DOI: 10.1002/ejoc.200500872

Diels–Alder Reactions of 2′-Hydroxychalcones with *ortho*-Benzoquinodimethane: A New Synthesis of 3-Aryl-2-naphthyl 2-Hydroxyphenyl Ketones

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Keywords: 2-Naphthyl ketones / Benzophenones / Diels–Alder reactions / Microwave irradiation / Benzoxanthones

Diels–Alder reactions of the 2′-hydroxychalcones **1a–e** with *ortho*-benzoquinodimethane (**3**) yielded the 3-aryl-1,2,3,4-tetrahydro-2-naphthyl 2-hydroxyphenyl ketones **4a–e** in good yields. The dehydrogenation of the cycloadducts **4a–e** to 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a–e** was studied. Good results were obtained when DDQ was used as oxidant and microwave irradiation as energy source. Several benzoxanthone derivatives were also obtained as minor products. Structures of all new compounds were established by extensive NMR studies.

Introduction

The benzophenone skeleton is a characteristic moiety of a large number of natural and synthetic products that present a wide-range of biological activities, including *anti*-inflammatory,[1] antitumour,[2,3] fungicidal,[4] *anti*-malarial[5] and antimitotic[3] activity. Certain derivatives have also been introduced as UV adsorbents for sunscreen purposes,[6] whereas others exhibit moderate inhibitory activity of farnesyltransferase.[7] In fact inhibition of this enzyme has become a major strategy for development of novel potential anticancer drugs.

Some studies indicate that certain medicinal properties of plants could result from the activity of both 2-hydroxybenzophenones and xanthones;[8] the former are the biogenic precursors of the latter.[9] It seems, from a structural point of view, that 2-hydroxybenzophenones have the structural requirement for interaction with ATP-binding sites. Thus, they also can be regarded as potential P-glycoprotein modulators,[10] the gene responsible for the active transport of chemotherapeutic drugs out of the cells. In addition, balanol (**I**) (Figure 1), having a 2-hydroxybenzophenone moiety, was isolated from the fungus *Verticillium balanoides* and *Fusarium merismoides*.[11] The total synthesis of this natural compounds[12] and of several analogues, maintaining the benzophenone moiety, has attracted the interest of the scientific community.[13] This interest is mainly due to the high inhibitory activity of the fungal metabolite against protein kinase C, a class of isoenzymes associated with a variety of disorders, which include cancer, cardiovascular disorders, asthma, diabetes, central nervous system dysfunction and AIDS.[11,12]

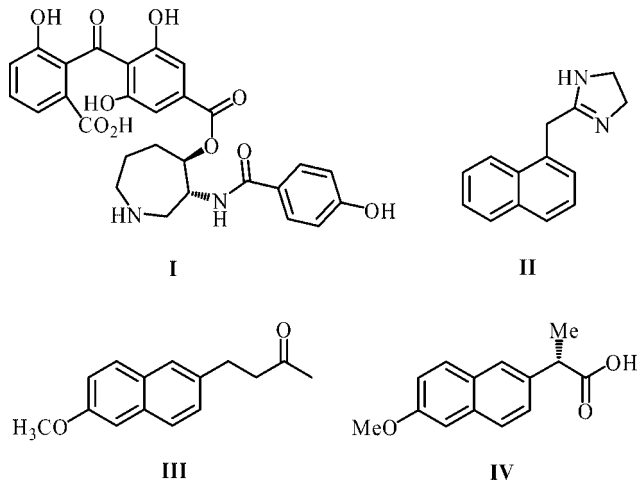

Figure 1. Structure of biologicaly active compounds having 2-hydroxybenzophenone or naphthalene moieties.

The naphthalene skeleton is also present in a large number of clinically used drugs, such as naphazoline (**II**), (a cardiovascular agent),[13,14] nabumetone (**III**) and naproxen (**IV**), *anti*-inflammatory agents with analgesic and antipyretic properties[13,15] (Figure 1). Recently, important pharmacological properties, such as potential vasorelaxant[16] and antitumour activities[13] were reported for compounds bearing naphthalene moieties.

In the last five years, we have been interested in the reactivity of several chromones as dienophiles in Diels–Alder reactions with very reactive dienes.[17,18] As an extension of these studies, and taking into consideration the potential applications of compounds bearing 2-hydroxybenzophe-

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none and naphthalene moieties, we decided to study the Diels–Alder reactions of 2′-hydroxychalcones with the highly reactive diene *ortho*-benzoquinodimethane. The oxidation of the resulting cycloadducts was also studied. This synthetic strategy constitutes a new route for the synthesis of some new functionalised 2-hydroxybenzophenones.

Microwave-accelerated synthesis has attracted a substantial amount of attention in recent years, and, as a consequence, a great number of reports have been published in the last decade advocating the advantages of using microwave irradiation to carry out organic synthesis.[19] Significant increases in rates, yields and purities of products have frequently been observed employing this non-conventional and energy-efficient heating method.[19] Typically, the oxidation of the cycloadducts obtained from the Diels–Alder reactions of 2′-hydroxychalcones with *ortho*-benzoquinodimethane requires refluxing at high temperatures and/or with long reactions times. Therefore, we decided to explore whether microwave irradiation could be used to enhance the efficiency of this type of reaction. We report here a simple and general procedure for the synthesis of 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a**–**e** from the oxidation of cycloadducts **4a**–**e** using microwave irradiation as energy source.

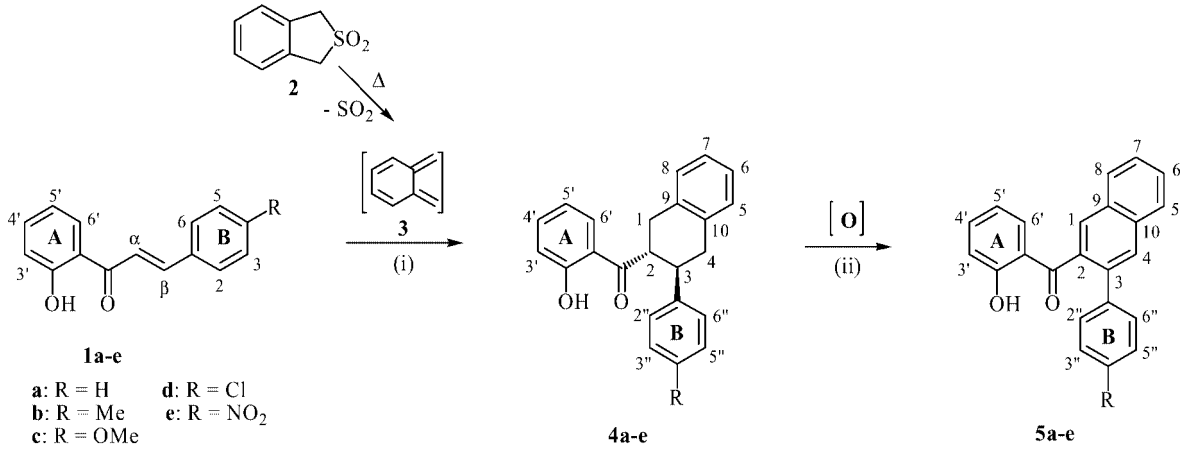
Results and Discussion

Syntheses

Our study started with the Diels–Alder reaction of the appropriate 2′-hydroxychalcones **1a**–**e** with *ortho*-benzoquinodimethane (**3**), formed in situ by thermal extrusion of sulfur dioxide from 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**2**)[20] (Scheme 1). Because the double bond of chalcones is conjugated with the carbonyl group, these compounds are expected to be good dienophiles. In fact their cycloaddition reactions with *ortho*-benzoquinodimethane can be accomplished in refluxing 1,2,4-trichlorobenzene and the expected cycloadducts, 3-aryl-1,2,3,4-tetrahydro-2-naphthyl 2-hydroxyphenyl ketones **4a**–**e**, were obtained in good yields (>70%). The B ring substituents do not significantly affect the yields of cycloaddition reactions.

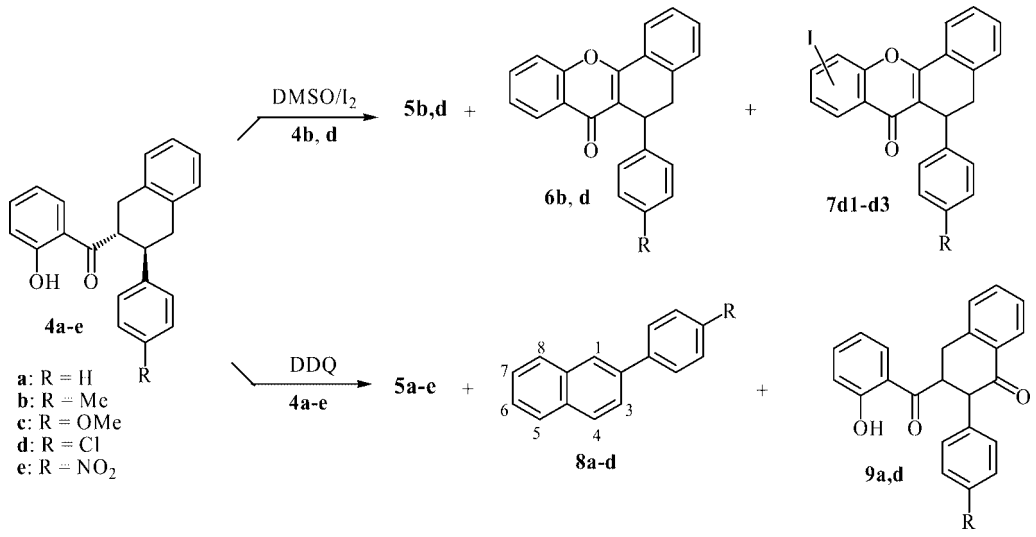
In order to achieve the synthesis of our target compounds, the 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a**–**e**, the cycloadducts **4a**–**e** were submitted to oxidation procedures. In the first attempt, the cycloadducts **4a**–**e** were subjected to bromination with NBS, in the presence of benzoyl peroxide, and the products were then dehydrobrominated by treatment with triethylamine. This method has been successfully applied in the dehydrogenation of other tetrahydronaphthyl derivatives.[17] However, in the present case, the desired products **5a**–**e** were only obtained in poor yields (≈ 10%). In the second attempt we performed the oxidation of cycloadducts **4b**,**d** using the oxidising agent system DMSO/I_2, which was already used in the oxidation of tetrahydroxanthone-type compounds.[18] In this case, the TLC of the reaction mixture revealed the presence of several products. The major fractions were isolated by preparative TLC and analysed by NMR spectroscopy. The NMR spectra of the major products, which were obtained in moderate yields (≈ 30%), show a dihydroxanthone **6b**,**d**[21] profile (Scheme 2). The expected products **5b**,**d** were obtained in poor yields (<10%) and the NMR spectra of other minor products indicate the presence of iodinated dihydroxanthones **7d1**–**d3** (R = Cl).[22] These results indicate that the oxidation of cycloadducts **4b**,**d** with a DMSO/I_2 mixture led to the formation of the chromone nucleus followed by the iodination of the most activated aromatic positions.[23] However, the complete aromatisation of these compounds was not obtained under these experimental conditions.

Because 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is known as a powerful oxidant, particularly useful for dehydrogenation to form aromatic compounds,[24] the next attempt consisted in the treatment of cycloadducts **4a**–**e** with an excess of DDQ, in refluxing 1,4-dioxane. However, when compounds **4a**,**b** were treated in these conditions, the target benzophenones **5a**,**b** were obtained in poor



(i) 1,2,4-trichlorobenzene, reflux; (ii) DDQ, dioxane, reflux

Scheme 1.



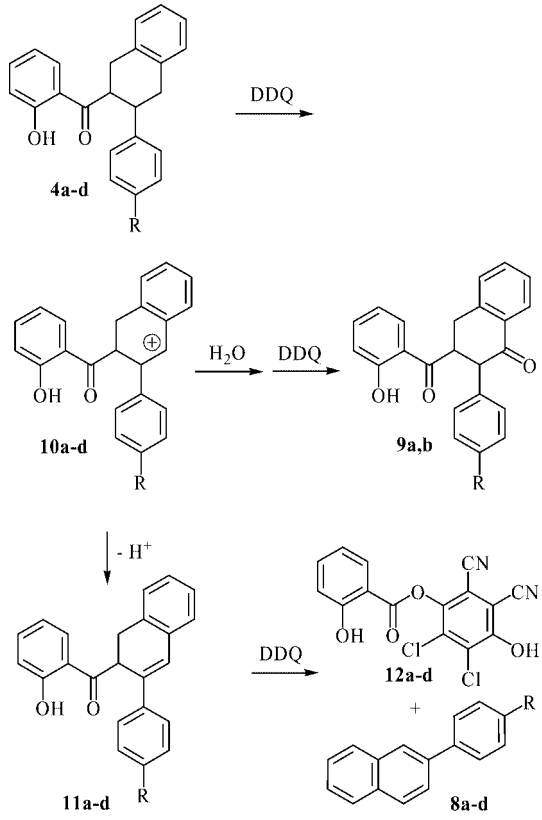
Scheme 2.

yields (15–18%) and compounds **8a**,**b** (7–21%) and **9a**,**d** (7–9%) were also isolated as by-products (Scheme 2). By using dry 1,4-dioxane the desired products **5a**–**e** were obtained in moderate yields (33–34%) for the cycloadducts **4a**,**d** and in poor yields (15–23%) for the other cycloadducts **4b**,**c**,**e**. Nevertheless, this method proved to be the one that allowed the synthesis of the desired 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a**–**e**. Chromatographic separation of the reaction mixtures allowed the recovery of some starting materials (7–15%) and the isolation of the compounds **8a**–**d** (except for R = NO_2) as by-products (Scheme 2).

The dehydrogenation mechanism of cyclohexanes by DDQ starts with a hydride transfer to DDQ and the consequent carbocation formation. In the case of the cycloadducts **4a**–**e** the carbocation must be localised in the more stable benzylic carbon atoms C-1, C-3 or C-4.[25] A carbocation at C-2 is unfavourable because it is adjacent to a carbonyl group. However, our results seem to indicate the formation of carbocation at C-4 in **10a**,**b**, because we have isolated the diketones **9a**,**d**. The formation of the 1,2,3,4-tetrahydro-2-naphthyl 2-hydroxyphenyl ketones **9a**,**d** can be explained by the addition of water to the intermediate **10a**,**d** followed by the oxidation of the resulting benzyl alcohol (Scheme 3). It is important to mention that compounds **9a**,**d** were not detected when dry 1,4-dioxane was used, indicating that their formations requires the presence of water.

The carbocations **10a**–**d** can also loose a proton to give the 3-aryl-1,2-dihydro-2-naphthyl-2-hydroxyphenyl ketones **11a**–**d**, which can then transfer a hydride followed by an acylium cation to DDQ to give 2-phenylnaphthalenes **8a**–**d** and the corresponding esters **12a**–**d** (Scheme 3).[26] Other examples of C–O coupling in oxidation reactions with DDQ have been described;[25] the failed attempts to isolate the esters **12a**–**d** could be due to their instability as it has been reported for similar compounds.[27]

Because the obtained results were not totally satisfactory, and taking into account that microwave radiation can be an alternative to conventional heating for introducing energy into reactions,[19] we decided to perform the oxidation of the cycloadducts **4a**–**e** by microwave irradiation. We used the conditions recently described by us in the oxidation of some hydroaromatic compounds with DDQ under microwave irradiation.[28] The mixture of cycloadducts **4a**–**e** with DDQ in 1,2,4-trichlorobenzene was irradiated at 170 °C for 30 minutes. Under these conditions, the 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a**–**e** were obtained in good yields (55–66%) and in notably shorter reactions times (Table 1).

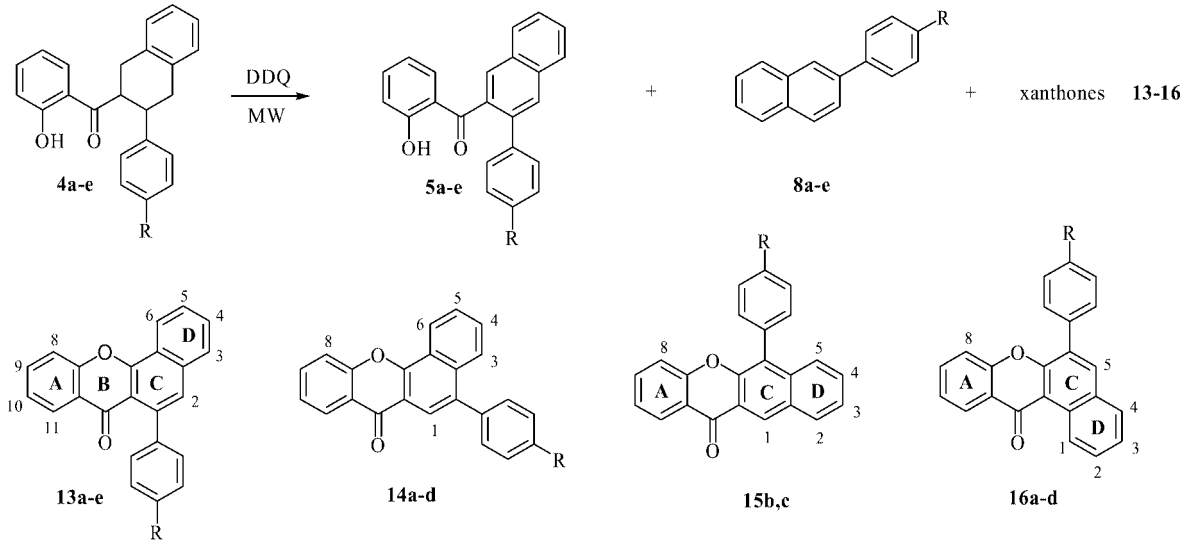


Scheme 3.

Table 1. Yields (%) obtained in the oxidation reactions of cycloadducts **4a**–**e**.

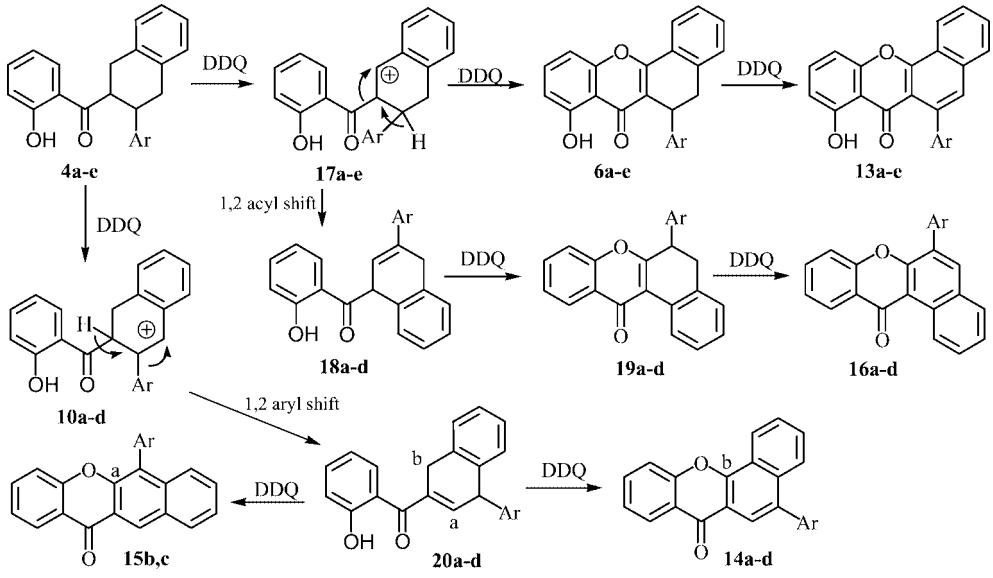
Entry	Reactant	Classical conditions[a]		Microwave[b]						
		5a–**e**	**8a**–**d**	**5a**–**e**	**8a**–**e**	**9a**,**d**	**13a**–**e**	**14a**–**d**	**15b**,**c**	**16a**–**d**
1	**4a**	33	11	66	5	5	7	1	–	5
2	**4b**	23	21	65	5	–	8	4	2	7
3	**4c**	23	19	60	4	–	5	4	17	3
4	**4d**	34	12	61	5	9	3	1	–	4
5	**4e**	15	–	55	7	–	13	–	–	–

[a] DDQ (5 mol relative to the amount of **4a**–**e**), freshly distilled 1,4-dioxane, reflux, 48 h. [b] DDQ (5 mol relative to the amount of **4a**–**e**), 1,2,4-trichlorobenzene, microwave irradiation: 36 min.



Scheme 4.

Several changes in temperatures and in reaction time allowed the establishment of the best conditions for the synthesis of 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a**–**e** and also for the isolation of 2-phenylnaphthalenes **8a**–**e** and several benzoxanthones (1-arylbenzo[*c*]xanthones **13a**–**e**, 2-arylbenzo[*c*]xanthones **14a**–**d**, 6-arylbenzo[*b*]xanthones **15b**,**c** and 6-arylbenzo[*a*]xanthones **16a**–**d**) as minor products (Table 1, Scheme 4). In two cases, the compounds **9a**,**d** (5–9%) were obtained as by-products, which could be due to the use of less dried cycloadducts **4a**,**b**. In order to confirm this fact, the oxidation of cycloadduct **4a** was performed by adding 0.1 mL of water to the reaction mixture.



Scheme 5.

Under these conditions the yield of compound **9a** was doubled (12%).

The improved yields of 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a**–**e** were expected, along with the formation of by-products. The unexpected results were the four types of benzoxanthones obtained as by-products. The formation of 1-arylbenzo[*c*]xanthones **13a**–**e** can be explained by the fact, also detected with other oxidizing agents, that cycloadducts **4a**–**e** in DDQ could generate the chromone moieties **6a**–**e**, which could be oxidised to the corresponding xanthones **13a**–**e** (Scheme 5). The formation of the other by-products can be explained by the formation of benzylic cations **10a**–**d** and **17a**–**e**, due to the reaction of **4a**–**e** with DDQ, followed by an 1,2-aryl or benzoyl shift, giving the intermediates **18a**–**d** and **20a**–**d** which afforded the obtained xanthones **14a**–**d**, **15b**,**c** and **16a**–**d** after cyclodehydrogenation as depicted in Scheme 5. A similar type of intermediate and rearrangement was postulated to explain the pyrone derivatives from lignans.[29] The strong deactivating effect of the nitro group can explain why these by-products were not detected in the oxidation of 2-hydroxyphenyl 3-(4-nitrophenyl)-2-naphthyl ketone (**4e**).

Nuclear Magnetic Resonance Spectroscopy

The ^{1}H NMR spectra of the cycloadducts **4a**–**e** present signals in the aromatic and aliphatic regions, besides the signal at δ = 12.17–12.36 ppm, which is due to the resonance of hydroxylic proton (2′-O*H*) involved in an intramolecular hydrogen bond with the carbonyl group. The resonances appearing in the aliphatic region are due to protons 1-H, 2-H, 3-H and 4-H. In terms of stereochemistry of these compounds, the most important resonances are those of 2-H and 3-H, which appear, in most cases, as double doublet of doublets at δ = 4.14–4.23 and 3.48–3.68 ppm, respectively. The coupling constants $^3J_{2\text{-H},3\text{-H}} \approx 11$ Hz indicate a *trans* configuration of these two protons, which is consistent with the stereospecificity of the Diels–Alder reaction (the starting 2′-hydroxychalcones **1a**–**e** have *trans* configuration).

In the aromatic region of the ^{1}H NMR spectra of **4a**–**e**, one can detect the common structural feature of the ring A, which appears in each case as ABCD spin systems corresponding to 3′-H, 4′-H, 5′-H and 6′-H proton resonances. 6′-H and 3′-H resonances appear in most cases as double doublets whereas those of 4′-H and 5′-H appear as double doublet of doublets. The resonances of 4′-H and 6′-H appear at higher frequencies (δ = 7.41–7.47 and 7.78–7.84 ppm, respectively) than those corresponding to 3′-H and 5′-H (δ = 6.89–6.93 and 6.84–6.90 ppm, respectively). This is due to the mesomeric and anisotropic deshielding effect of the carbonyl group in 6′-H and resonance effect on 4′-H. Another important feature is the presence of an AB spin system characteristic of the *para*-substituted B ring in cycloadducts **4b**–**e**.

The resonances of all other protons and the unequivocal assignment of the carbon resonances of the cycloadducts **4b**–**e** were determined with the aid of HSQC and HMBC spectra. Figure 2 (A) shows the most important connectivities found in the HMBC spectra of these compounds.

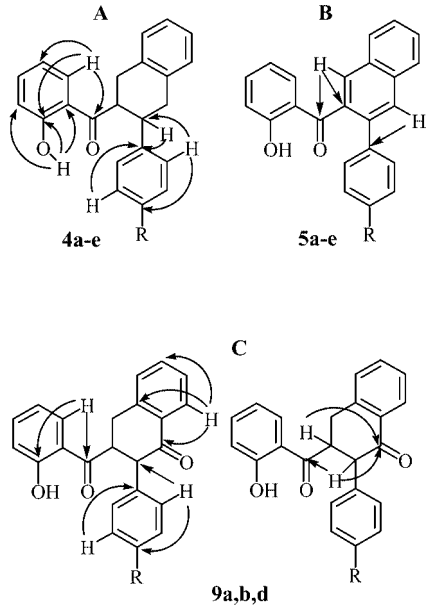


Figure 2. Important connectivities found in the HMBC spectra of compounds **4a**–**e**, **5a**–**e** and **9a**,**b**,**d**.

The ^{1}H NMR spectra of compounds **5a**–**e** also present the signal corresponding to the resonance of the hydroxylic proton (2′-O*H*) (δ = 11.88–12.08 ppm, as a singlet). In the aromatic region of these spectra, one can also observe the common structural features of the rings A and B of compounds **4a**–**e**. However the resonances which immediately indicate the oxidation of cycloadducts **4a**–**e** are those of 1-H and 4-H, which appear as singlets at δ = 7.94–8.04 and 7.92–7.98 ppm, respectively. The resonances of all carbon atoms of 2-hydroxybenzophenones **5a**–**e** were determined with the aid of HSQC and HMBC experiments. The most important connectivities found in the HMBC spectra allowed the unequivocal assignment of the quaternary carbon resonances and the confirmation of those corresponding to 1-H and 4-H (Figure 2, B).

The main characteristics of the ^{1}H NMR spectra of compounds **8a**–**e** are the resonances of the 1-H (d, $\delta \approx$ 7.9 ppm), 3-H (dd, $\delta \approx$ 7.7 ppm) and 4-H (br. s, $\delta \approx$ 8.0 ppm) protons. Another important spectroscopic aspect of the ^{13}C NMR spectroscopic data of these compounds is the absence of the characteristic carbon resonance due to the carbonyl group. The assignment of the protonated carbon resonances of compounds **8a**–**e** was based on the analysis of their HSQC spectra, whereas those of the quaternary carbon atoms were based on the connectivities found in their HMBC spectra.

The ^{1}H NMR spectra of 3-aryl-4-oxo-1,2,3,4-tetrahydro-2-naphthyl 2-hydroxyphenyl ketones **9a**,**d** indicate a partial oxidation of the corresponding cycloadducts **4a**,**d**, because the resonances corresponding to only four protons were observed in the aliphatic region of these spectra. However, unequivocal supports for this structure are the presence of two

carbonyl carbon resonances at $\delta \approx 197$ and ca. 205 ppm in their ^{13}C NMR spectra. These data and the analysis of their HMBC spectra (Figure 2, C) provide unequivocal support for the proposed structures.

An important characteristic of the ^{1}H NMR spectra of 1-arylbenzo[*c*]xanthones **13a**–**e** is the absence of the singlet peak due to the 2′-O*H* group. The proton resonances of H-2 appear as singlets at $\delta \approx 7.5$ ppm and indicate the presence of a fully aromatic C ring. Other relevant features of the ^{1}H NMR spectra of **13a**–**e** are the characteristic A and D ring resonances: i) 11-H ($\delta \approx 8.3$ ppm) and 9-H ($\approx \delta =$ 7.7 ppm) appeared at higher frequency values than those of 8-H ($\delta \approx 7.3$ ppm) and 10-H ($\delta \approx 7.3$ ppm), because of both anisotropic and mesomeric deshielding effects of the carbonyl group for 11-H and only the latter for 9-H; ii) 6-H ($\delta \approx 8.7$ ppm) appeared at higher frequency values than those of protons 3-H ($\delta \approx 7.9$ ppm) because of the through-space deshielding effect of the heterocyclic oxygen atom.

The ^{13}C NMR spectra of compounds **13a**–**e** confirm the xanthone-type structure, because typical carbonyl carbon resonances ($\delta \approx 176$–178 ppm) of xanthone-type compounds have been identified.[30] The assignment of the protonated carbon resonances of compounds **13a**–**e** was based on the analysis of their HSQC spectra, whereas those of the quaternary carbon atoms were based on the connectivity found in their HMBC spectra (Figure 3, see part A, shown as an example). The ^{1}H NMR spectra of 2-arylbenzo[*c*]xanthones **14a**–**d** confirm the presence of a fully aromatic nucleus of benzo[*c*]xanthone like in 1-arylbenzo[*c*]xanthones **13a**–**e**. The main difference is the singlet at $\delta \approx 8.2$ ppm, which presents a chemical shift characteristic of a proton near a carbonyl group[27] and deshielded by its anisotropic and mesomeric effects. The signal is consequently attributed to the resonance of proton 1-H. These data and the analysis of their HMBC spectra (Figure 3, B) provide unequivocal support for the proposed structures. The most noticeable feature in the characterization of the 6-arylbenzo[*b*]xanthones **15b**,**c** is the singlet at $\delta \approx 9.0$ ppm due to the proton H-1 resonance.[18,31] These xanthones present several signals both in ^{1}H and ^{13}C NMR spectra, which are similar to those of the other xanthones. Their differentiation and simultaneous unequivocal support for the proposed structure were achieved by the connectivities found in HMBC spectra (Figure 3, C). Finally, the features in the 6-arylbenzo[*a*]xanthones **16a**–**d** characterization are: i) the singlet at $\delta \approx$ 8.1 ppm corresponding to the resonance of proton H-5; ii) the doublet at $\delta \approx 10.1$ ppm due to the resonance of proton H-1, which is the most deshielded proton as a consequence of the anisotropic effect of the carbonyl group. The connectivities found in HMBC spectra (Figure 3, D) allowed the confirmation for the resonance assignments of protonated carbon atoms and the unequivocal assignment of the quaternary carbon atoms.

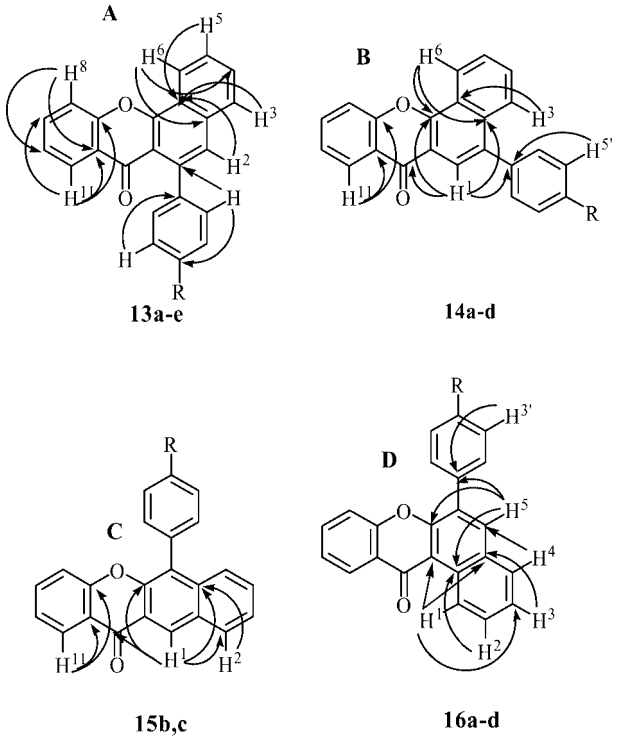


Figure 3. Important connectivities found in the HMBC spectra of compounds **13a**–**e**, **14a**–**d**, **15b**,**c** and **16a**–**d**.

Experimental Section

General Remarks: Melting points were measured with a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. NMR spectra were recorded with Bruker Avance 300 spectrometers (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C), in $CDCl_3$ as solvent, if not stated otherwise. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz; internal standard was TMS. Unequivocal ^{13}C assignments were made with the aid of 2D *g*HSQC and *g*HMBC (delays for one bond and long-range J C/H couplings were optimised for 145 and 7 Hz, respectively) experiments. Electron impact (EI = 70 eV) MS were recorded with VG Autospec Q and M spectrometers. Elemental analyses were obtained with a LECO 932 CHNS analyser. Reactions under microwave irradiation were performed with an Ethos SYNTH microwave labstation (Milestone) using glassware setup for atmospheric-pressure reactions (temperature measurement with a fiber-optic probe). Preparative thin-layer chromatography was performed with Merck silica gel 60 DGF_{254}. Column chromatography was performed with Merck silica gel 60, 70–230 mesh. All chemicals and solvents used were obtained from commercial sources and used as received or dried using standard procedures.

2′-Hydroxychalcones 1a–e: Prepared by base-catalysed aldol condensation as previously reported.[32]

1,3-Dihydrobenzo[*c*]thiophene 2,2-Dioxide (2): Prepared according to a literature procedure.[20]

General Procedure for the Synthesis of 3-Aryl-1,2,3,4-tetrahydro-2-naphthyl 2-Hydroxyphenyl Ketones 4a–e: 1,3-Dihydrobenzo[*c*]thiophene 2,2-dioxide (**2**) (0.443 g, 2.64 mmol) was added to a solution of the appropriate 2′-hydroxychalcone **1a**–**e** (2.2 mmol) in 1,2,4-trichlorobenzene (40 mL). The mixture was refluxed under nitrogen for 18 h. After this period the reaction mixture was purified by silica gel column chromatography eluting with light petroleum ether to remove the 1,2,4-trichlorobenzene and with dichloromethane to collect the cycloadducts **4a**–**e**.

2-Hydroxyphenyl 3-Phenyl-1,2,3,4-tetrahydro-2-naphthyl Ketone (4a): Yield 70% (508 mg). M.p. 93–94 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 3.04–3.22 (m, 4 H, 1,4-H), 3.52 (ddd, J = 11.2, 10.6 and 5.7 Hz, 1 H, 3-H), 4.22 (ddd, J = 10.6, 9.2 and 7.4 Hz, 1 H, 2-H), 6.86 (ddd, J = 7.9, 7.7 and 1.1 Hz, 1 H, 5′-H), 6.90 (dd, J = 8.2 and 1.1 Hz, 1 H, 3′-H), 7.09–7.18 (m, 5 H, 2′′,3′′,4′′,5′′,6′′-H), 7.20–7.24 (m, 4 H, 5,6,7,8-H), 7.42 (ddd, J = 8.2, 7.7 and 1.6 Hz, 1 H, 4′-H), 7.82 (dd, J = 7.9 and 1.6 Hz, 1 H, 6′-H), 12.35 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 34.8 (C-4), 37.9 (C-1), 42.7 (C-3), 46.4 (C-2), 118.6 (C-3′), 118.8 (C-5′), 119.1 (C-1′), 126.3 (C-4′′), 126.1 and 126.6 (C-6 and C-7), 127.1 (C-2′′,6′′), 128.4 and 128.6 (C-5 and C-8), 128.5 (C-3′′,5′′), 129.6 (C-6′), 134.4 and 135.7 (C-9 and C-10), 136.5 (C-4′), 143.8 (C-1′′), 162.9 (C-2′), 208.5 (C=O). EI-MS: *m*/*z* (%) = 328 (26) [M$^{+\cdot}$], 310 (20), 237 (15), 219 (13), 206 (6), 192 (30), 129 (9), 121 (100), 91 (30), 77 (7), 65 (17). $C_{23}H_{20}O_2$ (328.40): calcd. C 84.12, H 6.14; found C 83.99, H 5.96.

2-Hydroxyphenyl 3-(4-Methylphenyl)-1,2,3,4-tetrahydro-2-naphthyl Ketone (4b): Yield 95% (714 mg). M.p. 103–105 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 2.25 (s, 3 H, 4′′-C*H*$_3$), 3.01–3.21 (m, 4 H, 1,4-H), 3.50 (ddd, J = 11.2, 10.5 and 5.6 Hz, 1 H, 3-H), 4.21 (dt, J = 10.5 and 6.8 Hz, 1 H, 2-H), 6.87 (ddd, J = 8.3, 7.3 and 1.1 Hz, 1 H, 5′-H), 6.91 (dd, J = 8.1 and 1.1 Hz, 1 H, 3′-H), 7.02 (d, J = 8.1 Hz, 2 H, 3′′,5′′-H), 7.11 (d, J = 8.1 Hz, 2 H, 2′′,6′′-H), 7.13–7.20 (m, 4 H, 5,6,7,8-H), 7.44 (ddd, J = 8.1, 7.3 and 1.5 Hz, 1 H, 4′-H), 7.84 (dd, J = 8.3 and 1.5 Hz, 1 H, 6′-H), 12.35 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 21.0 (4′′-*C*H$_3$), 34.9 (C-4), 38.2 (C-1), 42.2 (C-3), 46.4 (C-2), 118.6 (C-3′), 118.9 (C-5′), 119.1 (C-1′), 126.1 and 126.3 (C-6 and C-7), 127.0 (C-2′′,6′′), 128.4 and 128.7 (C-5 and C-8), 129.3 (C-3′′,5′′), 129.7 (C-6′), 134.5 and 135.9 (C-9 and C-10), 136.1 (C-4′′), 136.5 (C-4′), 140.8 (C-1′′), 163.0 (C-2′), 208.6 (C=O). EI-MS: *m*/*z* (%) = 342 (30) [M$^{+\cdot}$], 324 (10), 237 (173), 219 (13), 206 (23), 129 (8), 121 (100), 105 (28), 91 (6), 77 (5), 65 (14). $C_{24}H_{22}O_2$ (342.43): calcd. C 84.18, H 6.48; found C 84.34, H 6.66.

2-Hydroxyphenyl 3-(4-Methoxyphenyl)-1,2,3,4-tetrahydro-2-naphthyl Ketone (4c): Yield 87% (687 mg). M.p. 100–103 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 3.08–3.20 (m, 4 H, 1,4-H), 3.48 (ddd, J = 11.1, 10.7 and 5.7 Hz, 1 H, 3-H), 3.72 (s, 3 H, 4′′-OC*H*$_3$), 4.16 (dt, J = 10.7 and 8.3 Hz, 1 H, 2-H), 6.75 (d, J = 8.4 Hz, 2 H, 3′′,5′′-H), 6.86 (ddd, J = 8.1, 7.9 and 0.8 Hz, 1 H, 5′-H), 6.91 (d, J = 8.1 Hz, 1 H, 3′-H), 7.11–7.20 (m, 4 H, 5,6,7,8-H), 7.14 (d, J = 8.4 Hz, 2 H, 2′′,6′′-H), 7.43 (ddd, J = 8.1, 7.9 and 1.1 Hz, 1 H, 4′-H), 7.81 (dd, J = 8.1 and 1.1 Hz, 1 H, 6′-H), 12.36 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 34.8 (C-4), 38.0 (C-1), 42.0 (C-3), 46.7 (C-2), 55.1 (4′′-O*C*H$_3$), 114.0 (C-3′′,5′′), 118.6 (C-3′), 118.9 (C-5′), 119.2 (C-1′), 126.1 and 126.3 (C-6 and C-7), 128.1 (C-2′′,6′′), 128.4 and 128.7 (C-5 and C-8), 129.7 (C-6′), 134.5 and 135.8 (C-9 and C-10), 135.8 (C-1′′), 136.5 (C-4′), 158.1 (C-4′′), 163.0 (C-2′), 208.7 (C=O). EI-MS: *m*/*z* (%) = 358 (12) [M$^{+\cdot}$], 340 (3), 237 (3), 222 (10), 129 (5), 121 (100), 104 (6), 77 (4), 65 (8). $C_{24}H_{22}O_3$ (358.43): calcd. C 80.42, H 6.19; found C 80.20, H 6.09.

3-(4-Chlorophenyl)-1,2,3,4-tetrahydro-2-naphthyl 2-Hydroxyphenyl Ketone (4d): Yield 75% (599 mg). Yellow oil. ^{1}H NMR: δ = 2.97–3.17 (m, 4 H, 1,4-H), 3.49 (ddd, J = 11.3, 10.7 and 5.6 Hz, 1 H, 3-H), 4.14 (ddd, J = 10.7, 10.4 and 6.2 Hz, 1 H, 2-H), 6.84 (ddd, J = 7.9, 7.7 and 1.1 Hz, 1 H, 5′-H), 6.89 (dd, J = 8.1 and 1.1 Hz, 1 H, 3′-H), 7.07–7.21 (m, 8 H, 5,6,7,8-H and 2′′,3′′,5′′,6′′-H), 7.41 (ddd, J = 8.1, 7.7 and 1.6 Hz, 1 H, 4′-H), 7.78 (dd, J = 7.9 and 1.6 Hz, 1 H, 6′-H), 12.31 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 34.7 (C-4), 37.7 (C-1), 42.0 (C-3), 46.4 (C-2), 118.7 (C-3′), 118.91 (C-5′), 118.89 (C-1′), 126.2 and 126.4 (C-6 and C-7), 128.51 (C-2′′,6′′), 128.2 and 128.57 (C-5 and C-8), 128.6 (C-3′′,5′′), 129.5 (C-6′), 132.1 (C-1′′), 134.1 and 135.3 (C-9 and C-10), 136.6 (C-4′), 142.3 (C-4′′), 162.9 (C-2′), 208.1 (C=O). EI-MS: *m*/*z* (%) = 362 (30) [M$^{+\cdot}$], 344 (15), 237 (21), 226 (24), 219 (17), 121 (100), 104 (10), 84 (10), 65 (7). FAB-HRMS ($C_{23}H_{19}O_2Cl$ [M + H]$^+$): calcd. 362.1076, found 362.1074.

2-Hydroxyphenyl 3-(4-Nitrophenyl)-1,2,3,4-tetrahydro-2-naphthyl Ketone (4e): Yield 80% (656 mg). M.p. 148–149 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 3.03–3.28 (m, 4 H, 1,4-H), 3.68 (ddd, J = 11.3, 11.0 and 5.5 Hz, 1 H, 3-H), 4.23 (dt, J = 11.0 and 5.3 Hz, 1 H, 2-H), 6.90 (ddd, J = 8.1, 7.4 and 1.1 Hz, 1 H, 5′-H), 6.93 (dd, J = 8.1 and 1.1 Hz, 1 H, 3′-H), 7.14–7.22 (m, 4 H, 5,6,7,8-H), 7.40 (d, J = 8.8 Hz, 2 H, 2′′,6′′-H), 7.47 (ddd, J = 8.1, 7.4 and 1.6 Hz, 1 H, 4′-H), 7.82 (dd, J = 8.1 and 1.6 Hz, 1 H, 6′-H), 8.09 (d, J = 8.8 Hz, 2 H, 3′′,5′′-H), 12.17 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 34.9 (C-4), 37.5 (C-1), 42.6 (C-3), 46.5 (C-2), 118.7 (C-1′), 118.9 (C-3′), 119.1 (C-5′), 123.9 (C-3′′,5′′), 126.5 and 126.6 (C-6 and C-7), 128.1 (C-2′′,6′′), 128.5 and 128.6 (C-5 and C-8), 129.4 (C-6′), 133.9 and 134.7 (C-9 and C-10), 137.0 (C-4′), 146.6 (C-1′′), 151.7 (C-4′′), 163.1 (C-2′), 207.5 (C=O). EI-MS: *m*/*z* (%) = 373 (29) [M$^{+\cdot}$], 356 (22), 235 (29), 147 (5), 128 (6), 121 (100), 93 (10), 65 (11). $C_{23}H_{19}O_4N$ (373.40): calcd. C 73.98, H 5.13, N 3.75; found C 73.63, H 4.79, N 4.03.

General Procedure for the Synthesis of 3-Aryl-2-naphthyl 2-hydroxyphenyl Ketones 5a-e under Classical Heating Conditions. Method A: DDQ (0.292 g, 1.3 mmol) was added to a solution of the appropriate 3-aryl-1,2,3,4-tetrahydro-2-naphthyl 2-hydroxyphenyl ketone **4a**,**b** (0.259 mmol) in 1,4-dioxane (10 mL). The reaction mixture was refluxed under nitrogen for 48 hours. After this period the reaction mixture was washed with water and purified by preparative TLC eluting with a 1:1 mixture of dichloromethane/light petroleum ether, leading to the isolation of three main spots, in each case. The spot of higher R_f value was identified as being 2-phenylnaphthalenes **8a**,**b** (**8a**, 7%; **8b**, 21%), the middle R_f value spot was identified as being (3-aryl-2-naphthyl) (2-hydroxyphenyl) ketones **5a**,**b** (**5a**, 15%, **5b**, 18%), the compounds with lower R_f values were identified as ketones **9a**,**b** (**9a**, 7%; **9b**, 9%).

Method B: The procedure was identical to that described for method A except that freshly dried 1,4-dioxane was used as solvent. Purification of the reaction mixture by preparative TLC afforded compounds **8a**–**d** and **5a**–**e** (yields indicated in Table 1). Some unchanged starting material was also recovered: **4a**, 8%; **4b**, 11%; **4c**, 12%; **4d**, 7%; **4e**, 15%.

2-Hydroxyphenyl 3-Phenyl-2-naphthyl Ketone (5a): Yellow oil. ^{1}H NMR: δ = 6.70 (dt, J = 7.6 and 1.0 Hz, 1 H, 5′-H), 6.96 (d, J = 8.1 Hz, 1 H, 3′-H), 7.22–7.30 (m, 3 H, 3′′,4′′,5′′-H), 7.33–7.42 (m, 4 H, 4′,6′-H and 2′′,6′′-H), 7.54–7.65 (m, 2 H, 6,7-H), 7.90–7.97 (m, 2 H, 5,8-H), 7.96 (s, 1 H, 1-H), 7.97 (s, 1 H, 4-H), 12.03 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 118.0 (C-3′), 118.7 (C-5′), 120.2 (C-1′), 127.4 (C-4′′), 127.0 and 128.0 (C-6 and C-7), 128.0 (C-5), 128.3 (C-8), 128.5 (C-3′′,5′′), 128.85 (C-2′′,6′′), 128.89 (C-1), 129.4 (C-4), 131.3 (C-2), 133.6 (C-6′), 134.0 (C-10), 135.9 (C-9) 136.5 (C-4′), 138.0 (C-3), 140.0 (C-1′′), 162.9 (C-2′), 203.6 (C=O). EI-MS: *m*/*z* (%) = 324 (100) [M$^{+\cdot}$], 323 (63), 305 (28), 276 (6), 247 (37), 231 (23), 204 (56), 202 (43), 153 (10), 121 (39), 93 (12), 65 (15). FAB-HRMS ($C_{23}H_{16}O_2$ [M + H]$^+$): calcd. 324.1150, found 324.1141.

2-Hydroxyphenyl 3-(4-Methylphenyl)-2-naphthyl Ketone (5b): M.p. 133–135 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 2.31 (s, 3 H, 4′′-C*H*$_3$), 6.77 (ddd, J = 8.4, 7.4 and 1.1 Hz, 1 H, 5′-H), 6.98 (dd, J = 8.5 and 1.1 Hz, 1 H, 3′-H), 7.11 (d, J = 8.2 Hz, 2 H, 3′′,5′′-H), 7.28 (d, J = 8.2 Hz, 2 H, 2′′,6′′-H), 7.40 (d, J = 8.4 Hz, 1 H, 6′-H), 7.42 (dd, J = 8.5 and 7.4 Hz, 1 H, 4′-H), 7.53–7.64 (m,

2 H, 6,7-H), 7.89–7.94 (m, 2 H, 5,8-H), 7.92 (s, 1 H, 1-H), 7.94 (s, 1 H, 4-H), 12.05 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 21.1 (4′′-*C*H$_3$), 118.1 (C-3′), 118.7 (C-5′), 120.2 (C-1′), 126.9 and 127.89 (C-6 and C-7), 127.93 (C-5), 128.8 (C-8), 128.3 (C-1), 128.7 (C-2′′,6′′), 129.3 (C-4 and C-3′′,5′′), 131.2 (C-2), 133.7 (C-6′), 134.0 (C-10), 135.9 (C-9), 136.5 (C-4′), 137.1 (C-1′′), 137.2 (C-3), 138.0 (C-4′′), 162.9 (C-2′), 203.7 (C=O). EI-MS: *m*/*z* (%) = 338 (100) [M$^{+\cdot}$], 337 (59), 319 (19), 305 (19), 247 (32), 245 (18), 218 (45), 215 (20), 202 (34), 169 (10), 121 (28), 93 (10), 65 (12). $C_{24}H_{18}O_2$ (338.40): calcd. C 85.18, H 5.36; found C 84.97, H 5.28.

2-Hydroxyphenyl 3-(4-Methoxyphenyl)-2-naphthyl Ketone (5c): Yellow oil. ^{1}H NMR: δ = 3.77 (s, 3 H, 4′′-OC*H*$_3$), 6.70 (ddd, *J* = 8.2, 7.5 and 0.8 Hz, 1 H, 5′-H), 6.84 (d, *J* = 8.7 Hz, 2 H, 3′′,5′′-H), 6.97 (dd, *J* = 8.1 and 0.8 Hz, 1 H, 3′-H), 7.31 (d, *J* = 8.7 Hz, 2 H, 2′′,6′′-H), 7.35 (dd, *J* = 8.2 and 1.6 Hz, 1 H, 6′-H), 7.40 (ddd, *J* = 8.1, 7.5 and 1.6 Hz, 1 H, 4′-H), 7.52–7.63 (m, 2 H, 6,7-H), 7.92 (s, 1 H, 1-H), 7.94 (s, 1 H, 4-H), 7.89–7.94 (m, 2 H, 5,8-H), 12.08 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 55.2 (4′′-O*C*H$_3$), 114.0 (C-3′′,5′′), 118.1 (C-3′), 118.7 (C-5′), 120.1 (C-1′), 126.8 and 127.9 (C-6 and C-7), 127.9 (C-5), 128.3 (C-8), 128.7 (C-1), 129.0 (C-4), 130.0 (C-2′′,6′′), 131.1 (C-2), 132.4 (C-1′′), 133.6 (C-6′), 134.0 (C-10), 136.0 (C-9) 136.5 (C-4′), 137.5 (C-3), 159.0 (C-4′′), 162.9 (C-2′), 203.9 (C=O). EI-MS: *m*/*z* (%) = 354 (100) [M$^{+\cdot}$] 353 (41), 335 (7), 305 (13), 261 (15), 247 (20), 234 (29), 218 (11), 202 (11), 189 (22), 177 (11), 121 (30), 93 (9), 65 (11). FAB-HRMS ($C_{24}H_{18}O_3$ [M + H]$^+$): calcd. 354.1256, found 354.1248.

3-(4-Chlorophenyl)-2-naphthyl 2-Hydroxyphenyl Ketone (5d): M.p. 98–101 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 6.73 (ddd, *J* = 8.2, 7.1 and 0.9 Hz, 1 H, 5′-H), 6.99 (d, *J* = 8.1 Hz, 1 H, 3′-H), 7.11 (d, *J* = 8.2 Hz, 2 H, 3′′,5′′-H), 7.28 (d, *J* = 8.2 Hz, 2 H, 2′′,6′′-H), 7.36 (dd, *J* = 8.2 and 1.6 Hz, 1 H, 6′-H), 7.43 (ddd, *J* = 8.1, 7.1 and 1.6 Hz, 1 H, 4′-H), 7.58–7.64 (m, 2 H, 6,7-H), 7.91–7.96 (m, 2 H, 5,8-H), 7.92 (s, 1 H, 1-H), 7.97 (s, 1 H, 4-H), 11.99 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 118.3 (C-3′), 118.8 (C-5′), 120.1 (C-1′), 127.2 and 128.0 (C-6 and C-7), 128.1 (C-5), 128.4 (C-1), 128.7 (C-2′′,6′′), 129.1 (C-8), 129.4 (C-4), 130.1 (C-3′′,5′′), 131.4 (C-2), 133.5 (C-6′), 133.6 (C-1′′), 133.9 (C-10), 135.6 (C-9) 136.7 (C-4′), 136.9 (C-3), 138.5 (C-4′′), 163.0 (C-2′), 203.3 (C=O). EI-MS: *m*/*z* (%) = 358 (100) [M$^{+\cdot}$], 357 (60), 341 (17), 305 (17), 265 (23), 247 (45), 238 (63), 230 (15), 202 (56), 179 (7), 162 (14), 153 (7), 138 (8), 121 (53), 93 (17), 65 (22). $C_{23}H_{15}O_2Cl$ (358.82): calcd. C 76.99, H 4.21; found C 76.59, H 4.11.

2-Hydroxyphenyl 3-(4-Nitrophenyl)-2-naphthyl Ketone (5e): Yellow oil. ^{1}H NMR: δ = 6.77 (ddd, *J* = 7.7, 7.5 and 0.9 Hz, 1 H, 5′-H), 7.01 (dd, *J* = 0.9 and 8.1 Hz, 1 H, 3′-H), 7.43 (dd, *J* = 7.7 and 1.7 Hz, 1 H, 6′-H), 7.46 (ddd, *J* = 8.1, 7.5 and 1.7 Hz, 1 H, 4′-H), 7.55 (d, *J* = 8.8 Hz, 2 H, 2′′,6′′-H), 7.64–7.71 (m, 2 H, 6,7-H), 7.94–8.00 (m, 2 H, 5,8-H), 7.98 (s, 1 H, 1-H), 8.04 (s, 1 H, 4-H), 8.19 (d, *J* = 8.8 Hz, 2 H, 3′′,5′′-H), 11.88 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 118.5 (C-3′), 119.0 (C-5′), 119.9 (C-1′), 123.8 (C-3′′,5′′), 127.9 and 128.6 (C-6 and C-7), 128.2 (C-5), 128.6 (C-8), 129.67 (C-2′′,6′′), 129.72 (C-1), 130.0 (C-4), 131.8 (C-2), 133.3 (C-6′), 133.8 (C-10), 135.2 (C-9) 135.7 (C-3), 137.0 (C-4′), 146.8 (C-1′′), 147.0 (C-4′′), 163.1 (C-2′), 202.6 (C=O). EI-MS: *m*/*z* (%) = 369 (100) [M$^{+\cdot}$], 368 (59), 352 (15), 339 (9), 322 (11), 305 (10), 276 (13), 249 (65), 230 (28), 202 (33), 189 (7), 161 (10), 121 (77), 93 (18), 65 (21). FAB-HRMS ($C_{23}H_{15}O_4N$ [M + H]$^+$): calcd. 369.1001, found 369.0989.

2-Phenylnaphthalene (8a): M.p. 94–97 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 7.39 (t, *J* = 7.3 Hz, 1 H, 4′-H), 7.46–7.54 (m, 4 H, 6,7,3′,5′-H), 7.58 (d, *J* = 7.3 Hz, 2 H, 2′,6′-H). 7.76 (dd, *J* = 8.5 and 1.6 Hz, 1 H, 3-H), 7.86–7.92 (m, 2 H, 5,8-H), 7.93 (d, *J* = 8.5 Hz, 1 H, 4-H), 8.05 (d, *J* = 1.6 Hz, 1 H, 1-H). ^{13}C NMR: δ = 125.6 (C-3), 125.8 (C-1), 125.9 and 126.3 (C-6 and C-7), 127.3 (C-4′), 127.4 (C-2′,6′), 127.6 (C-5), 128.2 (C-8), 128.4 (C-4), 128.8 (C-3′,5′), 132.6 (C-10) 133.6 (C-9), 138.5 (C-3), 141.1 (C-1′). EI-MS: *m*/*z* (%) = 204 (100) [M$^{+\cdot}$], 203 (22), 202 (36), 176 (6), 101 (14), 89 (8), 76 (5). FAB-HRMS ($C_{16}H_{12}$ [M + H]$^+$): calcd. 204.0939, found 204.0934.

2-(4-Methylphenyl)naphthalene (8b): M.p. 75–78 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 2.43 (s, 3 H, 4′-C*H*$_3$), 7.30 (d, *J* = 8.1 Hz, 2 H, 3′,5′-H), 7.44–7.52 (m, 2 H, 6,7-H), 7.63 (d, *J* = 8.1 Hz, 2 H, 2′,6′-H), 7.74 (dd, *J* = 8.6 and 1.6 Hz, 1 H, 3-H), 7.84–7.90 (m, 2 H, 5,8-H), 7.90 (d, *J* = 8.6 Hz, 1 H, 4-H), 8.02 (br. s, 1 H, 1-H). ^{13}C NMR: δ = 21.1 (4′-*C*H$_3$), 125.4 (C-1), 125.5 (C-3), 125.8 and 126.2 (C-6 and C-7), 127.2 (C-2′,6′), 127.6 (C-5), 128.1 (C-8), 128.3 (C-4), 129.6 (C-3′,5′), 132.5 (C-10) 133.7 (C-9), 137.2 (C-4′), 138.2 (C-1′), 138.5 (C-2). EI-MS: *m*/*z* (%) = 218 (100) [M$^{+\cdot}$], 217 (25), 215 (23), 202 (26), 189 (8), 109 (10), 101 (5), 65 (2). FAB-HRMS ($C_{17}H_{14}$ [M + H]$^+$): calcd. 218.1096, found 218.1104.

2-(4-Methoxyphenyl)naphthalene (8c): M.p. 135–137 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 3.87 (s, 3 H, 4′-OC*H*$_3$), 7.02 (d, *J* = 8.8 Hz, 2 H, 3′,5′-H), 7.43–7.52 (m, 2 H, 6,7-H), 7.66 (d, *J* = 8.8 Hz, 2 H, 2′,6′-H), 7.72 (dd, *J* = 8.5 and 1.8 Hz, 1 H, 3-H), 7.83–7.89 (m, 2 H, 5,8-H), 7.89 (d, *J* = 8.5 Hz, 1 H, 4-H), 7.99 (br. s, 1 H, 1-H). ^{13}C NMR: δ = 55.4 (4′-O*C*H$_3$), 114.3 (C-3′,5′), 125.0 (C-1), 125.4 (C-3), 125.6 and 126.2 (C-6 and C-7), 127.6 (C-5), 128.0 (C-8), 128.3 (C-4), 128.4 (C-2′,6′), 132.3 (C-10) 133.6 (C-1′), 133.7 (C-9), 138.1 (C-2),159.2 (C-4′). EI-MS: *m*/*z* (%) = 234 (100) [M$^{+\cdot}$], 219 (39), 202 (7), 191 (25), 189 (23), 165 (13), 117 (13), 83 (5). $C_{17}H_{14}O$ (234.29): calcd. C 87.15, H 6.02; found C 87.61, H 5.84.

2-(4-Chlorophenyl)naphthalene (8d): M.p. 133–134 °C (recrystallisation from ethanol). ^{1}H NMR: δ = 7.46 (d, *J* = 8.5 Hz, 2 H, 3′,5′-H), 7.50–7.55 (m, 2 H, 6,7-H), 7.65 (d, *J* = 8.5 Hz, 2 H, 2′,6′-H), 7.70 (dd, *J* = 8.6 and 1.8 Hz, 1 H, 3-H), 7.86–7.91 (m, 2 H, 5,8-H), 7.92 (d, *J* = 8.6 Hz, 1 H, 4-H), 8.01 (br. s, 1 H, 1-H). ^{13}C NMR: δ = 125.2 (C-3), 125.7 (C-1), 126.1 and 126.4 (C-6 and C-7), 127.6 (C-5), 128.2 (C-8), 128.6 (C-4), 128.6 (C-2′,6′), 129.0 (C-3′,5′), 132.6 (C-10), 133.4 (C-4′), 133.6 (C-9), 137.2 (C-2), 139.5 (C-1′). EI-MS: *m*/*z* (%) = 238 (100) [M$^{+\cdot}$], 202 (43), 176 (6), 119 (12), 101 (19), 88 (9), 75 (4). FAB-HRMS ($C_{16}H_{11}Cl$ [M + H]$^+$): calcd. 238.0549, found 218.0557.

2-Hydroxyphenyl 3-Phenyl-4-oxo-1,2,3,4-tetrahydro-2-naphthyl Ketone (9a): ^{1}H NMR: δ = 3.28 (dd, *J* = 16.5 and 4.7 Hz, 1 H, 1$_{trans}$-H) 3.39 (dd, *J* = 16.5 and 10.1 Hz, 1 H, 1$_{cis}$-H), 4.32 (d, *J* = 10.3 Hz, 1 H, 3-H), 4.62 (ddd, *J* = 10.3, 10.1 and 4.7 Hz, 1 H, 2-H), 6.85 (ddd, *J* = 7.7, 7.5 and 0.9 Hz, 1 H, 5′-H), 6.93 (dd, *J* = 8.4 and 0.9 Hz, 1 H, 3′-H), 7.15–7.27 (m, 5 H, 8,2′′,3′′,4′′,5′′,6′′-H), 7.40–7.47 (m, 2 H, 6,4′-H), 7.56 (dt, *J* = 7.5 and 1.3 Hz, 1 H, 7-H), 7.70 (dd, *J* = 7.5 and 1.3 Hz, 1 H, 6′-H), 8.14 (br. d, *J* = 7.8 Hz, 1 H, 5-H), 12.11 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 33.1 (C-1), 48.1 (C-2), 55.6 (C-3), 118.2 (C-1′), 118.9 (C-3′), 119.1 (C-5′), 127.3 (C-4′′), 127.6 (C-6), 127.9 (C-5), 128.6 (C-8), 128.7 (C-2′′,6′′), 128.9 (C-3′′,5′′), 129.5 (C-6′), 132.2 (C-10), 134.1 (C-7), 137.0 (C-4′), 137.9 (C-1′′), 140.5 (C-9), 163.3 (C-2′), 197.0 (C-4), 205.3 (C=O). EI-MS: *m*/*z* (%) = 342 (9) [M$^{+\cdot}$], 322 (5), 221 (100), 191 (5), 178 (5), 165 (5), 121 (53), 91 (24), 77 (5), 65 (20). EI-HRMS ($C_{23}H_{18}O_3$): calcd. 342.1256, found 342.1251.

2-Hydroxyphenyl 3-(4-Methylphenyl)-4-oxo-1,2,3,4-tetrahydro-2-naphthyl Ketone (9b): ^{1}H NMR: δ = 2.25 (s, 3 H, 4′′-C*H*$_3$), 3.27 (dd, *J* = 16.5 and 4.9 Hz, 1 H, 1$_{trans}$-H) 3.37 (dd, *J* = 16.5 and 10.0 Hz, 1 H, 1$_{cis}$-H), 4.29 (d, *J* = 10.3 Hz, 1 H, 3-H), 4.61(ddd, *J* = 10.3, 10.0 and 4.9 Hz, 1 H, 2-H), 6.86 (ddd, *J* = 7.9, 7.7 and

1.1 Hz, 1 H, 5′-H), 6.94 (dd, *J* = 8.1 and 1.1 Hz, 1 H, 3′-H), 7.05 (s, 4 H, 2′′,3′′,5′′,6′′-H), 7.25 (d, *J* = 7.0 Hz, 1 H, 8-H), 7.41 (dd, *J* = 7.8 and 7.0 Hz, 1 H, 6-H), 7.45 (ddd, *J* = 8.1, 7.7 and 1.5 Hz, 1 H, 4′-H), 7.54 (dt, *J* = 7.0 and 1.4 Hz, 1 H, 7-H), 7.72 (dd, *J* = 7.9 and 1.5 Hz, 1 H, 6′-H), 8.13 (dd, *J* = 7.8 and 1.4 Hz, 1 H, 5-H), 12.13 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 21.0 (4′′-CH_3), 33.1 (C-1), 48.0 (C-2), 55.1 (C-3), 118.2 (C-1′), 118.9 (C-3′), 119.1 (C-5′), 127.5 (C-6), 127.8 (C-5), 128.5 (C-8), 128.7 (C-2′′,6′′), 129.4 (C-3′′,5′′), 129.5 (C-6′), 132.2 (C-10), 134.0 (C-7), 134.8 (C-4′′), 136.85 (C-1′′), 136.91 (C-4′), 140.4 (C-9), 163.2 (C-2′), 197.1 (C-4), 205.4 (C=O). EI-MS: *m*/*z* (%) = 356 (11) [M$^{+\cdot}$], 235 (100), 207 (5), 191 (7), 143 (11), 121 (44), 105 (15), 90 (15), 65 (18). EI-HRMS ($C_{24}H_{20}O_3$): calcd. 356.1412, found 356.1412.

General Procedure for the Synthesis of 2-Hydroxyphenyl 3-Phenyl-2-naphthyl Ketones 5a-e under Microwave Irradiation: A mixture of the appropriate 2-hydroxyphenyl 3-phenyl-1,2,3,4-tetrahydro-2-naphthyl ketone **4a**–**e** (0.235 mmol), DDQ (0.159 g, 0.7 mmol) in 1,2,4-trichlorobenzene (10 mL), in a two-necked glassware apparatus, provided with magnetic stirring bar, fiber-optic temperature control and reflux condenser was heated for 36 minutes according to the following microwave program: step 1: 6 minutes, ramp to 170 °C, 800 W maximum power; step 2: 30 minutes, hold at 170 °C, 800 W maximum power. The crude product was purified by flash chromatography on silica gel eluting with light petroleum ether to remove the 1,2,4-trichlorobenzene and with a 1:1 mixture of light petroleum ether/dichloromethane to afford the 2-arylnaphthalenes **8a**–**e** (**8a**, 5%; **8b**, 5%; **8c**, 4%; **8d**, 5%; **8e**, 7%), 3-aryl-2-naphthyl 2-hydroxyphenyl ketones **5a**–**e** (**5a**, 66%; **5b**, 65%; **5c**, 60%; **5d**, 61%; **5e**, 44%), 2-hydroxyphenyl 3-phenyl-4-oxo-1,2,3,4-tetrahydro-2-naphthyl ketones **9a**,**d** (**9a**, 5%; **9d**, 9%). After the eluent was changed to dichloromethane, a mixture of benzoxanthones was eluted (except for R = NO_2, only 1-phenylbenzo[*c*]xanthone **13e** was obtained, 13%). The mixture of benzoxanthones was purified by preparative TLC eluting with a 8:2 mixture of dichloromethane/light petroleum ether, leading to the isolation of 1-arylbenzo[*c*]xanthones **13a**–**d** (**13a**, 7%; **13b**, 8%; **13c**, **5%**%; **13d**, 3%), 2-arylbenzo[*c*]xanthones **14a**–**d** (**14a**, 1%; **14b**, 4%; **14c**, 4%; **14d**, 1%), 6-arylbenzo[*b*]xanthones **15b**,**c** (**15b**, 2%; **15c**, 17%) and 6-arylbenzo[*a*]xanthones **16a**–**d** (**16a**, 5%; **16b**, 7%; **16c**, 3%; **16d**, 4%).

2-(4-Nitrophenyl)naphthalene (8e): ^{1}H NMR: δ = 8.35 (d, *J* = 8.8 Hz, 2 H, 3′,5′-H), 7.54–7.57 (m, 2 H, 6,7-H), 7.88 (d, *J* = 8.8 Hz, 2 H, 2′,6′-H), 7.75 (dd, *J* = 8.6 and 1.5 Hz, 1 H, 3-H), 7.86–7.94 (m, 2 H, 5,8-H), 7.98 (d, *J* = 8.6 Hz, 1 H, 4-H), 8.11 (d, *J* = 1.5 Hz, 1 H, 1-H). ^{13}C NMR: δ = 124.2 (C-3′,5′), 124.9 (C-3), 126.8 (C-1), 126.8 and 126.9 (C-6 and C-7), 127.7 (C-5), 128.0 (C-2′,6′), 128.4 (C-8), 129.0 (C-4), 133.2 (C-10) 133.6 (C-9), 136.0 (C-2), 147.1 (C-4′), 147.6 (C-1′). EI-MS: *m*/*z* (%) = 249 (100) [M$^{+\cdot}$], 219 (10), 202 (59), 191 (10), 176 (5), 152 (5), 101 (11), 88(5). FAB-HRMS ($C_{16}H_{11}NO_2$ [M + H]$^+$): calcd. 249.0790, found 249.0793.

3-(4-Chlorophenyl)-4-oxo-1,2,3,4-tetrahydro-2-naphthyl 2-Hydroxyphenyl Ketone (9d): ^{1}H NMR: δ = 3.27 (dd, *J* = 16.5 and 4.5 Hz, 1 H, 1_{trans}-H) 3.39 (dd, *J* = 16.5 and 10.8 Hz, 1 H, 1_{cis}-H), 4.32 (d, *J* = 11.0 Hz, 1 H, 3-H), 4.60 (ddd, *J* = 11.0, 10.8 and 4.5 Hz, 1 H, 2-H), 6.87 (ddd, *J* = 7.9, 7.7 and 1.1 Hz, 1 H, 5′-H), 6.96 (dd, *J* = 8.2 and 1.1 Hz, 1 H, 3′-H), 7.10 (d, *J* = 8.5 Hz, 2 H, 2′′,6′′-H), 7.23 (d, *J* = 8.5 Hz, 2 H, 3′′,5′′-H), 7.27 (d, *J* = 6.9 Hz, 1 H, 8-H), 7.42 (dd, *J* = 7.7 and 7.5 Hz, 1 H, 6-H), 7.47 (ddd, *J* = 8.2, 7.7 and 1.5 Hz, 1 H, 4′-H), 7.57 (ddd, *J* = 7.5, 6.9 and 1.4 Hz, 1 H, 7-H), 7.70 (dd, *J* = 7.9 and 1.5 Hz, 1 H, 6′-H), 8.13 (dd, *J* = 7.7 and 1.4 Hz, 1 H, 5-H), 12.09 (s, 1 H, 2′-O*H*). ^{13}C NMR: δ = 33.4 (C-1), 48.0 (C-2), 55.1 (C-3), 118.2 (C-1′), 119.0 (C-3′), 119.2 (C-5′), 127.7 (C-6), 127.9 (C-5), 128.6 (C-8), 128.8 (C-3′′,5′′), 129.3 (C-6′), 130.4 (C-2′′,6′′), 131.9 (C-10), 133.2 (C-4′′), 134.2 (C-7), 136.3 (C-1′′), 137.2 (C-4′), 140.4 (C-9), 163.4 (C-2′), 196.6 (C-4), 204.8 (C=O). EI-MS: *m*/*z* (%) = 376 (8) [M$^{+\cdot}$], 358 (5), 255 (100), 220 (6), 191 (13), 165 (6), 121 (77), 90 (27), 65 (28). EI-HRMS ($C_{23}H_{17}O_3{}^{35}Cl$): calcd. 376.0866, found 376.0857. EI-HRMS ($C_{23}H_{17}O_3{}^{37}Cl$): calcd. 378.0837, found 378.0832.

1-Phenylbenzo[*c*]xanthone (13a): ^{1}H NMR: δ = 7.37–7.49 (m, 6 H, 10,2′,3′,4′,5′,6′-H), 7.55 (s, 1 H, 2-H), 7.68–7.79 (m, 4 H, 5,4,9,8-H), 7.91 (dd, *J* = 8.2 and 1.7 Hz, 1 H, 3-H), 8.26 (dd, *J* = 8.0 and 1.5 Hz, 1 H, 11-H), 8.74 (dd, *J* = 8.2 and 1.7 Hz, 1 H, 6-H). ^{13}C NMR: δ = 116.2 (C-12a), 117.5 (C-8), 123.1 (C-6), 123.4 (C-11a), 124.4 (C-10), 126.5 (C-2), 126.8 (C-11), 126.9 (C-5), 127.0 (C-4′), 127.6 (C-2′,6′), 127.9 (C-3), 128.6 (C-3′,5′), 130.1 (C-4), 131.1 (C-6a), 134.1 (C-9), 135.3 (C-2a), 138.7 (C-1), 142.3 (C-1′), 154.9 (C-6b), 155.0 (C-7a), 176.6 (C-12). EI-MS: *m*/*z* (%) = 322 (66) [M$^{+\cdot}$], 321 (100), 305 (7), 292 (6), 205 (4), 189 (4), 160 (11), 118 (4). EI-HRMS ($C_{23}H_{14}O_2$): calcd. 322.0994, found 322.0988.

1-(4-Methylphenyl)benzo[*c*]xanthone (13b): ^{1}H NMR: δ = 2.46 (s, 3 H, 4′′-CH_3), 7.27 (d, *J* = 7.6 Hz, 2 H, 3′,5′-H), 7.34 (d, *J* = 7.6 Hz, 2 H, 2′,6′-H), 7.39 (dd, *J* = 7.7 and 7.4 Hz, 1 H, 10-H), 7.54 (s, 1 H, 2-H), 7.67–7.76 (m, 4 H, 4,5,8,9-H), 7.89 (d, *J* = 7.7 Hz, 1 H, 3-H), 8.27 (dd, *J* = 7.7 and 1.4 Hz, 1 H, 11-H), 8.73 (d, *J* = 8.8 Hz, 1 H, 6-H). ^{13}C NMR: δ = 21.4 (4′′-*C*H$_3$), 116.1 (C-12a), 117.5 (C-8), 123.0 (C-6), 123.5 (C-11a), 123.7 (C-6a), 124.4 (C-10), 126.5 (C-2), 126.8 (C-5), 126.9 (C-11), 127.8 (C-3), 128.3 (C-2′,6′), 128.5 (C-3′,5′), 130.0 (C-4), 134.1 (C-9), 135.3 (C-2a), 138.8 (C-1), 136.4 (C-4′), 139.4 (C-1′), 154.9 (C-6b), 155.1 (C-7a), 176.6 (C-12). EI-MS: *m*/*z* (%) = 336 (70) [M$^{+\cdot}$], 335 (100), 319 (9), 305 (5), 167 (7), 161 (19). EI-HRMS ($C_{24}H_{16}O_2$): calcd. 336.1150, found 336.1160.

1-(4-Methoxyphenyl)benzo[*c*]xanthone (13c): ^{1}H NMR: δ = 3.90 (s, 3 H, 4′′-OCH_3), 7.01 (d, *J* = 8.7 Hz, 2 H, 3′,5′-H), 7.37–7.42 (m, 1 H, 10-H), 7.36 (d, *J* = 8.7 Hz, 2 H, 2′,6′-H), 7.54 (s, 1 H, 2-H), 7. 69 (dd, *J* = 8.3 and 1.0 Hz, 1 H, 8-H), 7.71–7.79 (m, 3 H, 4,5,9-H), 7.89 (dd, *J* = 7.2 and 1.9 Hz, 1 H, 3-H), 8.28 (dd, *J* = 7.9 and 1.6 Hz, 1 H, 11-H), 8.73 (dd, *J* = 8.0 and 1.5 Hz, 1 H, 6-H). ^{13}C NMR: δ = 55.2 (4′′-O*C*H$_3$), 113.0 (C-3′,5′), 116.0 (C-12a), 117.5 (C-8), 123.0 (C-6), 123.4 (C-6a), 123.7 (C-11a), 124.4 (C-10), 126.6 (C-2), 126.77 (C-11), 126.84 (C-5), 127.9 (C-3), 129.7 (C-2′,6′), 130.0 (C-4), 134.1 (C-9), 134.6 (C-1′), 135.3 (C-2a), 138.4 (C-1), 154.95 (C-6b), 154.99 (C-7a), 158.6 (C-4′), 176.8 (C-12). EI-MS: *m*/*z* (%) = 352 (100) [M$^{+\cdot}$], 351 (87), 337 (11), 309 (16), 292 (7), 279 (17), 252 (5), 169 (10), 154 (18). EI-HRMS ($C_{24}H_{16}O_3$): calcd. 352.1099, found 352.1097.

1-(4-Chlorophenyl)benzo[*c*]xanthone (13d): ^{1}H NMR: δ = 7.34–7.42 (m, 1 H, 10-H), 7.35 (d, *J* = 8.3 Hz, 2 H, 3′,5′-H), 7.43 (d, *J* = 8.3 Hz, 2 H, 2′,6′-H), 7.51 (s, 1 H, 2-H), 7. 70 (dd, *J* = 8.4 and 1.0 Hz, 1 H, 8-H), 7.72–7.80 (m, 3 H, 4,5,9-H), 7.91 (dd, *J* = 7.0 and 2.2 Hz, 1 H, 3-H), 8.26 (dd, *J* = 7.9 and 1.6 Hz, 1 H, 11-H), 8.74 (dd, *J* = 8.3 and 2.0 Hz, 1 H, 6-H). ^{13}C NMR: δ = 115.7 (C-12a), 117.6 (C-8), 123.1 (C-6), 123.2 (C-11a), 123.9 (C-6a), 124.5 (C-10), 126.5 (C-2), 126.7 (C-11), 127.1 (C-5), 127.7 (C-2′,6′), 127.9 (C-3), 130.0 (C-3′,5′), 130.2 (C-4), 132.9 (C-4′), 134.3 (C-9), 135.2 (C-2a), 137.4 (C-1), 140.7 (C-1′), 155.0 (C-6b,7a), 176.7 (C-12). EI-MS: *m*/*z* (%) = 358 (32) [M$^{+\cdot}$, ^{37}Cl],356 (72) [M$^{+\cdot}$, ^{35}Cl], 72), 355 (100), 339 (10), 292 (6), 263 (10), 161 (35), 146 (5), 132 (8). EI-HRMS ($C_{23}H_{13}O_2{}^{35}Cl$): calcd. 356.0604, found 356.0589. EI-HRMS ($C_{23}H_{13}O_2{}^{37}Cl$): calcd. 358.0575, found 358.0564.

1-(4-Nitrophenyl)benzo[*c*]xanthone (13e): ^{1}H NMR: δ = 7.44 (ddd, *J* = 8.0, 7.0 and 1.1 Hz, 1 H, 10-H), 7.54 (s, 1 H, 2-H), 7.57 (d, *J* = 8.7 Hz, 2 H, 2′,6′-H), 7.73 (d, *J* = 8.6 Hz, 1 H, 8-H), 7.78–7.82 (m, 3 H, 5,4,9-H), 7.94 (dd, *J* = 7.3 and 1.5 Hz, 1 H, 3-H), 8.24

(dd, *J* = 8.0 and 1.5 Hz, 1 H, 11-H), 8.33 (d, *J* = 8.7 Hz, 2 H, 3′,5′-H), 8.78 (dd, *J* = 7.9 and 1.4 Hz, 1 H, 6-H). ^{13}C NMR: δ = 115.4 (C-12a), 117.7 (C-8), 122.9 (C-3′,5′), 123.0 (C-11a), 123.2 (C-6), 124.2 (C-6a), 124.8 (C-10), 126.4 (C-2), 126.7 (C-11), 127.7 (C-5), 128.1 (C-3), 129.6 (C-2′,6′), 130.6 (C-4), 134.6 (C-9), 135.1 (C-2a), 136.2 (C-1), 146.8 (C-4′), 149.4 (C-1′), 155.06 (C-6b), 155.12 (C-7a), 176.5 (C-12). EI-MS: *m*/*z* (%) = 367 (95) [M^{+}], 366 (100), 337 (9), 320 (40), 292 (14), 279 (5), 266 (18), 160 (16), 131 (7), 121 (19), 57 (9). EI-HRMS ($C_{23}H_{13}NO_4$): calcd. 367.0845, found 367.0832.

2-Phenylbenzo[*c*]xanthone (14a): ^{1}H NMR: δ = 7.38–7.54 (m, 6 H, 10,2′,3′,4′,5′,6′-H), 7.66–7.76 (m, 3 H, 4,5,8-H), 7.82 (ddd, *J* = 8.4, 6.9 and 1.6 Hz, 1 H, 9-H), 8.01 (dd, *J* = 8.1 and 1.5 Hz, 1 H, 3-H), 8.24 (s, 1 H, 1-H), 8.44 (dd, *J* = 8.0 and 1.5 Hz, 1 H, 11-H), 8.80 (dd, *J* = 8.7 and 1.6 Hz, 1 H, 6-H). ^{13}C NMR: δ = 117.1 (C-12a), 118.1 (C-8), 121.9 (C-1), 122.5 (C-11a), 123.1 (C-6), 124.4 (C-6a), 124.5 (C-10), 126.6 (C-11), 126.7 (C-3), 126.8 (C-5), 127.6 (C-4′), 128.4 (C-2′,6′), 129.6 (C-4), 130.1 (C-3′,5′), 134.4 (C-9), 135.1 (C-2a), 136.6 (C-2), 139.5 (C-1′), 153.1 (C-6b), 155.8 (C-7a), 176.9 (C-12). EI-MS: *m*/*z* (%) = 322 (100) [M$^{+\cdot}$], 321 (46), 292 (12), 263 (10), 189 (8), 149 (9), 118 (14). EI-HRMS ($C_{23}H_{14}O_2$): calcd. 322.0994, found 322.0990.

2-(4-Methylphenyl)benzo[*c*]xanthone (14b): ^{1}H NMR: δ = 2.48 (s, 3 H, 4′-CH_3), 7.34 (d, *J* = 8.1 Hz, 2 H, 3′,5′-H), 7.44 (d, *J* = 8.1 Hz, 2 H, 2′,6′-H), 7.48–7.53 (m, 1 H, 10-H), 7.66–7.71 (m, 2 H, 4,5-H), 7.75 (d, *J* = 7.8 Hz, 1 H, 8-H), 7.82 (ddd, *J* = 7.8, 6.9 and 1.5 Hz, 1 H, 9-H), 8.04 (d, *J* = 7.3 Hz, 1 H, 3-H), 8.23 (s, 1 H, 1-H), 8.44 (dd, *J* = 7.9 and 1.5 Hz, 1 H, 11-H), 8.80 (dd, *J* = 8.3 and 1.6 Hz, 1 H, 6-H). ^{13}C NMR: δ = 21.3 (4′-*C*H$_3$), 117.1 (C-12a), 118.1 (C-8), 121.8 (C-1), 122.5 (C-11a), 123.1 (C-6), 124.4 (C-6a,10), 126.6 (C-11), 126.7 (C-3), 126.8 (C-5), 129.1 (C-3′,5′), 129.5 (C-4), 130.0 (C-2′,6′), 134.4 (C-9), 135.2 (C-2a), 135.9 (C-2), 136.5 (C-1′), 137.4 (C-4′), 153.1 (C-6b), 155.8 (C-7a), 177.0 (C-12). EI-MS: *m*/*z* (%) = 336 (100) [M$^{+\cdot}$], 321 (10), 305 (5), 292 (10), 263 (5), 160 (5), 118 (19). EI-HRMS ($C_{24}H_{16}O_2$): calcd. 336.1150, found 336.1143.

2-(4-Methoxyphenyl)benzo[*c*]xanthone (14c): ^{1}H NMR: δ = 3.92 (s, 3 H, 4′-OCH_3), 7.06 (d, *J* = 8.5 Hz, 2 H, 3′,5′-H), 7.47–7.49 (m, 1 H, 10-H), 7.48 (d, *J* = 8.5 Hz, 2 H, 2′,6′-H), 7.68–7.74 (m, 2 H, 4,5-H), 7.74 (d, *J* = 8.2 Hz, 1 H, 8-H), 7.82 (ddd, *J* = 8.2, 7.1 and 1.4 Hz, 1 H, 9-H), 8.04 (d, *J* = 8.1 Hz, 1 H, 3-H), 8.22 (s, 1 H, 1-H), 8.44 (dd, *J* = 7.9 and 1.4 Hz, 1 H, 11-H), 8.79 (d, *J* = 8.0 Hz, 1 H, 6-H). ^{13}C NMR: δ = 55.4 (4′-O*C*H$_3$), 113.9 (C-3′,5′), 117.1 (C-12a), 118.1 (C-8), 121.8 (C-1), 122.5 (C-11a), 123.1 (C-6), 124.4 (C-6a,10), 126.6 (C-11), 126.7 (C-3,5), 129.5 (C-4), 131.2 (C-2′,6′), 131.8 (C-1′), 134.4 (C-9), 135.3 (C-2a), 136.3 (C-2), 152.9 (C-6b), 155.8 (C-7a), 159.2 (C-4′), 177.1 (C-12). EI-MS: *m*/*z* (%) = 352 (100) [M$^{+\cdot}$], 337 (28), 309 (10), 279 (15), 252 (6), 176 (11), 169 (5), 154 (9). EI-HRMS ($C_{24}H_{16}O_3$): calcd. 352.1099, found 352.1090.

2-(4-Chlorophenyl)benzo[*c*]xanthone (14d): ^{1}H NMR: δ = 7.47–7.52 (m, 5 H, 10,2′,3′,5′,6′-H), 7.71–7.77 (m, 3 H, 4,5,8-H), 7.82 (ddd, *J* = 8.2, 7.1 and 1.5 Hz, 1 H, 9-H), 7.95 (d, *J* = 8.0 Hz, 1 H, 3-H), 8.22 (s, 1 H, 1-H),8.44 (dd, *J* = 8.0 and 1.5 Hz, 1 H, 11-H), 8.80 (d, *J* = 8.0 Hz, 1 H, 6-H). ^{13}C NMR: δ = 117.0 (C-12a), 118.2 (C-8), 122.0 (C-1), 122.5 (C-11a), 123.3 (C-6), 124.5 (C-6a), 124.6 (C-10), 126.3 (C-3), 126.6 (C-11), 126.9 (C-5), 128.7 (C-2′,6′), 129.8 (C-4), 131.4 (C-3′,5′), 133.8 (C-4′), 134.5 (C-9), 134.9 (C-2a), 135.3 (C-2), 137.9 (C-1′), 153.2 (C-6b), 155.8 (C-7a), 176.9 (C-12). EI-MS: *m*/*z* (%) = 358 (46) [M$^{+\cdot}$, ^{37}Cl], 356 (100) [M$^{+\cdot}$, ^{35}Cl], 355 (22), 320 (15), 292 (20), 263 (16), 189 (6), 161 (10), 132 (7). EI-HRMS ($C_{23}H_{13}O_2{}^{35}Cl$): calcd. 356.0604, found 356.0595. EI-HRMS ($C_{23}H_{13}O_2{}^{37}Cl$): calcd. 358.0575, found 358.0573.

6-(4-Methylphenyl)benzo[*b*]xanthone (15b): ^{1}H NMR: δ = 2.54 (s, 3 H, 4′-CH_3), 7.29 (d, *J* = 8.2 Hz, 1 H, 11-H), 7.33 (dd, *J* = 7.7 and 7.4 Hz, 1 H, 9-H), 7.40 (s, 4 H, 2′,3′,5′,6′-H), 7.48–7.55 (m, 2 H, 2,3-H), 7.66 (ddd, *J* = 8.2, 7.4 and 1.7 Hz, 1 H, 10-H), 7.73–7.77 (m, 1 H, 4-H), 8.11–8.14 (m, 1 H, 1-H), 8.37 (dd, *J* = 7.7 and 1.7 Hz, 1 H, 8-H), 9.00 (s, 1 H, 5-H). ^{13}C NMR: δ = 21.4 (4′-*C*H$_3$), 118.2 (C-11), 120.8 (C-7a), 121.1 (C-6a), 123.4 (C-9), 125.3 (C-2), 125.8 (C-4), 126.4 (C-6), 126.8 (C-8), 127.7 (C-5), 128.8 (C-3), 129.1 (C-3′,5′), 129.5 (C-12b), 130.0 (C-1), 130.9 (C-2′,6′), 131.3 (C-1′), 135.1 (C-10), 135.9 (C-4a), 137.5 (C-4′), 148.8 (C-12a), 156.7 (C-11a), 178.4 (C-7). EI-MS: *m*/*z* (%) = 336 (100) [M$^{+\cdot}$], 335 (17), 321 (11), 292 (8), 263 (4), 215 (4), 118 (7). EI-HRMS ($C_{24}H_{16}O_2$): calcd. 336.1150, found 336.1152.

6-(4-Methoxyphenyl)benzo[*b*]xanthone (15c): ^{1}H NMR: δ = 3.96 (s, 3 H, 4′-OCH_3), 7.14 (d, *J* = 8.7 Hz, 2 H, 3′,5′-H), 7.29 (d, *J* = 8.2 Hz, 1 H, 11-H), 7.34 (ddd, *J* = 7.9, 7.5 and 0.9 Hz, 1 H, 9-H), 7.43 (d, *J* = 8.7 Hz, 2 H, 2′,6′-H), 7.67 (ddd, *J* = 8.2, 7.5 and 1.7 Hz, 1 H, 10-H), 7.48–7.57 (m, 2 H, 2,3-H), 7.75–7.78 (m, 1 H, 4-H), 8.11–8.14 (m, 1 H, 1-H), 8.37 (dd, *J* = 7.9 and 1.7 Hz, 1 H, 8-H), 8.99 (s, 1 H, 5-H). ^{13}C NMR: δ = 55.4 (4′-O*C*H$_3$), 113.8 (C-3′,5′), 118.2 (C-11), 120.8 (C-7a), 121.1 (C-6a), 123.4 (C-9), 125.3 (C-2), 128.9 (C-3), 125.8 (C-4), 126.1 (C-1′), 126.5 (C-6), 126.8 (C-8), 127.7 (C-5), 129.6 (C-12b), 130.1 (C-1), 132.2 (C-2′,6′), 135.2 (C-10), 136.1 (C-4a), 149.0 (C-12a), 156.7 (C-11a), 159.3 (C-4′), 178.4 (C-7). EI-MS: *m*/*z* (%) = 352 (100) [M$^{+\cdot}$], 337 (16), 309 (6), 292 (8), 279 (10), 252 (8), 189 (7), 176 (7), 168 (5), 113 (4). $C_{24}H_{16}O_3$ (352.38): calcd. C 81.80, H 4.58; found C 81.56, H 4.72.

6-Phenylbenzo[*a*]xanthone (16a): ^{1}H NMR: δ = 7.42 (d, *J* = 8.0 Hz, 1 H, 8-H), 7.44 (dd, *J* = 8.3 and 8.1 Hz, 1 H, 10-H), 7.50–7.65 (m, 3 H, 3,3′,5′-H), 7.65–7.73 (m, 3 H, 9,2′,6′-H), 7.79 (ddd, *J* = 8.3, 7.1 and 1.2 Hz, 1 H, 2-H), 7.93 (d, *J* = 8.0 Hz, 1 H, 4-H), 8.15 (s, 1 H, 5-H), 8.45 (dd, *J* = 8.1 and 1.6 Hz, 1 H, 11-H), 10.13 (d, *J* = 8.3 Hz, 1 H, 1-H). ^{13}C NMR: δ = 115.0 (C-12a), 117.6 (C-8), 123.3 (C-11a), 124.4 (C-10), 126.4 (C-3), 126.5 (C-11), 126.8 (C-1), 128.0 (C-4′), 128.37 (C-2′,6′), 128.42 (C-4), 129.4 (C-2), 129.8 (C-3′,5′), 129.9 (C-4a), 130.7 (C-12b), 131.1 (C-6), 133.9 (C-9), 136.6 (C-1′), 137.1 (C-5), 154.4 (C-7a), 155.1 (C-6a), 178.8 (C-12). EI-MS: *m*/*z* (%) = 322 (100) [M$^{+\cdot}$], 321 (16), 294 (18), 265 (12), 245 (7), 205 (10), 181 (14), 168 (6), 121 (12). EI-HRMS ($C_{23}H_{14}O_2$): calcd. 322.0994, found 322.0990.

6-(4-Methylphenyl)benzo[*c*]xanthone (16b): ^{1}H NMR: δ = 2.50 (s, 3 H, 4′-CH_3), 7.38 (d, *J* = 8.2 Hz, 2 H, 3′,5′-H), 7.43–7.47 (m, 2 H, 10,8-H), 7.60–7.65 (m, 1 H, 3-H), 7.62 (d, *J* = 8.1 Hz, 2 H, 2′,6′-H), 7.67–7.73 (m, 1 H, 9-H), 7.79 (ddd, *J* = 8.2, 7.8 and 1.5 Hz, 1 H, 2-H), 7.94 (d, *J* = 8.1 Hz, 1 H, 4-H), 8.15 (s, 1 H, 5-H), 8.46 (dd, *J* = 8.2 and 1.8 Hz, 1 H, 11-H), 10.13 (d, *J* = 8.2 Hz, 1 H, 1-H). ^{13}C NMR: δ = 21.3 (4′-*C*H$_3$), 115.0 (C-12a), 117.7 (C-8), 123.3 (C-11a), 124.4 (C-10), 126.4 (C-3), 126.6 (C-11), 126.9 (C-1), 128.4 (C-4), 129.1 (C-3′,5′), 129.3 (C-2), 129.7 (C-2′,6′), 130.0 (C-4a), 130.7 (C-12b), 131.1 (C-6), 133.7 (C-1′), 133.9 (C-9), 136.9 (C-5), 137.9 (C-4′), 154.4 (C-7a), 155.3 (C-6a), 178.9 (C-12). EI-MS: *m*/*z* (%) = 336 (100) [M$^{+\cdot}$], 335 (17), 308 (6), 292 (5), 276 (5), 263 (5), 215 (4), 189 (4), 167 (6), 146 (4). EI-HRMS ($C_{24}H_{16}O_2$): calcd. 336.1150, found 336.1155.

6-(4-Methoxyphenyl)benzo[*c*]xanthone (16c): ^{1}H NMR: δ = 3.94 (s, 3 H, 4′-OCH_3), 7.10 (d, *J* = 8.6 Hz, 2 H, 3′,5′-H), 7.44–7.47 (m, 2 H, 10,8-H), 7.63 (dd, *J* = 8.1 and 7.4 Hz, 1 H, 2-H), 7.67 (d, *J* = 8.6 Hz, 2 H, 2′,6′-H), 7.71 (ddd, *J* = 8.0, 7.1 and 1.4 Hz, 1 H, 9-H), 7.79 (dd, *J* = 8.0 and 7.4 Hz, 1 H, 3-H), 7.94 (d, *J* = 8.0 Hz, 1 H, 4-H), 8.14 (s, 1 H, 5-H), 8.47 (dd, *J* = 8.2 and 1.4 Hz, 1 H, 11-H), 10.13 (d, *J* = 8.1 H, 1 Hz, 1-H). ^{13}C NMR: δ = 55.4 (4′-O*C*H$_3$), 113.8 (C-3′,5′), 115.2 (C-12a), 117.6 (C-8), 123.2 (C-11a), 124.4

(C-10), 126.7 (C-1,3,11), 127.8 (C-1′), 128.3 (C-4), 129.2 (C-2), 130.4 (C-4a,6,12b), 131.1 (C-2′,6′), 133.8 (C-9), 136.7 (C-5), 154.4 (C-7a), 155.3 (C-6a), 159.5 (C-4′), 179.1 (C-12). EI-MS: *m*/*z* (%) = 352 (100) [$M^{+\cdot}$], 337 (16), 309 (17), 279 (6), 252 (7), 176 (8), 154 (4). EI-HRMS ($C_{24}H_{16}O_3$): calcd. 352.1099, found 352.1098.

6-(4-Chlorophenyl)benzo[*a*]xanthone (16d): ^{1}H NMR: δ = 7.42–7.47 (m, 2 H, 10,8-H), 7.54 (d, *J* = 8.5 Hz, 2 H, 2′,6′-H), 7.61–7.67 (m, 1 H, 3-H), 7.66 (d, *J* = 8.5 Hz, 2 H, 3′,5′-H), 7.72 (dt, *J* = 7.7 and 1.7 H, 1 Hz, 9-H), 7.82 (ddd, *J* = 8.3, 7.8 and 1.4 Hz 1 H, 2-H), 7.95 (d, *J* = 8.0 Hz, 1 H, 4-H), 8.14 (s, 1 H, 5-H), 8.47 (dd, *J* = 8.0 and 1.7 Hz, 1 H, 11-H), 10.14 (d, *J* = 8.3 Hz, 1 H, 1-H). ^{13}C NMR: δ = 114.9 (C-12a), 117.5 (C-8), 123.3 (C-11a), 124.6 (C-10), 126.55 (C-11), 126.63 (C-3), 126.9 (C-1), 128.5 (C-4), 128.6 (C-2′,6′), 129.7 (C-2), 129.8 (C-12b), 129.9 (C-4′), 130.8 (C-4a), 131.6 (C-3′,5′), 134.0 (C-9), 134.2 (C-1′), 135.1 (C-6), 136.9 (C-5), 154.4 (C-7a), 154.9 (C-6a), 178.8 (C-12). EI-MS: *m*/*z* (%) = 358 (3) [$M^{+\cdot}$, ^{37}Cl], 356 (2) [$M^{+\cdot}$, ^{35}Cl], 255 (100), 220 (5), 202 (3), 191 (7), 165 (5), 121 (58), 90(15), 65 (13). EI-HRMS ($C_{23}H_{13}O_2{}^{35}Cl$): calcd. 356.0604, found 356.0605. EI-HRMS ($C_{23}H_{13}O_2{}^{37}Cl$): calcd. 358.0575, found 358.0586.

Acknowledgments

Sincere thanks are expressed to the University of Aveiro, "Fundação para a Ciência e a Tecnologia", Portugal, and FEDER for funding the Organic Chemistry Research Unit. C.M.B. thanks the Organic Chemistry Research Unit for a research grant.

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[21] Selected data for 1-(4-methylphenyl)-1,2-dihydrobenzo[*c*]xanthone (**6b**) (11%): ^{1}H NMR: δ = 2.20 (s, 3 H, 4′-CH_3), 3.16 (dd, *J* = 16.0 and 1.2 Hz, 1 H, H-2$_{trans}$), 3.53 (dd, *J* = 16.0 and 7.5 Hz, 1 H, H-2$_{cis}$), 4.70 (d, *J* = 7.5 Hz, 1 H, H-1), 6.93 (d, *J* = 8.1 Hz, 2 H, H-3′,5′), 7.07 (d, *J* = 8.1 Hz, 2 H, H-2′,6′), 7.20–7.23 (m, 1 H, H-3), 7.35–7.41 (m, 3 H, H-4,5,10), 7.58 (d, *J* = 7.8 Hz, 1 H, H-8), 7.68 (dt, *J* = 7.8 and 1.7 Hz, 1 H, H-9), 8.04–8.07 (m, 1 H, H-6), 8.21 (dd, *J* = 8.0 and 1.7 Hz, 1 H, H-11). ^{13}C NMR: δ = 20.9 (4′-CH_3), 34.3 (C-1), 35.0 (C-2), 117.9 (C-8), 119.2 (C-12a), 123.86 (C-6), 123.90 (C-11a), 124.8 (C-10), 126.0 (C-11), 127.0 and 131.5 (C-4 and C-5), 127.1 (C-2′,6′), 128.3 (C-6a), 128.95 (C-3), 129.01 (C-3′,5′), 133.4 (C-9) 136.1 (C-4′), 137.8 (C-2a), 139.6 (C-1′), 155.6 (C-7a), 158.0 (C-6b), 176.8 (C-12). EI-MS: *m*/*z* (%) = 338 (95) [$M^{+\cdot}$], 337 (86), 247 (100), 218 (16), 202 (14), 189 (18), 105 (10), 91 (12), 77 (6), 65 (7).

[22] Selected data for xanthones **7d**. 1-(4-chlorophenyl)-8-iodo-1,2-dihydrobenzo[*c*]xanthone (**7d1**) (7%): ^{1}H NMR: δ = 3.14 (dd, *J* = 16.3 and 1.2 Hz, 1 H, H-2$_{trans}$), 3.55 (dd, *J* = 16.3 and 7.9 Hz, 1 H, H-2$_{cis}$), 4.67 (dd, *J* = 7.9 and 1.2 Hz, 1 H, H-1), 7.10 (s, 4 H, H-2′,3′,5′,6′), 7.13 (dd, *J* = 7.8 and 1.5 Hz, 1 H, H-9), 7.16 (t, *J* = 7.8 Hz, 1 H, H-10), 7.21–7.24 (m, 1 H, H-3), 7.44–7.47 (m, 2 H, H-4,5), 8.18 (dd, *J* = 7.8 and 1.5 Hz, 1 H, H-11), 8.24–8.27 (m, 1 H, H-6).
(4-Chlorophenyl)-10-iodo-1,2-dihydrobenzo[*c*]xanthone (**7d2**) (6%): ^{1}H NMR: δ = 3.13 (dd, *J* = 16.2 and 1.1 Hz, 1 H, H-2$_{trans}$), 3.53 (dd, *J* = 16.2 and 7.9 Hz, 1 H, H-2$_{cis}$), 4.68 (dd, *J* = 7.9 and 1.1 Hz, 1 H, H-1), 7.09 (s, 4 H, H-2′,3′,5′,6′), 7.21–7.24 (m, 1 H, H-3), 7.36 (d, *J* = 8.8 Hz, 1 H, H-8), 7.41–7.44

(m, 2 H, H-4,5), 7.95 (dd, J = 8.8 and 2.2 Hz, 1 H, H-9), 8.01–8.04 (m, 1 H, H-6), 8.53 (d, J = 2.2 Hz, 1 H, H-11).
(4-Chlorophenyl)-8,10-diiodo-1,2-dihydrobenzo[*c*]xanthone (**7d3**) (13%): ^{1}H NMR: δ = 3.14 (br. d, J = 16.3 Hz, 1 H, H-2$_{trans}$), 3.54 (dd, J = 16.3 and 8.0 Hz, 1 H, H-2$_{cis}$), 4.65 (dd, J = 8.0 and 1.2 Hz, 1 H, H-1), 7.09 (s, 4 H, H-2′,3′,5′,6′), 7.22–7.25 (m, 1 H, H-3), 7.44–7.47 (m, 2 H, H-4,5), 8.19–8.22 (m, 1 H, H-6), 8.39 (d, J = 2.1 Hz, 1 H, H-9), 8.47 (d, J = 2.1 Hz, 1 H, H-11).

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Received: November 5, 2005
Published Online: March 22, 2006

