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Article

Ceric ammonium sulfate (CAS) mediated oxidations of benzophenones possessing a phenolic substituent for the synthesis of xanthones and related products

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Ceric ammonium sulfate (CAS) mediated oxidations of benzophenones possessing a phenolic substituent for the synthesis of xanthones and related products

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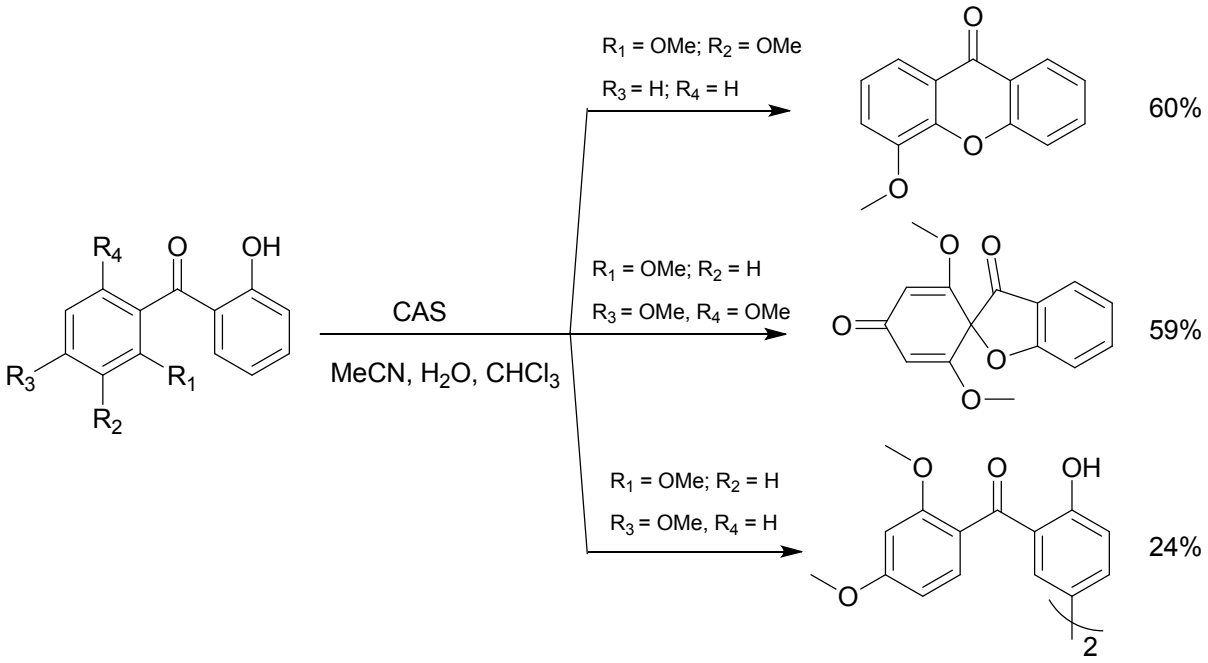
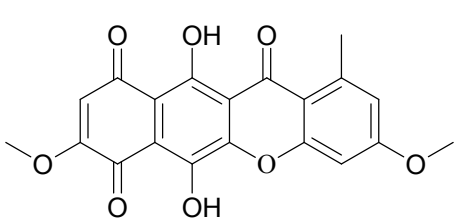
ABSTRACT: Work previously published by our group described novel methodology for the synthesis of xanthones and related products from phenolic benzophenones in a reaction mediated by ceric ammonium sulfate (CAS). In this paper we further explore this novel reaction by subjecting an additional set of phenolic benzophenones to CAS to afford a range of compounds, including xanthones, 9*H*-xanthen-2,9(4a*H*)-diones, 3*H*-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-3,4'-diones and biaryl compounds. A comparison of these reactions with the more commonly used oxidant ceric ammonium nitrate (CAN) was also conducted. Based on these results, greater insight into the reaction mechanism has been gained. In addition, the conversion of the synthesized xanthen-2,9(4a*H*)-diones to xanthones by treatment with sodium dithionite is described.



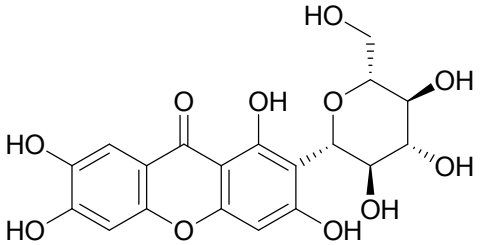
KEYWORDS (Word Style "BG_Keywords"). Benzophenones, ceric ammonium sulfate, oxidative addition, xanthone, spirofuran, xanthendiones

Introduction

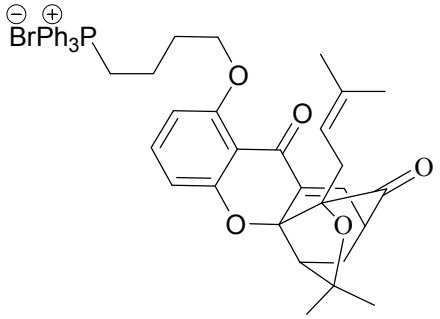
The remarkable biological activity of xanthones (dibenzo-γ-pyranones) has caught the attention of medicinal and synthetic chemists. These privileged scaffolds isolated from plants, lichens and fungi (examples in Figure 1)[1,2,3] have been found to display significant antitumour,[4] antioxidant,[2] antimalarial,[5] and anti-HIV activity.[6]



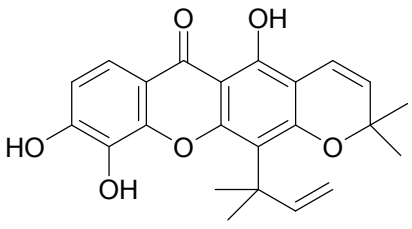
Bikaverin (antitumour)



Mangiferin (antioxidant)



Caged *Garcinia* xanthone CR135 (antimalarial)



Macluraxanthone (anti-HIV)

Figure 1 – A selection of naturally occurring xanthones

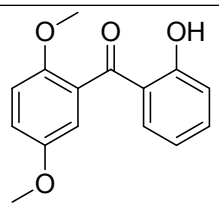
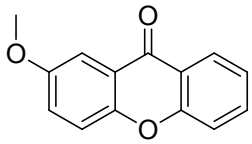
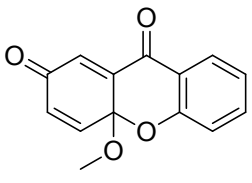
As a result many synthetic approaches to the assembly of the xanthone core have been developed.[2,7] In our laboratories a new method for the synthesis of xanthones and related compounds was disclosed in 2010.[8] We reported that in the presence of ceric ammonium nitrate (CAN) phenolic-containing benzophenones could undergo an oxidative cyclization to form xanthones and related products. However, after further experimentation it was ascertained that the reagent was ceric ammonium *sulfate* (CAS) and not ceric ammonium *nitrate* (CAN). A correction has been made to the *Journal of Organic Chemistry* manuscript (DOI: 10.1021/jo101873v).

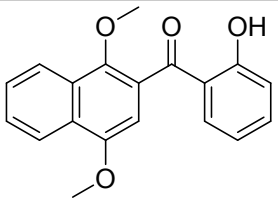
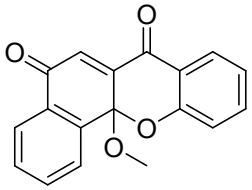
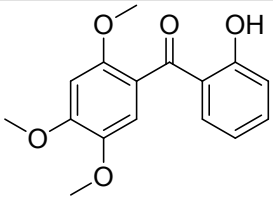
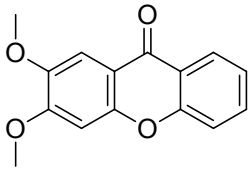
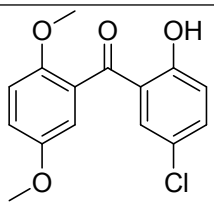
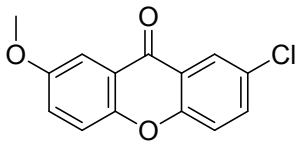
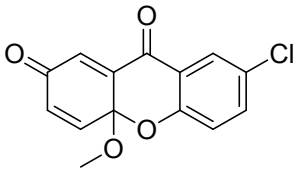
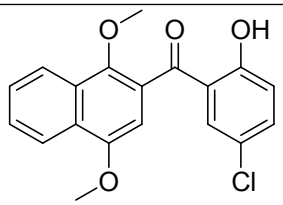
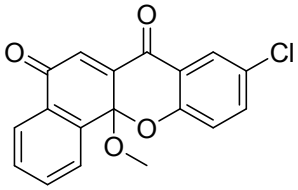
In this paper we report further findings on the use of CAS as a reagent for the preparation of xanthones and related compounds. Based on the results of the additional examples we further speculate on the mechanism of the reaction. In addition, the conversion of some of the xanthen-2,9(4a*H*)-diones into xanthones by treatment with sodium dithionite is described.

Results and Discussion

As a starting point we repeated the same reactions described in the *Journal of Organic Chemistry* paper[8] utilizing a recently purchased commercial source of CAS. Subjecting benzophenones **1-5** to optimized reaction conditions of between 3 and 4 equivalents of CAS (repeated in triplicate) afforded products **6-12** as shown in Table 1.[8] As before, and depending on the nature of the benzophenone the CAS-mediated oxidative cyclization reaction afforded a variety of products; including xanthones **6**, **9** and **10**, and 9*H*-xanthen-2,9(4a*H*)-diones **7**, **8**, **11** and **12**. These were the same products as described in the *Journal of Organic Chemistry* Note. However; some of the yields under these optimized reaction conditions were different to those previously described.[8]

Table 1 – CAS mediated oxidative cyclizations

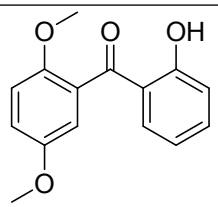
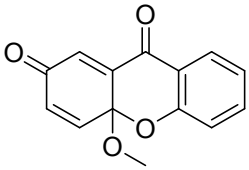
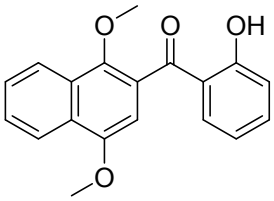
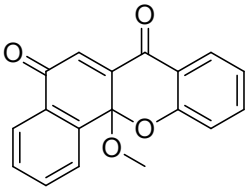
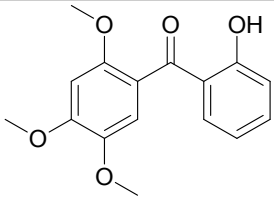
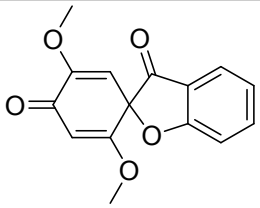
Benzophenone	Product(s) and yield	
		

1	**6** (30 %)	**7** (45 %)
 **2**	 **8** (81 %)	
 **3**	 **9** (70 %)	
 **4**	 **10** (28 %)	 **11** (50 %)
 **5**	 **12** (84 %)	

[a] *Reaction Conditions*: CAS (3 to 4 eq), MeCN/H_2O/$CHCl_3$, rt, 18 h

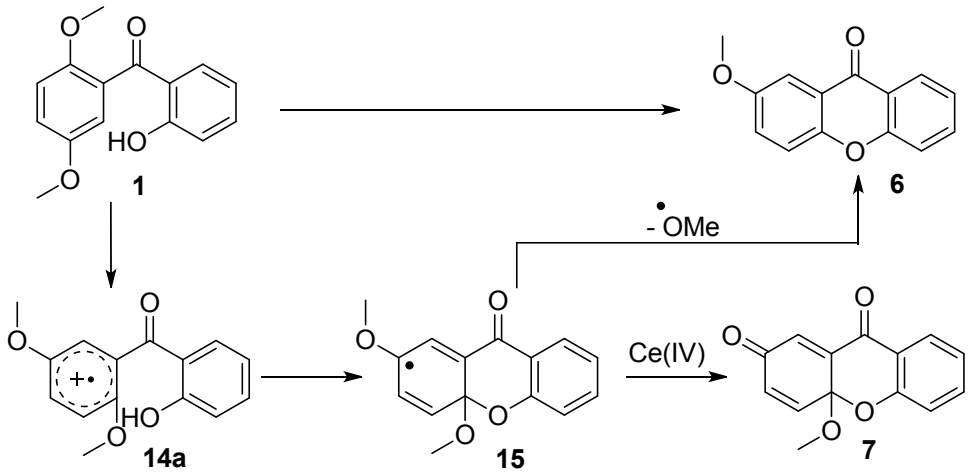
Since CAS is rarely used in organic synthesis, we repeated the first three reactions in Table 1 using CAN as the reagent (Table 2). Different results, in particular the yields, were obtained using CAN as the oxidant. Exposing **1** to CAN furnished **7** exclusively in a poor yield of 16% Naphthalene **2** was converted into **8,** but in a meagre yield **(**26%). The third reaction with CAN (**3** → **13**) gave a different product as to when CAS was used as the oxidant, albeit in a poor yield. These results demonstrate that CAS was a superior oxidant to CAN for these transformations.

Table 2 – CAN mediated oxidative cyclizations

Benzophenone	Product
 **1**	 **7** (16%)
 **2**	 **8** (26%)
 **3**	 **13** (13%)

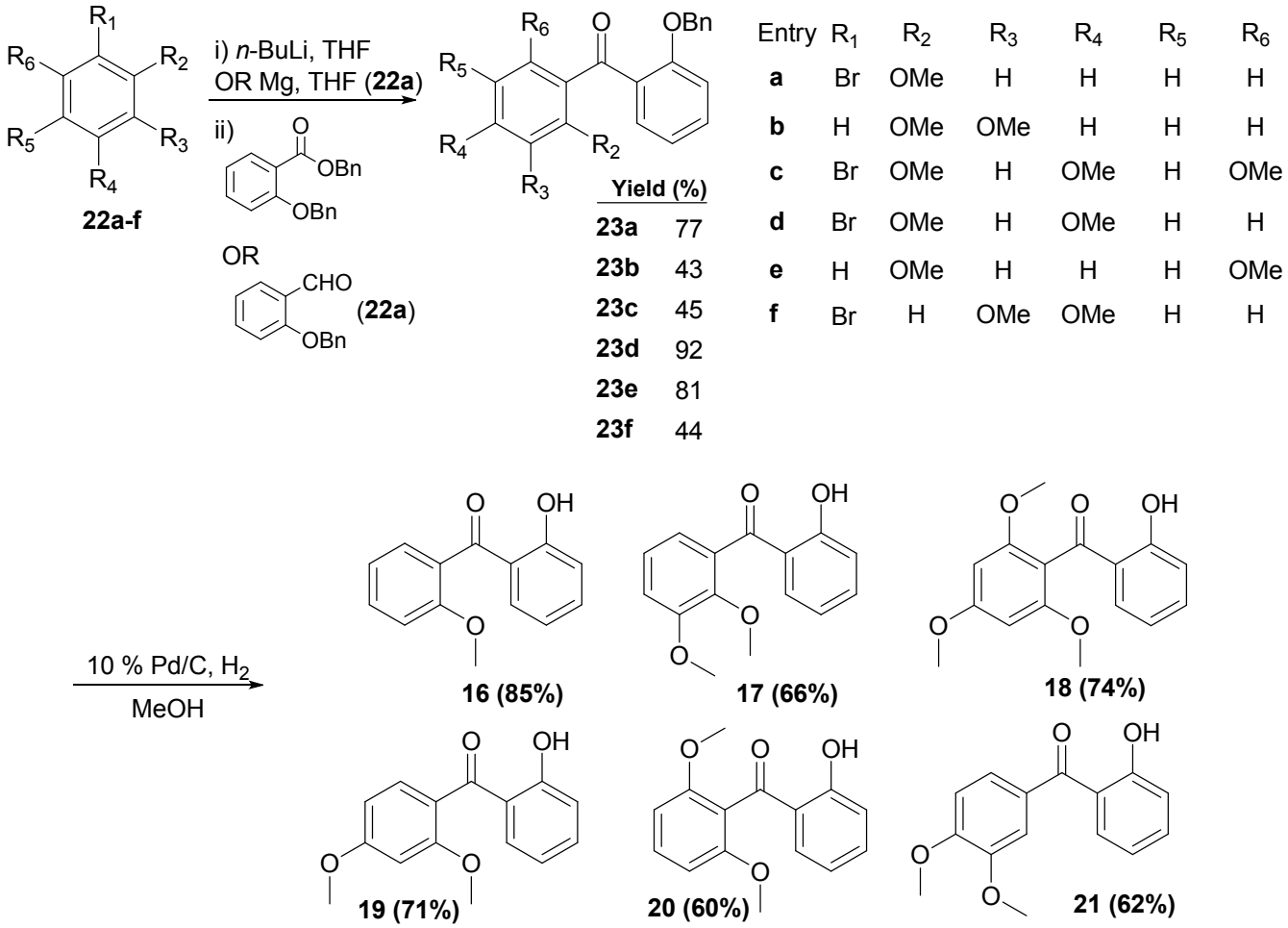
[a] *Reaction Conditions*: CAN (3-5 eq), MeCN/H_2O/$CHCl_3$, rt, 10 mins

At the time of the original publication[8] the major product *i.e*. xanthones (e.g. **6**) or diones (e.g. **8**) from the reaction could not be rationally predicted. A tentative mechanism (Scheme 1) was proposed in an attempt to explain the results,[8] in which the benzophenone would initially form a radical cation **14a** from **1**, which then allowed for the formation of **15**. This was proposed as it was in line with the mechanism suggested for the oxidation with CAN of *para*-dimethoxybenzenes to quinones.[9] Intermediate radical **15** could aromatize to form the xanthone **6**, although the loss of a methoxy radical seemed problematic in the conversion of **15** into **6**. Alternatively, the intermediate radical **15** could be converted into the dione **7** by reaction with a further equivalent of CAS in the presence of water. However, since only benzophenones possessing *at least two* methoxy substituents (with one *ortho* to the ketone bridge) on the benzene ring of the benzophenone lacking the phenol were investigated, this mechanism was speculative.



Scheme 1 – Previously proposed mechanism for the oxidative formation of xanthones

In order to gain a better understanding of the novel CAS reaction, a further set of benzophenones **16-21** containing a range of aromatic methoxy substitution patterns were synthesized from **22a-f**. This was achieved using methodology previously reported[8] by subjecting the substituted benzenes **22b-f** to *n*-butyllithium (or magnesium turnings in the case of **22a**) and benzyl 2-(benzyloxy)benzoate (or 2-(benzyloxy)benzaldehyde for **22a**) (Scheme 2) to afford ketones **23a-f**. Treatment of **23a-f** with hydrogen gas and palladium supported on carbon resulted in the desired benzophenones **16-21** containing a hydrogen-bonded phenol substituent.



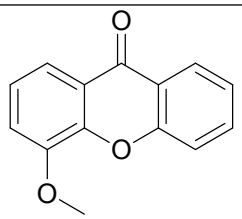
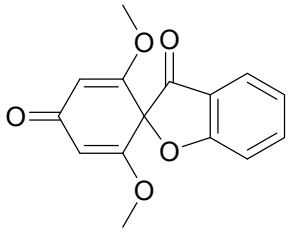
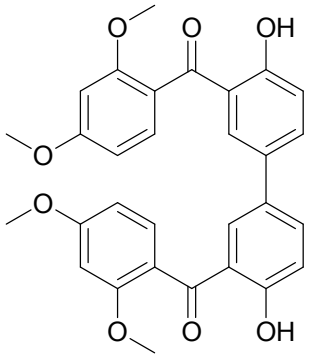
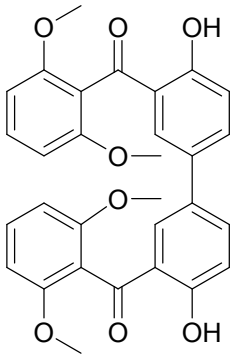
Entry	R_1	R_2	R_3	R_4	R_5	R_6
a	Br	OMe	H	H	H	H
b	H	OMe	OMe	H	H	H
c	Br	OMe	H	OMe	H	OMe
d	Br	OMe	H	OMe	H	H
e	H	OMe	H	H	H	OMe
f	Br	H	OMe	OMe	H	H

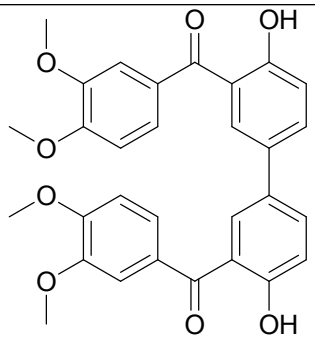
	Yield (%)
23a	77
23b	43
23c	45
23d	92
23e	81
23f	44

Scheme 2 – The synthesis of additional phenolic-containing benzophenones.

The phenol containing benzophenones **16-21** were exposed to 2-4 equivalents of CAS for 12 h. Each reaction mixture was analysed by TLC and, where possible, new compounds formed from the reaction were isolated and characterized. The reactions were performed in triplicate for each substrate to ensure reproducibility and the yields are reported averages (Table 3). Unfortunately, while all the mono-methoxybenzophenone **16** was consumed during the reaction, nothing from the reaction could be successfully characterized. *ortho*-Dimethoxybenzophenone **17** resulted in the synthesis of xanthone **24**. Trimethoxybenzophenone **18** allowed for the formation of the novel spirofuran **25**. The three remaining dimethoxybenzophenones **19-21** afforded the unexpected novel biaryl dimers **26**, **27** and **28** respectively, albeit in low yields.

Table 3 – Products resulting from exposing benzophenones 16-21 to CAS for 18 h

Benzophenone	Product	Average Yield of triplicate experiments
16	**None**	**-**
17	 **24**	**60%**
18	 **25**	**59%**
19	 **26**	**24%**
20	 **27**	**18%**

21	 **28**	**15%**

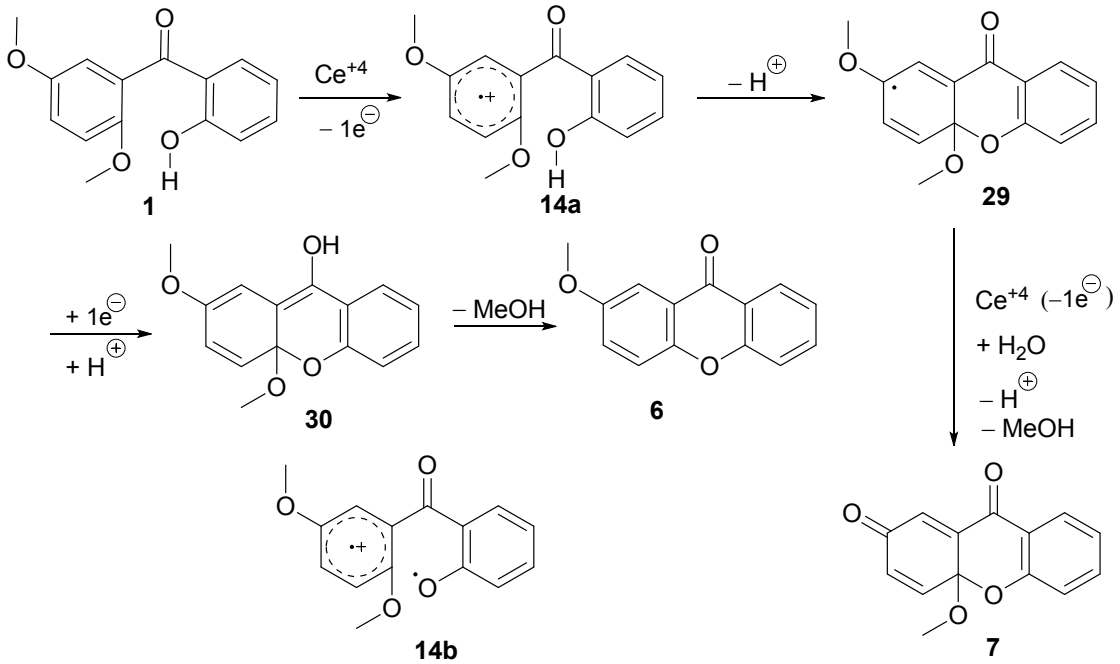
The structures of the dimers **26**-**28** were initially determined from NMR spectroscopic and HRMS data and the structure of **26** was later confirmed by obtaining the X-ray crystal structure (details available in the supplementary information). While the formation of these dimers was an unexpected result and unprecedented under these conditions, related dimers have been reported under oxidative CAN conditions.[10,11]

Combining the results previously obtained[8] and repeated under optimal conditions as shown in Table 1 with the new results obtained in Table 3 has allowed us to examine more fully the scope and limitations of the CAS-mediated reaction, as well as speculate on a more defined mechanism.

Firstly, for the CAS-mediated reaction to take place resulting in the formation of xanthones (e.g. **24**) diones, (e.g. **12**) or spiro-containing compounds (e.g. **25**) at least two aromatic methoxy substituents are required on the electron-rich benzene ring to assist in the formation of radical cations such as **14a** (Scheme 3). In addition, one of the methoxy substituents needs to be situated *ortho* to the ketone bridge and the second methoxy substituent needs to be situated either *ortho* (*e.g.* **17** → **24**) or *para* (*e.g.* **1** → **6** +**7**) to the first methoxy substituent on the same aromatic ring. Thus, we propose that oxidation of the benzophenone **1** occurs as shown in the example in Scheme 3 to afford the previously proposed radical cation **14a**. The oxidation of the electron-rich aromatic ring of **1** to afford the radical cation **14a** is expected as a result of evidence provided by ESR and UV spectroscopic measurements in the single electron transfer oxidation (SET) of 1,4-dimethoxybenzene.[12] In addition, it has often been speculated[13] that with electron rich aromatic compounds SET oxidations take place to afford aromatic radical cations

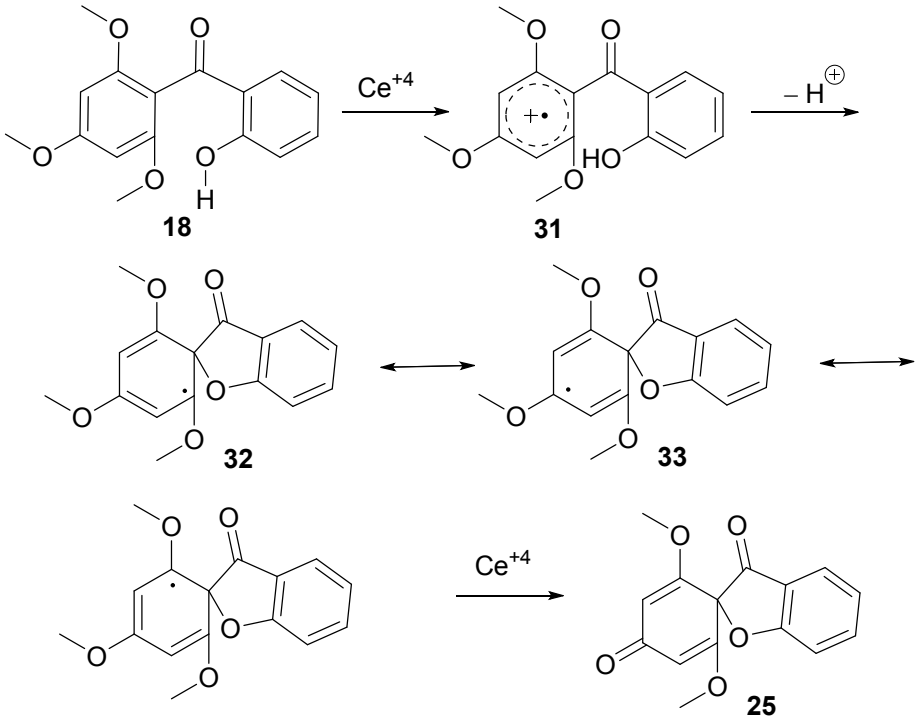
similar to **14a**. However, we cannot rule out the possibility of the reaction proceeding by way of the related phenoxy radical **14b**, particularly as the reactions of **19-21** lead to biaryl compounds that must be formed from oxidative coupling of the phenols.

Subsequent addition of the phenol of **14a** to the methoxy-containing radical cation benzene ring would afford the resonance stabilized ring closed radical intermediate **29** where the *para* positioned methoxy substituent of **29** provides further stabilization of the radical. If the reaction proceeds *via* the oxygen-centred radical **14b**, the key cyclization step would be homolytic in nature and would result in a cationic intermediate equivalent to radical **29**. In order for the intermediate **29** to regain aromaticity, to allow for the formation of xanthone **6,** formally the loss of a methoxy radical would have to take place. For this to occur, the driving force for reforming the aromatic ring would facilitate the process. Alternatively, reduction of the radical **29**, by oxidation of another molecule of **1** in the presence of a proton source would lead to the formation of enol **30**. Spontaneous elimination of methanol from **30** would allow for the formation of xanthone **6**. Alternatively, the ring closed intermediate **29** could undergo a further oxidation to afford the dione **7**, *via* the oxocarbenium ion, followed by the addition of water as shown in Scheme 3.



Scheme 3 – Proposed mechanism for the formation of xanthone 6 and dione 7

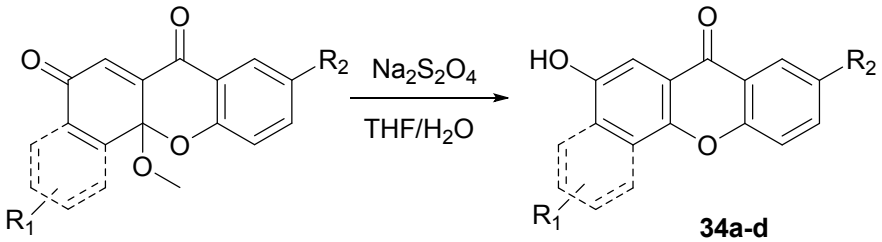
Alternatively, with the 1,3,5-trimethoxy-containing aromatic compound **18**, phenol addition, or phenoxy radical addition, to the radical cation **31** would result in radical intermediate **32**, which could be further stabilized through resonance by all three aromatic methoxy substituents (Scheme 4). Further oxidation of **33** followed by the addition of water, as before, would result in the formation of spirofuran **25**. It must be noted that in order for the spirofuran to form three aromatic methoxy substituents are required. This was also shown to be the case in the JOC Note we previously published.[8]



Scheme 4 – Proposed mechanism for the formation of spirofuran 25

Finally, the formation of the biaryl *para*-dimers **26-29** must occur by means of a classical oxidative phenoxy radical-mediated dimerization process from the corresponding phenols **21-23**, albeit in low yields. Clearly, the mechanistic rationale for this transformation would require an intermediate phenoxy-type radical, analogous to **14b**. In these examples, as the second methoxy substituent is not *ortho* or *para* to the methoxy substituent situated *ortho* to the ketone bridge the formation of xanthones or diones does not take place. In these reactions we were unable to detect or isolate any of the *ortho*-coupled biaryl dimers. However, we cannot exclude the formation of these types of products, or possibly products that would react further to form polymeric-type materials.

The unique dione structures of **7**, **8**, **11** and **12** are not naturally occurring scaffolds, however, they are structurally similar to the xanthone core. We therefore wished to develop methodology that could be used to transform these diones into their xanthone counterparts. Treatment of diones, **7**, **8**, **11** and **12** with sodium dithionite in a THF/H_2O suspension at room temperature afforded the hydroxy-containing xanthones **34a-d** as shown in Scheme 5.



34a-d

	R_1	R_2
7	H	H
11	H	Cl
8	naphthyl	H
12	naphthyl	Cl

	R_1	R_2	Yield
a	H	H	90%
b	H	Cl	75%
c	naphthyl	H	64%
d	naphthyl	Cl	68%

Scheme 5 – Conversion of diones to xanthones

Conclusion

In conclusion, we have further expanded upon the novel ceric ammonium sulfate (CAS) oxidative cyclization reaction developed in our labs. Although debatable, we believe that the first oxidation takes place on the more electron rich aromatic ring containing at least two aromatic methoxy substituents. Once the aromatic radical cation is formed this allows for the phenolic oxygen's lone pair or the phenoxy radical on the adjacent aromatic ring to add to the radical cation forming a new carbon-oxygen bond. Depending on the electronic nature of the benzophenone and the arrangement of the methoxy substituents, a variety of products are isolated including xanthones, 9*H*-xanthen-2,9(4a*H*)-diones, 3*H*-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-3,4'-diones, as well as the dimers **26**, **27** and **28**.

Further details of this oxidative mechanism have also been outlined. In summary, the xanthone and dione products require at least one methoxy substituent to allow for stabilization in the intermediate radical (for example, structure **29**) as in the formation of products **6** and **24** from **1** and **17** respectively. Utilizing hydroxyl benzophenones **19** and **20** does not allow for further stabilization of the intermediate radical by the aromatic methoxy substituents and results in the formation of dimers **26** and **27**. While

starting material **21** does possess a suitably positioned aromatic methoxy substituent, it does not bear an aromatic methoxy group at the site of nucleophilic attack. Hence exposure of **21** to CAS results in the formation of the biaryl compound **28**. Finally, the spiro-containing product **25** is formed as each of the three aromatic methoxy substituents allow for stabilization of the radical as shown in Scheme 4 which is uniquely present in starting material **18**.

In addition, it has been shown that CAS is superior to CAN for these types of transformations. In fact based on the yields for the oxidation reactions mediated by CAN it is clear that it is not a suitable reagent for these transformations. Furthermore, we have shown that the novel diones **7**, **8**, **11** and **12** could be converted into xanthones **34a-d** under reductive conditions.

Experimental

The solvents and reagents used for this project were purchased from ACE Chemicals or Sigma-Aldrich and used without purification unless otherwise stated. Acetonitrile (MeCN) was distilled over calcium hydride under nitrogen gas. Tetrahydrofuran (THF) was distilled over sodium wire and benzophenone under nitrogen gas. Thin layer chromatography (TLC) was performed on aluminium-backed ALUGRAM Sil G/$UV_2$54 plates that are pre-coated with 0.25 mm silica gel 60. The compounds were detected using ultraviolet light. Flash column chromatography was performed using silica gel (particle size 0.035-0.070 mm). ^{1}H NMR spectra were recorded on spectrometers operating at 500 MHz and 300 MHz respectively. All spectra were recorded in deuterated chloroform (C*D*Cl_3), deuterated methanol (CD_3O*D*) and deuterated dimethyl sulfoxide (d_6-DMSO) with all chemical shift values reported in parts per million referenced against 0.03% tetramethylsilane (TMS) as an internal standard. Coupling constants, *J*, are reported in Hertz (Hz). Commonly used abbreviations in assignments include: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. 75.47 MHz and 125 MHz ^{13}C NMR (^{1}H decoupled) spectra were recorded either at 75 MHz or 126 MHz. All spectra were recorded in C*D*Cl_3, CD_3O*D* or d_6-DMSO and the chemical shifts are reported on the δ scale in parts per million (ppm) relative to the central signal of C*D*Cl_3 taken as 77.0 ppm, CD_3O*D* as 49.0 ppm and d_6-DMSO as 39.5 ppm. Infrared spectra were recorded where all predominant absorptions are reported in terms of wavenumbers (ν/cm^{-1}). IR spectra were obtained only for compounds where no IR data was available

and for final compounds. High resolution mass spectra (HRMS) were recorded and quoted in relative abundance (*m/z*). HRMS was performed only on novel compounds where no MS data was available as well as for final compounds. Melting points were recorded and are reported without correction. Single crystal X-ray diffraction data were collected on a CCD area detector diffractometer with graphite monochromated Mo K α-radiation (50kV, 30mA) using the APEX 2 data collection software. The collection method involved ω-scans of width 0.5° and 512x512 bit data frames. Data reduction was carried out using the program *SAINT+* version 6.02.6 software and *SADABS* was used to make empirical absorption corrections.[14] *SHELXS-97* was used to solve crystal structures by direct methods.[14] After initial isotropic refinements of non-hydrogen atoms, further anisotropic refinements were done by full matrix least-squares calculations based on F^2 using *SHELXL-97*.[14] C-bound H atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms, with thermal displacement parameters 1.2 times of the parent C atom. Where possible, the coordinates and isotropic displacement parameters of the N–bound and O–bound H atoms involved in the hydrogen bonding interactions were allowed to refine freely. Diagrams and publication material were generated using *WinGX*[15] and *ORTEP-3* and the displacement ellipsoids shown at a 50% probability level.[16]

General experimental procedure for the Ceric Ammonium Sulfate (CAS) mediated oxidation of benzophenones **1-5**, and **16-21**. A $CHCl_3$ and MeCN solution (1:4 v/v) was used to dissolve the phenol-containing benzophenone derivatives. Once the benzophenone had completely dissolved, water (double the volume than that of the $CHCl_3$) was added and a suspension resulted. $CAS \cdot 2H_2O$ (2-4 eq) was added slowly and the suspension stirred at room temperature overnight. The mixture was then transferred to a separating funnel and EtOAc and water added. The water layer was run off and the organic layer was washed further with sat $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 concentrated *in vacuo* and purified by column chromatography to afford products **6-12** as described previously[8] but in the yields shown in Table 1. In addition, products **24-28** were also isolated.

2-Methoxy-9H-xanthen-9-one **(6) and** ***4a-methoxy-2H-xanthene-2,9(4aH)-dione*** **(7)**. The general procedure was followed using (2,5-dimethoxyphenyl)(2-hydroxyphenyl)methanone, (**1**) (0.400 g, 1.688

mmol) and CAS·$2H_2O$ (3.350 g, 5.296 mmol, 3.14 eq). Purification using flash column chromatography 10-20 % EtOAc/Hexane resulted in a white solid and yellow crystals being collected. Using NMR spectroscopy, the white powder was determined to be *2-methoxy-9H-xanthen-9-one,* **6** (0.142 g, 36 %) and the yellow crystals to be *4a-methoxy-2H-xanthene-2,9(4aH)-dione,* **7** (0.153 g, 36 %). *Note: the yields reported in the experimental were obtained for a single experiment, while the yields reported in Table 1 were the average yields obtained over at least three experiments.

***2-Methoxy-9H-xanthen-9-one* (6). M.p.** = 127-128 °C, lit 131-133 °C.[8] **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 8.36 (1H, dd, *J* = 8.0 and 1.7 Hz), 7.76 – 7.68 (2H, m), 7.49 (1H, dd, *J* = 8.5 and 1.2 Hz), 7.45 (1H, d, *J* = 9.1 Hz), 7.41 – 7.37 (1H, m), 7.37 – 7.33 (1H, m), 3.93 (3H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 177.1, 156.1, 156.0, 151.0, 134.6, 126.7, 124.9, 123.7, 122.2, 121.3, 119.4, 118.0, 105.9, 55.9; **IR** $\nu_{max.}$(cm^{-1}) = 2972, 2938, 2868, 2851, 1670, 1636, 1601, 1462, 1288, 1236, 1219, 1202, 1150, 1097, 1045, 1028, 1011, 959, 941, 854, 820, 785, 750, 698, 629. ***4a-Methoxy-2H-xanthene-2,9(4aH)-dione* (7)**. **M.p.** = 108-110 °C, 110-112 °C.[8] **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 8.02 (1H, dd, *J* = 7.9 and 1.8 Hz), 7.60 (1H, ddd, *J* = 8.3, 7.3 and 1.7 Hz), 7.18 (1H, ddd, *J* = 8.0, 7.3 and 1.1 Hz), 7.14 – 7.07 (2H, m), 6.89 (1H, d, *J* = 2.0 Hz), 6.44 (1H, dd, *J* = 10.4 and 2.0 Hz), 3.35 (3H, s). **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 185.0, 180.9, 157.0, 144.5, 140.1, 137.0, 130.7, 128.5, 127.5, 123.3, 121.7, 118.5, 95.1, 51.3; **IR** $\nu_{max.}$(cm^{-1}) = 2972, 2938, 2868, 2851, 1670, 1636, 1601, 1462, 1288, 1236, 1219, 1202, 1150, 1097, 1045, 1028, 1011, 959, 941, 854, 820, 785, 750, 698, 629.

***12a-Methoxy-5H-benzo[c]xanthene-5,7(12aH)-dione* (8).** (1,4-Dimethoxynaphthalen-2-yl)(2-hydroxyphenyl)methanone **2** (0.120 g, 0.434 mmol) in a 4:2:1 MeCN:H_2O:$CHCl_3$ solvent mixture was exposed to CAS·$2H_2O$ (0.824 g, 1.303 mmol, 3.00 eq) for 18 h. After purification by flash column chromatography in 20 % EtOAc/Hexane, an orange solid resulted. NMR spectroscopy was used to confirm the identity of *12a-methoxy-5H-benzo[c]xanthene-5,7(12aH)-dione*, **8** (0.092 g, 73 %). **M.p.** = 139-140 °C, lit 162-165 °C.[8] **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H = 8.15 (1H, dd, *J* = 7.9 and 1.4 Hz), 8.03 (2H, m), 7.80 (1H, td, *J* = 7.6 and 1.4 Hz), 7.62 (2H, m), 7.19 (1H, d, *J* = 1.4 Hz), 7.19 – 7.16 (2H, m), 3.03 (3H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 184.0, 180.9, 157.7, 143.7, 137.0, 136.6, 133.9, 130.8, 130.6, 130.2, 127.5, 126.9, 126.5, 123.2, 121.5, 118.6, 96.4, 51.3; **IR** $\nu_{max.}$(cm^{-1}) = 3069, 2936,

2833, 1726, 1691, 1666, 1607, 1458, 1387, 1294, 1267, 1219, 1134, 1103, 1067, 1016, 943, 870, 756, 737, 702, 660; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{18}H_{13}O_4$ 293.0814, found 293.0811.

***2,3-Dimethoxy-9H-xanthen-9-one* (9)**. Following the general procedure, (2-hydroxyphenyl)(2,4,5-trimethoxyphenyl)methanone **3** (0.167 g, 0.579 mmol) exposed to CAS·$2H_2O$ (1.466 g, 2.317 mmol, 4.00 eq) resulted in a single product that was determined to be *2,3-dimethoxy-9H-xanthen-9-one* **9**. This was collected as yellow crystals (0.122 g, 69 %). **M.p.** = 153-155 °C, lit 170-172 °C.[8] **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 8.35 (1H, ddd, *J* = 8.0, 1.8 and 0.5 Hz), 7.74 – 7.65 (2H, m), 7.47 (1H, ddd, *J* = 8.5, 1.1 and 0.5 Hz), 7.38 (1H, ddd, *J* = 8.2, 7.1 and 1.1 Hz), 6.93 (1H, s), 4.03 (3H, s), 4.01 (3H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 176.1, 156.1, 155.5, 152.5, 146.8, 134.0, 126.6, 123.8, 121.6, 117.7, 115.0, 105.5, 99.7, 56.5, 56.4; **IR** $\nu_{max.}$(cm^{-1}) = 2972, 2938, 2868, 2833, 1653, 1601, 1514, 1462, 1427, 1306, 1271, 1236, 1201, 1132, 1063, 1028, 1011, 941, 854, 820, 785, 750, 698, 646.

***2-Chloro-7-methoxy-9H-xanthen-9-one* (10) *and 7-chloro-4a-methoxy-2H-xanthene-2,9(4aH)-dione* (11).** When exposed to CAS·$2H_2O$ (2.644 g, 4.180 mmol, 4.00 eq), (5-chloro-2-hydroxyphenyl)(2,5-dimethoxyphenyl)methanone, **4** (0.306 g, 1.045 mmol) was transformed into two products. The two products were separated by flash column chromatography and collected as a light pink solid that was found to be *2-chloro-7-methoxy-9H-xanthen-9-one,* **10** (0.027 g, 26 %) and a yellow solid that was found to be *7-chloro-4a-methoxy-2H-xanthene-2,9(4aH)-dione,* **11** (0.114 g, 40 %).

***2-Chloro-7-methoxy-9H-xanthen-9-one* (10). M.p.** = 171-172 °C, lit 130-133 °C.[8] **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 8.31 (1H, d, *J* = 2.6 Hz), 7.69 (1H, d, *J* = 3.2 Hz), 7.65 (1H, dd, *J* = 8.9 and 2.6 Hz), 7.45 (2H, dd, *J* = 9.0 and 6.2 Hz), 7.35 (1H, dd, *J* = 9.1 and 3.1 Hz), 3.92 (3H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 176.0, 156.3, 154.4, 150.9, 134.7, 129.5, 126.0, 125.3, 122.1, 121.8, 119.7, 119.5, 105.8, 56.0; **IR** $\nu_{max.}$(cm^{-1}) = 3071, 2980, 2953, 2853, 1655, 1612, 1485, 1462, 1445, 1364, 1292, 1242, 1209, 1144, 1123, 1107, 1024, 993, 904, 872, 814, 785, 719, 687, 629.

***7-Chloro-4a-methoxy-2H-xanthene-2,9(4aH)-dione* (11). M.p.** = 143-144 °C, 122-124 °C.[8] **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.97 (1H, d, *J* = 2.7 Hz), 7.54 (1H, dd, *J* = 8.7 and 2.7 Hz), 7.08 (2H, dd, *J* = 9.5 and 8.7 Hz), 6.89 (1 H, d, *J* = 2.0 Hz), 6.45 (1H, dd, *J* = 10.4 and 2.0 Hz), 3.35 (3H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 184.7, 180.0, 155.4, 143.8, 139.7, 136.7, 130.9, 129.0, 129.0,

126.9, 122.6, 120.2, 95.3, 51.4; **IR** $\nu_{max.}(cm^{-1})$ = 3071, 3005, 2945, 2831, 1668, 1643, 1603, 1468, 1422, 1288, 1267, 1203, 1142, 1099, 1003, 945, 837, 821, 779, 714, 677.

9-Chloro-12a-methoxy-5H-benzo[c]xanthene-5,7(12aH)-dione **(12).** The general procedure was followed using (5-chloro-2-hydroxyphenyl)(1,4-dimethoxynaphthalen-2-yl)methanone, **5** (0.183 g, 0.534 mmol) and CAS·$2H_2O$ (1.351 g, 2.136 mmol, 4.00 eq) resulting in the formation of *9-chloro-12a-methoxy-5H-benzo[c]xanthene-5,7(12aH)-dione,* **12**. This was collected as a yellow solid (0.146 g, 84 %). **M.p.** = 158-160 °C, lit 162-165 °C.[8] **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 8.16 (1H, ddd, *J* = 7.8, 1.4 and 0.6 Hz), 8.03 – 7.97 (2H, m), 7.81 (1H, ddd, *J* = 7.9, 7.4 and 1.4 Hz), 7.63 (1H, td, *J* = 7.6 and 1.3 Hz), 7.56 (1H, dd, *J* = 8.8 and 2.7 Hz), 7.21 (1H, s), 7.19 – 7.13 (1H, m), 3.02 (H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 183.7, 180.1, 156.2, 143.0, 136.7, 136.2, 134.0, 131.1, 130.8, 130.4, 128.9, 127.0, 126.9, 126.5, 122.4, 120.2, 96.7, 51.4; **IR** $\nu_{max.}(cm^{-1})$ = 3109, 2974, 2936, 2820, 1682, 1663, 1624, 1605, 1470, 1412, 1258, 1200, 1142, 1123, 1065, 1026, 987, 949, 891, 833, 775, 737, 718, 679, 660, 621.

General experimental procedure for the Ceric Ammonium Nitrate (CAN) mediated oxidation of benzophenones **1-3**. A $CHCl_3$ and MeCN solution (1:4 v/v) was used to dissolve the phenol-containing benzophenone derivatives. Water (half the volume of the acetonitrile) was used to dissolve the CAN (3-5 eq) and this was added dropwise to the rapidly stirring solution at rt. After 10 mins, TLC analysis of the reaction mixture showed no more starting material remained and the reaction was quenched with aq. $NaHCO_3$. The resulting precipitate was filtered off and washed with EtOAc and the filtrate transferred to a separating funnel. Further portions of EtOAc and water added to the separating funnel, the organic layer collected and dried over anhydrous Na_2SO_4. After concentration *in vacuo*, the mixture was purified by column chromatography to afford products **7, 8** and **13.**

4a-methoxy-2H-xanthene-2,9(4aH)-dione **(7)**. The general procedure was followed using (2,5-dimethoxyphenyl)(2-hydroxyphenyl)methanone, (**1**) (0.100 g, 0.387 mmol) and CAN (1.058 g, 1.936 mmol, 5.0 eq). Purification using flash column chromatography 10-20 % EtOAc/Hexane resulted in yellow crystals being collected that were found to be **7** (0.015 g, 16 %).

12a-Methoxy-5H-benzo[c]xanthene-5,7(12aH)-dione **(8).** (1,4-Dimethoxynaphthalen-2-yl)(2-hydroxyphenyl)methanone **2** (0.200 g, 0.642 mmol) and CAN (1.052 g, 1.927 mmol, 3.0 eq) were combined according to the general procedure. The orange solid that was found to be **8** (0.048 g, 26 %).

2'',5-Dimethoxy-3H-spiro[benzofuran-2,1'-cyclochexa[2,5]diene]3,4'-dione **(13).** Benzophenone **3** (0.260 g, 0.902 mmol) in MeCN (15 ml) and CAN (1.711 g, 2.706 mmol, 3.0 eq) were combined following the general procedure. After 10 mins no starting material was observed on the TLC plate and a new spot was evident. After the work up procedure, drying over anhydrous Na_2SO_4 and concentration *in vacuo* the product was purified by flash column chromatography with 10-20 % EtOAc/Hexane as the eluent. A white solid was collected (0.036 g, 13 %) and determined to be **13** following characterization by NMR spectroscopy. **M.p.** = 103-105 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.77 – 7.67 (2H, m, H-5 and H-7), 7.26 – 7.21 (1H, m, H-4), 7.18 (1H, ddd, *J* = 7.9, 7.2 and 0.8 Hz, H-6), 5.77 (1H, s, H-12), 5.20 (1H, s, H-9), 3.69 (3H, s, H-14), 3.68 (3H, s, H-15); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 195.4, 181.3, 172.5, 168.0, 153.3, 139.0, 125.7, 122.7, 119.9, 113.9, 104.0, 103.0, 86.1, 56.6, 55.6: **IR (ν_m.cm^{-1})** = 3063, 2938, 2852, 1719, 1666, 1643, 1601, 1506, 1456, 1402, 1337, 1261, 1205, 1171, 1099, 1084, 1032, 991, 924, 887, 850, 750, 706, 629; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{15}H_{13}O_5$ 273.0757, found 273.0650.

(2-Hydroxyphenyl)(2-methoxyphenyl)methanone **(16)**.[17] In a 2-neck round bottomed flask, dry magnesium (0.183g, 7.54 mmol, 1.60 eq) was weighed out and a stirrer bar added, followed by a rubber septum and condenser. The entire chamber was then evacuated, further dried under evacuation and the chamber filled with nitrogen (repeated 3 times). Once filled with nitrogen for the final time, THF (5 ml) was injected followed by the 2-bromoanisole (1.32 g, 7.07 mmol, 1.50 eq). Heat was applied as necessary to initiate the Grignard reagent formation and then the reaction left to stir until all the magnesium was consumed (approximately 30 min) under a nitrogen atmosphere. To the brown solution, a further 5 ml of THF was added and cooled to 0 °C. 2-(Benzyloxy)benzaldehyde (1.00 g, 4.71 mmol) was dissolved in THF (5 ml) and injected dropwise into the cooled Grignard solution. An immediate color change is observed and a bright yellow color developed while the reaction was left to stir at 0 °C for 2 h. 1M HCl (10 ml) was added to the reaction with vigorous stirring for 10 min, the suspension

transferred to a separation funnel and the aqueous layer removed. The organic layer was further washed with brine before being dried with anhydrous $MgSO_4$ and concentrated *in vacuo*. The product was then purified by column chromatography with using 10-20 % EtOAc/Hexane as the eluent and (2-(benzyloxy)phenyl)(2-methoxyphenyl)methanol was collected as a yellow oil (1.48 g, 99 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.38 – 7.20 (7H, m), 7.18 (1H, dd, *J* = 7.5 and 1.7 Hz), 7.00 – 6.90 (2H, m), 6.87 (2H, d, *J* = 7.7 Hz), 6.43 (1H, d, *J* = 5.5 Hz), 5.05 (2H, d, *J* = 3.8 Hz), 3.77 (3H, s), 3.35 (1H, d, *J* = 5.4 Hz); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 156.9, 155.8, 136.9, 131.6, 131.2, 128.5, 128.3, 127.9, 127.9, 127.8, 127.33, 120.8, 120.6, 111.7, 110.5, 70.1, 67.3, 55.4; **IR** $\nu_{max.}$(cm^{-1}) = 3560, 3442, 3030, 2940, 2839, 1601, 1488, 1449, 1381, 1287, 1238, 1105, 1015, 870, 745, 695, 651; **ESI-MS TOF** (*m/z*) calculated $[M+Na]^+$ for $C_{21}H_{20}O_3Na$ 343.1310, found 343.1302. In a round bottomed flask, (2-(benzyloxy)phenyl)(2-methoxyphenyl)methanol,[18] (1.00 g, 4.71 mmol, 1 eq) was dissolved in 20 ml CH_2Cl_2. To this solution 1.00 g of flash chromatography silica was added followed by PCC (1.49 g, 6.92 mmol, 1.5 eq) in portions. This reaction mixture was stirred under nitrogen for 2 h, a thick brown by product results as the reaction progresses. Once the reaction is completed (as determined by TLC) the reaction was filtered through a glass fritted funnel lined with Celite and flash silica and this plug washed with EtOAc. The filtrate was concentrated *in vacuo* and the resulting product *(2-(benzyloxy)phenyl)(2-methoxyphenyl)methanone* **23a** collected as a viscous yellow oil (1.131 g, 77 %) used with no further purification. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.60 (1H, dd, *J* = 7.6 and 1.8 Hz, 7.52 (1H, dd, *J* = 7.6 and 1.8 Hz), 7.40 (2H, m), 7.22 – 7.17 (3H, m), 7.07 – 7.00 (1H, m), 7.00 – 6.90 (4H, m), 6.82 (1H, dd, *J* = 8.4 and 0.9 Hz), 4.93 (2H, s), 3.59 (3H, d, *J* = 0.6 Hz); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 195.5, 158.3, 157.2, 136.4, 132.6, 132.5, 130.9, 130.6, 130.4, 130.3, 128.2, 127.4, 126.7, 120.8, 120.3, 112.4, 111.6, 70.1, 55.6; **IR** $\nu_{max.}$(cm^{-1}) = 3027, 2944, 2837, 1642, 1596, 1484, 1446, 1382, 1308, 1248, 1161, 1103, 1022, 924, 853, 750, 695, 638. Benzophenone **23a** (1.131 g, 3.716 mmol) and 10 % Pd/C (0.113 g, 10 mass %) in 30 ml of MeOH under a H_2 atmosphere resulted in the formation of benzophenone **16** (0.717 g, 85 %) as a yellow solid after filtration and concentration which was used with no further purification. **M.p.** = 74-75 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.19 (1H, s), 7.51 – 7.41 (2H, m), 7.33 (1H, dd, *J* = 8.0 and 1.8 Hz), 7.28 (1H, dd, *J* = 7.5 and 1.8 Hz), 7.08 – 6.98

(3H, m), 6.79 (1H, ddd, J = 8.1, 7.2 and 1.2 Hz), 3.76 (3H, s); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 202.1, 162.9, 156.6, 136.4, 133.8, 131.9, 128.8, 127.8, 120.5, 120.2, 118.7, 118.0, 111.5, 55.6; **IR** (solid) ν_{max} (cm^{-1}) = 3026, 2968, 2939, 2835, 1601, 1483, 1463, 1447, 1333, 1306, 1279, 1244, 1146, 1117, 1101, 1020, 932, 824, 793, 748, 698, 640; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{14}H_{13}O_3$ 229.0865, found 229.0866.[17]

General procedures for the synthesis of benzophenones **17-21**. The relevant substituted benzene **22b-f** (1.1 eq) was added to a dry 2-necked flask before the flask was fitted with a rubber septum, stirrer bar and attached to a nitrogen line. The flask was evacuated and charged with nitrogen three times before dry THF was added to dilute the benzene. The solution was cooled to -78 °C and *n*-BuLi (1.1 eq) was added dropwise and the reaction mixture stirred at -78°C for 30 mins. In a separate 2-neck flask, benzyl 2-(benzyloxy)benzoate (1 eq) was added, fitted with a stirrer bar and rubber septum and attached to a nitrogen line. The second flask was evacuated and charged with nitrogen three times before the addition of dry THF. Once the ester had completely dissolved, the solution was cooled to -78 °C with high stirring. The lithiated solution from the first flask was added to the ester solution dropwise over several mins. The mixture was left to react at -78 °C for 1-2 h under nitrogen before being quenched with saturated NH_4Cl and warmed to rt. The suspension was extracted with water and washed with EtOAc. The organic layer was further washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting products **23b-f** were purified by flash column chromatography with 10-20 % EtOAc/Hexane as the eluent and characterised by NMR spectroscopy. As the next step 10% palladium on activated carbon (10 mass %) was added to the freshly synthesized benzophenones **23b-f** (1 eq) and the contents carefully dissolved in MeOH. The resulting suspension was then exposed to a H_2 atmosphere at ambient pressure, stirred at room temperature for 12 h. The suspension was filtered through a Celite/flash silica plug to remove the palladium catalyst, washed with EtOAc and concentrated *in vacuo*. If all the palladium was successfully removed the product was used with no further purification, if not the product was purified by silica column chromatography (20% EtOAc/Hexane) resulting in the synthesis of benzophenones **17-21**.

***(2,3-Dimethoxyphenyl)(2-hydroxyphenyl)methanone* (17).**[19] Veratrole **22b** (2.39 g, 17.30 mmol, 1.1 eq) was treated with *n*-BuLi (13.5 ml, 1.28M, 17.30 mmol, 1.1 eq) at -78 °C in dry THF. This solution was added to benzyl 2-(benzyloxy)benzoate (5.00 g, 15.73 mmol) and the general procedure followed. After purification by flash column chromatography, *(2-(benzyloxy)phenyl)(2,3-dimethoxyphenyl)methanone* **23b** was collected as a liquid (2.35 g, 43 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H = 7.62 (1H, dd, *J* = 7.6 and 1.8 Hz), 7.43 (1H, ddd, *J* = 8.3, 7.4 and 1.8 Hz), 7.19 (3H, dd, *J* = 5.1 and 2.0 Hz), 7.07 (1H, dd, *J* = 7.7 and 1.7 Hz), 7.03 (2H, t, *J* = 7.8 Hz), 6.96 (4H, ddd, *J* = 7.9, 5.2 and 1.2 Hz), 4.93 (2H, s), 3.80 (3H, s), 3.52 (3H, s); **^{13}C{H} NMR** (125 MHz, $CDCl_3$): δ_C = 195.7, 157.4, 152.7, 148.0, 136.3, 135.8, 132.9, 130.5, 130.3, 128.2, 127.5, 126.8, 123.6, 121.1, 120.7, 115.1, 112.5, 70.1, 61.3, 56.0; **IR** ν_{max}.(cm^{-1}) = 2943, 2889, 2835, 1647, 1593, 1566, 1485, 1458, 1431, 1377, 1296, 1269, 1242, 1161, 1107, 1080, 1053, 1026, 999, 972, 837, 756, 702, 621; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{22}H_{21}O_4$ 349.1440, found 349.1442. Methanol was used to dissolve **23b** (2.35 g, 6.76 mmol) and 5 % Pd/C (0.24 g, 10 mass %) added. After stirring under a H_2 atmosphere and purification according to the general procedure, benzophenone **17** was collected as a white solid (1.16 g, 66 %). **M.p.** = 75-77 °C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 12.16 (1H, s), 7.45 (1H, ddd, *J* = 8.7, 7.2 and 1.8 Hz), 7.35 (1H, dd, *J* = 8.0 and 1.7 Hz), 7.11 (1H, d, *J* = 7.5 Hz), 7.03 (2H, m), 6.85 (1H, dd, *J* = 7.4 and 1.7 Hz), 6.79 (1H, ddd, *J* = 8.2, 7.2 and 1.2 Hz), 3.90 (3H, s), 3.77 (3H, s); **^{13}C{H} NMR** ($CDCl_3$, 75 MHz) δ 201.8, 162.9, 152.8, 146.2, 136.7, 133.9, 133.0, 124.1, 120.1, 119.8, 118.8, 118.0, 114.4, 61.7, 55.9; **IR** (solid) ν_{max} (cm^{-1}) = 3678, 2984, 2868, 2839, 2810, 1624, 1595, 1566, 1479, 1450, 1422, 1335, 1306, 1248, 1161, 1074, 1045, 1016, 959, 843, 814, 785, 756, 698, 669, 611; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{15}H_{15}O_4$ 259.0970, found 259.0972.

***(2-Hydroxyphenyl)(2,4,6-trimethoxyphenyl)methanone* (18).**[20] Combining 2-bromo-1,3,5-trimethoxybenzene **22c** (4.27 g, 17.28 mmol, 1.1 eq), *n*-BuLi (13.5 ml, 17.28 mmol, 1.28 M, 1.1 eq) and benzyl 2-(benzyloxy)benzoate (5.00 g, 15.71 mmol, 1 eq) according to the general procedure resulted in the formation of a yellow oil that was determined to be *(2-(benzyloxy)phenyl)(2,4,6-trimethoxyphenyl)methanone* **23c** (2.65 g, 45 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.72 (1H, dd, *J* = 7.7 and 1.9 Hz), 7.35 (1H, ddd, *J* = 8.3, 7.3 and 1.9 Hz), 7.24 (3H, dd, *J* = 5.0 and 1.9 Hz), 7.12 (2H, dd,

J = 6.7 and 2.9 Hz), 7.00 – 6.88 (2H, m), 5.96 (2H, s), 4.89 (2H, s), 3.72 (3H, s), 3.52 (6H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 193.3, 162.1, 158.8, 157.9, 136.5, 133.1, 131.3, 130.3, 128.1, 127.5, 127.3, 120.5, 114.8, 113.0, 90.8, 70.3, 55.8, 55.2; **IR** ν_{max} (cm^{-1}) = 3001, 2978, 2931, 2862, 2839, 1659, 1485, 1458, 1431, 1377, 1296, 1242, 1161, 1107, 1026, 999, 918, 891, 849, 802, 779, 756, 733, 687, 640, 617; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{23}H_{23}O_5$ 379.1545, found 379.1546. The benzyl group of **22c** (2.342 g, 6.19 mmol) was removed using 5 % Pd/C (0.234 g, 10 mass %) under a H_2 atmosphere as described in the general procedure. After filtration the product was recrystallized from isopropyl alcohol resulting in the collection of light yellow crystals of **18** (1.322 g, 74 %). **M.p.** = 144-146 °C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 12.23 (1H, s), 7.44 (1H, ddd, *J* = 8.6, 7.1 and 1.8 Hz), 7.32 (1H, dd, *J* = 8.0 and 1.8), 7.00 (1H, dd, *J* = 8.4 and 1.2 Hz), 6.78 (1H, ddd, *J* = 8.2, 7.2 and 1.1 Hz), 6.17 (2H, s), 3.86 (3H, s), 3.71 (6H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 201.1, 162.8, 162.6, 158.4, 136.2, 133.2, 121.4, 118.7, 117.8, 109.7, 90.7, 55.9, 55.5; **IR** (solid) ν_{max} (cm^{-1}) = 3686, 2970, 2943, 2930, 2862, 2862, 2849, 1607, 1580, 1485, 1404, 1337, 1296, 1242, 1229, 1202, 1188, 1148, 1121, 1053, 1026, 1013, 959, 932, 824, 797, 756, 716; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{16}H_{17}O_5$ 289.1076, found 289.1082.[20]

(2,4-Dimethoxyphenyl)(2-hydroxyphenyl)methanone* (19)**.[21] Combining 1-bromo-2,4-dimethoxybenzene **22d** (3.77 g, 17.30 mmol, 1.1 eq), *n*-BuLi (13.5 ml, 17.30 mmol, 1.28 M, 1.1 eq) and benzyl 2-(benzyloxy)benzoate (5.00 g, 15.73 mmol, 1 eq) according to the general procedure resulted in the formation of a yellow oil that was determined to be *(2-(benzyloxy)phenyl)(2,4-dimethoxyphenyl)methanone* **23d** (5.03 g, 92 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.58 (1H, dd, *J* = 8.7 and 1.3 Hz), 7.50 (1H, dd, *J* = 7.5 and 1.8 Hz), 7.42 – 7.34 (1H, m), 7.24 – 7.17 (3H, m), 7.06 – 6.96 (3H, m), 6.94 (1H, dd, *J* = 8.4 and 1.0 Hz), 6.48 (1H, dd, *J* = 8.6 and 2.3 Hz), 6.33 (1H, d, *J* = 2.2 Hz), 4.95 (2H, s), 3.81 (3H, s), 3.57 (3H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 194.1, 164.1, 160.7, 156.6, 136.6, 133.0, 132.0, 131.7, 129.8, 128.1, 127.4, 126.6, 123.2, 120.8, 112.3, 104.7, 98.6, 70.1, 55.6, 55.4; **IR** ν_{max}.(cm^{-1}) = 3013, 2947, 2843, 1624, 1601, 1504, 1483, 1433, 1333, 1306, 1285, 1242, 1209, 1150, 1144, 1030, 945, 826, 758; **ESI-MS TOF (m/z***)** calculated $[M+H]^+$ for $C_{22}H_{21}O_4$ 349.1440, found 349.1438. Ketone **23d** (4.86 g, 13.99 mmol) and 5 % Pd/C (0.486 g, 10 mass %) were combined

according to the general hydrogenation procedure. A yellow oil was collected after purification and confirmed to be **19** (2.58 g, 71 %). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 12.24 (1H, s), 7.42 (2H, m, *J* = 8.3, 7.9 and 1.7 Hz), 7.27 (1H, d, *J* = 8.1 Hz), 7.00 (1H, dd, *J* = 8.4 and 1.2 Hz), 6.79 (1H, ddd, *J* = 8.1, 7.2 and 1.1 Hz), 6.59 – 6.46 (2H, m), 3.86 (3H, s), 3.74 (3H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 125 MHz) δ 201.2, 163.2, 162.8, 158.6, 136.1, 133.8, 131.0, 120.7, 120.5, 118.5, 118.0, 104.6, 98.9, 55.6, 55.5; **IR** ν_{max} (cm^{-1}) = 2936, 2839, 1605, 1508, 1470, 1412, 1335, 1315, 1277, 1238, 1200, 1161, 1123, 1026, 949, 949, 910, 949, 910, 833, 795, 756, 737, 698, 640, 621; **ESI-MS TOF** (*m/z*) calcd for $C_{15}H_{15}O_4$ 259.0970, found 259.0974.

***(2,6-Dimethoxyphenyl)(2-hydroxyphenyl)methanone* (20)**.[19] 1,3-dimethoxybenzene **22e** (2.39 g, 17.30 mmol, 1.1 eq) and *n*-BuLi (13.5 ml, 1.28 M, 17.30 mmol, 1.1 eq) at -78 °C in dry THF. This solution was added to benzyl 2-(benzyloxy)benzoate (5.00 g, 15.73 mmol, 1 eq) also at -78 °C and the reaction mixture stirred for 2 h. The reaction was quenched and purified as outlined in the general procedure and *(2-(benzyloxy)phenyl)(2,6-dimethoxyphenyl)methanone* **23e** was collected as a peach solid (4.41 g, 81 %). **M.p.** = 85-87 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.77 (1H, dd, *J* = 7.7 and 1.8 Hz), 7.37 (1H, ddd, *J* = 8.4, 7.3 and 1.9 Hz), 7.30 (2H, d, *J* = 4.6 Hz), 7.24 (2H, dd, *J* = 5.2 and 1.8 Hz), 7.15 (1H, d, *J* = 8.5 Hz), 7.13 – 7.09 (1H, m), 6.96 (1H, dd, *J* = 7.6 and 1.0 Hz), 6.94 – 6.87 (1H, m), 6.42 (2H, d, *J* = 8.4 Hz), 4.90 (2H, s), 3.55 (6H, s); **^{13}C**{H} **NMR** (75 MHz, $CDCl_3$): δ_C = 194.1, 158.3, 157.3, 136.4, 133.6, 131.7, 130.1, 128.2, 127.4, 127.2, 126.9, 120.5, 113.2, 104.2, 70.3, 55.8; **IR** ν_{max}.(cm^{-1}) = 2943, 2889, 2835, 2376, 1674, 1593, 1485, 1458, 1431, 1296, 1269, 1242, 1161, 1107, 1026, 999, 945, 918, 864, 783, 756, 729, 702, 621; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{22}H_{21}O_4$ 349.1440, found 349.1440. Following the general procedure, benzophenone **23e** (4.08 g, 11.71 mmol) H_2 gas and 5 % Pd/C (0.41 g, 10 mass %) was used to remove the benzyl group resulting in the collection of a yellow solid that was confirmed to be **20** (1.82 g, 60 %). **M.p.** = 104-107°C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 12.15 (1H, s), 7.44 (1H, ddd, *J* = 8.7, 7.2 and 1.8 Hz), 7.36 (1H, t, *J* = 8.4 Hz), 7.28 (1H, dd, *J* = 7.9 and 1.7 Hz), 7.01 (1H, dd, *J* = 8.4 and 1.1 Hz), 6.77 (1H, ddd, *J* = 8.1, 7.2 and 1.1 Hz), 6.62 (2H, d, *J* = 8.4 Hz), 3.71 (6H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 201.3, 162.5, 157.3, 136.4, 133.0, 131.3, 121.0, 118.9, 117.9, 116.5, 104.0, 55.9; **IR** (solid) ν_{max} (cm^{-1}) = 3699, 2978,

2936, 2851, 1620, 1578, 1472, 1450, 1366, 1344, 1302, 1281, 1238, 1132, 1111, 1069, 1026, 941, 835, 793, 772, 750, 729, 623; **ESI-MS TOF** (*m/z*) calcd for $C_{15}H_{15}O_4$ 259.0970, found 259.0971.

(3,4-Dimethoxyphenyl)(2-hydroxyphenyl)methanone* (21)**.[22] Combining 4-bromo-1,2-dimethoxybenzene **22f** (3.78 g, 17.30 mmol, 1.1 eq), *n*-BuLi (13.5 ml, 17.30 ml, 1.1 eq) and benzyl 2-(benzyloxy)benzoate (5.00 g, 15.73 mmol, 1 eq) according to the general procedure resulted in the formation of a yellow oil that was determined to be *(2-(benzyloxy)phenyl)(3,4-dimethoxyphenyl)methanone* **23f** (2.41 g, 44 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.58 (1H, d, *J* = 8.6 Hz), 7.50 (1H, dd, *J* = 7.5 and 1.8 Hz), 7.43 – 7.32 (1H, m), 7.23 – 7.16 (3H, m), 7.05 – 6.93 (4H, m), 6.48 (1H, dd, *J* = 8.6 and 2.3 Hz), 6.33 (1H, d, *J* = 2.3 Hz), 4.95 (2H, s), 3.81 (3H, s), 3.57 (3H, s); **^{13}C**{H} **NMR** (125 MHz, $CDCl_3$): δ_C = 194.1, 164.0, 160.7, 156.6, 136.6, 133.0, 132.0, 131.7, 129.8, 128.1, 127.4, 126.6, 123.2, 120.8, 112.3, 104.7, 98.5, 70.1, 55.6, 55.4; **IR** $\nu_{max.}$(cm^{-1}) = 3024, 2943, 2862, 2376, 1647, 1593, 1521, 1485, 1458, 1431, 1296, 1269, 1107, 1053, 1026, 918, 729, 702; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{22}H_{21}O_4$ 349.1440, found 349.1441. Benzyl protected benzophenone **23f** (2.21 g, 6.34 mmol) was reduced using 5 % Pd/C (0.221 g, 10 mass %) under a H_2 atmosphere. After purification by flash column chromatography, **21** was collected as a yellow solid (1.01 g, 62 %). **M.p.** = 86-89 °C, 76-78 °C.[23] **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 11.97 – 11.82 (1H, s), 7.70 – 7.64 (1 H, m), 7.50 (1H, ddd, *J*= 8.6, 7.1 and 1.6 Hz), 7.36 – 7.30 (2H, m), 7.10 – 7.05 (1H, m), 6.94 (1H, d, *J* = 7.9 Hz), 6.92 – 6.85 (1H, m), 3.97 (3H, s), 3.94 (3H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 199.9, 162.9, 152.7, 149.1, 135.8, 133.3, 130.5, 124.3, 119.5, 118.5, 118.4, 112.2, 110.1, 56.1, 56.1; **IR** (solid) ν_{max} (cm^{-1}) 3424, 3007, 2972, 2936, 2833, 1618, 1584, 1514, 1479, 1462, 1447, 1410, 1358, 1323, 1306, 1254, 1219, 1167, 1132, 1115, 1063, 1028, 976, 889, 854, 820, 802, 768, 750, 698, 646, 611; **ESI-MS TOF** ***(m/z) calculated $[M+H]^+$ for $C_{15}H_{15}O_4$ 259.0970, found 259.0974.

***4-Methoxy-9H-xanthen-9-one* (24).**[19] Benzophenone **17** (0.117 g, 0.453 mmol) was dissolved in MeCN (20 ml), distilled H_2O (10 ml) and $CHCl_3$ (5 ml) under N_2. CAS·$2H_2O$ (1.146 g, 1.812 mmol, 4.00 eq) was added and the reaction mixture stirred rapidly for 18 h. Only a single spot was visualized on the TLC plate. This product was characterised by NMR spectroscopy and determined to be **24** (0.061 g, 60 %). **M.p**. = 178 °C, 175-176 °C.[19] **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.35 (1H, ddd, *J* = 7.9, 1.7 and

0.5 Hz), 7.92 (1H, dd, *J* = 7.8 and 1.8 Hz), 7.74 (1H, ddd, *J* = 8.7, 7.0 and 1.8 Hz), 7.62 (1H, ddd, *J* = 8.5, 1.1 and 0.5 Hz), 7.40 (1H, ddd, *J* = 8.1, 7.1 and 1.2 Hz), 7.32 (2H, m), 4.04 (3H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 177.2, 156.0, 148.7, 146.6, 134.8, 126.7, 124.1, 123.4, 122.8, 121.7, 118.3, 117.7, 115.4, 56.5; **IR** (solid) ν_{max} (cm^{-1}) 2993, 2955, 2916, 2858, 2839, 1663, 1605, 1566, 1489, 1470, 1450, 1354, 1335, 1277, 1258, 1238, 1200, 1142, 1065, 1026, 968, 891, 853, 814, 756, 718, 679, 621; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{14}H_{11}O_3$ 227.0708, found 227.0704.

2',6'-Dimethoxy-3H-spiro[benzofuran-2,1'-cyclohexa[2,5]diene]-3,4'-dione **(25).** To a solution of **18** (0.300 g, 1.041 mmol) in MeCN (40 ml), H_2O (20 ml) and $CHCl_3$ (10 ml), CAS·$2H_2O$ (2.634 g, 4.164 mmol, 4.00 eq) was added and stirred for 18 h. After purification by flash column chromatography, white crystals were collected and identified as **25** (0.166 g, 59 %). **M.p.** = 194-196 °C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.75 – 7.63 (2H, m), 7.26 – 7.20 (1H, m), 7.17 (1H, ddd, *J* = 7.9, 7.2 and 0.8 Hz), 5.64 (2H, d, *J* = 1.0 Hz), 3.64 (6H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 194.4, 186.8, 173.8, 164.8, 138.6, 125.3, 122.7, 120.1, 113.5, 103.5, 84.3, 56.5; **IR** (solid) ν_{max} (cm^{-1}) 2972, 2938, 2920, 2868, 2816, 1722, 1670, 1636, 1601, 1462, 1358, 1323, 1306, 1236, 1219, 1184, 1150, 1097, 1063, 993, 924, 889, 854, 768, 716, 629; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{15}H_{13}O_5$ 273.0763, found 273.0764.

(4,4'-Dihydroxy-[1,1'-biphenyl]-3,3'-diyl)bis((2,4-dimethoxyphenyl)methanone) **(26).** Benzophenone **19** (0.521 g, 2.017 mmol) was dissolved in MeCN (40 ml), H_2O (20 ml) and $CHCl_3$ (5 ml) and CAS·$2H_2O$ (2.552 g, 4.035 mmol, 2.00 eq) was added. After stirring overnight under a N_2 atmosphere and purification by flash column chromatography, **26** (0.082 g, 24 %) was isolated as a white solid. **M.p.** = 171-175 °C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 12.15 (1H, s), 7.51 (1H, dd, *J* = 8.6 and 2.4 Hz), 7.42 (1H, d, *J* = 2.4 Hz), 7.28 (1H, d, *J* = 8.4 Hz), 7.04 (1H, d, *J* = 8.6 Hz), 6.55 (1H, dd, *J* = 8.4 and 2.3 Hz), 6.51 (1H, d, *J* = 2.2 Hz), 3.91 (3H, s), 3.61 (3H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 201.1, 163.3, 162.0, 158.5, 134.4, 131.3, 131.1, 130.8, 120.7, 120.5, 118.5, 104.7, 99.1, 55.6, 55.5; **IR** (solid) ν_{max} (cm^{-1}) 2972, 2938, 2851, 1601, 1584, 1514, 1462, 1410, 1323, 1288, 1236, 1202, 1167, 1132, 1115, 1028, 976, 941, 820, 785, 768, 611; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{30}H_{27}O_8$ 515.1706, found 515.1702.

***(4,4'-Dihydroxy-[1,1'-biphenyl]-3,3'-diyl)bis((2,6-dimethoxyphenyl)methanone)* (27).** A solution of MeCN (30 ml), H_2O (15 ml) and $CHCl_3$ (7.5 ml) was used to dissolve benzophenone **20** (0.291 g, 1.127 mmol) and CAS·$2H_2O$ (2.138 g, 3.380 mmol, 3.00 eq) was added with high stirring for 18 h. Following purification by flash column chromatography **27** was collected as a yellow oil (0.052 g, 18 %). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 12.13 (1H, s), 7.50 (1H, dd, *J* = 8.7 and 2.4 Hz), 7.42 – 7.33 (1H, m), 7.22 (1H, d, *J* = 2.4 Hz), 7.04 (1H, d, *J* = 8.6 Hz), 6.59 (2H, d, *J* = 8.4), 3.63 (6H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 201.1, 161.8, 157.3, 134.9, 131.3, 131.2, 130.5, 120.9, 118.4, 116.3, 104.1, 55.9; **IR** ν_{max} (cm^{-1}) 3009, 2978, 2947, 2839, 1636, 1589, 1466, 1435, 1327, 1281, 1250, 1219, 1157, 1111, 1049, 1034, 941, 833, 787, 756, 725, 632; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{30}H_{27}O_8$ 515.1706, found 515.1707.

***(4,4'-Dihydroxy-[1,1'-biphenyl]-3,3'-diyl)bis((3,4-dimethoxyphenyl)methanone)* (28).** Benzophenone **21** (0.409 g, 1.584 mmol) was dissolved in MeCN (20 ml), H_2O (10 ml) and $CHCl_3$ (5 ml). To this rapidly stirring solution CAS·$2H_2O$ (2.00 g, 3.167 mmol, 2.00 eq) was added under a N_2 atmosphere and stirred overnight. Following purification by flash column chromatography, a yellow solid was collected that was determined to be **28** (0.062 g, 15 %). **M.p.** = 148-150 °C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 11.78 (1H, s), 7.78 (1H, d, *J* = 2.4 Hz), 7.64 (1H, dd, *J* = 8.6 and 2.4 Hz), 7.35 (1H, d, *J* = 2.0 Hz), 7.32 (1H, dd, *J* = 8.2 and 2.0 Hz), 7.13 (1H, d, *J* = 8.6 Hz), 6.86 (1H, d, *J* = 8.2 Hz), 3.96 (3H, s), 3.90 (3H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 199.5, 162.1, 153.0, 149.2, 133.9, 130.9, 130.6, 130.2, 124.5, 119.6, 119.0, 112.1, 109.9, 56.1, 56.0; **IR** (solid) ν_{max} (cm^{-1}) 3013, 2974, 2974, 2936, 2858, 2839, 1624, 1566, 1508, 1470, 1412, 1335, 1258, 1238, 1200, 1180, 1142, 1065, 1026, 872, 814, 795, 756, 698, 660, 621; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ $C_{30}H_{27}O_8$ 515.1706, found 515.1704.

General experimental procedure for the conversion of diones to xanthones (**34a-d**). In a 25 ml round bottomed flask, dione, **7**, **8**, **11** and **12** (1 eq) was dissolved in freshly distilled THF (5 ml). To this 5 ml of water was added and 3 equivalents of sodium dithionite was added to the solution while being stirred at a high speed. Just after the addition of the sodium dithionite a colour change of the mixture was noted and the solution was stirred for a further 15 mins. The reaction was monitored by TLC and when no

further starting material was observed the mixture was transferred to a separation funnel and diluted with 15 ml water and 15 ml diethyl ether. The water layer was removed and the organic layer washed with a further 15 ml of water. Concentrated aq. NaOH (15 ml) was added to the organic layer, the separation funnel stoppered and shaken vigorously. A notable change in colour was observed during shaking. The aqueous layer (now highly coloured) was collected. Further addition of conc. NaOH along with vigorous shaking was repeated until no further colour change was observed in the aqueous layer. The basic aqueous layers that were collected, combined and neutralized by portionwise addition of solid ammonium chloride until a solid precipitated out of solution, the solid collected by filtration and dried in a desiccator overnight. The solids were characterised by NMR, infrared and mass spectroscopy.

2-Hydroxy-9H-xanthen-9-one **(34a)**.[23] Dione **7** (0.100 g, 0.413 mmol) was reduced to **34a** with sodium dithionite (0.216 g, 1.239 mmol, 3.00 eq). The product **34a** was collected as a cream coloured powder (0.079 g, 90 %). **M.p**. = >310 °C. **^{1}H NMR** (CD_3OD, 300 MHz) δ 8.25 (1H, dd, *J* = 8.1 and 1.7 Hz), 7.81 (1H, ddd, *J* = 8.7, 7.1 and 1.7 Hz), 7.60 – 7.54 (2 H, m), 7.49 (1H, d, *J* = 9.1 Hz), 7.43 (1H, ddd, *J* = 8.1, 7.0 and 1.1 Hz), 7.33 (1H, dd, *J* = 9.1 and 3.0 Hz); **^{13}C**{H} **NMR** (CD_3OD, 75 MHz) δ 179.0, 157.7, 155.4, 151.6, 136.3, 127.2, 125.9, 125.0, 123.2, 122.0, 120.5, 119.2, 109.8; **IR** (solid) ν_{max}(cm^{-1}) 3302, 3069, 2947, 2872, 1651, 1614, 1597, 1460, 1342, 1302, 1223, 1146, 1190, 1130, 871, 816, 787, 748, 711, 619; **ESI-MS TOF** (*m/z*) calculated $[M-H]^-$ for $C_{13}H_7O_3$ 211.0401, found 211.0399.

2-Chloro-7-hydroxy-9H-xanthen-9-one **(34b)**.[24] The reduction of dione **11** (0.257 g, 0.929 mmol) was performed using sodium dithionite (0.485 g, 2.786 mmol, 3.00 eq) resulting in the formation of a beige powder **34b** (0.171 g, 75 %) after the work up given in the general procedure. **M.p.** = 250 °C, lit 221-222 °C.[22] **^{1}H NMR** (*d*-DMSO, 500 MHz) δ 7.85 (1H, d, *J* = 2.6 Hz), 7.45 (1H, dd, *J* = 9.0 and 2.7 Hz), 7.26 (1H, d, *J* = 8.9 Hz), 7.21 (1H, d, *J* = 3.0 Hz), 7.17 (1H, d, *J* = 9.1 Hz), 7.01 (1H, dd, *J* = 9.0 and 3.0 Hz); **^{13}C**{H} **NMR** (*d*-DMSO, 126 MHz) δ 180.3, 158.6, 158.4, 154.0, 138.7, 133.0, 128.83, 128.76, 125.5, 124.0, 123.1, 112.4; **IR** (solid) ν_{max} (cm^{-1}) 3312, 2984, 2959, 2878, 1651, 1616, 1476, 1375, 1285, 12238, 1150, 1059, 1034, 1030, 891, 889, 820, 795, 733, 689, 629; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{13}H_8O_3Cl$ 247.0162, found 247.0157.

5-Hydroxy-7H-benzo[c]xanthen-7-one **(34c)**. In the presence of sodium dithionite (0.179 g, 1.026 mmol, 3.00 eq), dione **8** (0.100 g, 0.342 mmol) was reduced to **34c** following the general procedure resulting in the formation of a yellow solid (0.057 g, 64 %). **M.p.** = decomposed at 260 °C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.64 (1H, dt, *J* = 6.8 and 3.4 Hz), 8.34 (1H, dt, *J* = 7.0 and 3.5 Hz), 8.27 – 8.19 (1H, m), 7.94 – 7.84 (2H, m), 7.80 (2H, dt, *J* = 6.4 and 3.5 Hz), 7.50 (1H, ddd, *J* = 8.1, 5.8 and 2.3 Hz), 7.42 (1H, s); **^{13}C**{H} **NMR** ($CDCl_3$, 75 MHz) δ 175.5, 155.1, 151.4, 146.1, 134.4, 129.4, 128.7, 127.4, 125.6, 124.5, 124.2, 123.0, 122.4, 121.1, 118.3, 117.9, 99.1; **IR** (solid) ν_{max}(cm^{-1}) 3329, 3074, 1624, 1607, 1581, 1470, 1420, 1286, 1265, 1234, 1130, 1076, 1022, 889, 858, 842, 771, 745, 698, 661, 635;**ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{17}H_{11}O_3$ 263.0708, found 263.0716.

9-Chloro-5-hydroxy-7H-benzo[c]xanthen-7-one **(34d).** Following the general procedure, dione **12** (0.146 g, 0.447 mmol) was reduced by sodium dithionite (0.233 g, 1.341 mmol, 3.00 eq). The product was collected as a yellow solid and determined to be **34d** (0.090 g, 68 %). **M.p.** = decomposed >270 °C. **^{1}H NMR** (*d*-DMSO, 500 MHz) δ 8.63 – 8.56 (1H, m), 8.29 – 8.24 (1H, m), 8.08 (1H, d, *J* = 1.5 Hz), 7.88 (2H, d, *J* = 1.6 Hz), 7.83 – 7.77 (2H, m), 7.38 (1H, s); **^{13}C**{H} **NMR** (*d*-DMSO, 126 MHz) δ 175.0, 154.2, 150.6, 147.4, 134.9, 129.9, 129.2, 128.3, 124.9, 123.2, 123.15, 123.09, 122.6, 121.4, 117.8, 99.7; **IR** (solid) ν_{max}(cm^{-1}) 3323, 2981, 2924, 2868, 1626, 1601, 1685, 1452, 1402, 1267, 1117, 1057, 1034, 1016, 893, 585, 812, 766, 710, 665, 615; **ESI-MS TOF** (*m/z*) calculated $[M+H]^+$ for $C_{17}H_{10}O_3Cl$ 297.0318, found 297.0312.

SUPPORTING INFORMATION PARAGRAPH Supporting Information is available containing ^{1}H and ^{13}C NMR spectra and crystallographic information file (CIF) for compound **26**.

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