosulphate (100 ml, 2 M) followed by water (50 ml), dried over magnesium sulphate, filtered, and concentrated under reduced pressure. The residue was washed with petroleum ether (2 × 30 ml), the filtrate concentrated to precipitate the residual starting material (2 g, 23%), and the remaining solid was recrystallised from dichloromethane/petrol to give the compound **3** as white needles (11 g, 67%), m.p. 133–134 °C (Found: C, 39.35; H, 2.3. $C_9H_7IO_2$ calcd.: C, 39.4; H, 2.6%); δ 7.57 (2H, m, H5, H7); 6.82 (1H, d, J 8 Hz, H8); 2.99 (2H, m, CH_2 pyrone); 2.78 (2H, m, CH_2 pyrone); m/z 275 (MH^+).

Ethyl 6-(3,4-dihydro-2H-1-benzopyran-2-one)propenoate (4). Compound **2** (227 mg, 1 mmol) was heated with ethyl acrylate (0.3 ml, 3 mmol), palladium acetate (5 mg, 2%), tri-*o*-tolylphosphine (25 mg, 8%), and triethylamine (2 ml) at 100 °C for 24 h. The mixture was then cooled, diluted with ether, and filtered to remove the triethylamine hydrobromide crystals. The filtrate was concentrated at reduced pressure and subjected to column chromatography to give the compound **4** as shiny white plates (150 mg, 61%), m.p. 76 °C (Found: C, 68.4; H, 5.6. $C_{14}H_{14}O_4$ calcd.: C, 68.3; H, 5.7%); δ 7.63 (1H, d, J 16 Hz, alkene-H); 7.43 (1H, dd, J 2, 8 Hz, H7);

7.37 (1H, d, *J* 2 Hz, H5); 7.06 (1H, d, *J* 8 Hz, H8); 6.37 (1H, d, *J* 16 Hz, alkene-H); 4.30 (2H, q, *J* 7 Hz, OCH_2); 3.04 (2H, m, CH_2 pyrone); 2.82 (2H, m, CH_2 pyrone); 1.34 (3H, t, *J* 7 Hz, Me); $\delta(^{13}C)\{^1H\}$ 167.7 (C), 166.7 (C), 153.3 (C), 143.1 (CH), 130.9 (C), 128.1 (CH), 127.7 (CH), 123.1 (C), 118.2 (CH), 117.5 (CH), 60.6 (CH_2), 29.0 (CH_2), 23.7 (CH_2), 14.3 (CH_3); *m/z* 247 (MH^+); followed by ethyl (3-*N*,*N'*-diethylpropanamide-4-hydroxyphenyl)propenoate (**5**) as a white powder (100 mg, 31%), m.p. 138–139 °C (Found: C, 67.4; H, 7.9; N, 4.6. $C_{18}H_{25}NO_4$ calcd.: C, 67.6; H, 7.9; N, 4.4%); δ 10.38 (1H, s, phenol-H); 7.61 (1H, d, *J* 16 Hz, alkene-H); 7.33 (1H, dd, *J* 2, 8 Hz, H7); 7.24 (1H, d, *J* 2 Hz, H5); 6.92 (1H, d, *J* 8 Hz, H8); 6.27 (1H, d, *J* 16 Hz, alkene-H); 4.25 (2H, q, *J* 7 Hz, OCH_2); 3.39 (2H, q, *J* 7 Hz, NCH_2); 3.29 (2H, q, *J* 7 Hz, NCH_2); 2.95 (2H,m, CH_2 pyrone); 2.74 (2H, m, CH_2 pyrone); 1.33 (3H, t, *J* 7 Hz, OCH_2Me); 1.14 (3H, t, *J* 7 Hz, NCH_2Me); 1.11 (3H, t, *J* 7 Hz, NCH_2Me); *m/z* 320 (MH^+).

*6-(Trimethylsilylethynyl)-3,4-dihydro-2H-1-benzopyran-2-one (**6**).* Compound (**2**) (227 mg, 1 mmol) was heated with trimethylsilylacetylene (0.22 ml, 2 mmol), palladium acetate (5 mg, 2%), triphenylphospine (21 mg, 8%), and triethylamine (2 ml) at 100 °C for 24 h. The mixture was worked-up in the same manner as in the preparation of **4** to give the compound **6** as fluffy white needles (195 mg, 80%), m.p. 83–84 °C (Found: C, 68.8; H, 6.8. $C_{14}H_{16}O_2Si$ calcd.: C, 68.8; H, 6.6%); δ 7.35 (2H, m, H5, H7); 6.98 (1H, d, *J* 8 Hz, H8); 2.99 (2H, m, CH_2 pyrone); 2.78 (2H, m, CH_2 pyrone); 0.25 (9H, s, $SiMe_3$); *m/z* 245 (MH^+).

*6-Ethynyl-3,4-dihydro-2H-1-benzopyran-2-one (**7**).* A mixture of cesium fluoride (31 mg, 0.2mmol), and **6** (50 mg, 0.2 mmol) and acetonitrile (2 ml) was stirred at 18 °C for 4 h by which time TLC indicated that the starting material had been consumed. The solution was diluted with ether, filtered, concentrated, and subjected to column chromatography to give the compound **7** as pale yellow needles (27 mg, 79%), m.p. 145 °C (Found: C, 77.0; H, 4.7. $C_{11}H_8O_2$ calcd.: C, 76.7; H, 4.7%); δ 7.39 (2H, m, H5, H7); 7.01 (1H, d, *J* 8 Hz, H8); 3.06 (1H, s, acetylinic-H); 2.91 (2H, m, CH_2 pyrone); 2.81 (2H, m, CH_2 pyrone); *m/z* 191 (MNH_4^+), 172 (MH^+).

*Methyl(5-hydroxy-3-trimethylsilylethynylphenyl)propionate (**8**).* Potassium carbonate (5 mg) was suspended in methanol (0.5 ml) and **6** (50 mg, 0.2 mmol) was added. The mixture was stirred at 18 °C for 3h, filtered, concentrated, and subjected to column chromatography to yield 40 mg (71%) of a pale solid which was identified as the compound **8**; δ 7.2 (2H, m, H5, H7); 6.78 (1H, d, *J* 8 Hz, H8); 3.68 (3H, s, OMe); 2.90 (2H, m, CH_2 pyrone); 2.75 (2H, m, CH_2 pyrone); 0.25 (9H, s, $SiMe_3$); *m/z* 277 (MH^+).

*General procedure of palladium catalysed tin cross coupling reactions of **2**.* A Schlenk tube was charged with **2** (227 mg, 1 mmol), the organostannane (1.5 equiv.), palladium acetate (5 mg, 2%), triphenylphospine (21 mg, 8%), and triethylamine (2 ml). The vessel was degassed by two freeze thaw cycles and heated to 100 °C for 24 h. The mixture was cooled then concentrated under vacuum, and the residue was purified by column chromatography, followed by trituration with petroleum ether (to remove any organotin residues) and recrystallised from ether/petrol or dichloromethane.

*6-Vinyl-3,4-dihydro-2H-1-benzopyrone-2-one (**9**).* Compound **2** was heated with vinyltributyltin (475 mg, 1.5 mmol), triethylamine, and the catalyst mixture to give the compound **9** as white needles (115 mg, 64%), m.p. 88 °C (Found: C, 76.0; H, 6.1. $C_{11}H_{10}O_2$ calcd.: C, 75.8; H, 5.8%); δ 7.29 (1H, dd, *J* 2, 8 Hz, H7); 7.25 (1H, d, *J*

2Hz, H5); 7.01 (1H, d, *J* 8 Hz, H8); 6.66 (1H, dd, *J* 12, 17 Hz, int. alkene-H); 5.69 (1H, d, *J* 17 Hz, *trans* alkene-H); 5.23 (1H, d, *J* 12 Hz, *cis*-alkene-H); 2.92 (2H, m, CH_2 pyrone); 2.79 (2H, m, CH_2 pyrone); ^{13}C {^1H} 168.2 (C), 151.6 (C), 135.6 (CH), 134.1 (C), 126.1 (CH), 125.7 (CH), 122.6 (C), 117.0 (CH), 113.8 (CH_2), 29.2 (CH_2), 23.8 (CH_2); *m/z* 174 (M^+).

*6-Phenyl-3,4-dihydro-2H-1-benzopyran-2-one (**10**).* Compound **2** heated with phenyltributyltin (550 mg, 1.5 mmol), triethylamine, and the catalyst mixture to give the compound **10** as white needles (170 mg, 76%), m.p. 93–94°C (Found: C, 80.3; H, 5.5. $C_{15}H_{12}O_2$ calcd.: C, 80.3; H, 5.4%); δ 7.5 (7H, m, aromatic-H); 7.13 (1H, d, *J* 8 Hz, H8); 3.08 (2H, m, CH_2 pyrone); 2.84 (2H, m, CH_2 pyrone); *m/z* 224 (M^+).

*6-Phenylethynyl-3,4-dihydro-2H-1-benzopyran-2-one (**11**).* Compound **2** was heated with phenylethynyltributyltin (600 mg, 1.5 mmol), triethylamine, and the catalyst mixture to give the compound **11** as shiny white plates (150 mg, 61%), m.p. 155–156°C (Found: C, 82.3; H, 4.8. $C_{17}H_{12}O_2$ calcd.: C, 82.2; H, 4.9%); δ 7.45 (7H, m, aromatic-H); 7.05 (1H, d, *J* 8 Hz, H8); 3.03 (2H, m, CH_2 pyrone); 2.82 (2H, m, CH_2 pyrone); *m/z* 248 (M^+).

*Carbonylation of **2**.* A Fischer–Porter bottle was charged with **2** (680 mg, 3 mmol), butanol (5 ml), triethylamine (3 ml), palladium chloride (21 mg, 4%), and triphenylphosphine (63 mg, 8%). The vessel was flushed with carbon monoxide, charged to a pressure of 3 atm, and kept at 85°C for 60 h. The system was cooled and vented, and the mixture diluted with ether. The solution was filtered to remove the triethylamine hydrobromide, then concentrated and subjected to column chromatography to yield butyl (5-bromo-2-hydroxyphenyl)propionate (**12**) as a pale oil (60 mg, 6%), δ 7.55 (1H, s, phenol-H); 7.2 (2H, m, H5, H7); 6.80 (1H, d, *J* 8 Hz, H8); 4.15 (2H, t, *J* 7 Hz, OCH_2); 2.92 (2H, m, CH_2 pyrone); 2.80 (2H, m, CH_2 pyrone), 1.60 (2H, quintet, *J* 7 Hz, $OCH_2CH_2CH_2$); 1.4 (2H, sextet, *J* 7 Hz, $CH_2CH_2CH_3$); 0.95 (3H, t, *J* 7 Hz, Me); *m/z* 300 [MH^+(^{79}Br)] and 302 [MH^+(^{81}Br)]; followed by butyl(3-butoxycarbonyl-6-hydroxyphenyl)propionate (**14**) as a pale oil (590 mg, 60%), δ 8.05 (12 H, broad, phenol-H); 7.85 (2H, m, H5, H7); 6.90 (1H, d, *J* 8 Hz, H8); 4.30 (2H, t, *J* 7 Hz, OCH_2); 4.12 (2H, t, *J* 7 Hz, OCH_2); 2.95 (2H, m, CH_2 pyrone); 2.77 (2H, M, CH_2 pyrone); 1.75 (2H, quintet, *J* 7 Hz, $OCH_2CH_2CH_2$); 1.60 (2H, t, *J* 7 Hz, $OCH_2CH_2CH_2$); 1.48 (2H, sextet, *J* 7Hz, $CH_2CH_2CH_3$); 1.25 (2H, sextet, *J* 7 Hz, $CH_2CH_2CH_3$);0.98 (3H, t, *J* 7 Hz, Me); 0.91 (3H, t, *J* 7 Hz, Me); m/z 323 (MH^+), followed by the dimeric product **16** as a pale oil (290 mg, 32%); δ 8.43 (1H, broad, phenol-H); 7.98 (4H, m, aromatic-H); 7.21 (1H, d, *J* 8Hz, aromatic-H); 6.97 (1H, d, *J* 8 Hz, aromatic-H); 4.35 (2H, t, *J* 7 Hz, OCH_2); 4.11 (2H, t, *J* 7 Hz, OCH_2); 4.03 (2H, t, *J* 7 Hz, OCH_2); 2.98 (4H, m, 2 × CH_2 pyrone); 2.80 (2H, m, CH_2 pyrone); 2.65 (2H, m, CH_2 pyrone); 1.77 (2H, quintet, *J* 7 Hz, $OCH_2CH_2CH_2$); 1.25–1.68 (10H, m, int. alkyl-H); 1.00 (3H, t, *J* 7 Hz, Me); 0.92 (3H, t, *J* 7 Hz, Me); 0.88 (3H, t, *J* 7 Hz, Me); *m/z* 588 ($MNH4^+$), 571 (MH^+).

*Butyl(3,4-dihydro-2H-1-benzopyran-2-one)-6-carboxylate (**17**).* Compounds **14** (570 mg, 1.77 mmol) and **16** (290 mg, 0.47 mmol) were dissolved in toluene (15 ml) and *p*-toluenesulphonic acid (50 mg) was added. The mixture was refluxed under nitrogen for 20 h then cooled and concentrated. The residue was subjected to column chromatography to give the title compound **17** (500 mg, 74%) as white fluffy needles, m.p. 67°C (Found: C, 68.0; H, 6.5. $C_{14}H_{16}O_3$ calcd.: C, 67.7; H, 6.5%); δ

7.96 (1H, dd, *J* 2, 8 Hz, H7); 7.92 (1H, d, *J* 2 Hz, H5); 7.10 (1H, d, *J* 8 Hz, H8); 4.32 (2H, t, *J* 7 Hz, OCH_2); 3.08 (2H, m, CH_2 pyrone); 2.83 (2H, m, CH_2 pyrone); 1.76 (2H, quintet, *J* 7 Hz, $OCH_2CH_2CH_2$); 1.48 (2H, sextet, *J* 7 Hz, $CH_2CH_2CH_3$); 0.99 (3H, t, *J* 7 Hz, Me); *m/z* 266 ($MNH4^+$), 249 (MH^+), followed by **14** (125 mg, 15%) identical to a previously isolated sample.

General procedure of palladium catalysed tin cross couplings of **3** *under a carbon monoxide atmosphere.* These reactions can be performed under one atmosphere of carbon monoxide but to avoid recharging the vessel was charged to 3 atm. The Fischer–Porter bottle was charged with palladium acetate (12 mg, 2%), triphenylphosphine (21 mg, 4%), the organostannane (1.5 equiv.), and THF (5ml), and the vessel sealed. The mixture was stirred until homogeneous, flushed with carbon monoxide, and pressurised to 1 atm. Compound **3** (550 mg, 2 mmol) in THF (5 ml) was added from a syringe, the vessel was again flushed with carbon monoxide then pressurised to 3 atm. and kept at the required temperature. The reaction time depended on the organostannane used, when reaction was complete the system was cooled, and vented, and the solution diluted with ether, then filtered through Celite to remove the palladium black precipitate. The filtrate was concentrated and the residue purified by column chromatography followed by recrystallisation from ether or dichloromethane.

*6-Phenylpropynol-3,4-dihydro-2H-1-benzopyran-2-one (**18**).* Compound **3** was heated with phenylethynyltributylstannane (1.12 g, 3 mmol), THF, and the catalyst mixture to 40–45 °C for 6 h under carbon monoxide to give the compound **18** as shiny cream plates (455 mg, 81%), m.p. 132–133 °C (Found: C, 78.2; H, 4.5. $C_{18}H_{12}O_3$ calcd.: C, 78.25; H, 4.4%); δ 8.17 (1H, dd, *J* 2, 8 Hz, H7 coumarin); 8.08 (1H, d, *J* 2Hz, H5 coumarin); 7.70 (2H, m, 2× phenyl-H); 7.45 (3H, m, 3× phenyl-H); 7.19 (1H, d, *J* 8 Hz, H8 coumarin); 3.13 (2H, m, CH_2 pyrone); 2.86 (2H, m, CH_2 pyrone); *m/z* 277 (MH^+).

*6-Acryloyl-3,4-dihydro-2H-1-benzopyran-2-one (**19**).* Compound **3** was heated with vinyltributyltin (950 mg, 3 mmol), THF, and the catalyst mixture to 50–55 °C for 24 h under carbon monoxide to give the compound **19** as white needles, m.p. 92–93 °C (Found; C, 71.0; H, 4.9. $C_{12}H_{10}O_3$ calcd.: C, 71.3; H, 5.0%); δ 7.87 (2H, m, H5, H7); 7.15 (2H, m, H8 and int. alkene-H); 6.46 (1H, dd, *J* 2, 17 Hz, *trans* alkene-H); 5.95 (1H, dd, *J* 2, 10 Hz, *cis* alkene-H); 3.10 (2H, m, CH_2 pyrone); 2.85 (2H, m, CH_2 pyrone); *m/z* 203 (MH^+).

*6-Benzoyl-3,4-dihydro-2H-1-benzopyran-2-one (**20**).* Compound **3** was heated with phenyltributyltin (1.1 g, 3 mmol), THF, and the catalyst mixture to 65–70 °C for 24 h under carbon monoxide to give the compound **20** as fine white needles (320 mg, 62%), m.p. 122 °C (Found: C, 76.4; H, 4.9. $C_{16}H_{12}O_3$ calcd.: C, 76.2; H, 4.8%); δ 7.75 (4H, m, 4× aromatic-H); 7.63 (1H, m, aromatic-H); 7.55 (2H, m, 2× aromatic-H); 7.15 (1H, d, *J* 8 Hz, H8 coumarin); 3.10 (2H, m, CH_2 pyrone); 2.86 (2H,m, CH_2 pyrone); *m/z* 253 (MH^+).

*6-Acetyl-3,4-dihyro-2H-1-benzopyran-2-one (**21**).* Compound **3** was heated with tetramethyltin (537 mg, 3 mmol), THF, and the catalyst mixture to 65 °C for 24 h under carbon monoxide to give the compound **21** as pale yellow plates (280 mg, 74%). m.p. 81–82 °C (Found: C, 69.6; H, 5.4. $C_{11}H_{10}O_3$ calcd.: C, 69.5; H, 5.3%); δ 7.88 (2H, m, H5, H7); 7.13 (2H, d, *J* 8Hz, H8); 3.09 (2H, m, CH_2 pyrone); 2.84 (2H, m, CH_2 pyrone); 2.60 (3H, s, Me); *m/z* 191 (MH^+).

6-Pentanoyl-3,4-dihydro-2H-1-benzopyran-2-one (22). Compound **3** was heated with tetrabutyltin (1.04 g, 3 mmol), THF, and the catalyst mixture to 85 °C for 24 h under carbon monoxide to give the compound **22** as fine colourless needles (340 mg, 74%); m.p. 73–74 °C (Found: C, 72.6; H, 7.2. $C_{14}H_{16}O_3$ calcd.: C, 72.4; H, 6.9%); δ 7.87 (2H, m, H5, H7), 7.12 (1H, d, J 8 Hz, H8); 3.09 (2H, m, CH_2 pyrone); 2.94 (2H, t, J 7 Hz, $COCH_2$); 2.84 (2H, m, CH_2 pyrone); 1.73 (2H, quintet, J 7 Hz, $CH_2CH_2CH_2$); 1.42 (2H, sextet, J 7 Hz, $CH_2CH_2CH_3$); 0.97 (3H, t, J 7 Hz, Me); m/z 233 (MH^+).

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