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Diels–Alder reactions of chromone-3-carboxaldehydes with *ortho*-benzoquinodimethane. New synthesis of benzo[*b*]xanthones

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Abstract—An efficient new route to the benzo[*b*]xanthone system has been developed and applied to the synthesis of several new derivatives. The cycloaddition reactions of chromone-3-carboxaldehydes **12**, reacting as dienophiles, with *ortho*-benzoquinodimethane **7** gave a diastereomeric mixture of cycloadducts **8** and **9**. The formation of these compounds results from the Diels–Alder reactions of **12** and **7** followed by the in situ deformylation. The oxidation of adducts **8** and **9** with dimethyl sulfoxide in the presence of iodine gave the novel benzo[*b*]xanthones **11** in good yields.

1. Introduction

The enone moiety of the parent chromone does not function as dienophile in cycloaddition reactions. However, the presence of an electron-withdrawing substituent at C-3 enhances the dienophilicity of such 2,3-double bond. These 3-substituted chromones are very versatile molecules, reacting as Michael acceptors, with concomitant opening of the pyrone ring; some of them can react as heterodienes and as dienophiles. The majority of the reactions of this type of chromones are nucleophilic additions leading mainly to new heterocyclic compounds as condensation products.[1]

Although chromone-3-carboxaldehydes constitute the most studied class of chromones bearing electron-withdrawing substituent at C-3,[2] their use as 2π components in cycloaddition reactions are scarce. They have been only used as dienophiles in Diels–Alder reactions with electron-rich dienes (2,3-dimethyl-1,3-butadiene and 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene—Danishefsky's diene), giving xanthone-type compounds.[3] Chromones bearing a 3-cyano substituent have also been used as dienophiles in the same type of cycloaddition reactions with the Danishefsky's diene, in order to prepare xanthone derivatives possessing important biological activities.[4] We describe here for the first time Diels–Alder reactions of chromone-3-carboxaldehydes with *ortho*-benzoquinodimethane, followed by oxidation of the formed cycloadducts, leading to benzo[*b*]xanthones. Our results confirm that chromone-3-carboxaldehydes can be used as dienophiles; the corresponding cycloaddition reactions followed by oxidation constitute a new method for the synthesis of novel benzo[*b*]xanthones.

The great interest on xanthones is due to their abundance in nature[5] and mainly to their important biological properties, such as inhibitors of monoamineoxygenase enzymes (MAO-A and MAO-B),[5] acting as anti-inflammatory, anti-oxidant and anti-ulcer agents,[6] as bronchodilatators in the treatment of asthma[7] and also as in vivo and in vitro anti-tumour drugs.[8] However the most prominent activities of this type of compounds are shown by some xanthone based analogues of the anthracycline anti-tumour agents[9] and the antibiotic bikaverin **1**, a natural fungal metabolite with a benzo[*b*]xanthone skeleton.[10] Some synthetic benzo[*b*]xanthone analogues like **2**, **3** and **4** (Scheme 1) proved to be cytotoxic in vitro against a human breast cancer MCF-7 cell line[11] and against leukaemia L1210 cells.[12]

General synthetic approaches to xanthones involve the connection of two aryl fragments to form the internal pyranone ring.[9,11,13] Besides these classical syntheses, other methods have been also developed, such as cycloadditon reactions of 2-styrylchromones with appropriate dienophiles[14] and photooxidative cyclizations of 2-styrylchromones.[15] Other synthesis of benzo[*b*]xanthone type compounds have been carried out by photooxidative cyclizations of appropriate styrylxanthones,[16] by irradiation of 2-benzyl- and 2-benzhydryl-3-benzoylchromones with UV light[17] and by decomposition of *ortho*-carboxynaphthalenediazonium tetrafluoroborates in the presence of phenols.[18] A few specific synthetic methods were also developed for the synthesis of bikaverin **1**.[10,19] We describe here a new method for the synthesis of novel benzo[*b*]-xanthones **11**, from Diels–Alder reactions of chromone-3-carboxaldehydes **12**, as dienophiles, with the highly reactive

Keywords: Diels–Alder reactions; chromone-3-carboxaldehydes; *ortho*-benzoquinodimethane; benzo[*b*]xanthones; oxidation reactions.

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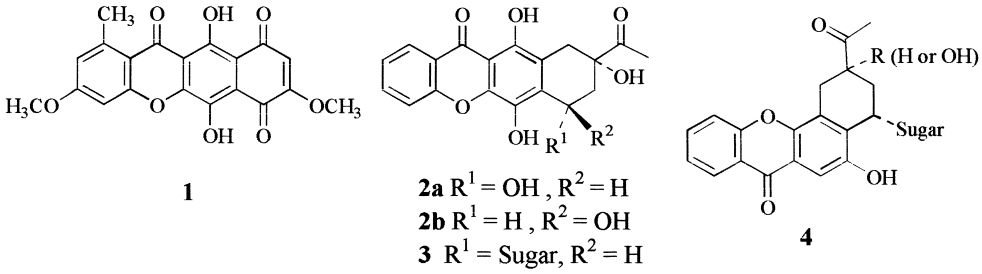


Scheme 1.

diene *ortho*-benzoquinodimethane **7**, followed by oxidation of the obtained cycloadducts **8** and **9**.

2. Results and discussion

2.1. Chemistry

Initial experiments considered the Diels–Alder reactions of the unsubstituted chromone **5** with *ortho*-benzoquinodimethane **7**, formed in situ by thermal extrusion of sulfur dioxide from 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide **6**,[20] with or without a Lewis acid as catalyst (Table 1, Scheme 2). Low yields have been obtained in all cases, and when $AlCl_3$, $TiCl_4$ or higher pressure was used the cycloadducts **8a** and **9a** were not isolated. The formation of the *trans*-diastereomer **8a** can be explained by a thermal enolisation of the *cis*-diastereomer **9a**. The benxo[*b*]-xanthone **11a** and (2-hydroxyphenyl)-2-naphthylketone **10a** were also isolated in almost all cases. Presumably xanthone **11a** has been obtained by the in situ oxidation of cycloadducts **8a** and **9a**, whereas **10a** involves the pyran ring opening during the oxidation process.

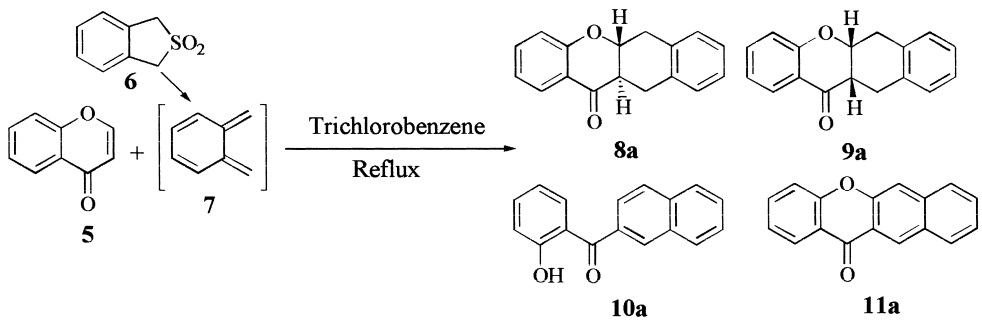
Since the yields obtained were not acceptable and taking into account the dienophilicity of chromones bearing electron withdrawing substituents at C-3, we carried out Diels–Alder reactions of chromone-3-carboxaldehydes **12** with *ortho*-benzoquinodimethane **7**, obtaining a diastereomeric mixture of benzo[*b*]-1,6,6a,12a-tetrahydroxanthones, **8** and **9**, in good yields (Table 2, Scheme 3). These cycloaddition reactions might give rise to the expected adduct **13**, a β-ketoaldehyde which was prone to deformylation under the reactions conditions, yielding the mixture of diastereomers **8** and **9**, which could be separated by thin layer chromatography (TLC). This type of deformylation was already reported by Wallace et al.,[3] from reactions carried out at high temperatures. In some cases, small amounts of the opened compound **10a**,**f**,**g** were also isolated (Table 2); however when using 6-nitrochromone-3-carboxaldehyde **12j** as starting material the opened compound **10j** was formed in appreciable amount (38.5%). This fact seems to indicate that the pyran ring opening is facilitated by the presence of an electron withdrawing substituent in the *para* position of the heterocyclic oxygen.

From the reaction of 5-acetoxychromone-3-carboxaldehyde **12h** with *ortho*-benzoquinodimethane **7** four compounds **8h** (32%), **9h** (21%) and **8i** (12.5%), **9i** (9.5%) have

Table 1. Reaction conditions and yields obtained in the Diels–Alder reactions of the unsubstituted chromone **5** with *ortho*-benzoquinodimethane **7**

Entry	Sulfone **6** (equiv.)	Catalyst	Pressure (atm)	Time (h)	Yield (%)			
					10a	**8a+9a**	**11a**	**5**[a]
1	2.5	–	–	72	17	5.5	12.5	54
2	1.5	–	4.5	20	6.5	–	7.5	83
3	2	$ZnCl_2$	–	26	15	7.5	–	55.5
4	1.5	$TiCl_4$	–	24	10	–	11	38.5
5	1.5	$AlCl_3$	–	14	11.5	–	14	68

[a] Recovered starting material.



Scheme 2.

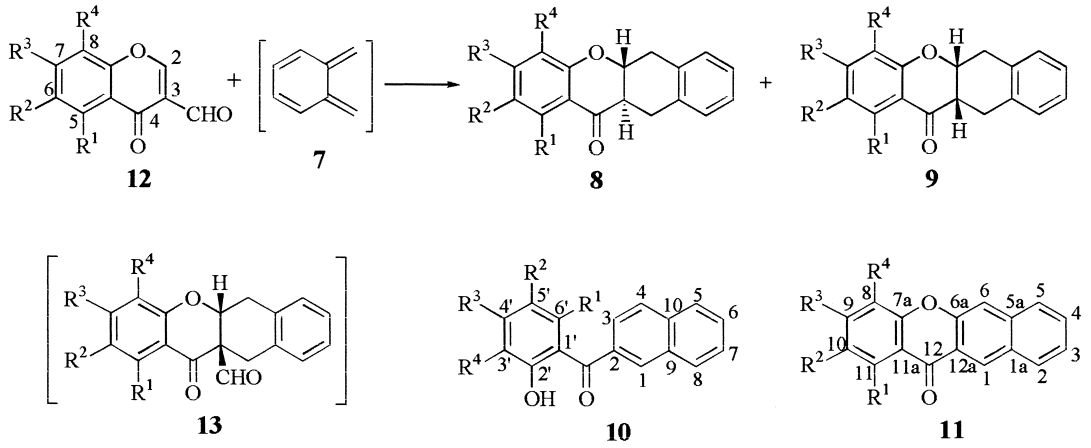
Table 2. Conditions and yields obtained in the Diels–Alder reactions of the chromone-3-carboxaldehydes **12** with *ortho*-benzoquinodimethane **7**

Entry		R^1	R^2	R^3	R^4	Time (h)	Yield (%)		
							8	**9**	**10**
1	**a**	H	H	H	H	6:30	51	44	4
2	**b**	H	CH_3	H	H	5:30	50.5	43.5	–
3	**c**	H	Cl	H	H	5	52	42	–
4	**d**	H	Br	H	H	3:30	54	42	–
5	**e**	H	Br	H	Br	5	54	37	–
6	**f**	H	H	OCH_3	H	5:30	44	41	2.3
7	**g**	OCH_3	H	H	H	5	42	48.5	2.4
8	**h**	OAc	H	H	H	4:30	32	21	–
9	**i**	OH	H	H	H	5	49.5	40	–
10	**j**	H	NO_2	H	H	5	23	12.5	38.5

To circumvent the bromination step during the conversion of the diastereomeric mixture of **8** and **9** into **11**, we decided to perform this transformation with DMSO/I_2, a reagent mixture which has been used by our group in the cyclodehydrogenation of 2′-hydroxychalcones and 2′-hydroxycinnamylideneacetophenones into the corresponding chromones.[21] In this way the expected benzo[*b*]xanthones **11** have been obtained in very good yields (88–98%).

2.2. NMR spectroscopy

The most important features of the ^{1}H NMR spectra of the benzotetrahydroxanthones **8** and **9** are the resonances appearing in their aliphatic region, due to H-1, H-6, H-6a and H-12a. However the resonances which immediately



Scheme 3.

been isolated. Compounds **8h** and **9h** are the expected cycloadducts (two diastereomers), while the presence of **8i** and **9i** suggests that a deacetylation process also accompanied the cycloaddition reaction.

Procedures for the transformation of the benzo[*b*]-1,6,6a,12a-tetrahydroxanthones, **8** and **9**, into benzo[*b*]-xanthones **11** have also been attempted. Oxidation of these cycloadducts with chloranil and with sulphur were unsuccessful, while treatment of the **8c** and **9c** mixture with an excess of limonene and 10% Pd/C gave **11c** in 28.5% yield; benzylic bromination with NBS (2.05 equiv.), in the presence of AIBN, followed by dehydrobromination by treatment with triethylamine, has afforded benzoxanthone **13c** contaminated with a small amount of another product. TLC analysis of this mixture revealed the presence of two very close spots and their separation by preparative TLC was not successful. The ^{1}H NMR spectrum of this mixture revealed that the minor component is quite similar to that due to **13c** (there are minor shifts in the resonances of similar protons). The main difference is in the resonance of H-6 which is missing for the unknown compound. Based on these data and on the fact that the mass spectrum of this mixture presented peaks with the profile of a chlorobromobenzoxanthone derivative, *m/z* at 258 (^{35}Cl, ^{79}Br) and 260 (^{35}Cl, ^{81}Br), we believe that this new compound is the 6-bromo-10-chlorobenzo[*b*]-xanthone.

indicate the presence of the *trans* **8** or the *cis* **9** cycloadducts are those of H-6a; in the case of **9** they appear as narrow multiplets (δ 4.89–5.05 ppm) while in the case of **8** they appears as a double doublet of doublets (δ 4.53–4.73 ppm). The coupling constants $^3J_{H6a-H12a}$~12–13 Hz in the latter case indicate a *trans* configuration of these two protons. In the case of compounds **9** the coupling constants $^3J_{H6a-H12a}$~2–3 Hz, measured in some cases from the signal of H-12a, suggest a *cis* configuration of these protons. This configuration was confirmed by the close proximity of H-6a and H-12a found in the NOESY spectra of these adducts **9**.

The resonances of all other protons of compounds **8** and **9**, mainly those of the referred aliphatic region, and their coupling constants were determined by the aid of COSY, HETCOR (or HSQC), HMBC and NOESY spectra. These 2D spectra also allowed the unequivocal assignment of the carbon resonances; those of the quaternary carbons were mainly assigned by the connectivities found in the HMBC spectra (Fig. 1). In the case of compounds **8i** and **9i** the presence of a hydroxyl proton involved in a hydrogen bond with the carbonyl group was identified by the resonance at δ 11.66–11.82 ppm.

The ^{1}H NMR spectra of compounds **10a**,**f**,**g**,**j** present signals in the aromatic region and another at δ 12.06–12.76 ppm for **10a**,**f**,**j** and at δ 10.80 ppm for **10g**. These data together with a carbon resonance at δ 199.7–201.5 ppm indicate that

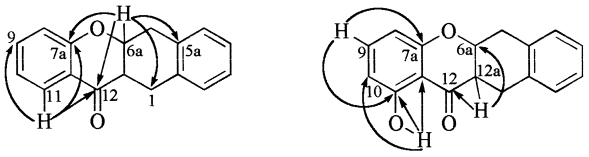


Figure 1. Important connectivities found in the HMBC spectra of the cycloadducts **8** and **9**.

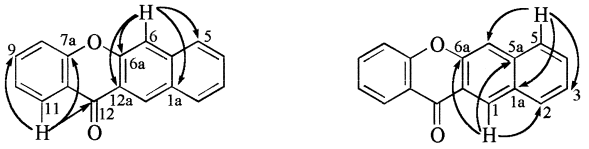


Figure 2. Important connectivities found in the HMBC spectra of the benzoxanthones **11**.

the cycloadducts **8a**,**f**,**g**,**j** and **9a**,**f**,**g**,**j** have been oxidised with concomitant pyran ring opening. The signals at δ 10.80–12.76 ppm are due to the resonances of hydroxyl protons (2′-OH) involved in intramolecular hydrogen bonds with a carbonyl group. The resonance of the 2′-OH of **10g** appears at lower frequency value relatively to those of **10a**,**f**,**j**, this is probably due to the steric effect between the 6′-methoxyl group and the 2-naphthyl group. This effect implies lack of conjugation between the 2-naphthyl and the carbonyl groups, decreasing the strength of the hydrogen bond.[22] The connectivities found in the HMBC spectra of compounds **10a**,**f**,**g**,**j** (2′-OH→C-1′, C-2′ and C-3′; H-1→C-3, C-8 and C-10; H-4→C-2, C-9 and C-5) allowed the confirmation for the resonance assignments of protonated carbons and the unequivocal assignment of those of quaternary carbons.

The most deshielded protons of compounds **11** are H-1 (δ 8.87–8.96 ppm) and H-11 (δ 8.13–8.45 ppm, save for **11g**,**i** which have substituents at that position and for **11j** since its spectrum was run in a different solvent), due to the mesomeric and anisotropic deshielding effect of the carbonyl group. The unequivocal assignment of H-1 and its differentiation of H-6 (δ 7.80–8.04 ppm) was not only based in their frequency values, but also on the connectivities found in the HMBC spectra of these compounds, as shown in Fig. 2. These connectivities allowed the confirmation of some protonated carbons and the unequivocal assignments of the quaternary carbons (C-1a, C-5a, C-6a, C-7a, C-12 and 12a).

3. Experimental

3.1. General

Melting points were determined on a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, if not stated otherwise, on Bruker AMX 300 and DRX 300 spectrometers operating at 300.13 and 75.47 MHz, respectively; the chemical shifts are expressed in δ (ppm) values relative to TMS as internal reference and the coupling constants (J) are expressed in Hz. ^{1}H Assignments were made using 2D COSY and NOESY (mixing time of 800 ms) experiments, while ^{13}C assignments were made using 2D HETCOR or HSQC and HMBC experiments (long range C/H coupling constants were optimised to 4 and 7 Hz). Mass spectra (EI, 70 eV) were measured on VG Autospec Q an M mass spectrometers. Elemental analyses were obtained on a LECO 932 CHN analyser. Preparative TLC was carried on Riedel silica gel 60 DGF_{254}, and column chromatography on Merck silica gel 60, 70–230 mesh.

3.2. General procedure for chromone-3-carboxaldehydes 12

The chromone-3-carboxaldehydes **12** used in this work have been prepared by Vilsmeir formylation of appropriate 2′-hydroxyacetophenones.[22] However, the procedure has been slightly improved. Phosphorous oxychloride (30 mmol) was added to dry DMF (10 mL) and the resulting mixture stirred for 15 min. Then the appropriate 2′-hydroxyacetophenone (10 mmol) was added and the reaction mixture kept at 60°C for 16 h for 2′-hydroxy-4′-methoxyacetophenone and 6′-acetoxy-2′-hydroxyacetophenone and 4–5 h for the others. After this period the reaction mixture was poured into an ice water mixture and stirred for 2 h. The obtained solid was removed by filtration, taken in chloroform (100 mL) and washed with water. The solvent was evaporated to dryness and the residue recrystallised from ethanol, giving chromone-3-carboxaldehydes **12** in good yields (61–94%). It is important to notice that using our procedure the yield of compounds **12e** (94%), **12f** (61%), **12g** (77%) and **12j** (69%) significantly increased in relation with literature data.[23]

3.3. General procedure for the Diels–Alder reactions of chromone-3-carboxaldehydes 12 with *ortho*-benzoquinodimethane 7: synthesis of cycloadducts benzo[*b*]-1,6,6a,12a-tetrahydroxanthones 8 and 9

Chromone-3-carboxaldehydes **12** (1.15 mmol) and 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide **6** (212.5 mg, 1.26 mmol) in 1,2,4-trichlorobenzene (5 mL) were refluxed at 250°C, under nitrogen for the appropriate reaction time (Table 2). After reaction cooling, the solvent was removed by column chromatography (silica gel, light petroleum as eluent) and then the cycloadducts were eluted with dichloromethane. The solvent was evaporated to dryness and the residue was separated by preparative TLC, using an appropriate mixture of solvents (with polarities ranging from light petroleum to chloroform). The cycloadducts **8** and **9** were recrystallised from ethanol.

3.3.1. *trans*-Benzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8a) (51%). Mp 180–182°C; ^{1}H NMR δ 2.90–3.00 (m, 1H, H-12a), 3.00 (dd, J=15.1, 9.0 Hz, 1H, H-1), 3.30 (dd, J=16.0, 10.4 Hz, 1H, H-6), 3.43 (dd, J=16.0, 6.0 Hz, 1H, H-6), 3.50 (dd, J=15.1, 3.6 Hz, 1H, H-1), 4.60 (ddd, J=12.8, 10.4, 6.0 Hz, 1H, H-6a), 7.02 (d, J=8.3 Hz, 1H, H-8), 7.05 (ddd, J=7.6, 7.2, 1.0 Hz, 1H, H-10), 7.18–7.22 (m, 4H, H-2,3,4,5), 7.51 (ddd, J=8.3, 7.2, 1.8 Hz, 1H, H-9), 7.94 (dd, J=7.6, 1.8 Hz, 1H, H-11); ^{13}C NMR δ 28.0 (C-1), 36.0 (C-6), 46.0 (C-12a), 77.2 (C-6a), 117.8 (C-8), 120.7 (C-11a), 121.5 (C-10), 126.4 and 126.7 (C-3 and C-4), 127.2 (C-11), 129.0 and 129.1 (C-2 and C-5), 132.6 (C-5a), 133.8

(C-1a), 136.0 (C-9), 161.1 (C-7a), 193.6 (C-12); MS (EI) *m/z* (rel. int.) 251 [$(M+1)^+$, 42], 250 ($M^{+\cdot}$, 100), 249 [$(M-1)^+$, 52], 232 (43), 231 (73), 130 (29), 129 (41), 128 (40), 121 (55), 120 (24), 115 (34), 92 (27), 77 (8). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.68. Found: C, 81.51; H, 5.65.

3.3.2. *cis*-Benzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9a) (44%). Mp 124–125°C; ^{1}H NMR δ 2.87–3.09 (m, 3H, 2×H-1 and H-12a), 3.19 (dd, *J*=18.0, 4.4 Hz, 1H, H-6), 3.30 (dd, *J*=18.0, 3.3 Hz, 1H, H-6), 4.92–4.96 (m, 1H, H-6a), 6.96 (d, *J*=8.4 Hz, 1H, H-8), 7.03 (ddd, *J*=7.7, 7.3, 1.0 Hz, 1H, H-10), 7.11–7.18 (m, 4H, H-2,3,4,5), 7.47 (ddd, *J*=8.4, 7.3, 1.7 Hz, 1H, H-9), 7.93 (dd, *J*=7.7, 1.7 Hz, 1H, H-11); ^{13}C NMR δ 26.2 (C-1), 32.8 (C-6), 44.8 (C-12a), 75.0 (C-6a), 118.0 (C-8), 119.2 (C-11a), 121.5 (C-10), 126.2 and 126.5 (C-3 and C-4), 127.5 (C-11), 128.8 and 129.3 (C-2 and C-5), 131.7 (C-5a), 133.7 (C-1a), 136.0 (C-9), 160.9 (C-7a), 194.8 (C-12); MS (EI) *m/z* (rel. int.) 251 [$(M+1)^+$, 21], 250 ($M^{+\cdot}$, 100), 249 [$(M-1)^+$, 25], 232 (30), 231 (90), 130 (17), 129 (56), 128 (51), 121 (74), 120 (13), 115 (21), 104 (23), 92 (21), 77 (12). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.68. Found: C, 81.57; H, 5.67.

3.3.3. *trans*-10-Methylbenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8b) (51%). Mp 159–161°C; ^{1}H NMR δ 2.32 (s, 3H, C*H*$_3$), 2.86–2.98 (m, 2H, H-1 and H-12a), 3.26 (dd, *J*=15.9, 10.2 Hz, 1H, H-6), 3.39 (dd, *J*=15.9, 6.0 Hz, 1H, H-6), 3.43–3.54 (m, 1H, H-1), 4.53 (ddd, *J*=12.5, 10.2, 6.0 Hz, 1H, H-6a), 6.91 (d, *J*=8.4 Hz, 1H, H-8), 7.16–7.21 (m, 4H, H-2,3,4,5), 7.31 (dd, *J*=8.4, 1.9 Hz, 1H, H-9), 7.72 (d, *J*=1.9 Hz, 1H, H-11); ^{13}C NMR δ 20.4 (s, *C*H$_3$), 28.1 (C-1), 36.0 (C-6), 46.0 (C-12a), 77.3 (C-6a), 117.6 (C-8), 120.3 (C-11a), 126.4 and 126.6 (C-3 and C-4), 126.7 (C-11), 129.0 and 129.1 (C-2 and C-5), 130.9 (C-10), 132.6 (C-5a), 133.8 (C-1a), 137.1 (C-9), 159.2 (C-7a), 193.8 (C-12); MS (EI) *m/z* (rel. int.) 265 [$(M+1)^+$, 27], 264 ($M^{+\cdot}$, 73), 263 [$(M-1)^+$, 32], 246 (34), 245 (100), 231 (10), 135 (59), 134 (35), 130 (16), 129 (38), 128 (47), 127 (22), 115 (22), 104 (10), 91 (11), 78 (27), 77 (27); Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.76; H, 6.13.

3.3.4. *cis*-10-Methylbenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9b) (43%). Mp 123–124°C; ^{1}H NMR δ 2.31 (s, 3H, C*H*$_3$), 2.89 (dd, *J*=13.0, 2.9 Hz, 1H, H-1), 2.91–2.96 (m, 1H, H-12a), 3.06 (dd, *J*=13.0, 5.1 Hz, 1H, H-1), 3.18 (dd, *J*=18.0, 4.2 Hz, 1H, H-6), 3.29 (dd, *J*=18.0, 3.3 Hz, 1H, H-6), 4.89–4.92 (m, 1H, H-6a), 6.86 (d, *J*=8.4 Hz, 1H, H-8), 7.09–7.18 (m, 4H, H-2,3,4,5), 7.29 (dd, *J*=8.4, 2.4 Hz, 1H, H-9), 7.72 (d, *J*=2.4 Hz, 1H, H-11); ^{13}C NMR δ 20.4 (*C*H$_3$), 26.2 (C-1), 32.9 (C-6), 44.8 (C-12a), 74.9 (C-6a), 117.7 (C-8), 118.8 (C-11a), 126.2 and 126.5 (C-3 and C-4), 127.0 (C-11), 128.7 and 129.2 (C-2 and C-5), 131.0 (C-10), 131.7 (C-5a), 133.8 (C-1a), 137.1 (C-9), 158.9 (C-7a), 195.1 (C-12); MS (EI) *m/z* (rel. int.) 265 [$(M+1)^+$, 34], 264 ($M^{+\cdot}$, 100), 263 [$(M-1)^+$, 29], 246 (35), 245 (76), 135 (80), 134 (37), 130 (13), 129 (44), 128 (49), 127 (18), 115 (17), 104 (21), 78 (29), 77 (15). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.80; H 6.09.

3.3.5. *trans*-10-Chlorobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8c) (52%). Mp 182–184°C; ^{1}H NMR δ 2.89–3.00 (m, 1H, H-12a), 3.00 (dd, *J*=15.0, 9.0 Hz, 1H, H-1), 3.29 (dd, *J*=16.1, 10.4 Hz, 1H, H-6), 3.43 (dd, *J*=16.1, 6.1 Hz, 1H, H-6), 3.50 (dd, *J*=15.0, 3.4 Hz, 1H, H-1), 4.60 (ddd, *J*=12.8, 10.4, 6.1 Hz, 1H, H-6a), 6.99 (d, *J*=8.8 Hz, 1H, H-8), 7.18–7.21 (m, 4H, H-2,3,4,5), 7.45 (dd, *J*=8.8, 2.7 Hz, 1H, H-9), 7.89 (d, *J*=2.7 Hz, 1H, H-11); ^{13}C NMR δ 27.9 (C-1), 35.8 (C-6), 45.8 (C-12a), 77.7 (C-6a), 119.6 (C-8), 121.4 (C-11a), 126.5 (C-11 and C-3 or C-4), 126.7 (C-3 or C-4), 127.0 (C-10), 129.0 and 129.1 (C-2 and C-5), 132.3 (C-5a), 133.5 (C-1a), 135.8 (C-9), 159.6 (C-7a), 192.5 (C-12); MS (EI) *m/z* (rel. int.) 287 [$(M+1)^+$, ^{37}Cl, 11], 286 ($M^{+\cdot}$, ^{37}Cl, 44), 285 [$(M-1)^+$, ^{37}Cl; $(M+1)^+$, ^{35}Cl; 35], 284 ($M^{+\cdot}$, ^{35}Cl, 99), 283 [$(M-1)^+$, ^{35}Cl, 29], 268 (16), 267 (40), 266 (37), 265 (82), 249 (14), 231 (9), 157 (33), 156 (15), 155 (67), 154 (16), 130 (38), 129 (100), 128 (63), 127 (32), 126 (20), 116 (22), 115 (34), 104 (15), 103, (10), 102 (11), 101 (10), 99 (12), 98 (9), 91 (11), 77 (22). Anal. Calcd for $C_{17}H_{13}ClO_2$: C, 71.71; H, 4.60. Found: C, 71.49; H, 4.83.

3.3.6. *cis*-10-Chlorobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9c) (42%). Mp 136–137°C; ^{1}H NMR δ 2.91 (dd, *J*=12.1, 4.0 Hz, 1H, H-1), 2.97 (ddd, *J*=8.8, 4.0, 2.0 Hz, 1H, H-12a), 3.06 (dd, *J*=12.1, 8.8 Hz, 1H, H-1), 3.20 (dd, *J*=18.0, 4.5 Hz, 1H, H-6), 3.30 (dd, *J*=18.0, 3.4 Hz, 1H, H-6), 4.93–4.96 (m, 1H, H-6a), 6.92 (d, *J*=8.8 Hz, 1H, H-8), 7.12–7.20 (m, 4H, H-2,3,4,5), 7.41 (dd, *J*=8.8, 2.6 Hz, 1H, H-9), 7.88 (d, *J*=2.6 Hz, 1H, H-11); ^{13}C NMR δ 26.0 (C-1), 32.7 (C-6), 44.5 (C-12a), 75.3 (C-6a), 119.7 (C-8), 120.1 (C-11a), 126.4 and 126.7 (C-3 and C-4), 126.8 (C-11), 127.1 (C-10), 128.8 and 129.3 (C-2 and C-5), 131.5 (C-5a), 133.4 (C-1a), 135.9 (C-9), 159.3 (C-7a), 193.6 (C-12); MS (EI) *m/z* (rel. int.) 287 [$(M+1)^+$, ^{37}Cl, 8], 286 ($M^{+\cdot}$, ^{37}Cl, 32), 285 [$(M-1)^+$, ^{37}Cl; $(M+1)^+$, ^{35}Cl; 24], 284 ($M^{+\cdot}$, ^{35}Cl, 73), 283 [$(M-1)^+$, ^{35}Cl, 18], 268 (12), 267 (31), 266 (27), 265 (59), 249 (9), 231 (6), 157 (24), 156 (15), 155 (55), 154 (18), 130 (36), 129 (100), 128 (64), 127 (31), 126 (22), 116 (10), 115 (30), 104 (32), 103 (13), 102 (10), 101 (9), 99 (11), 98 (10), 91 (7), 78 (13), 77 (16). Anal. Calcd for $C_{17}H_{13}ClO_2$: C, 71.71; H, 4.60. Found: C, 71.83; H, 4.72.

3.3.7. *trans*-10-Bromobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8d) (54%). Mp>294°C; ^{1}H NMR δ 2.87–2.97 (m, 1H, H-12a), 2.93 (dd, *J*=14.6, 8.9 Hz, 1H, H-1), 3.28 (dd, *J*=16.0, 10.4 Hz, 1H, H-6), 3.42 (dd, *J*=16.0, 6.1 Hz, 1H, H-6), 3.49 (dd, *J*=14.6, 2.9 Hz, 1H, H-1), 4.58 (ddd, *J*=12.8, 10.4, 6.1 Hz, 1H, H-6a), 6.93 (d, *J*=8.8 Hz, 1H, H-8), 7.17–7.20 (m, 4H, H-2,3,4,5), 7.57 (dd, *J*=8.8, 2.5 Hz, 1H, H-9), 8.03 (d, *J*=2.5 Hz, 1H, H-11); ^{13}C NMR δ 27.9 (C-1), 35.8 (C-6), 45.8 (C-12a), 77.6 (C-6a), 114.1 (C-10), 119.9 (C-8), 121.9 (C-11a), 126.5 and 126.8 (C-3 and C-4), 129.6 (C-11), 132.3 (C-5a), 133.5 (C-1a), 138.6 (C-9), 160.0 (C-7a), 192.3 (C-12); MS (EI) *m/z* (rel. int.) 331 [$(M+1)^+$, ^{81}Br, 22], 330 ($M^{+\cdot}$, ^{81}Br, 81), 329 [$(M-1)^+$, ^{81}Br; $(M+1)^+$, ^{79}Br; 35], 328 ($M^{+\cdot}$, ^{79}Br, 78), 327 [$(M-1)^+$, ^{79}Br, 18], 313 (10), 312 (24), 311 (54), 310 (25), 309 (51), 249 (16), 231 (11), 202 (13), 201 (41), 200 (17), 199 (42), 198 (11), 172 (11), 170 (10), 164 (9), 130 (39), 129 (100), 128 (72), 127 (32), 121 (10), 116 (24), 115 (39), 105 (10), 104 (11), 103 (12), 102 (8), 91 (12), 77 (15). Anal. Calcd for $C_{17}H_{13}BrO_2$: C, 62.03; H, 3.98. Found: C, 61.81; H, 4.07.

3.3.8. *cis*-10-Bromobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9d) (42%). Mp 158–160°C; ^{1}H NMR δ 2.90 (dd, J=12.1, 3.4 Hz, 1H, H-1), 2.93–2.99 (m, 1H, H-12a), 3.05 (dd, J=12.1, 9.0 Hz, 1H, H-1), 3.19 (dd, J=18.0, 4.2 Hz, 1H, H-6), 3.30 (dd, J=18.0, 3.3 Hz, 1H, H-6), 4.92–4.95 (m, 1H, H-6a), 6.86 (d, J=8.8 Hz, 1H, H-8), 7.09–7.17 (m, 4H, H-2,3,4,5), 7.54 (dd, J=8.8, 2.5 Hz, 1H, H-9), 8.03 (d, J=2.5 Hz, 1H, H-11); ^{13}C NMR δ 26.0 (C-1), 32.7 (C-6), 44.4 (C-12a), 75.2 (C-6a), 114.2 (C-10), 120.1 (C-8), 120.6 (C-11a), 126.4 and 126.6 (C-3 and C-4), 128.8 and 129.3 (C-2 and C-5), 130.0 (C-11), 131.4 (C-5a), 133.4 (C-1a), 138.6 (C-9), 159.8 (C-7a), 193.4 (C-12); MS (EI) m/z (rel. int.) 331 [$(M+1)^+$, ^{81}Br, 24], 330 ($M^{+\cdot}$, ^{81}Br, 88), 329 [$(M-1)^+$, ^{81}Br, $(M+1)^+$, ^{79}Br, 36], 328 ($M^{+\cdot}$, ^{79}Br, 90), 327 [$(M-1)^+$, ^{79}Br, 19], 313 (9), 312 (30), 311 (62), 310 (31), 309 (59), 249 (15), 231 (9), 201 (45), 200 (18), 199 (44), 172 (9), 170 (8), 130 (35), 129 (100), 128 (71), 127 (29), 121 (7), 116 (9), 115 (30), 104 (26), 103 (10), 77 (11). Anal. Calcd for $C_{17}H_{13}BrO_2 \cdot 0.25H_2O$: C, 61.13; H, 4.04. Found: C, 61.28; H, 4.29. HRMS (EI) calcd for $C_{17}H_{13}{}^{81}BrO_2$: 330.0078. Found: 330.0091.

3.3.9. *trans*-8,10-Dibromobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8e) (54%). Mp 190–192°C. ^{1}H NMR δ 2.95 (dd, J=16.1, 11.6 Hz, 1H, H-1), 2.97–3.06 (m, 1H, H-12a), 3.39 (dd, J=16.2, 10.4 Hz, 1H, H-6), 3.49 (dd, J=16.1, 4.1 Hz, 1H, H-1), 3.54 (dd, J=16.2, 6.0 Hz, 1H, H-6), 4.66 (ddd, J=13.1, 10.4, 6.0 Hz, 1H, H-6a), 7.18–7.21 (m, 4H, H-2,3,4,5), 7.87 (d, J=2.4 Hz, 1H, H-9), 8.00 (d, J=2.4 Hz, 1H, H-11); ^{13}C NMR δ 27.9 (C-1), 35.7 (C-6), 45.5 (C-12a), 78.4 (C-6a), 112.7 (C-8), 114.0 (C-10), 122.5 (C-11a), 126.6 and 126.8 (C-3 and C-4), 128.9 (C-2 or C-5), 129.1 (C-11 and C-2 or C-5), 132.1 (C-5a), 133.2 (C-1a), 141.1 (C-9), 156.7 (C-7a), 191.6 (C-12); MS (EI) m/z (rel. int.) 410 ($M^{+\cdot}$, ^{81}Br, 11), 409 (40), 408 ($M^{+\cdot}$, ^{79}Br^{81}Br, 70), 407 (19), 406 ($M^{+\cdot}$, ^{79}Br, 41), 405 (7), 392 (14), 391 (27), 390 (24), 389 (41), 388 (14), 387 (24), 281 (17), 280 (10), 279 (30), 278 (12), 277 (18), 199 (15), 197 (12), 143 (10), 141 (8), 130 (31), 129 (100), 128 (59), 127 (23), 116 (21), 115 (27), 91 (8), 77 (10). Anal. Calcd for $C_{17}H_{12}Br_2O_2$: C, 50.03; H, 2.96. Found: C, 50.08; H, 3.14.

3.3.10. *cis*-8,10-Dibromobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9e) (37%). Mp 160–162°C; ^{1}H NMR δ 2.90 (dd, J=14.1, 4.5 Hz, 1H, H-1), 3.04 (ddd, J=10.3, 4.5, 2.8 Hz, 1H, H-12a), 3.11 (dd, J=14.1, 10.3 Hz, 1H, H-1), 3.24 (dd, J=18.1, 4.9 Hz, 1H, H-6), 3.37 (dd, J=18.1, 3.9 Hz, 1H, H-6), 5.02–5.06 (m, 1H, H-6a), 7.14–7.21 (m, 4H, H-2,3,4,5), 7.85 (d, J=2.5 Hz, 1H, H-9), 8.00 (d, J=2.5 Hz, 1H, H-11); ^{13}C NMR δ 25.9 (C-1), 32.2 (C-6), 44.2 (C-12a), 76.2 (C-6a), 113.0 (C-8), 114.0 (C-10), 121.4 (C-11a), 126.4 and 126.7 (C-3 and C-4), 128.8 and 129.3 (C-2 and C-5), 129.4 (C-11), 131.4 (C-5a), 133.1 (C-1a), 141.2 (C-9), 156.4 (C-7a), 192.5 (C-12); MS (EI) m/z (rel. int.) 410 ($M^{+\cdot}$, ^{81}Br, 61), 409 (32), 408 ($M^{+\cdot}$, ^{79}Br^{81}Br, 100), 407 (27), 406 ($M^{+\cdot}$, ^{79}Br, 60), 392 (22), 391 (39), 390 (37), 389 (62), 388 (22), 387 (35), 281 (20), 280 (12), 279 (35), 278 (17), 277 (20), 276 (9), 199 (12), 197 (19), 143 (8), 141 (8), 130 (38), 129 (97), 128 (58), 127 (23), 116 (10), 115 (24), 104 (21), 103 (8), 91 (8), 77 (13). Anal. Calcd for $C_{17}H_{12}Br_2O_2$: C, 50.03; H, 2.96. Found: C, 49.69; H 3.09.

3.3.11. *trans*-9-Methoxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8f) (44%). Mp 184–186°C; ^{1}H NMR δ 2.86–2.97 (m, 1H, H-12a), 2.91 (dd, J=22.8, 11.4 Hz, 1H, H-1), 3.27 (dd, J=16.0, 10.1 Hz, 1H, H-6), 3.40 (dd, J=16.0, 6.0 Hz, 1H, H-6), 3.49 (dd, J=22.8, 11.4 Hz, 1H, H-1), 3.85 (s, 3H, OCH_3), 4,57 (ddd, J=12.1, 10.1, 6.0 Hz, 1H, H-6a), 6.46 (d, J=2.4 Hz, 1H, H-8), 6.61 (dd, J=8.8, 2.4 Hz, 1H, H-10), 7.17–7.22 (m, 4H, H-2,3,4,5), 7.87 (d, J=8.8 Hz, 1H, H-11); ^{13}C NMR δ 28.1 (C-1), 36.0 (C-6), 45.6 (C-12a), 55.6 (OCH$_3$), 77.8 (C-6a), 100.6 (C-8), 110.1 (C-10), 114.6 (C-11a), 126.4 and 126.6 (C-3 and C-4), 128.9 and 129.1 (C-2 and C-5), 129.0 (s, C-11), 132.6 (C-5a), 134.0 (C-1a), 163.1 (C-7a), 166.0 (C-9), 192.1 (C-12); MS (EI) m/z (rel. int.) 281 [$(M+1)^+$, 30], 280 ($M^{+\cdot}$, 100), 279 [$(M-1)^+$, 55], 262 (19), 261 (55), 249 (7), 152 (15), 151 (84), 150 (24), 130 (15), 129 (33), 128 (36), 127 (18), 122 (19), 115 (22), 107 (14), 104 (4), 94 (7), 79 (12), 77 (9). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.17; H, 5.72.

3.3.12. *cis*-9-Methoxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9f) (41%). Mp 182–184°C; ^{1}H NMR δ 2.87 (dd, J=12.5, 2.3 Hz, 1H, H-1), 2.83–2.89 (m, 1H, H-12a), 3.03 (dd, J=12.5, 6.0 Hz, 1H, H-1), 3.19 (dd, J=18.0, 4.3 Hz, 1H, H-6), 3.29 (dd, J=18.0, 3.1 Hz, 1H, H-6), 3.81 (s, 3H, OCH_3), 4.91–4.94 (m, 1H, H-6a), 6.40 (d, J=2.4 Hz, 1H, H-8), 6.60 (dd, J=8.8, 2.4 Hz, 1H, H-10), 7.10–7.17 (m, 4H, H-2,3,4,5), 7.86 (d, J=8.8 Hz, 1H, H-11); ^{13}C NMR δ 26.4 (C-1), 33.0 (C-6), 44.5 (C-12a), 55.6 (OCH$_3$), 75.4 (C-6a), 100.8 (C-8), 110.3 (C-10), 113.0 (C-11a), 126.3 and 126.5 (C-3 and C-4), 128.8, 129.2 and 129.3 (C-2, C-5 and C-11), 131.7 (C-5a), 133.9 (C-1a), 162.9 (C-7a), 166.1 (C-9), 193.7 (C-12); MS (EI) m/z (rel. int.) 281 [$(M+1)^+$, 30], 280 ($M^{+\cdot}$, 100), 279 [$(M-1)^+$, 43], 262 (18), 261 (54), 249 (5), 152 (15), 151 (87), 150 (22), 130 (14), 129 (43), 128 (48), 127 (19), 122 (18), 115 (20), 107 (15), 104 (17), 95 (9), 79 (13), 77 (10). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.43; H, 5.76.

3.3.13. *trans*-11-Methoxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8g) (42%). Mp 193–194°C; ^{1}H NMR δ 2.88–2.98 (m, 1H, H-12a), 2.98 (dd, J=11.1, 3.0 Hz, 1H, H-1), 3.24 (dd, J=16.3, 10.2 Hz, 1H, H-6), 3.40 (dd, J=16.3, 6.0 Hz, 1H, H-6), 3.47 (dd, J=11.1, 7.5 Hz, 1H, H-1), 3.94 (s, 3H, OCH_3), 4.56 (ddd, J=13.0, 10.2, 6.0 Hz, 1H, H-6a), 6.54 (dd, J=8.4, 0.8 Hz, 1H, H-8), 6.62 (dd, J=8.4, 0.8 Hz, 1H, H-10), 7.17–7.23 (m, 4H, H-2,3,4,5), 7.41 (t, J=8.4 Hz, 1H, H-9); ^{13}C NMR δ 28.1 (C-1), 36.0 (C-6), 46.6 (C-12a), 56.1 (OCH_3), 77.2 (C-6a), 103.8 (C-8), 109.9 (C-10), 126.0 (C-11a), 126.3 and 126.6 (C-3 and C-4), 129.0 and 129.1 (C-2 and C-5), 132.5 (C-5a), 134.1 (C-1a), 135.9 (C-9), 160.8 (C-11), 162.6 (C-7a), 192.3 (C-12); MS (EI) m/z (rel. int.) 281 [$(M+1)^+$, 27], 280 ($M^{+\cdot}$, 100), 279 [$(M-1)^+$, 36], 262 (21), 261 (52), 247 (9), 231 (8), 151 (54), 150 (47), 130 (14), 129 (27), 128 (30), 127 (15), 122 (24), 115 (20), 107 (28), 104 (9), 91 (7), 77 (10). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.13; H, 5.79.

3.3.14. *cis*-11-Methoxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9g) (48.5%). Mp 116–118°C; ^{1}H NMR δ 2.83–2.90 (m, 1H, H-12a), 2.91 (dd, J=13.5, 6.2 Hz, 1H, H-1),

3.04 (dd, *J*=13.5, 4.7 Hz, 1H, H-1), 3.15 (dd, *J*=18.1, 3.9 Hz, 1H, H-6), 3.25 (dd, *J*=18.1, 3.0 Hz, 1H, H-6), 3.91 (s, 3H, OC*H*$_3$), 4.86–4.89 (m, 1H, H-6a), 6.53 (t, *J*=8.2 Hz, 2H, H-8,10), 7.08–7.15 (m, 4H, H-2,3,4,5), 7.35 (t, *J*=8.2 Hz, 1H, H-9); ^{13}C NMR δ 26.3 (C-1), 32.6 (C-6), 45.7 (C-12a), 56.0 (O*C*H$_3$), 74.2 (C-6a), 103.8 (C-8), 109.3 (C-11a), 110.0 (C-10), 126.1 and 126.3 (C-3 and C-4), 128.7 and 129.1 (C-2 and C-5), 131.6 (C-5a), 133.8 (C-1a), 135.8 (C-9), 161.1 (C-11), 162.4 (C-7a), 193.7 (C-12); MS (EI) *m/z* (rel. int.) 281 [(M+1)$^+$, 28], 280 (M$^{+\cdot}$, 100), 279 [(M−1)$^+$, 34], 262 (23), 261 (58), 247 (9), 231 (7), 151 (49), 150 (38), 130 (10), 129 (28), 128 (32), 127 (13), 122 (18), 115 (14), 107 (25), 104 (9), 77 (7). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.13; H 5.73.

3.3.15. *trans*-11-Acetoxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8h) (32%). Mp 163–165°C; ^{1}H NMR δ 2.42 (s, 3H, OCOC*H*$_3$), 2.87–3.02 (m, 2H, H-1 and 12a), 3.35–3.47 (m, 1H, H-1), 3.26 (dd, *J*=16.1, 10.3 Hz, 1H, H-6), 3.42 (dd, *J*=16.1, 6.0 Hz, 1H, H-6), 4.63 (ddd, *J*=12.9, 10.3, 6.0 Hz, 1H, H-6a), 6.69 (dd, *J*=8.1, 1.1 Hz, 1H, H-8), 6.95 (dd, *J*=8.4, 1.1 Hz, 1H, H-10), 7.17–7.20 (m, 4H, H-2,3,4,5), 7.48 (dd, *J*=8.4, 8.1 Hz, 1H, H-9); ^{13}C NMR δ 21.1 (OCO*C*H$_3$), 27.8 (C-1), 35.9 (C-6), 46.2 (C-12a), 76.9 (C-6a), 113.5 (C-11a), 116.0 (C-8,10), 126.4 and 126.7 (C-3 and C-4), 128.9 and 129.0 (C-2 and C-5), 132.3 (C-5a), 133.6 (C-1a), 135.7 (C-9), 150.1 (C-11), 162.1 (C-7a), 169.7 (O*C*OCH$_3$), 191.9 (C-12); MS (EI) *m/z* (rel. int.) 308 (M$^{+\cdot}$, 100), 267 (19), 266 (100), 265 (15), 248 (26), 247 (38), 137 (56), 136 (14), 130 (10), 129 (30), 128 (25), 127 (10), 115 (14), 108 (9), 85 (33), 83 (50). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.74; H, 5.17.

3.3.16. *cis*-11-Acetoxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9h) (21%). Mp 142–143°C; ^{1}H NMR δ 2.39 (s, 3H, OCOC*H*$_3$), 2.83–2.93 (m, 1H, H-1), 2.87 (ddd, *J*=12.6, 6.2, 2.4 Hz, 1H, H-12a), 3.07 (dd, *J*=17.1, 12.6 Hz, 1H, H-1), 3.17 (dd, *J*=18.1, 4.6 Hz, 1H, H-6), 3.29 (dd, *J*=18.1, 3.3 Hz, 1H, H-6), 4.94–4.97 (m, 1H, H-6a), 6.68 (dd, *J*=8.2, 2.1 Hz, 1H, H-8), 6,87 (dd, *J*=8.2, 1.1 Hz, 1H, H-10), 7.08–7.18 (m, 4H, H-2,3,4,5), 7.44 (t, *J*=8.2 Hz, 1H, H-9); ^{13}C NMR δ 21.1 (OCO*C*H$_3$), 26.0 (C-1), 32.7 (C-6), 45.3 (C-12a), 74.6 (C-6a), 112.1 (C-11a), 116.07 and 116.14 (C-8 and C-10), 126.3 and 126.6 (C-3 and C-4), 128.8 and 129.3 (C-2 and C-5), 131.5 (C-5a), 133.6 (C-1a), 135.6 (C-9), 150.7 (C-11), 162.0 (C-7a), 169.7 (O*C*OCH$_3$), 193.1 (C-12); MS (EI) *m/z* (rel. int.) 308 (M$^{+\cdot}$, 36), 267 (19), 266 (100), 265 (21), 256 (18), 249 (10), 248 (45), 247 (61), 168 (41), 149 (26), 137 (65), 136 (16), 130 (12), 129 (44), 128 (38), 127 (13), 118 (19). Anal. Calcd for $C_{19}H_{16}O_4 \cdot 0.25H_2O$: C, 71.84; H, 5.35. Found: C, 71.54; H, 5.72. HRMS (EI) calcd for $C_{19}H_{16}O_4$: 308.1049. Found: 308.1061.

3.3.17. *trans*-11-Hydroxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8i) (49.5%). Mp 167–169°C; ^{1}H NMR δ 2.92 (dd, *J*=16.5, 11.7 Hz, 1H, H-1), 3.04 (ddd, *J*=12.8, 11.7, 5.2 Hz, 1H, H-12a), 3.26 (dd, *J*=16.0, 10.5 Hz, 1H, H-6), 3.42 (dd, *J*=16.0, 6.0 Hz, 1H, H-6), 3.50 (dd, *J*=16.5, 5.2 Hz, 1H, H-1), 4.57 (ddd, *J*=12.8, 10.5, 6.0 Hz, 1H, H-6a), 6.48 (dd, *J*=8.3, 0.7 Hz, 1H, H-8), 6.54 (d, *J*=8.3 Hz, 1H, H-10), 7.18–7.21 (m, 4H, H-2,3,4,5), 7.39 (t, *J*=8.3 Hz, 1H, H-9), 11.82 (s, 1H, O*H*); ^{13}C NMR δ 27.7 (C-1), 35.7 (C-6), 45.5 (C-12a), 76.9 (C-6a), 107.2 (C-8), 107.9 (C-11a), 109.5 (C-10), 126.6 and 126.7 (C-3 and C-4), 129.0 and 129.1 (C-2 and C-5), 132.4 (C-5a), 133.3 (C-1a), 138.3 (C-9), 161.1 (C-7a), 162.2 (C-11), 199.5 (C-12); MS (EI); *m/z* (rel. int.) 267 [(M+1)$^+$, 20], 266 (M$^{+\cdot}$, 100), 265 [(M−1)$^+$, 22], 248 (32), 247 (62), 137 (59), 136 (12), 130 (8), 129 (26), 128 (26), 115 (12), 108 (9), 104 (7). Anal. Calcd for $C_{17}H_{12}O_3$: C, 76.68; H, 5.30. Found: C, 76.62; H, 5.49.

3.3.18. *cis*-11-Hydroxybenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9i) (40%). Mp 139–141°C; ^{1}H NMR δ 2.95 (ddd, *J*=12.4, 6.3, 2.5 Hz, 1H, H-12a), 2.97 (dd, *J*=16.9, 6.3 Hz, 1H, H-1), 3.12 (dd, *J*=16.9, 12.4 Hz, 1H, H-1), 3.21 (dd, *J*=17.8, 4.0 Hz, 1H, H-6), 3.31 (dd, *J*=17.8, 3.2 Hz, 1H, H-6), 4.90–4.94 (m, 1H, H-6a), 6.42 (dd, *J*=8.3, 0.7 Hz, 1H, H-8), 6.53 (dd, *J*=8.3, 0.7 Hz, 1H, H-10), 7.11–7.20 (m, 4H, H-2,3,4,5), 7.36 (t, *J*=8.3 Hz, 1H, H-9), 11.66 (s, 1H, O*H*); ^{13}C NMR δ 25.5 (C-1), 32.7 (C-6), 44.3 (C-12a), 74.5 (C-6a), 106.5 (C-11a), 107.5 (C-8), 109.5 (C-10), 126.4 and 126.7 (C-3 and C-4), 128.7 and 129.3 (C-2 and C-5), 131.5 (C-5a), 133.3 (C-1a), 138.2 (C-9), 160.9 (C-7a), 162.6 (C-11), 201.1 (C-12); MS (EI) *m/z* (rel. int.) 267 [(M+1)$^+$, 27], 266 (M$^{+\cdot}$, 100), 265 [(M−1)$^+$, 25], 248 (44), 247 (69), 137 (68), 136 (20), 130 (13), 129 (39), 128 (40), 115 (17), 108 (20), 104 (18). Anal. Calcd for $C_{17}H_{12}O_3$: C, 76.68; H, 5.30. Found: C, 76.65; H, 5.34.

3.3.19. *trans*-10-Nitrobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (8j) (23%). Mp 215–218°C; ^{1}H NMR δ 3.00 (dd, *J*=16.4, 11.9 Hz, 1H, H-1), 3.03–3.12 (m, 1H, H-12a), 3.35 (dd, *J*=16.0, 10.3 Hz, 1H, H-6), 3.51 (dd, *J*=16.0, 6.1 Hz, 1H, H-6), 3.50–3.60 (m, 1H, H-1), 4.73 (ddd, *J*=13.0, 10.3, 6.1 Hz, 1H, H-6a), 7.16 (d, *J*=9.2 Hz, 1H, H-8), 7.20–7.23 (m, 4H, H-2,3,4,5), 8.37 (dd, *J*=9.2, 2.9 Hz, 1H, H-9), 8.83 (d, *J*=2.9 Hz, 1H, H-11); ^{13}C NMR δ 27.8 (C-1), 35.7 (C-6), 45.8 (C-12a), 78.4 (C-6a), 119.2 (C-8), 120.2 (C-11a), 123.8 (C-11), 126.7 and 127.0 (C-3,4), 128.9 and 129.0 (C-2,5), 130.4 (C-9), 131.8 (C-5a), 133.1 (C-1a), 142.2 (C-10), 165.0 (C-7a), 191,5 (C-12); MS (EI) *m/z* (rel. int.) 296 [(M+1)$^+$, 28], 295 (M$^{+\cdot}$, 100), 294 [(M−1)$^+$, 21], 277 (39), 276 (65), 230 (16), 202 (6), 166 (31), 150 (9), 130 (32), 129 (100), 128 (87), 127 (29), 120 (16), 115 (32), 104 (22), 91 (17), 77 (12). Anal. Calcd for $C_{17}H_{13}NO_4 \cdot 0.25H_2O$: C, 68.04; H, 4.50; N, 4.67. Found: C, 67.93; H, 4.66; N, 4.83. HRMS (EI) calcd for $C_{17}H_{13}NO_4$: 295.0845. Found: 295.0836.

3.3.20. *cis*-10-Nitrobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone (9j) (12.5%).[24] ^{1}H NMR (500.13 MHz) δ 2.96 (dd, *J*=15.9, 5.9 Hz, 1H, H-1), 3.03–3.07 (m, 1H, H-1), 3.11 (ddd, *J*=10.5, 5.9, 2.3 Hz, 1H, H-12a), 3.26 (dd, *J*=18.0, 4.5 Hz, 1H, H-6), 3.32–3.38 (m, 1H, H-6), 5.07–5.09 (m, 1H, H-6a), 7.10 (d, *J*=9.1 Hz, 1H, H-8), 7.14–7.20 (m, 4H, H-2,3,4,5), 8.34 (dd, *J*=9.1, 2.8, 1H, H-9), 8.83 (d, *J*=2.8 Hz, 1H, H-11); ^{13}C NMR (125.76 MHz) δ 25.8 (C-1), 32.4 (C-6), 44.3 (C-12a), 76.1 (C-6a), 119.3 (C-8), 120.2 (C-11a), 124.2 (C-11), 126.7 and 126.9 (C-3 and C-4), 128.9 and 129.3 (C-2 and C-5), 130.4 (C-9), 131.0 (C-5a), 132.8 (C-1a), 142.3 (C-10), 164.8 (C-7a), 192.4 (C-12).

3.3.21. (2-Hydroxyphenyl)-2-naphthylketone (10a) (4%). Mp 79–80°C; ^{1}H NMR δ 6.90 (ddd, *J*=8.0, 7.2, 1.0 Hz, 1H,

H-5′), 7.11 (dd, *J*=8.3, 1.0 Hz, 1H, H-3′), 7.54 (ddd, *J*=8.3, 7.2, 1.5 Hz, 1H, H-4′), 7.59 (dt, *J*=6.9, 2.5 Hz, 1H, H-7), 7.63 (dt, *J*=6.9, 2.5 Hz, 1H, H-6), 7.68 (dd, *J*=8.0, 1.5 Hz, 1H, H-6′), 7.78 (dd, *J*=8.4, 1.6 Hz, 1H, H-3), 7.93 (dd, *J*=6.9, 2.5 Hz, 1H, H-5), 7.95 (dd, *J*=6.9, 2.5 Hz, 1H, H-8), 7.98 (d, *J*=8.4 Hz, 1H, H-4), 8.19 (d, *J*=1.6 Hz, 1H, H-1), 12.06 (s, 1H, 2′-O*H*); ^{13}C NMR δ 118.4 (C-3′), 118.7 (C-5′), 119.3 (C-1′), 125.3 (C-3), 127.0 (C-7), 127.8 (C-5), 128.2 (C-6), 128.4 (C-4), 129.2 (C-8), 130.4 (C-1), 132.1 (C-2), 133.7 (C-6′), 134.8 (C-10), 135.1 (C-9), 136.3 (C-4′), 163.2 (C-2′), 201.5 (C=O); MS (EI) *m/z* (rel. int.) 249 [(M+1)$^+$, 25], 248 (M$^{+\cdot}$, 94), 247 [(M−1)$^+$, 100], 231 (17), 189 (8), 155 (31), 129 (9), 128 (57), 127 (54), 126 (15), 124 (12), 121 (40), 101 (9), 93 (12). Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 81.90; H, 4.49.

3.3.22. (2-Hydroxy-4-methoxyphenyl)-2-naphthylketone (10f) (2.3%). Yellowish oil; ^{1}H NMR δ 3.89 (s, 3H, OC*H*$_3$), 6.44 (dd, *J*=8.9, 2.5 Hz, 1H, H-5′), 6.56 (d, *J*=2.5 Hz, 1H, H-3′), 7.56–7.65 (m, 2H, H-6,7), 7.60 (d, *J*=8.9 Hz, 1H, H-6′), 7.74 (dd, *J*=8.3, 1.7 Hz, 1H, H-3), 7.91–7.96 (m, 2H, H-5,8), 7.97 (d, *J*=8.3 Hz, 1H, H-4), 8.14 (d, *J*=1.7 Hz, 1H, H-1), 12.76 (s, 1H, 2′-O*H*); ^{13}C NMR: δ 55.7 (O*C*H$_3$), 101.1 (C-3′), 107.5 (C-5′), 113.3 (C-1′), 125.3 (C-3), 126.9 (C-7), 127.8 (C-5), 128.0 (C-6), 128.3 (C-4), 129.1 (C-8), 129.8 (C-1), 132.2 (C-9), 134.6 (C-10), 135.3 (C-6′), 135.5 (C-2), 166.2 and 166.3 (C-2′ and C-4′), 199.9 (C=O). HRMS (EI) calcd for $C_{18}H_{14}O_3$: 278.0943. Found 278.0939.

3.3.23. (2-Hydroxy-6-methoxyphenyl)-2-naphthylketone (10g) (2.4%). Yellowish oil; ^{1}H NMR δ 3.48 (s, 3H, OC*H*$_3$), 6.46 (d, *J*=8.3 Hz, 1H, H-5′), 6.72 (dd, *J*=8.3, 0.5 Hz, 1H, H-3′), 7.43 (t, *J*=8.3 Hz, 1H, H-4′), 7.53 (ddd, *J*=8.0, 7.0, 1.2 Hz, 1H, H-7), 7.59 (ddd, *J*=8.1, 7.0, 1.3 Hz, 1H, H-6), 7.67 (dd, *J*=8.6, 1.7 Hz, 1H, H-3), 7.85 (d, *J*=8.6 Hz, 1H, H-4), 7.88 (d, *J*=8.1 Hz, 1H, H-5), 7.93(d, *J*=8.0 Hz, 1H, H-8), 8.19 (s, 1H, H-1), 10.8 (s, 1H, 2′-O*H*); ^{13}C NMR δ 55.3 (O*C*H$_3$), 102.3 (C-5′), 110.4 (C-3′), 111.8 (C-1′), 125.0 (C-3), 126.4 (C-7), 127.2 (C-4), 127.7 (C-5), 127.9 (C-6), 129.3 (C-8), 129.4 (C-1), 132.4 (C-9), 134.9 (C-10), 135.6 (C-4′), 138.1 (C-2), 160.1 (C-6′), 161.9 (C-2′), 199.7 (C=O). HRMS (EI) calcd for $C_{18}H_{14}O_3$: 278.0943. Found 278.0931.

3.3.24. (2-Hydroxy-5-nitrophenyl)-2-naphthylketone (10j) (38.5%). Mp 175–176°C; ^{1}H NMR δ 7.23 (d, *J*=9.2 Hz, 1H, H-3′), 7.64 (ddd, *J*=8.0, 6.8, 1.2 Hz, 1H, H-7), 7.69 (ddd, *J*=8.1, 6.8, 1.3 Hz, 1H, H-6), 7.80 (dd, *J*=8.5, 1.7 Hz, 1H, H-3), 7.97 (d, *J*=8.1 Hz, 1H, H-5), 8.00 (d, *J*=8.0 Hz, 1H, H-8), 8.04 (d, *J*=8.5 Hz, 1H, H-4), 8.24 (d, *J*=1.7 Hz, 1H, H-1), 8.42 (dd, *J*=9.2, 2.7 Hz, 1H, H-4′), 8.69 (d, *J*=2.7 Hz, 1H, H-6′), 12.73 (s, 1H, 2′-O*H*); ^{13}C NMR δ 118.2 (C-1′), 119.6 (C-3′), 124.8 (C-3), 127.5 (C-7), 128.0 (C-5), 129.0 (C-6), 129.1 (C-4), 129.4 (C-8), 129.7 (C-6′), 130.9 (C-4′), 131.0 (C-1), 132.2 (C-9), 133.5 (C-2), 135.3 (C-10), 139.5 (C-5′), 168.0 (C-2′), 200.4 (C=O); MS (EI) *m/z* (rel. int.) 294 [(M+1)$^+$, 25], 293 (M$^{+\cdot}$, 100), 292 [(M−1), 79], 276 (11), 246 (16), 218 (4), 189 (10), 166 (8), 155 (45), 128 (52), 127 (74), 126 (12), 120 (13). Anal. Calcd for $C_{17}H_{11}NO_4 \cdot 0.25H_2O$: C, 68.50; H, 3.86; N, 4.70. Found: C, 68.56; H, 4.05; N, 5.10. HRMS (EI) calcd for $C_{17}H_{11}NO_4$: 293.0688. Found: 293.0682.

3.4. General procedure for the synthesis of benzo[*b*]xanthones 11

A mixture of compounds **8** and **9** (0.4 mmol) and iodine (10.2 mg, 0.04 mmol) in DMSO (5 mL) was refluxed for 2 h. After cooling, the reaction mixture was poured into ice and water. A small amount of $Na_2S_2O_3$ was added and the reaction mixture stirred for some minutes. The obtained yellow solid was filtered and washed with water. The residue was taken in chloroform and washed with water. The recrystallisation of the obtained residue in ethanol gave compounds **11** in good yields.

3.4.1. Benzo[*b*]xanthone (11a) (98%). Mp 214–215°C; ^{1}H NMR δ 7.38 (ddd, *J*=7.9, 7.0, 0.9 Hz, 1H, H-10), 7.51 (ddd, *J*=8.2, 6.9, 1.2 Hz, 1H, H-3), 7.52 (d, *J*=8.1 Hz, 1H, H-8), 7.63 (ddd, *J*=8.1, 6.9, 1.3 Hz, 1H, H-4), 7.76 (ddd, *J*=8.1, 7.0, 1.7 Hz, 1H, H-9), 7.92 (s, 1H, H-6), 7.93 (d, *J*=8.1 Hz, 1H, H-5), 8.09 (d, *J*=8.2 Hz, 1H, H-2), 8.34 (dd, *J*=7.9, 1.7 Hz, 1H, H-11), 8.96 (s, 1H, H-1); ^{13}C NMR δ 113.5 (C-6), 117.8 (C-8), 121.0 and 121.3 (C-11a and C-12a), 123.4 (C-10), 125.5 (C-3), 126.3 (C-11), 126.9 (C-5), 128.3 (C-1), 129.0 (C-4), 129.5 (C-1a), 129.7 (C-2), 135.3 (C-9), 136.7 (C-5a), 152.2 (C-6a), 156.7 (C-7a), 178.0 (C-12); MS (EI) *m/z* (rel. int.) 247 [(M+1)$^+$, 23], 246 (M$^{+\cdot}$, 100), 218 (21), 189 (25). Anal. Calcd for $C_{17}H_{10}O_2 \cdot 0.25H_2O$: C, 81.35; H, 4.18. Found: C, 81.38; H, 4.31. HRMS (EI) calcd for $C_{17}H_{10}O_2$: 246.0681. Found: 246.0678.

3.4.2. 10-Methylbenzo[*b*]xanthone (11b) (97%). Mp 176–177°C; ^{1}H NMR δ 2.46 (s, 3H, C*H*$_3$), 7.37 (d, *J*=8.6 Hz, 1H, H-8), 7.48 (ddd, *J*=8.2, 6.9, 1.1 Hz, 1H, H-3), 7.53 (dd, *J*=8.6, 2.2 Hz, 1H, H-9), 7.59 (ddd, *J*=8.3, 6.9, 1.2 Hz, 1H, H-4), 7.85 (s, 1H, H-6), 7.89 (d, *J*=8.3 Hz, 1H, H-5), 8.05 (d, *J*=8.2 Hz, 1H, H-2), 8.13 (d, *J*=2.2 Hz, 1H, H-11), 8.91 (s, 1H, H-1); ^{13}C NMR δ 20.8 (*C*H$_3$), 113.4 (C-6), 117.6 (C-8), 120.7 (C-11a), 121.3 (C-12a), 125.4 (C-3), 126.3 (C-11), 127.0 (C-5), 128.3 (C-1), 128.9 (C-4), 129.4 (C-1a), 129.7 (C-2), 133.1 (C-10), 136.5 (C-9), 136.6 (C-5a), 152.3 (C-6a), 154.9 (C-7a), 178.1 (C-12); MS (EI) *m/z* (rel. int.) 261 [(M+1)$^+$, 29], 260 (M$^{+\cdot}$, 100), 259 [(M−1)$^+$, 20], 232 (9), 231 (25), 203 (7), 202 (17). Anal. Calcd for $C_{18}H_{12}O_2 \cdot 0.25H_2O$: C, 81.57; H, 4.72. Found: C, 81.67; H, 4.62. HRMS (EI) calcd for $C_{18}H_{12}O_2$: 260.0837. Found: 260.0831.

3.4.3. 10-Chlorobenzo[*b*]xanthone (11c) (94%). Mp 225°C; ^{1}H NMR δ 7.41 (d, *J*=8.9 Hz, 1H, H-8), 7.49 (ddd, *J*=8.2, 6.9, 1.0 Hz, 1H, H-3), 7.59 (ddd, *J*=8.2, 6.9, 1.0 Hz, 1H, H-4), 7.64 (dd, *J*=8.9, 2.6 Hz, 1H, H-9), 7.84 (s, 1H, H-6), 7.88 (d, *J*=8.2 Hz, 1H, H-5), 8.03 (d, *J*=8.2 Hz, 1H, H-2), 8.28 (d, *J*=2.6 Hz, 1H, H-11), 8.94 (s, 1H, H-1); ^{13}C NMR δ 113.7 (C-6), 119.6 (C-8), 120.8 (C-12a), 122.0 (C-11a), 125.7 (C-3), 126.3 (C-11), 127.1 (C-5), 128.6 (C-1), 129.2 (C-10), 129.3 (C-4), 129.7 (C-1a), 129.8 (C-2), 135.2 (C-9), 136.8 (C-5a), 152.0 (C-6a), 155.1 (C-7a), 176.8 (C-12); MS (EI) *m/z* (rel. int.) 283 [(M+1)$^+$, ^{37}Cl, 8], 282 (M$^{+\cdot}$, ^{37}Cl, 43), 281 [(M−1)$^+$, ^{37}Cl; (M+1)$^+$, ^{35}Cl; 25], 280 (M$^{+\cdot}$, ^{35}Cl, 100), 252 (13), 189 (16). Anal. Calcd for $C_{17}H_9ClO_2 \cdot 0.25H_2O$: C, 71.52; H, 3.33. Found: C, 71.85; H, 3.54. Found: C, 81.67; H, 4.62. HRMS (EI) calcd for $C_{17}H_9{}^{37}ClO_2$: 282.0262. Found: 282.0261.

3.4.4. 10-Bromobenzo[*b*]xanthone (11d) (96%). Mp 206–208°C; ^{1}H NMR δ 7.37 (d, J=8.9 Hz, 1H, H-8), 7.51 (ddd, J=8.2, 6.9, 1.1 Hz, 1H, H-3), 7.62 (ddd, J=8.3, 6.9, 1.3 Hz, 1H, H-4), 7.79 (dd, J=8.9, 2.5 Hz, 1H, H-9), 7.86 (s, 1H, H-6), 7.89 (d, J=8.3 Hz, 1H, H-5), 8.04 (d, J=8.2 Hz, 1H, H-2), 8.45 (d, J=2.5 Hz, 1H, H-11), 8.89 (s, 1H, H-1); ^{13}C NMR δ 113.7 (C-6), 116.4 (C-10), 119.9 (C-8), 120.8 (C-12a), 122.3 (C-11a), 125.8 (C-3), 127.1 (C-5), 128.6 (C-1), 129.3 (C-4), 129.4 (C-11), 129.6 (C-1a), 129.8 (C-2), 136.8 (C-5a), 138.0 (C-9), 151.9 (C-6a), 155.4 (C-7a), 176.8 (C-12); MS (EI) *m/z* (rel. int.) 327 [$(M+1)^+$, ^{81}Br, 22], 326 ($M^{+\cdot}$, ^{81}Br, 100), 325 [$(M-1)^+$, ^{81}Br, $(M+1)^+$, ^{79}Br, 23], 324 ($M^{+\cdot}$, ^{79}Br, 99), 298 (7), 296 (7), 217 (8), 190 (6), 189 (36), 188 (7), 187 (12), 163 (10), 95 (13), 78 (15). Anal. Calcd for $C_{17}H_9BrO_2{\cdot}0.25H_2O$: C, 61.88; H, 2.88. Found: C, 62.10; H, 2.71. HRMS (EI) calcd for $C_{17}H_9{}^{81}BrO_2$: 325.9765. Found: 325.9771.

3.4.5. 8,10-Dibromobenzo[*b*]xanthone (11e) (94%). Mp 266–268°C; ^{1}H NMR δ 7.55 (ddd, J=8.0, 6.9, 1.0 Hz, 1H, H-3), 7.66 (ddd, J=8.2, 6.9, 1.2 Hz, 1H, H-4), 7.94 (d, J=8.2 Hz, 1H, H-5), 8.04 (s, 1H, H-6), 8.05 (d, J=8.0 Hz, 1H, H-2), 8.08 (d, J=2.5 Hz, 1H, H-9), 8.42 (d, J=2.5 Hz, 1H, H-11), 8.91 (s, 1H, H-1); ^{13}C NMR δ 112.6 (C-8), 114.3 (C-6), 116.3 (C-10), 120.3 (C-12a), 123.2 (C-11a), 126.1 (C-3), 127.2 (C-5), 128.8 (C-1), 129.0 (C-11), 129.6 (C-4), 129.9 (C-2), 130.1 (C-1a), 137.0 (C-5a), 140.6 (C-9), 151.7 (C-6a), 152.3 (C-7a), 176.2 (C-12); MS (EI) *m/z* (rel. int.) 407 [$(M+1)^+$, ^{81}Br, 15], 406 ($M^{+\cdot}$, ^{81}Br, 60), 405 (28), 404 ($M^{+\cdot}$, ^{79}Br^{81}Br, 100), 403 (15), 402 ($M^{+\cdot}$, ^{79}Br, 61), 269 (13), 267 (14), 216 (20), 202 (8), 188 (18), 187 (29), 114 (10), 107 (10), 94 (9). Anal. Calcd for $C_{17}H_8Br_2O_2{\cdot}0.25H_2O$: C, 47.32; H, 2.55. Found: C, 47.40; H, 2.19. HRMS (EI) calcd for $C_{17}H_8{}^{81}Br_2O_2$: 405.8850. Found: 405.8856.

3.4.6. 9-Methoxybenzo[*b*]xanthone (11f) (88%). Mp 190–192°C; ^{1}H NMR δ 3.95 (s, 3H, OCH_3), 6.88 (d, J=2.3 Hz, 1H, H-8), 6.92 (dd, J=8.8, 2.3 Hz, 1H, H-10), 7.49 (ddd, J=8.2, 6.9, 1.2 Hz, 1H, H-3), 7.60 (ddd, J=8.2, 6.9, 1.3 Hz, 1H, H-4), 7.84 (s, 1H, H-6), 7.90 (d, J=8.2 Hz, 1H, H-5), 8.06 (d, J=8.2 Hz, 1H, H-2), 8.28 (d, J=8.8 Hz, 1H, H-11), 8.91 (s, 1H, H-1); ^{13}C NMR δ 55.9 (OCH_3), 100.2 (C-8), 112.7 (C-10), 113.3 (C-6), 115.1 (C-11a), 121.5 (C-12a), 125.4 (C-3), 127.0 (C-5), 128.2 (C-1), 128.6 (C-11), 128.8 (C-4), 129.6 (C-1a), 129.7 (C-2), 136.4 (C-5a), 152.4 (C-6a), 158.6 (C-7a), 165.5 (C-9), 177.0 (C-12); MS (EI) *m/z* (rel. int.) 277 [$(M+1)^+$, 25], 276 ($M^{+\cdot}$, 100), 233 (11), 205 (11), 176 (7). HRMS (EI) calcd for $C_{18}H_{12}O_3$: 276.0786. Found: 276.0780.

3.4.7. 11-Methoxybenzo[*b*]xanthone (11g) (91%). Mp 229–231°C; ^{1}H NMR δ 4.05 (s, 3H, OCH_3), 6.79 (dd, J=8.3, 0.7 Hz, 1H, H-10), 7.06 (dd, J=8.3, 0.7 Hz, 1H, H-8), 7.47 (ddd, J=8.2, 6.9, 1.2 Hz, 1H, H-3), 7.58 (ddd, J=8.2, 6.9, 1.2 Hz, 1H, H-4), 7.61 (t, J=8.3 Hz, 1H, H-9), 7.80 (s, 1H, H-6), 7.87 (d, J=8.2 Hz, 1H, H-5), 8.05 (d, J=8.2 Hz, 1H, H-2), 8.87 (s, 1H, H-1); ^{13}C NMR δ 56.4 (OCH_3), 105.1 (C-10), 109.9 (C-8), 111.8 (C-11a), 112.7 (C-6), 122.5 (C-12a), 125.2 (C-3), 126.9 (C-5), 128.3 (C-1), 128.7 (C-4), 129.6 (C-1a), 129.8 (C-2), 135.3 (C-9), 136.4 (C-5a), 151.5 (C-6a), 158.6 (C-7a), 161.0 (C-11), 177.1 (C-12); MS (EI) *m/z* (rel. int.) 277 [$(M+1)^+$, 23], 276 ($M^{+\cdot}$, 100), 275 [$(M-1)^+$, 38], 259 (10), 248 (14), 247 (72), 246 (24), 231 (10), 230 (38), 218 (17), 189 (27), 176 (10), 138(10), 109 (19), 95 (17). Anal. Calcd for $C_{18}H_{12}O_3{\cdot}0.25H_2O$: C, 76.92; H, 4.45. Found: C, 76.26; H, 4.54. HRMS (EI) calcd for $C_{18}H_{12}O_3$: 276.0786. Found: 276.0778.

3.4.8. 11-Hydroxybenzo[*b*]xanthone (11i) (91%). Mp 212–214°C; ^{1}H NMR δ 6.81 (dd, J=8.3, 0.8 Hz, 1H, H-10), 6.94 (dd, J=8.3, 0.8 Hz, 1H, H-8), 7.52 (ddd, J=8.3, 6.8, 1.2 Hz, 1H, H-3), 7.62 (t, J=8.3 Hz, 1H, H-9), 7.64 (ddd, J=8.3, 6.8, 1.2 Hz, 1H, H-4), 7.87 (s, 1H, H-6), 7.92 (d, J=8.3 Hz, 1H, H-5), 8.07 (d, J=8.3 Hz, 1H, H-2), 8.89 (s, 1H, H-1), 12.69 (s, 1H, O*H*); ^{13}C NMR δ 106.9 (C-8), 108.3 (C-11a), 110.3 (C-10), 113.5 (C-6), 120.1 (C-12a), 125.7 (C-3), 127.1 (C-5), 127.9 (C-1), 129.5 (C-1a,4), 129.8 (C-2), 137.1 (C-5a), 137.4 (C-9), 151.9 (C-6a), 156.7 (C-7a), 162.3 (C-11), 183.0 (C-12); MS (EI) *m/z* (rel. int.) 263 [$(M+1)^+$, 27], 262 ($M^{+\cdot}$, 100), 205 (10), 176 (9). HRMS (EI) calcd for $C_{17}H_{10}O_3$: 262.0630. Found: 262.0635.

3.4.9. 10-Nitrobenzo[*b*]xanthone (11j) (92%). Mp 258–260°C; ^{1}H NMR ($CDCl_3$+TFA) δ 7.61 (ddd, J=8.3, 7.0, 1.1 Hz, 1H, H.3), 7.73 (d, J=9.2 Hz, 1H, H-8), 7.71–7.76 (m, 1H, H-4), 8.00 (d, J=8.4 Hz, 1H, H-5), 8.05 (s, 1H, H-6), 8.14 (d, J=8.3 Hz, 1H, H-2), 8.64 (dd, J=9.2, 2.8 Hz, 1H, H-9), 9.00 (s, 1H, H-1), 9.24 (d, J=2.8 Hz, 1H, H-11); ^{13}C NMR ($CDCl_3$+TFA) δ 114.7 (C-6), 119.6 (C-12a), 120.0 (C-8), 120.2 (C-11a), 124.1 (C-11), 126.9 (C-3), 127.4 (C-5), 129.6 (C-1), 130.2 (C-2), 130.4 (C-9,1a), 130.7 (C-4), 137.8 (C-5a), 143.5 (C-10), 151.7 (C-6a), 160.4 (C-7a), 179.3 (C-12); MS (EI) *m/z* (rel. int.) 292 [$(M+1)^+$, 27], 291 ($M^{+\cdot}$, 100), 261 (12), 245 (33), 217 (14), 205 (10), 190 (11), 189 (49), 188 (11), 187 (19), 163 (10), 114 (9). Anal. Calcd for $C_{17}H_9NO_4{\cdot}0.25H_2O$: C, 67.94; N, 4.66; H, 3.33. Found: C, 67.87; N, 5.01; H, 3.62. HRMS (EI) calcd for $C_{17}H_9NO_4$: 291.0532. Found: 291.0526.

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24. The isolation of *cis*-10-nitrobenzo[*b*]-1,6,6a,12a-tetrahydroxanthone **9j** from its diastereomer **8j** was not possible, since during the separation process **9j** was always partially converted into **8j**. The NMR characterization of **9j** was made from a mixture of these two diastereomers enriched in **9j**.