Hydroxy-substituted triarylcarbenium bromides. Synthesis, structure, derivatization and facile conversion to highly substituted xanthenes †

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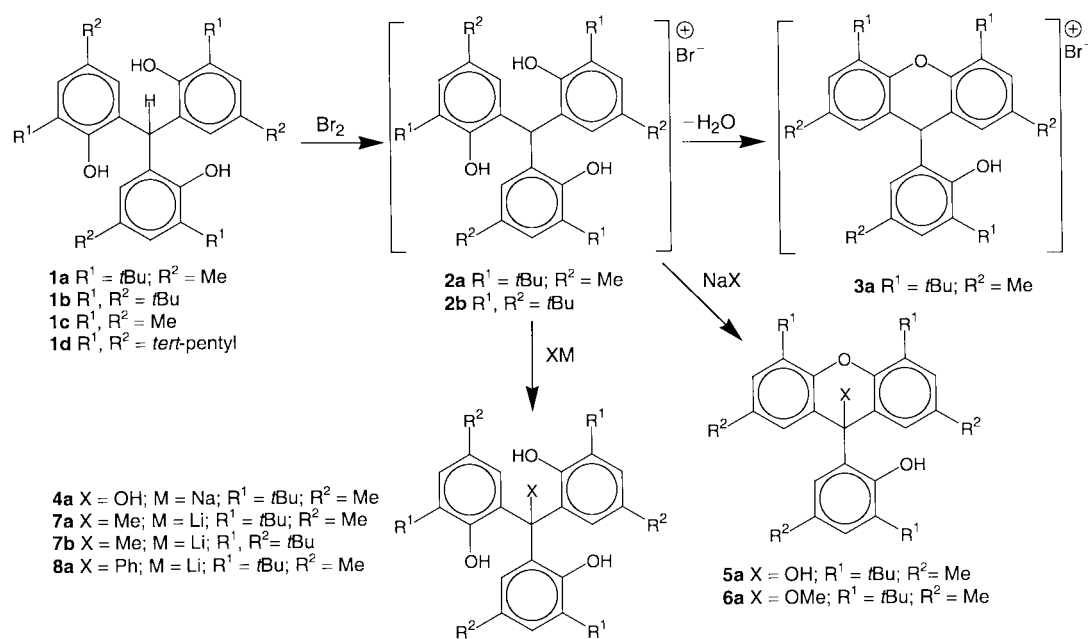
The tris(3,5-dialkyl-2-hydroxyphenyl)carbenium bromides (**2a**) (3-*tert*-butyl, 5-methyl) and **2b** (3,5-di-*tert*-butyl) have been prepared by the oxidation of the corresponding tris(3,5-dialkyl-2-hydroxyphenyl)methanes with bromine. Compound **2a** has been fully characterized by a single crystal X-ray study, which shows that the bromide, atypically, does not bind to the central carbon atom. The materials **2** are reactive, and the trityl alcohol (**4a**), methyl (**7a**, **7b**) and phenyl (**8a**) derivatives can be readily prepared in good yield by reaction of **2** with the appropriate anions; X-ray structures for **4a**, **7b** (as its lithium salt) and **8a** are reported. In solution, **2a** and **4a** undergo a facile, uncatalyzed, controllable intramolecular dehydration to produce the corresponding xanthene derivatives; X-ray structures for the xanthene carbocation (bromide salt) (**3a**) and the 9-hydroxy derivative (**5a**) are also reported.

Introduction

Recently, we have been exploring the chemistry of the tris-(3,5-dialkyl-2-hydroxyphenyl)methanes (**1a**–**1d**) and have found these C_3 symmetric compounds to exhibit a pronounced tendency to adopt a conformation both in solution and in the solid state wherein the oxygen donor atoms are all held in alignment with the proton on the methine group linking the phenolic arms.[1] Due to the rigidity of this platform, these molecules share many traits with the calix[*n*]arene macrocycles and seem to exhibit similarly diverse chemistry. The peripheral hydroxy groups can be derivatized using the well-established methodology employed for the calixarene systems.[1] In all of the compounds characterized to date, the three arms of the molecule all point up with respect to the central methine hydrogen (Type 1, Fig. 1a). In the solid state, **1b** forms a very weakly associated, hydrogen-bonded dimer (shortest H···O contact 2.368 Å), and although NOE studies suggest the aromatic rings rotate freely about the central carbon linker in **1**, the rotation ceases when the hydroxy groups are derivatized due to the steric bulk of the *tert*-butyl groups at the periphery of the molecule. Prior to substitution of the hydroxy groups, however, the NMR data intimate a second conformation can be adopted by **1** with the hydroxy groups orientated in a direction opposite to the central methine hydrogen (Type 2, Fig. 1b). With this dramatic change in conformation, the Type 2 system should exhibit properties markedly different from those of the Type 1 systems previously

† Further details of the X-ray crystal structure analyses together with the complete numbering schemes used in the X-ray structures are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b001032o/

1a R¹ = *t*Bu; R² = Me
1b R¹, R² = *t*Bu
1c R¹, R² = Me
1d R¹, R² = *tert*-pentyl

2a R¹ = *t*Bu; R² = Me
2b R¹, R² = *t*Bu

3a R¹ = *t*Bu; R² = Me

4a X = OH; M = Na; R¹ = *t*Bu; R² = Me
7a X = Me; M = Li; R¹ = *t*Bu; R² = Me
7b X = Me; M = Li; R¹, R² = *t*Bu
8a X = Ph; M = Li; R¹ = *t*Bu; R² = Me

5a X = OH; R¹ = *t*Bu; R² = Me
6a X = OMe; R¹ = *t*Bu; R² = Me

Scheme 1

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J. Chem. Soc., Perkin Trans. 1, 2000, 1741–1748 **1741**

(a)

HO

OH   H

OH

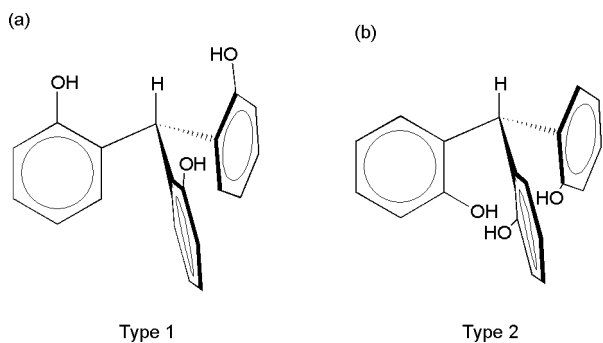Type 1

(b)

H

OH
HO

Type 2

Fig. 1

characterized, and they may serve as interesting ligands for transition metals. Intent on the synthesis of these molecules, we pursued the transformation of the methine hydrogen in **1** to other moieties.

Two methods, in particular, present themselves for derivatizing the central methine of triarylmethanes. First, the hydrogen should be sufficiently reactive for it to be deprotonated by strong bases, such as alkyllithiums, to form carbanions. This carbanion can, in turn, react with alkylating agents, generating the substituted product.[2] Unfortunately this methodology is not immediately applicable to **1** since the bases initially deprotonate the phenolic oxygens to produce aggregates, in which the methine hydrogen is protected in a cage like structure, blocking its reaction.[3] If the phenolic groups were first protected with an unreactive moiety (such as a methyl group), this strategy may succeed, although the subsequent deprotection step(s) may be sterically difficult and/or often require very harsh conditions.[4] The second route, *via* oxidation of the methine in **1** to produce the carbocation (carbenium ion), was thus pursued. Herein we report the results of these studies.

Results and discussion

An examination of the literature reveals oxidations of triarylmethanes are readily accomplished by means of nitrosium tetrafluoroborate.[5] Although a rapid reaction was clearly noted, all attempts to use this methodology with **1a** failed, and only extensive decomposition was observed. Instead, a procedure was developed based loosely on early research concerning the reaction of bis(2-hydroxyphenyl)phenylmethane with bromine to give the corresponding pentabromo species.[6] Since the positions *ortho* and *para* to the hydroxy groups are blocked in **1**, we reasoned this methodology can only lead to reaction at the central carbon position. Thus, the reaction of tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)methane **1a** with an excess of bromine produces a rapid intense dark green coloration. After 2 hours, and removal of the solvent and excess bromine, the carbocation **2a** was formed in essentially quantitative yield.

Although **2a** was completely stable in the solid state and could be stored for long periods in air at room temperature, solutions of **2a** were moderately unstable, and decomposition to 9-(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)-4,5-di-*tert*-butyl-2,7-dimethylxanthen-9-ylium bromide (**3a**) (*vide infra*) was observed spectroscopically. An analogous compound derived from tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane (**1b**) was also prepared, yielding the corresponding adduct **2b** when treated with bromine. Unfortunately, solutions of this material were found to be even less stable than **2a** in solution.

Since triphenylmethyl bromide is a colorless solid with the bromine covalently bound to the central carbon,[7] the very intense coloration for **2** implied the bromine may not be associated with the central carbon, so we undertook a crystallographic analysis of the system. Slow evaporation of a chloroform solution of **2a** at 4 °C yielded very dark green blocks suitable for X-ray structural analysis. The structure of
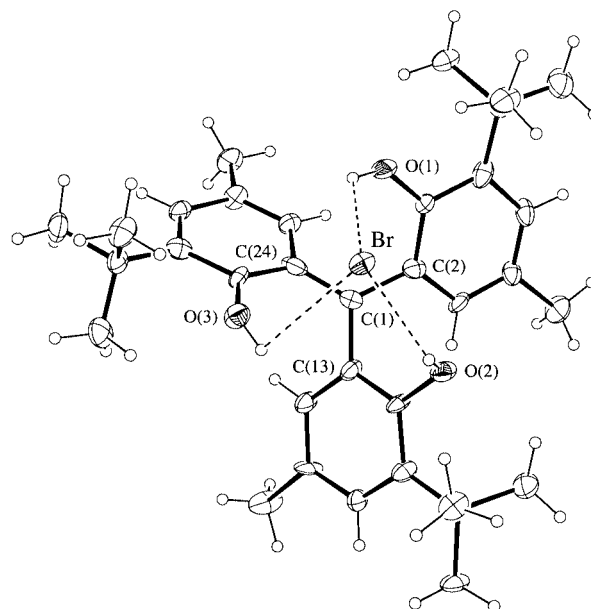

Fig. 2 Structure of **2a**·CHCl₃ (30% probability ellipsoids). The complete numbering scheme is depicted in the electronic supplementary data. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.50(1); C(1)–C(13) 1.50(1); C(1)–C(24) 1.40(1); C(1)···Br 3.34(1); O(1)···Br 3.151; O(2)···Br 3.132; O(3)···Br 3.178; O(1)H···Br 2.572; O(2)H···Br 2.458. O(1)–H–Br 124.5; O(2)–H–Br 133.7.

2a·CHCl₃ is shown in Fig. 2, while crystal and data collection parameters are given in Table 1.

In the solid state, the bromine is not bonded to the central carbon atom, but resides at a distance of 3.34(2) Å, and forms closer approaches [3.13(2), 3.14(2) and 3.16(2) Å] to the phenolic oxygens. For the structure of triphenylmethyl bromide, an average distance (3 independent molecules) of 2.009 Å was measured.[7] The absence of a carbon–bromine bond in **2a** almost certainly can be attributed to an electronic effect, since the steric constraints at the other side of the molecule are such that a bromine atom could be accommodated. Our inability to prepare the fluorinated compound, but success in the synthesis of the methyl- and phenyl-substituted materials (*vide infra*), further supports this notion. The carbocation is not completely planar, with the central carbon C(1) slightly puckered 0.104 Å above the plane defined by C(2), C(13) and C(24), in contrast to the average distance of 0.40(2) Å measured for C(1) in the structure of **1a**.[8]

Although the data were not of sufficient quality to locate with certainty the absolute positions of the phenolic hydrogen atoms, small peaks were located in the difference Fourier maps near the oxygens, and these were assigned as hydrogens and refined. In two cases, the position for the hydrogen atoms refined in an orientation directing towards the bromine with H···Br contacts of 2.57(1) and 2.46(1) Å for O(1)H···Br and O(2)H···Br, respectively. The third hydrogen refined at a location 3.07(2) Å distant from the bromine. As in **1b**, the aromatic rings are canted with respect to the core [C(2), C(13) and C(24)] by 37.9(4), 40.9(4) and 41.2(3)° for the rings bound to O(1), O(2) and O(3), respectively. Somewhat larger angles of 42.96(4), 46.81(4) and 49.75(4)° were measured for the three rings of the three independent molecules in the structure of **1a**, and these are typical twist angles for triarylmethyl cations.[9] Two very disordered chloroform solvents each with site occupancy of one half were also located in electron density maps, but these were not involved in any interactions with **2a**.

Solutions of **2** slowly decompose in unreactive organic solvents, and complete decomposition was effected in one day at room temperature to give a new, dark orange material. Nonetheless, NMR data for **2** could be readily obtained. From a comparison of the ¹H NMR spectrum of **2a** with that of the

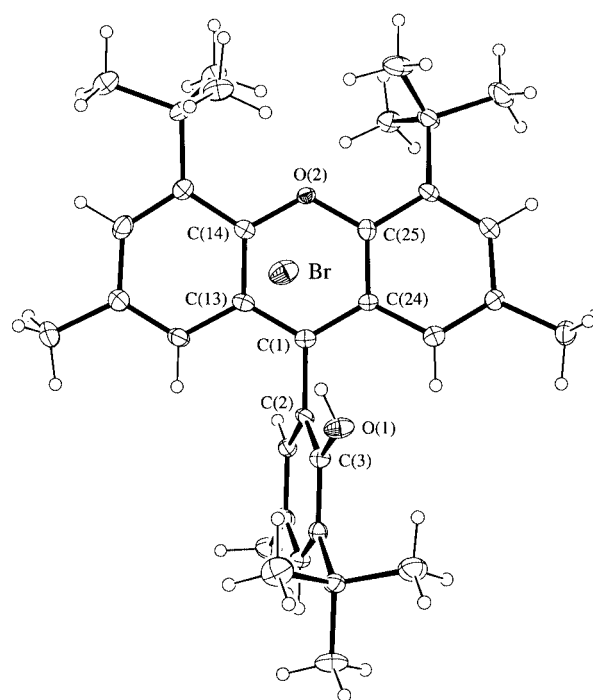**Table 1** X-Ray data for the presented crystal structures

	1a	2a·CHCl₃	3a·CH₂Cl₂	4a·2Me₂CO	5a	7b Lithium salt·4⅔THF	8a·0.8Me₂CO
Total reflections	28036	19643	18656	10563	9535	25905	4408
Unique reflections	6209	6266	5935	6651	6746	8046	4263
R(int)	0.0582	0.0631	0.0752	0.0339	0.0229	0.2046	0.0566
Temperature/K	173(2)	173(2)	173(2)	173(2)	173(2)	172(3)	173(2)
Chemical formula	$C_{34}H_{46}O_3$	$C_{35}H_{46}O_3Cl_3Br$	$C_{35}H_{45}O_2Cl_2Br$	$C_{40}H_{58}O_6$	$C_{34}H_{44}O_3$	$C_{62.67}H_{100.33}O_{7.67}Li_3$	$C_{42.4}H_{54.8}O_{3.8}$
Formula weight	502.71	700.98	648.52	634.86	500.69	997.27	625.26
Crystal system	Hexagonal	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{3}$	$P2_12_12$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
μ(Mo-Kα)/mm^{-1}	0.068	1.415	1.406	0.073	0.071	0.068	0.066
a/Å	22.3915(7)	19.085(1)	9.3103(5)	10.2038(6)	11.1823(6)	20.984(1)	11.956(2)
b/Å	—	19.464(1)	12.5249(7)	13.5294(8)	12.6574(7)	10.8817(7)	12.740(2)
c/Å	10.4686(5)	9.5618(5)	28.920(2)	14.9405(9)	12.8089(7)	27.237(2)	13.430(2)
α/°	—	—	—	96.034(1)	103.779(1)	—	97.043(5)
β/°	—	—	—	94.077(1)	108.435(1)	98.486(2)	90.828(4)
γ/°	—	—	—	110.752(1)	111.672(1)	—	105.813(3)
V/Å³	4545.5(3)	3552.0(3)	3372.4(3)	1905.0(2)	1463.1(1)	6151.2(7)	1951.0(5)
Z	6	4	4	2	2	4	2
R_1 [$I \geq 2\sigma(I)$ data]	0.0480 [4116]	0.0777 [5434]	0.0471 [5060]	0.0676 [4830]	0.0487 [5849]	0.0882 [3153]	0.0738 [2473]
wR_2 (all data)	0.1111	0.2043	0.1109	0.1667	0.1378	0.2676	0.2028
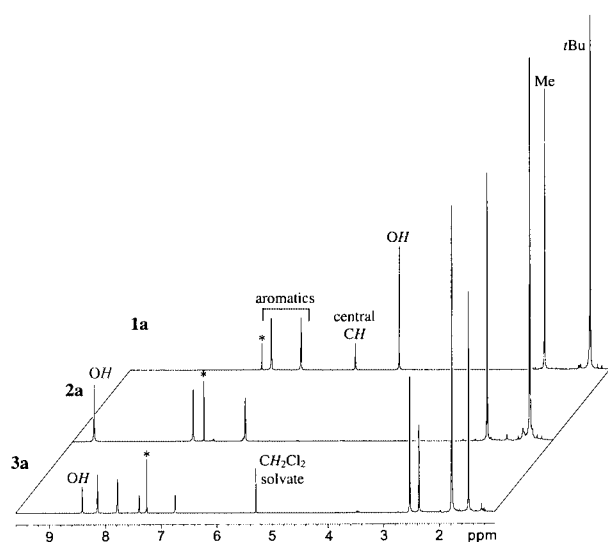
Fig. 3 Comparison of ^{1}H NMR (300 MHz) spectra of **1a**, **2a** and **3a** in CDCl₃ solvent. Residual CHCl₃ is denoted by *.

Fig. 4 ORTEP diagram of **3a**·CH₂Cl₂, normal to the xanthene plane. The complete numbering scheme is depicted in electronic supplementary data. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.492(5); C(1)–C(13) 1.397(5); C(1)–C(24) 1.407(5); C(14)–O(2) 1.360(4); C(25)–O(2) 1.352(4); C(1)···Br 3.467(7); O(1)···Br 3.161(7); O(1)H···Br 2.384(6). O(1)–H–Br 166.2(3); C(13)–C(1)–C(24) 119.8(3); C(14)–O(2)–C(25) 121.8(3).

starting material **1a** (Fig. 3), the most notable change, besides the absence of the methine proton, was the large upfield shift (4.43 ppm) of the hydroxy proton signals to 9.22 ppm, possibly due to the electron deficient delocalized ring system. In the ^{13}C NMR spectrum, the central carbon appeared at 195.4 ppm, in sharp contrast to the value of 42.4 ppm measured for **1a**.[1] Additionally, the resonance for the *ipso* phenolic carbon in **2a** was found at 161.3 ppm, a position 10.2 ppm upfield relative to **1a**.

As **2a** slowly decomposed, it was clear from ^{1}H NMR spectroscopy that only one product was formed and that this new material was no longer C_3 symmetric, since only two of the aromatic rings were equivalent. In addition, the phenolic hydrogen resonance, located at 8.41 ppm, revealed only one proton on integration. Addition of methanol directly to solid **2a** greatly facilitated the reaction, with complete decomposition of **2a** effected in only a few seconds. In order to determine the absolute conformation and connectivity of this material, a crystal structure determination was undertaken (Fig. 4).

The structure revealed the product to be a 9-arylxanthenylium bromide (**3a**), resulting from an intramolecular dehydration involving two of the phenolic rings. The reaction was surprisingly facile, even at −20 °C. Condensations of this type have never been observed for the starting methane **1a**, which, like bis(2-hydroxyphenyl)methane,[10] has been found to be stable

with respect to cyclodehydration. Typically, 9-substituted xanthenes are synthesized by the cyclization of *ortho*-methoxy-substituted triarylmethanols facilitated by pyridinium chloride at 205 °C,[11] or by reaction of xanthone with a Grignard reagent.[12] Furthermore, 9-substituted xanthene derivatives have been isolated in low yield from certain reactions of various substituted phenoxymagnesium bromides with triethyl orthoformate.[13] In this particular system, the cyclization was suggested to proceed *via* a pathway involving carbocations analogous to **3a**, which were not isolated. The condensation observed in the present work lends additional validity to the proposed scheme.

Although a number of 9-arylxanthenylium salts have been structurally characterized,[14] **3a** represents the first example to
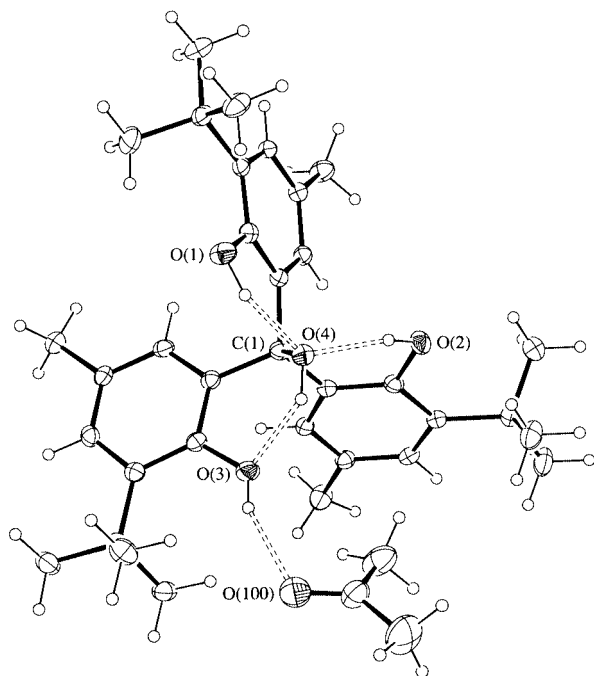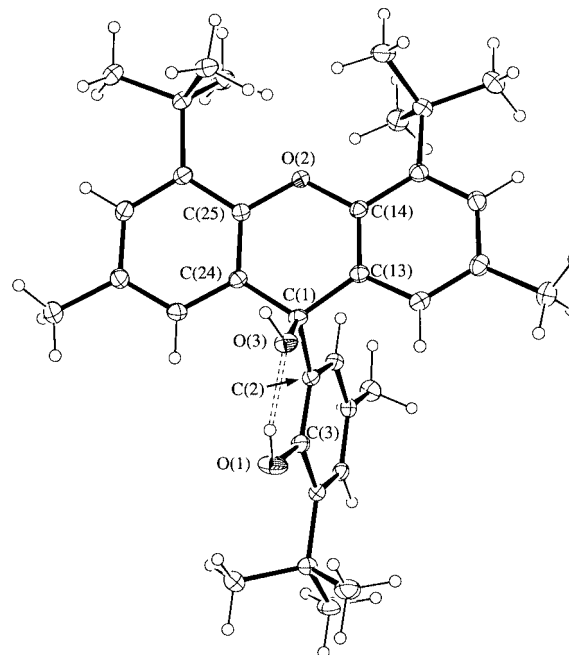
Fig. 5 Structure of **4a**·2Me₂CO (30% probability ellipsoids). The remaining acetone solvate has been omitted, for clarity. The complete numbering scheme is depicted in the electronic supplementary data. Selected bond lengths (Å) and angles (°): C(1)–O(4) 1.474(3); O(1)···O(4) 2.605(6); O(2)···O(4) 2.649(6); O(4)···O(3) 2.601(6); O(3)···O(100) 2.747(6); O(1)H···O(4) 1.783(5); O(2)H···O(4) 1.848(5); O(4)H···O(3) 1.925(5); O(3)H···O(100) 2.062(5). O(1)–H–O(4) 143.9(3); O(2)–H–O(4) 153.5(3); O(4)–H–O(3) 130.0(3); O(3)–H–O(100) 151.4(3).

Fig. 6 Structure of **5a** (30% probability ellipsoids). The complete numbering scheme is depicted in the electronic supplementary data. Selected bond lengths (Å) and angles (°): C(1)–O(3) 1.458(1); O(2)···O(3) 2.540(2); O(3)H···O(2) 1.749(2); C(1)–C(2) 1.458(1); C(1)–C(13) 1.512(2); C(1)–C(24) 1.509(2); O(1)–C(3) 1.368(2); C(14)–O(1) 1.388(1); C(25)–O(2) 1.391(1). O(3)–C(1)–C(2) 107.74(9); C(1)–O(3)–H 148.4(1); C(13)–C(1)–C(24) 111.54(9); C(14)–O(2)–C(25) 120.01(9).

contain a 9-hydroxyphenyl substituent. Unlike the structure of **2a**, the core, defined by C(1), C(2), C(13) and C(24) is absolutely planar, with no atom deviating from the least-squares plane drawn through these atoms by more than 0.008(3) Å for C(1). In the solid state, the bromine is not situated directly above C(1), but rather, in reference to Fig. 4 which is drawn normal to the xanthene plane, it is shifted significantly up, and slightly to the left, while residing ~3.32 Å above the ring system. Additionally, the hydroxy hydrogen atom (located and refined) hydrogen-bonds to the bromine, with a fairly short H···Br contact of 2.384(6) Å. Consistent with the dark coloration of **3a**, the xanthene ring system is completely delocalized, as evidenced by the similar bond lengths and angles of the atoms involved, though the xanthene ring system is not completely planar, with a significant twist of 14.8(9)° between the planes defined by C(13)–C(23) and C(24)–C(34). If a completely planar conformation were realized, there would be a significant steric interaction between the two xanthene *tert*-butyl groups, for which a dihedral angle of 29.1° is measured. The phenolic ring is also twisted relative to the xanthene plane by 72.5(1)°.

Reactivity of tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)-carbenium bromide (2a)

The carbocation **2a** should be a reactive material, more so even than triphenylmethyl bromide, and therefore may serve as a useful precursor for the derivatization of the central carbon atom. With this in mind, a number of different reagents were added to the material. When **2a**, dissolved in chloroform, was shaken with saturated sodium bicarbonate, the organic phase rapidly turned from dark green to pale yellow, and the C_3 symmetric triarylmethanol (**4a**) was produced. From spectroscopic data, it was difficult to determine if the preferred conformation of **4a** was Type 1 or Type 2 (Fig. 1), and for this reason, as well as to examine hydrogen-bonding interactions, the solid-state structure of the material was determined. Colorless blocks

suitable for crystallographic analysis were grown from a saturated acetone solution of **4a** at −20 °C. An ORTEP diagram of **4a** is shown in Fig. 5, while collection and crystal data is presented in Table 1.

From an examination of the structure, it was immediately apparent that the compound is orientated in a Type 1 fashion. All four hydroxy hydrogens were located in difference maps and refined without constraint, and these OHs are all involved in hydrogen-bonding interactions. Two of the phenolic protons, O(1)H and O(2)H, form hydrogen-bonds to the central hydroxy, with O···H contacts of 1.783(5) and 1.848(5) Å, respectively, while the proton on the central hydroxy forms a weaker bond to O(3) at a distance of 1.925(5) Å. The remaining hydroxy group is hydrogen-bonded to a molecule of acetone solvent with an O(3)H–O(100) contact of 2.062(5) Å. The central carbon–oxygen distance [C(1)–O(4)] is typical, 1.474(3) Å; the related compounds tris(2-methoxyphenyl)-methanol [1.446(2) Å][15] and tris(4-methoxyphenyl)methanol [1.459(3) and 1.441(3) Å][16] show similar O–C bond lengths. The aromatic rings are not perpendicular with respect to the core [defined by C(2), C(13) and C(24)], but instead are canted by 48.5(1), 47.64(8) and 48.8(1)° for the rings attached to O(1), O(2) and O(3), respectively.

Solutions of **4a** were unstable and decomposed over the course of a few days at room temperature to produce the 9-arylxanthene (**5a**), identified by the loss of C_3 symmetry in the NMR spectrum and by analogy with the spectrum of **3a**. The compound **5a** was also subjected to complete characterization by a single crystal X-ray analysis (Fig. 6).

As depicted in Fig. 6, the phenolic hydrogen atom interacts with the central hydroxy group at a distance of 1.749(2) Å, but the central hydroxy proton does not exhibit any hydrogen bonding. As for **3a**, the two aromatic rings of the xanthene moiety in **5a** are not coplanar, but twisted by 13.80(6)°. The phenolic ring cants relative to the xanthene plane at an angle of 78.67(3)°. In contrast to the structure of **3a**, no delocalization of the xanthene group is evident, with C(1)–C(13) and C(1)–C(24) distances 0.1 Å longer than in **3a**. The bonds formed to

O(2) are also slightly extended (0.03 Å), but the remaining structural features are typical.

The ^{1}H NMR spectrum of **5a** is similar to that of **3a**, except for a large shift upfield for the 2-hydroxyphenyl proton from 8.41 in **3a** to 10.29 ppm in **5a**, likely due to the strong hydrogen-bonding interaction between this proton and the central hydroxy group. For comparison, this resonance can be found at 7.15 ppm for **4a** and 4.79 ppm for **1a**. Lacking a hydrogen bond, the central hydroxy resonance is further downfield at 3.22 ppm; the central hydroxy in **4a** appears at 6.67 ppm. In the ^{13}C NMR spectra, the central carbon resonances occur at 87.7 and 76.7 ppm for **4a** and **5a**, respectively. The IR spectrum of **5a** exhibits two main stretches at 3529 and 3295 cm^{-1}, and these bands may be assigned to the 9-hydroxy and phenolic hydroxy groups, respectively, based on the hydrogen-bonding criterion.

In an attempt to add a methoxy group to the carbocation, **2a** was reacted with an excess of sodium methoxide, but this reaction cleanly converted **2a** to the 9-aryl-9-methoxyxanthene derivative (**6a**). In all likelihood, the triarylmethoxymethane formed as an intermediate in this reaction, however this material was neither isolated nor detected in the procedure. Presumably, in a manner analogous to **5a**, the phenolic hydroxy hydrogen bonds to the methoxide, since the resonance for this proton is found at almost the same position (10.54 ppm) as **5a** in the ^{1}H NMR spectrum, and the infrared spectrum exhibits a similar OH stretch at 3243 cm^{-1}.

We also explored the synthesis of the fluorine analog of **1a**, both by the standard methodology, and by the reaction of **2a** with hydrogen fluoride. Normally, triarylmethanes can be readily fluorinated in a one-pot reaction with nitrosium teraﬂuoroborate and pyridinium poly(hydrogen fluoride) (PPHF).[5] However, when **1a** was reacted in this manner, the mixture turned dark brown and a large number of products were formed. Since oxidation of triphenylmethane with NOBF$_4$ produced a carbocation, we reasoned that **2a** should be a suitable substitute, so a large excess of PPHF was added to a dichloromethane solution of **2a**. After work-up, which involved neutralizing the PPHF with sodium bicarbonate solution, **4a** was identified as the major product, with a small amount of **5a** also present. Steric constraints do not seem to be sufficient as to prevent fluorine from covalently binding to the central carbon, but the hydroxy groups may preclude the addition of the very electronegative atom by rendering the central carbon electron deficient.

Addition of a hydrophobic moiety at the central carbon was thought to possibly induce inversion to a Type 2 system, and a suitable procedure to substitute various groups at this position was designed. Treatment of triphenylmethyl chloride with Grignard reagents readily produced various 1,1,1-triphenyl-alkanes or -aryls,[17] and 4,8,12-trioxa-4,8,12,12c-tetrahydrodi-benzo[cd,mn]pyrene (trioxatricornan) derivatives can be prepared by reaction of the corresponding tetrafluoroborate salt with methyllithium.[18] Although the compounds **2** have reactive hydroxy groups, we anticipated that the addition of at least four equivalents of a metal alkyl or aryl should allow for reaction at the central carbon. Accordingly, when **2a** or **2b**, dissolved in ether, were reacted with six equivalents of methyllithium, the dark green solutions slowly turned yellow–orange. After addition of water, and separation, yellow residues were collected, containing the corresponding 1,1,1-tris(3,5-dialkyl-2-hydroxyphenyl)ethanes (**7a** and **7b**).

As discussed above, ^{1}H NMR NOE studies have suggested the aromatic rings in **1a** and **1b** freely rotate about the central carbon linker. NOE experiments similarly revealed that the rings in **7a** and **7b** rotate, and the preferred conformation (Type 1 *versus* Type 2, Fig. 1) for **7** was unknown. Unlike **1a** and **1b**, the compounds **7a** and **7b** were, somewhat surprisingly, extremely soluble in all organic solvents, and exhaustive attempts at crystallization by evaporation were futile. Additionally, **7b** proved to be unstable in non-alcoholic solvents and
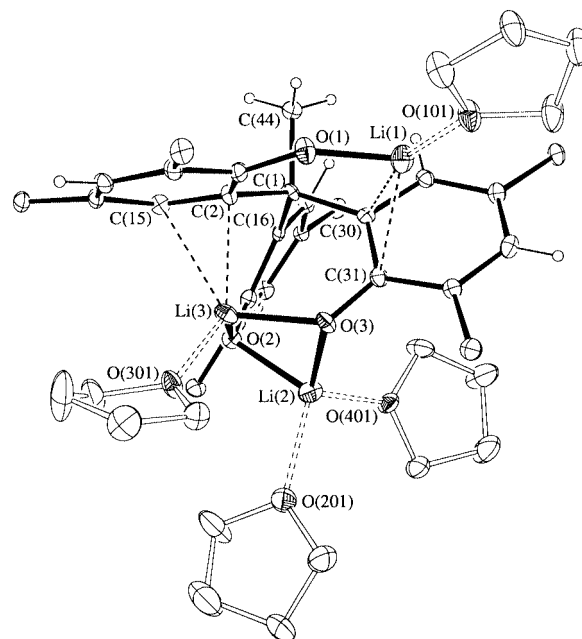
Fig. 7 Structure of **7b** lithium salt·$4\frac{2}{3}$THF (20% probability ellipsoids). The non-coordinating THF solvate, the *tert*-butyl methyl groups, and the THF hydrogens have been omitted for clarity. The triarylmethane fragment is drawn with solid lines, while THFs are represented by open bonds. The complete numbering scheme is depicted in the electronic supplementary data. Selected bond lengths (Å) and angles (°): C(1)–C(44) 1.568(8); C(1)–C(2) 1.547(8); C(1)–C(16) 1.575(9); C(1)–C(30) 1.555(9); Li(1)–O(1) 1.76(1); Li(2)–O(2) 1.91(1); Li(2)–O(3) 1.97(1); Li(3)–O(2) 1.86(1); Li(3)–O(3) 1.87(1); Li(1)–O(101) 1.89(1); Li(2)–O(201) 2.14(1); Li(2)–O(401) 1.96(1); Li(3)–O(301) 1.92(1); Li(1)···C(30) 2.36(1); Li(1)···C(31) 2.48(2); Li(3)···C(2) 2.23(1); Li(3)···C(15) 2.53(1). O(1)–Li(1)–O(101) 116.4(8); O(2)–Li(2)–O(201) 113.4(6); O(2)–Li(2)–O(401) 117.3(7); O(2)–Li(3)–O(301) 114.3(6); O(3)–Li(3)–O(301) 109.4(6); Li(2)–O(2)–Li(3) 80.1(6); Li(2)–O(3)–Li(3) 78.2(6); Li(1)–O(1)–C(3) 145.0(6); Li(3)–O(2)–C(17) 128.6(5); Li(2)–O(2)–C(17) 112.9(6); Li(2)–O(3)–C(31) 110.5(6); Li(3)–O(3)–C(31) 130.0(6).

readily decomposed to a variety of uncharacterized compounds in only a few minutes. For these reasons, crystallization attempts of the initially formed lithium salts prepared in the synthesis of **7** were carried out. A small number of crystals were eventually isolated after slow evaporation of solvent from a THF solution of the lithium salt of **7b**, and this compound was characterized by X-ray crystallography (Fig. 7).

Inspection of the structure immediately reveals that the conformation of the organic fragment now closely resembles that of Type 2. In sharp contrast, the lithium salt of **1b** is a hexanuclear complex, comprising of two organic fragments adopting a Type 1 (Fig. 1a) conformation, with the two methine hydrogens pointing directly at one another in the cage-like structure.[3] As seen in Fig. 7, two of the aromatic rings, with the corresponding hydroxy groups O(2) and O(3), are canted down by 64.4(2) and 65.3(3)°, respectively, with respect to the central methyl group [C(44)], while the remaining ring is canted just slightly up [10.9(3)°]. Concomitant with this observation, while Li(2) and Li(3) show approximately tetrahedral coordination environments by bridging adjacent hydroxy groups, Li(1) cannot quite reach a second oxygen and forms only two bonds: to O(1) and a ligating THF. Additionally, two lithium atoms exhibit significant interactions with aromatic ring bonds; Li(1) interacts with the C(30)–C(31) bond at 2.36(1) and 2.48(2) Å, and Li(3) interacts with the C(2)–C(15) linkage at 2.23(1) and 2.53(1) Å, respectively. Together with these interactions, Li(1) and Li(3) each coordinate a single THF molecule, while the lower steric requirements of Li(2) allow the binding of two THFs, although the Li(2)–O(201) distance is longer than the others at 2.14(1) Å. The Li(1)–O(1) distance at 1.76(1) Å is very short, and is comparable to the shortest distance previously
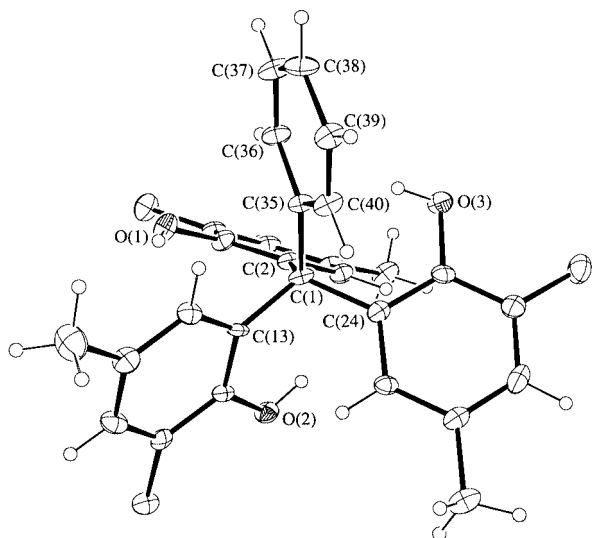
Fig. 8 Structure of **8a**·0.8Me$_2$CO (30% probability ellipsoids). The acetone solvates and *tert*-butyl methyl groups have been omitted. The complete numbering scheme is depicted in the electronic supplementary data. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.589(6); C(1)–C(13) 1.558(7); C(1)–C(24) 1.556(6); C(1)–C(35) 1.545(6). C(2)–C(1)–C(13) 106.5(4); C(2)–C(1)–C(24) 110.7(3); C(2)–C(1)–C(35) 111.4(4); C(13)–C(1)–C(24) 111.7(4); C(13)–C(1)–C(35) 111.0(4); C(24)–C(1)–C(35) 105.7(4).

measured for [Li$_3$(μ$_2$-OAr)] (where ArOH = 2,6-diphenyl-3,5-di-*tert*-butylphenol) at 1.775(7) Å.[19] The remaining Li–OAr distances are much longer (1.85–1.97 Å) and typical for lithium–phenoxide bond lengths.[19]

While the C(1)–aryl and C(1)–C(44) bond lengths are typical for triphenylalkyl systems,[20] C(1) adopts a substantially distorted tetrahedral geometry, possibly due to significant strain exerted by the lithium binding motif. Maximum deviations of 98.8(5) and 115.4(5)° for C(44)–C(1)–C(2) and C(2)–C(1)–C(30) angles, respectively, were measured.

The spectroscopic data for **7a** and **7b** are consistent with a C_3 symmetric compound, and remarkably similar to the corresponding starting materials **1a** and **1b**. A single hydroxy resonance can be found at 5.13 and 5.01 ppm for **7a** and **7b**, respectively, compared with 4.79 and 4.83 ppm for **1a** and **1b**. A more significant downfield shift is observed in the ^{13}C NMR for the central carbon, which in **7a** and **7b** resonated at 49.6 and 50.4 ppm, while occurring at 42.4 and 42.5 ppm for **1a** and **1b**, respectively. Comparison of the infrared spectral data demonstrated that **7a** and **7b** exhibit higher (33 and 32 cm^{-1}, respectively) frequencies for the OH stretches relative to **1a** and **1b**.

The carbocation **2a** was also treated with phenyllithium in a manner analogous for the synthesis of **7**. ^{1}H NMR analysis confirmed the incorporation of the phenyl moiety, although all three substituted aromatic rings were now rendered inequivalent, with their associated hydroxy resonances appearing at three different chemical shifts. The latter observation implies rotation of the aromatic rings occurs at a rate slower than the timescale of the NMR experiment. Since the absolute geometry of the compound was unknown, full characterization by X-ray crystallography was undertaken. Fig. 8 displays a side-on view of the structure of **8a**, while Table 1 gives collection and refinement data.

Clearly the compound is extremely sterically crowded, although perhaps slightly less so than the methyl derivatives **7**.[21] In order to accommodate the phenyl group, one of the aromatic rings has rotated 180° relative to the C(2), C(16), C(30) plane, but the remaining hydroxys still point up with respect to the added phenyl group. The phenyl is effectively locked in position by the two hydroxy substituents, and in an unsymmetrical fashion, rendering the two substituted rings non-equivalent. Unlike the structure of the lithium salt of **7b**, examination of

the bond angle data reveals the geometry about the central carbon linker is almost perfectly tetrahedral, while the bond length values show the C–Ar distances are approximately equal and average to 1.56(2) Å, typical for tetraaryl substituted carbons.[20] Relative to the plane drawn through C(2), C(16) and C(30), the rings are canted at different angles; 32.5(2) and 37.7(2)° for the two rings with hydroxys [O(1) and O(3)] pointing up with respect to the phenyl group, while the ring whose hydroxy groups points down [O(2)] is considerably closer to perpendicular, forming an angle of 78.7(2)°. Somewhat surprisingly, no intra- or inter-molecular hydrogen-bonding interactions are present between any of the hydroxy groups.

The ^{1}H NMR spectrum of **8a** is entirely consistent with the crystallographic observations. The two hydroxy resonances pointing up with respect to the phenyl ring, although inequivalent, appear at similar chemical shifts of 5.17 and 5.09 ppm, while the remaining hydroxy resonance occurs at 4.38 ppm. Congruent with this asymmetry, six Ar-*H* peaks are observed for the substituted rings, with three peaks for the Ar-C*H*$_3$ groups. All five protons on the introduced phenyl group are inequivalent, appearing as two multiplets.

In order to ascertain if the hydroxy substituted rings in **8a** rotate at elevated temperature, a sample of **8a** was dissolved in d$_8$-toluene and spectra were recorded at various temperatures. The two hydroxy resonances (appearing in toluene at 5.60 and 5.58 ppm) coalesced into a single signal at ~50–60 °C with a chemical shift of 5.53 ppm, consistent with the compound adopting mirror symmetry at this temperature. At higher temperatures (80–108 °C), a spectrum consistent with a molecule possessing C_3 symmetry emerged. A single, very broad hydroxy resonance was observed at 5.33 ppm, together with only two Ar-*H* signals from the three substituted aromatic rings, and single Ar-C*H*$_3$ (2.05 ppm) and *tert*-butyl (1.40 ppm) resonances. Based on these data, the aromatic rings appear to rotate at higher temperatures, and the compound should therefore be able to act as a system with Type 2 geometry.

Finally, **2a** was reacted with lithium aluminium hydride to readily regenerate **1a**. This methodology may have utility for incorporation of a deuterium label into the methine moiety of **1**.

Conclusions

The title compounds have been prepared and fully characterized. These compounds are reactive and of utility for the derivatization of the central carbon atom in the triarylmethanes **1**. The hydroxyphenyl rings in **2** render the carbocation electron deficient, so more electronegative atoms (or groups), such as the halogens, fail to bind. Hydroxide, methyl and phenyl derivatives, however, can be readily prepared and these materials may possess very interesting ligand properties of value in coordination chemistry; reactions to this end are currently being investigated. Additionally, the hydroxy groups in **2** and **4**, can give rise to an uncatalyzed cyclodehydration, giving the 9-hydroxyphenyl substituted xanthene compounds.

Experimental

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of N$_2$ on a vacuum line using standard Schlenk techniques. All solvents used were dried and distilled prior to use. NMR spectra were recorded on a Varian VXR 300 MHz spectrometer at 299.95 and 75.43 MHz for the proton and carbon channels, respectively, using CDCl$_3$ solvent, unless otherwise stated. IR spectra were recorded as KBr discs on a Bruker Vector 22 instrument at a resolution of 2 cm^{-1}. UV–Vis spectra were recorded on a Varian Cary 50 instrument using CHCl$_3$ as the solvent. Melting points were determined using a capillary melting point apparatus and are uncorrected. The tris(3,5-dialkyl-2-hydroxyphenyl)methanes **1a** (3-*tert*-butyl-

5-methyl) and **1b** (3-di-*tert*-butyl) were prepared following previously reported procedures.[1]

Tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)carbenium bromide (2a)

In a 100 ml Schlenk flask, **1a** (500 mg, 1.0 mmol) was dissolved in dry CCl_4 (50 ml), and cooled to 0 °C with an ice bath. Excess Br_2 (~0.2 ml) was added, rapidly turning the solution dark green. The reaction was stirred at 0 °C for 2.5 h, after which time the solvent and unreacted Br_2 were removed under vacuum, to leave a dark metallic green powder of **2a**. NMR analysis of the material obtained by this route indicated it was of sufficient purity for further reactions. Solutions of **2a** decompose to **3a** upon standing for a few hours.

Decomposes without melting (130 °C); λ_{max}/nm 639 (ε/dm³ mol^{-1} cm^{-1} 4 300), 435 (8 800), 381 (7 300), 277 (14 200); ν_{max}/cm^{-1} 3436m v. br, 3143w br (OH); δ_H 9.22 (s, 3H, O*H*), 7.46 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.52 (d, *J* 2.4 Hz, 3H, Ar-*H*), 2.17 (s, 9H, C*H₃*), 1.41 (s, 27H, *t*Bu); δ_C 195.4 (*C*$^+$), 161.3 (*C*$_{Ar}$OH), 141.6, 139.4, 135.3, 130.6, 130.3 (Ar-*C*), 35.1 [*C*(CH₃)₃], 29.4 [C(*C*H₃)₃], 20.5 (Ar-*C*H₃).

Tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)carbenium bromide (2b)

In a manner analogous to that described for **2a**, **1b** (500 mg, 0.795 mmol) was reacted with excess Br_2. The reaction proceeded more rapidly than that of **2a**, and a shorter reaction time of 1.5 h was used. Longer reaction times led to significant decomposition of the product.

Decomposes without melting (120 °C); λ_{max}/nm 633 (ε/dm³ mol^{-1} cm^{-1} 5 700), 437 (13 000), 385 (8 000), 277 (15 500); ν_{max}/cm^{-1} 3426m v. br, 3109w br (OH); δ_H 9.04 (s, 3H, O*H*), 7.74 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.68 (d, *J* 2.4 Hz, 3H, Ar-*H*), 1.43 (s, 27H, *t*Bu), 1.20 (s, 27H, *t*Bu); δ_C 197.1 (*C*$^+$), 160.5 (*C*$_{Ar}$OH), 143.4, 141.3, 136.4, 131.7, 130.6 (Ar-*C*), 35.4, 34.3 [*C*(CH₃)₃], 30.9, 29.6 [C(*C*H₃)₃].

9-(3-*tert*-Butyl-5-methyl-2-hydroxyphenyl)-4,5-di-*tert*-butyl-2,7-dimethylxanthen-9-ylium bromide (3a)

Compound **2a** (252 mg, 0.433 mmol) was reacted with MeOH (solvent) at room temperature to rapidly (10 seconds) produce a dark orange solution. The solvent was removed under vacuum to leave an orange residue. Crystallization from a vapor diffusion of ether into a saturated CH_2Cl_2 solution to gave **3a**·CH_2Cl_2 (224 mg, 92%).

Decomposes without melting (210 °C) (Found C, 71.7; H, 7.7. $C_{34}H_{43}O_2Br·\frac{1}{10}CH_2Cl_2$ requires C, 71.6; H, 7.6%); λ_{max}/nm 489 (ε/dm³ mol^{-1} cm^{-1} 3 600), 378 (22 400), 277 (39 600); ν_{max}/cm^{-1} 3434m v. br (OH); δ_H 8.41 (s, 1H, O*H*), 8.14 (d, *J* 2.4 Hz, 2H, xanthene Ar-*H*), 7.79 (d, *J* 2.4 Hz, 3H, xanthene Ar-*H*), 7.39 (d, *J* 2.4 Hz, 1H, phenol Ar-*H*), 6.75 (d, *J* 2.4 Hz, 1H, phenol Ar-*H*), 2.53 (s, 6H, xanthene C*H₃*), 2.37 (s, 3H, phenol C*H₃*), 1.78 (s, 18H, xanthene *t*Bu), 1.48 (s, 9H, xanthene *t*Bu); δ_C 172.4 (*C*$^+$), 156.0 (xanthene *C*$_{Ar}$O), 151.0 (phenol *C*$_{Ar}$OH), 142.7, 139.6, 139.4, 137.9, 130.9, 129.2, 128.1, 127.8, 126.4, 121.0 (Ar-*C*), 35.4 [xanthene *C*(CH₃)₃], 34.9 [phenol *C*(CH₃)₃], 30.7 [xanthene C(*C*H₃)₃], 29.3 [phenol C(*C*H₃)₃], 21.5 (xanthene *C*H₃), 20.6 (phenol *C*H₃).

Tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)methanol (4a)

In a separating funnel, **2a** (100 mg, 0.172 mmol) was dissolved in $CHCl_3$ (25 ml). Saturated aqueous $NaHCO_3$ (30 ml) was added to the dark green solution and the resulting mixture was vigorously shaken until the $CHCl_3$ layer was almost colorless (~5 minutes). The organic layer was collected and dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure to leave a pale green residue. A small quantity (~1 ml) of pentane was added and the white insoluble material was collected, washed and dried, and recrystallised from acetone to yield pure **4a**·2Me₂CO (85 mg, 78%). One of the molecules of

acetone solvent was rapidly lost after removal of the mother liquor, while the remaining acetone solvate is more tightly held and not lost even under vacuum. Solutions of **4a** slowly decompose to **6a** on standing.

Mp 133–134 °C (Found C, 76.9; H, 9.2. $C_{34}H_{46}O_4·Me_2CO$ requires C, 77.0; H, 9.1%); ν_{max}/cm^{-1} 3383m br, 3362m br (OH); δ_H 7.15 (s, 3H, Ar-O*H*), 7.13 (d, *J* 2.4 Hz, 3H, Ar-*H*), 6.67 (s, 1H, CO*H*), 6.10 (d, *J* 2.4 Hz, 3H, Ar-*H*), 2.12 (s, 9H, C*H₃*), 1.41 (s, 27H, *t*Bu); δ_C 152.2 (*C*$_{Ar}$OH), 137.9, 128.42, 128.40, 128.3, 127.0 (Ar-*C*), 87.3 (*C*OH), 34.6 [*C*(CH₃)₃], 29.9 [C(*C*H₃)₃], 21.0 (Ar-*C*H₃).

9-(3-*tert*-Butyl-5-methyl-2-hydroxyphenyl)-4,5-di-*tert*-butyl-2,7-dimethylxanthen-9-ol (5a)

Compound **2a** (100 mg, 0.172 mmol) was dissolved in ether in a separating funnel. Excess H_2O and Et_3N were added, and the mixture was vigorously shaken until the solution was almost colorless. The organic layer was collected and dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. The residue was dissolved in diethyl ether, and a small quantity of MeCN was added. The ether was allowed to evaporate depositing large colorless hexagons of **5a** (67 mg, 78%).

Mp 168–169 °C (Found C, 81.7; H, 9.6. $C_{34}H_{44}O_3$ requires C, 81.8; H, 9.25%); ν_{max}/cm^{-1} 3529m, 3295m br (OH); δ_H 10.29 (s, 1H, Ar-O*H*), 7.41 (d, *J* 2.4 Hz, 2H, xanthene Ar-*H*), 7.28 (d, *J* 2.4 Hz, 3H, xanthene Ar-*H*), 6.98 (d, *J* 2.4 Hz, 1H, phenol Ar-*H*), 6.14 (d, *J* 2.4 Hz, 1H, phenol Ar-*H*), 3.22 (s, 1H, CO*H*), 2.33 (s, 6H, xanthene C*H₃*), 2.07 (s, 3H, phenol C*H₃*), 1.69 (s, 18H, xanthene *t*Bu), 1.57 (s, 9H, xanthene *t*Bu); δ_C 151.5 (phenol *C*$_{Ar}$O), 146.1 (xanthene *C*$_{Ar}$OH), 137.3, 137.1, 132.1, 130.9, 129.0, 128.6, 127.4, 126.8, 126.5 (Ar-*C*), 76.7 (*C*OH), 35.1 [xanthene *C*(CH₃)₃], 35.0 [phenol *C*(CH₃)₃], 31.0 [xanthene C(*C*H₃)₃], 29.7 [phenol C(*C*H₃)₃], 20.94 (xanthene C*H₃*), 20.88 (phenol C*H₃*).

9-(3-*tert*-Butyl-5-methyl-2-hydroxyphenyl)-4,5-di-*tert*-butyl-2,7-dimethyl-9-methoxyxanthene (6a)

Compound **2a** (578 mg, 1.0 mmol) was dissolved in ether and NaOMe (300 mg, 5.55 mmol) was added. The solution slowly turned orange, then gray, and finally pale green at completion (2 h). The excess NaOMe was filtered off, and the solvent was removed under vacuum to leave a green–gray residue. The material was purified by crystallization from MeOH–pentane to give colorless blocks of **6a**·C_5H_{12} (460 mg, 90%).

Mp 180–182 °C (decomp.) (Found C, 82.1; H, 10.1. $C_{35}H_{47}O_3$·C_5H_{12} requires C, 81.7; H, 10.1%); ν_{max}/cm^{-1} 3421w v. br, 3243m (OH); δ_H 10.54 (s, 1H, Ar-O*H*), 7.25 (d, *J* 2.4 Hz, 2H, xanthene Ar-*H*), 7.22 (d, *J* 2.4 Hz, 3H, xanthene Ar-*H*), 6.92 (d, *J* 2.4 Hz, 1H, phenol Ar-*H*), 6.07 (d, *J* 2.4 Hz, 1H, phenol Ar-*H*), 2.93 (s, 3H, COC*H₃*), 2.29 (s, 6H, xanthene C*H₃*), 2.01 (s, 3H, phenol C*H₃*), 1.63 (s, 18H, xanthene *t*Bu), 1.53 (s, 9H, xanthene *t*Bu); δ_C 151.4 (phenol *C*$_{Ar}$O), 148.2 (xanthene *C*$_{Ar}$OH), 137.1, 136.7, 131.9, 129.6, 128.5, 127.6, 126.7, 126.3, 122.6 (Ar-*C*), 83.3 (*C*OCH₃), 50.3 (COC*H₃*), 35.0 [xanthene/phenol *C*(CH₃)₃], 30.9 [xanthene C(*C*H₃)₃], 29.7 [phenol C(*C*H₃)₃], 21.0 (xanthene C*H₃*), 20.9 (phenol C*H₃*).

1,1,1-Tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)ethane (7a)

An ether solution (40 ml) of **2a** (501 mg, 0.861 mmol) was cooled to −78 °C (acetone–dry ice) and MeLi (3.20 ml of 1.6 M in ether, 5.12 mmol) was added. The solution was maintained at −78 °C for 1 h and was then slowly allowed to warm to room temperature. During this time, the dark colored solution became pale yellow. Water was slowly added and the ether layer subsequently separated, and dried with $MgSO_4$. The solvent was removed under reduced pressure to leave a yellow residue, which was subjected to column chromatography, eluting with hexanes, to give **7a** as a pale yellow powder (267 mg, 60%). The material collected from the column was pure by NMR, although the crystalline material (hexanes −20 °C) is colorless.

Mp 168–170 °C (decomp.); m/z (FAB): 516.3507 (M$^+$, $C_{35}H_{48}O_3$ requires 516.3603); ν_{max}/cm^{-1} 3540m (OH); δ_H 7.11 (d, J 2.4 Hz, 3H, Ar-H), 6.81 (d, J 2.4 Hz, 3H, Ar-H), 5.13 (s, 3H, OH), 2.29 (s, 3H, CCH_3), 2.22 (s, 9H, Ar-CH_3), 1.34 (s, 27H, tBu); δ_C 151.9 (C_{Ar}OH), 139.1, 129.8, 129.7, 128.0, 126.2 (Ar-C), 49.6 (CCH$_3$), 34.9 [C(CH$_3$)$_3$], 29.7 [C(CH$_3$)$_3$], 25.3 (CCH$_3$), 21.3 (Ar-CH$_3$).

1,1,1-Tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)ethane (7b)

In a procedure analogous to that described for **7a**, **2b** (502 mg, 0.710 mmol) was reacted with MeLi (2.7 ml of 1.6 M in ether, 4.32 mmol). The product was very unstable, decomposing over only a few hours in non-alcoholic solvents. This reactivity hindered attempts to purify the compound by chromatography or crystallization. However, the crude material obtained (381 mg, 83%) was pure by ^{1}H NMR spectroscopy.

Mp 104–108 °C (decomp.); m/z (FAB): 642.5045 (M$^+$, $C_{44}H_{66}O_3$ requires 642.5012); ν_{max}/cm^{-1} 3535m (OH); δ_H 7.33 (d, J 2.4 Hz, 3H, Ar-H), 6.91 (d, J 2.4 Hz, 3H, Ar-H), 5.01 (s, 3H, OH), 2.37 (s, 3H, CCH_3), 1.36 (s, 27H, tBu), 1.18 (s, 27H, tBu); δ_C 151.7 (C_{Ar}OH), 142.9, 138.3, 129.8, 124.0, 122.8 (Ar-C), 50.4 (CCH$_3$), 35.3, 34.5 [C(CH$_3$)$_3$], 31.4, 29.9 [C(CH$_3$)$_3$], 25.3 (CCH$_3$).

Tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)phenylmethane (8a)

In a procedure analogous to that described for **7a**, PhLi (3.6 ml of 2 M in cyclohexane–ether, 7.16 mmol) was added to an ether solution of **2a** (694 mg, 1.19 mmol) at −78 °C. After workup, a bright yellow, oily residue was collected. Addition of MeCN (1 ml), with stirring, precipitated crude **8a** as a cream solid, which was collected by filtration and dried. The crude material was subsequently recrystallized by slow evaporation of a saturated acetone solution to produce colorless crystals of **8a**·0.8Me$_2$CO (332 mg, 45%). The stoichiometry of the acetone solvate was determined both by ^{1}H NMR integration and by structural analysis.

Mp 195–197 °C (melts with decomposition) (Found C, 81.6; H, 9.2. $C_{40}H_{50}O_3$·0.8Me$_2$CO requires C, 81.4; H, 8.85%); ν_{max}/cm^{-1} 3529m, 3295m br (OH); δ_H 7.45–7.28 (m, 4H, Ar-H), 7.19 (d, J 2.4 Hz, 1H, Ar-H), 7.17 (d, J 2.4 Hz, 1H, Ar-H), 7.14 (d, J 2.4 Hz, 1H, Ar-H), 7.09 (d, ^3J(H,H) 7.20 Hz, 3H, Ar-H), 7.07 (d, J 2.4 Hz, 3H, Ar-H), 6.73 (d, J 2.4 Hz, 3H, Ar-H), 6.72 (d, J 2.4 Hz, 3H, Ar-H), 5.17 (s, 1H, OH 'up'), 5.09 (s, 1H, OH 'up'), 4.38 (s, 1H, OH 'down'), 2.22 (s, 3H, Ar-CH_3), 2.20 (s, 9H, Ar-CH_3), 2.19 (s, 9H, Ar-CH_3), 1.30 (s, 9H, tBu), 1.27 (s, 18H, tBu); δ_C 152.61, 152.58, 151.7 (C_{Ar}OH), 140.2, 139.6, 139.2, 138.3, 133.7, 129.7, 129.4, 129.25, 129.22, 129.0, 128.9, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.7, 127.3 (Ar-C), 60.1 (Ar$_3$$C$Ph), 34.94, 34.86, 34.7 [C(CH$_3$)$_3$], 29.5, 29.3 [C(CH$_3$)$_3$], 21.4, 21.3, 21.2 (Ar-CH$_3$).

Tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)methane (1a)

Tris(3-*tert*-butyl-5-methyl-2-hydroxyphenyl)carbenium bromide **2a** (25 mg, 0.043 mmol) was dissolved in ether and LiAlH$_4$ (100 mg, excess) added. The solution immediately turned almost colorless. Water was carefully added dropwise, followed by 6 M HCl. After extraction with ether, drying with magnesium sulfate, and evaporation of the solvent, MeOH (1 ml) was added to the solid residue and swirled. The insoluble material was filtered to give **1a** (15 mg, 69%) as a white powder which exhibited the same spectral data as an authentic sample.[1]

X-ray crystallography ‡

The structure of **1a** revealed the presence of three independent molecules in the unit cell, each residing on a three-fold position.

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‡ CCDC reference number 207/420. See http://www.rsc.org/suppdata/p1/b0/b001032o/ for crystallographic files in .cif format.

The structure showed the molecules adopt the same general conformation, hydrogen-bonded dimers, seen previously in the structure of **1b**.[1] For the structures **2a**, **3a** and **8a** the disordered CHCl$_3$, CH$_2$Cl$_2$ and acetone solvates, respectively, were removed ("squeezed") from the data by use of the Platon for Windows software program.[22] The residual electron density removed corresponds to two half site-occupancy CHCl$_3$ molecules for **2a**, one full occupancy CH$_2$Cl$_2$ molecule for **3a**, and a single 0.8 site occupancy acetone for **8a**. Structural and refinement data for the complexes are presented in Table 1. ORTEP diagrams were drawn using the ORTEP-3 for Windows package.[23]

References

1 M. B. Dinger and M. J. Scott, *Eur. J. Org. Chem.*, in press.
2 W. Moene, M. Vos, M. Schakel, F. J. J. de Kanter, R. F. Schmitz and G. W. Klumpp, *Chem. Eur. J.*, 2000, **6**, 225; H. W. Gibson, S.-H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen and M. Bheda, *J. Org. Chem.*, 1993, **58**, 3748.
3 M. B. Dinger and M. J. Scott, *Inorg. Chem.*, 2000, **39**, 1238.
4 T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd edn., Wiley & Sons, 1999, p. 249.
5 G. A. Olah, J. G. Shih, B. P. Singh and B. G. B. Gupta, *J. Org. Chem.*, 1983, **48**, 3356.
6 Th. Zincke, *Ann.*, 1939, **363**, 246.
7 A. Dunand and R. Gerdil, *Acta Crystallogr.*, *Sect. B*, 1984, **40**, 59.
8 The structure of **1a** was also determined for the purposes of comparison with the derivatives presented herein. The bond length and angle data as well as the general conformation of the structure were found to be analogous to those of **1b**, discussed elsewhere.[1]
9 B. Kahr, J. E. Jackson, D. L. Ward and S.-H. Jang, *Acta Crystallogr.*, *Sect. B*, 1992, **48**, 329.
10 C. A. Buehler, D. E. Cooper and E. O. Scrudder, *J. Org. Chem.*, 1943, **8**, 316.
11 J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, 1964, **11**, 2252.
12 E. Weber, N. Dörpinghaus and I. Csöregh, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 2167.
13 G. Casiraghi, G. Casnati, M. Cornia and V. D'Azeglio, *Tetrahedron Lett.*, 1973, 679; G. Casiraghi, G. Casnati, M. Cornia and A. Pochini, *Gazz. Chim. Ital.*, 1978, **108**, 79.
14 C.-M. Liu, R.-G. Xiong, X.-Z. You and W. Chen, *Acta Chem. Scand.*, 1998, **52**, 883; H. Wang, R.-G. Xiong, C.-M. Liu, H.-Y. Chen, X.-Z. You and W. Chen, *Inorg. Chim. Acta*, 1997, **254**, 183; A. Rieker, A. Moosmayer, W. Winter, N. Neumayer and W. Hiller, *Z. Kristallogr.*, 1997, **212**, 161; J.-P. Dubost, J.-M. Leger, J.-C. Colleter, P. Levillain and D. Fompeydie, *C. R. Seances Acad. Sci.*, *Ser. 2*, 1981, **292**, 965.
15 I. L. J. Patterson, C. Glidewell and G. Ferguson, *Acta Crystallogr.*, *Sect. C*, 1998, **54**, 1970.
16 G. Ferguson, C. Glidewell and I. L. J. Patterson, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 420.
17 M. Gomberg and L. H. Cone, *Chem. Ber.*, 1906, **39**, 2957.
18 M. Lofthagen, R. VernonClark, K. K. Baldridge and J. S. Siegel, *J. Org. Chem.*, 1992, **57**, 61.
19 J. S. Vilardo, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1998, **17**, 769.
20 Cambridge Crystallographic Database: D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746; F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.
21 S. P. Verevkin, *J. Chem. Eng. Data*, 1999, **44**, 557.
22 A. L. Spek, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, C-34.
23 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, 565.