

Chemoselectivity in the Reaction of Metal Phenolates with Aromatic Dialdehydes

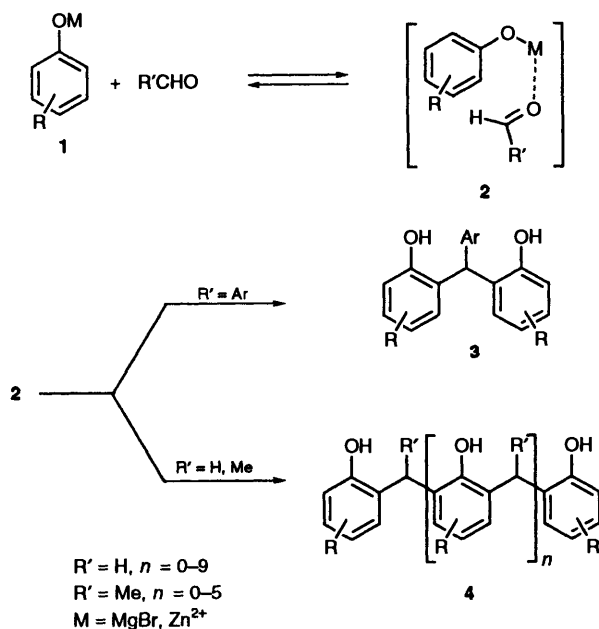
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Oxophilic metal phenolates undergo highly selective condensations with aromatic dialdehydes to produce compounds **6**, **7**, **11** and **12** resulting from di- or tetra-attack, depending upon the phenol-aldehyde molar ratio. 1,4-Anthraquinones **17** were synthesized by allowing 1,4-hydroquinones to react with phthalaldehyde (OPA).

The development of a selective synthetic methodology for the construction of phenol-aldehyde telomers is of current interest because of the potential of the latter in the stepwise synthesis of macrocyclic ligands such as calixarenes¹ and dendritic macromolecules such as the so-called 'starburst' polymers.²

In previous papers, we have reported that oxophilic metal phenolates react with aldehydes to provide a convenient route to 2,2'-dihydroxytriphenylmethanes **3**³ or telomers **4**⁴ (depending on the nature of the aldehyde). It was suggested that the reaction occurred *via* complex **2**⁵ whose crucial role was demonstrated by NMR analysis of appropriate reaction mixtures (see Scheme 1).⁶



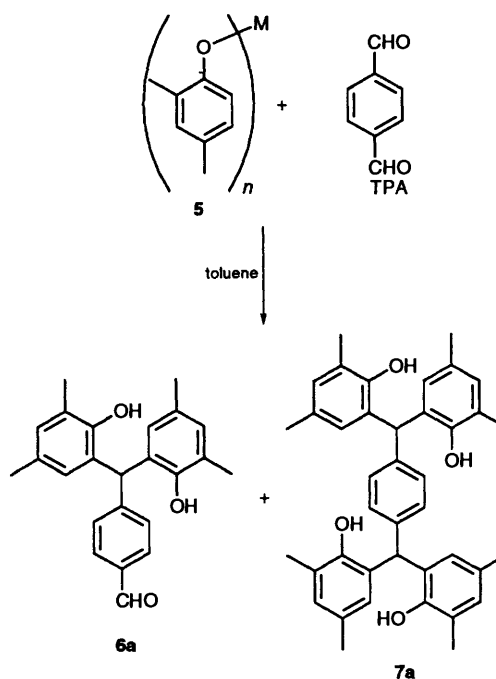
Scheme 1

Recently, we have studied the reactivity of metal phenolates with terephthalaldehyde (TPA), isophthalaldehyde (IPA) and phthalaldehyde (OPA) with the goal of preparing new synthons for phenolic macrocyclic ligands. We have also reinvestigated the condensation of OPA with hydroquinones to produce 1,4-anthraquinones, as previously described by Lepage and co-workers.⁷ We detail the outcome of these studies in this paper.

Results and Discussion

We first examined the reaction between various metal 2,4-dimethylphenolates⁵ with TPA to see how the metal ion M

affected the chemoselectivity of the process. Thus, potassium, bromomagnesium, tin and titanium 2,4-dimethylphenolates were allowed to react with TPA in dry toluene at 110 °C for 5 h (see Scheme 2).



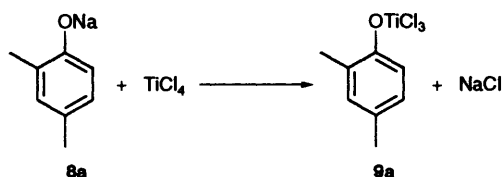
Scheme 2

The reaction was expected to afford the two products **6a** and **7a** as the result of di- and tetra-attack, respectively, by the phenolate **5** on the dialdehyde. Results given in Table 1 demonstrate the important influence of the acidic character and the coordinating power of the metal ion M. Thus, the highly coordinating counterions (Sn^{IV} and Ti^{IV}) are very powerful promoters of this reaction; with titanium(IV) compound **6a** was obtained in 85% yield for a 2:1 phenol-aldehyde ratio and compound **7a** in 88% yield for a 4:1 phenol-aldehyde ratio. More conveniently, the process was performed by treating TPA with sodium 2,4-dimethylphenolate **8a** in the presence of a stoichiometric amount of TiCl_4 in dry toluene at 110 °C; under these conditions, the more reactive trichlorotitanium phenolate **9a** is produced (see Scheme 3).

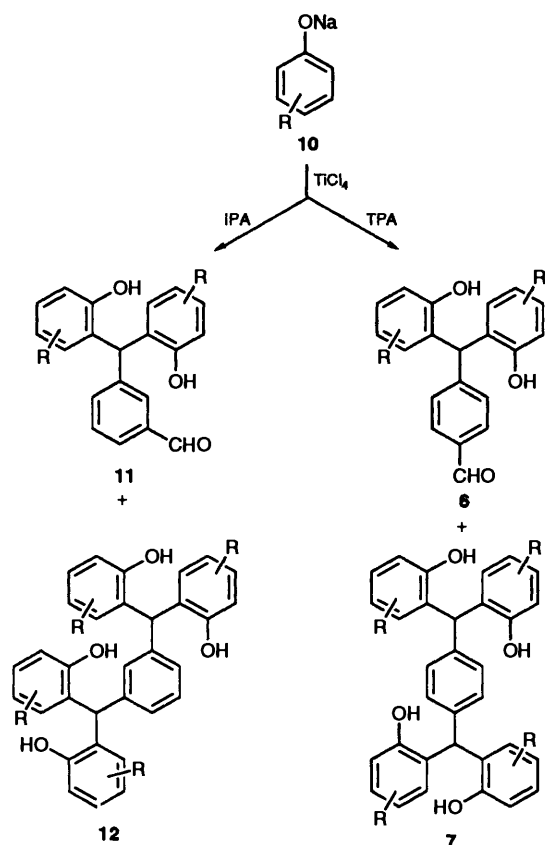
As earlier reported, compound **9a** and similar phenolates react with coordinated aldehydes to give alcohols or phenolic telomers with high chemoselectivity.⁸ With *p*-*tert*-butylphenol and IPA similar reactions gave the polyhydroxylated com-

Table 1 Reaction between 2,4-dimethylphenolates and TPA

Entry	M	n	Phenol-aldehyde ratio	Yield of 6a (%)	Yield of 7a (%)
1	K	1	2	10	3
2	K	1	4	5	18
3	MgBr	1	2	40	7
4	MgBr	1	4	8	50
5	Sn ^{IV}	4	2	68	7
6	Sn ^{IV}	4	4	10	73
7	Si ^{IV}	4	2	85	10
8	Ti ^{IV}	4	4	9	88



pounds 11a and 12a, which have potential as synthons for polyphenolic ligands⁹ (see Scheme 4). Compared with those of TPA, the reactions with IPA suffer from some steric hindrance as evidenced by the lower product yields (Table 2).

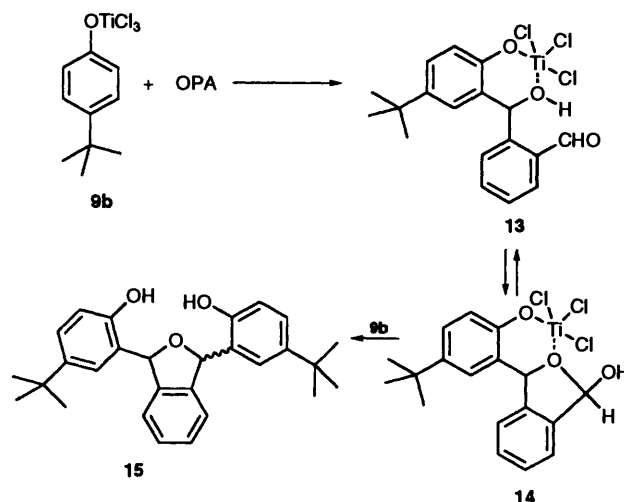


The reaction of trichlorotitanium 4-*tert*-butylphenolate **9b** with OPA under similar conditions failed to give triphenylmethane derivatives (see Scheme 4), a complex reaction mixture being produced from which the dihydroisobenzofuran derivative **15** (*cis* and *trans* mixture) was isolated as the main product (30%) by preparative TLC (see Scheme 5).

On the basis of these results and reports from the literature,¹⁰ we suggest that the intermediate **13**, formed by addition of **9b** to the CHO group of OPA, undergoes 'ring-chain tautomerism'¹¹

Table 2 Reaction between sodium phenolates and TPA or IPA, in the presence of TiCl₄

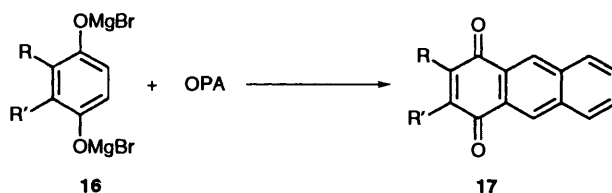
Entry	R	Aldehyde	Phenol-aldehyde ratio	Product (% yield)
1	2,4-Me ₂	TPA	2	6a (85)
2	4-Bu ^t	TPA	2	6b (88)
3	2,4-Me ₂	TPA	4	7a (86)
4	4-Bu ^t	TPA	4	7b (90)
5	2,4-Me ₂	IPA	2	11a (60)
6	4-Bu ^t	IPA	2	11b (85)
7	2,4-Me ₂	IPA	4	12a (62)
8	4-Bu ^t	IPA	4	12b (85)



to afford the cyclic isomer **14** and that this reacts with a second molecule of **9b**, replacing the acetalic OH group and leading to the final product **15**.

These results taken together prompted us to reinvestigate the vicinal bisalkylation of hydroquinones with OPA. The reaction was previously described to be promoted by stoichiometric quantities of bases such as pyridine and NaOH.⁷ In that study, the substrates were limited to substituted 1,4-hydroquinones. In fact, the 1,4-anthrahydroquinone initially obtained reacts further with a second molecule of OPA giving pentacene-6,13-quinone.

Adapting our methodology, we treated OPA with hydroquinone bis(magnesium bromide) salt **16c** in dry toluene under a nitrogen atmosphere at 110 °C for 1 h to give the expected 1,4-anthraquinone **17c** (70%) (see Scheme 6). Other hydroquinones



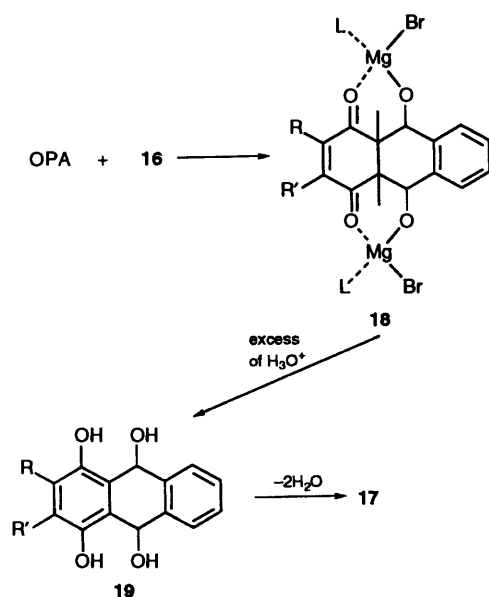
reacted similarly (see Table 3). The poor yield obtained with methoxyhydroquinone (entry 3) is explained in terms of coordination of the Lewis acid (MgBr) to the methoxy group which deactivates the substrate toward electrophilic attack.¹²

Our results on the vicinal bisacylation of hydroquinones¹³ and reports from the literature¹⁴ suggest that a simpler mechanistic scheme is in operation whereby the dichelation adduct **18** is the key intermediate. The 1,4-anthraquinones **17**

Table 3 Reaction between different 1,4-hydroquinone bis(magnesium bromides) and OPA

Entry	R	R'	Product (% yield)
1	H	H	17c (70)
2	Me	H	17d (85)
3	OMe	H	17e (20)
4	Me	Me	17f (88)

are obtained *via* a double dehydration of **19** according to the mechanism of the acid-promoted conversion of saligenin into 1,2-benzoquinone mono-methide¹⁵ (Scheme 7).

**Scheme 7**

Experimental

M.p.s were obtained on an Electrothermal melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker AC100 spectrometer at 100 MHz, on a Bruker CXP200 spectrometer at 200 MHz and on a Bruker AMX400 spectrometer at 400 MHz. Chemical shifts are expressed in ppm relative to tetramethylsilane as internal standard and *J* values are expressed in Hz. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Mass spectra were obtained on a Finnigan 1020 instrument at 70 eV and on a Finnigan SSQ 710 instrument in 'E.I. mode'. Microanalyses were carried out by Istituto di Chimica Farmaceutica dell'Università di Parma, Italy. Potassium, bromomagnesium and titanium phenolates were prepared as previously reported in the literature.¹⁶

Tin(IV) 2,4-Dimethylphenolate.—A solution of 2,4-dimethylphenol (1.22 g, 0.01 mol) in dry toluene (50 cm³) was added to a solution of tin(IV) tetraethoxide¹⁷ (0.75 g, 0.0025 mol) in dry toluene (50 cm³). The resulting solution was refluxed for 30 min and then slowly distilled to remove completely the ethanol formed (*ca.* 2 h). The solution of the phenolate was directly utilized.

Reaction between Metal 2,4-Dimethylphenolates 5 and TPA.—**General procedure.** A solution of TPA (0.67 g, 0.005 mol) in dry toluene (50 cm³) was added, under nitrogen, to a solution of the selected metal 2,4-dimethylphenolate [total phenol-aldehyde molar ratio = 2:1 or 4:1 (see Table 1)] in dry toluene

(50 cm³). The stirred reaction mixture was refluxed for 5 h and then cooled. Aqueous 10% HCl (100 cm³) was then rapidly added to the mixture after which it was extracted with Et₂O (3 × 50 cm³). The organic phase was dried (Na₂SO₄) and the solvent distilled off. The residue was chromatographed on silica gel plates with hexane–ethyl acetate (30%) to give the products.

Synthesis of Products 6, 11 and 15.—**General procedure.** A solution of the selected phenol (0.01 mol) in dry toluene (50 cm³) was added dropwise, under nitrogen, to a suspension of NaH (0.4 g, 0.01 mol) in dry toluene (50 cm³) and the mixture was heated at reflux for 30 min and then cooled. A solution of TiCl₄ (1.9 g, 0.01 mol) in dry toluene (30 cm³) was added to the mixture which was then refluxed for 15 min. A solution of the selected dialdehyde (0.67 g, 0.005 mol) in dry toluene (50 cm³) was added at room temp. to the mixture which was then refluxed for 2 h. After the reaction mixture had cooled it was quenched with aqueous 10% HCl (100 cm³) and extracted with Et₂O (3 × 50 cm³). The organic phase was dried (Na₂SO₄) and the solvent distilled off. The residue was chromatographed on silica gel plates with hexane–ethyl acetate (20–30%) to give the products.

Synthesis of Products 7 and 12.—**General procedure.** The reaction was carried out under the conditions reported for the synthesis of products 6, 11 and 15 (see General procedure) by using a phenol–aldehyde molar ratio of 4:1.

Synthesis of 1,4-Anthraquinones 17.—**General procedure.** To a solution of EtMgBr (0.01 mol) in dry tetrahydrofuran (THF) (50 cm³) a solution of the selected hydroquinone (5 mmol) in dry THF (50 cm³) was added under nitrogen and the reaction mixture was refluxed for 10 min. After the reaction mixture had cooled, the THF was distilled off and replaced with dry toluene (50 cm³). A solution of the OPA (0.67 g, 0.005 mol) in dry toluene (50 cm³) was then added dropwise to the mixture which was then refluxed for 1 h. After cooling to room temp., the mixture was quenched with aqueous 10% HCl (100 cm³) and extracted with CH₂Cl₂ (3 × 50 cm³). The combined extracts were dried (Na₂SO₄) and the solvent distilled off. The residue was chromatographed on silica gel plates with hexane–ethyl acetate (15–25%) to give the products.

4'-Formyl-2,2'-dihydroxy-3,3',5,5'-tetramethyltriphenylmethane 6a. A white solid, m.p. 96 °C (from benzene) (Found: C, 80.0; H, 6.8. C₂₄H₂₄O₃ requires C, 79.97; H, 6.71%); ν_{\max} (KBr)/cm⁻¹ 3500 (OH) and 1700 (C=O); δ_{H} (100 MHz, CDCl₃) 2.17 (6 H, s, Me), 2.20 (6 H, s, Me), 4.88 (2 H, s, OH), 5.95 (1 H, s, CH), 6.5 (2 H, br s, 6-H and 6'-H or 4-H and 4'-H), 6.7 (2 H, br s, 4-H and 4'-H or 6-H and 6'-H), 7.33 (2 H, d, *J* 8.2, 2''-H and 6''-H), 7.81 (2 H, d, *J* 8.2, 3''-H and 5''-H) and 9.98 (1 H, s, CHO); *m/z* 360 (M⁺, 40%), 239 (100) and 209 (35).

5,5'-Di-tert-butyl-2,2'-dihydroxy-4'-formyltriphenylmethane 6b. A white solid, m.p. 98 °C (from benzene) (Found: C, 80.8; H, 7.8. C₂₈H₃₂O₃ requires C, 80.73; H, 7.74%); ν_{\max} (KBr)/cm⁻¹ 3400 (OH) and 1690 (C=O); δ_{H} (100 MHz, CDCl₃) 1.18 (18 H, s, Me₃C), 5.7 (2 H, br s, OH), 6.09 (1 H, s, CH), 6.76 (2 H, d, *J* 8.3, 3-H and 3'-H), 6.97 (2 H, d, *J* 2.3, 6-H and 6'-H), 7.16 (2 H, dd, *J* 8.3 and 2.3, 4-H and 4'-H), 7.33 (2 H, d, *J* 8.1, 2''-H and 6''-H), 7.80 (2 H, d, *J* 8.1, 3''-H and 5''-H) and 9.97 (1 H, s, CHO); *m/z* 416 (M⁺, 85%), 401 (65), 359 (30) and 267 (100).

2,2'-Dihydroxy-3''-formyl-3,3',5,5'-tetramethyltriphenylmethane 11a. A pale yellow solid, m.p. 178 °C (from benzene) (Found: C, 79.9; H, 6.7. C₂₄H₂₄O₃ requires C, 79.97; H, 6.71%); ν_{\max} (KBr)/cm⁻¹ 3344 (OH) and 1686 (C=O); δ_{H} (100 MHz, CDCl₃) 2.16 (6 H, s, Me), 2.20 (6 H, s, Me), 5.0 (2 H, br s, OH), 5.97 (1 H, s, CH), 6.5 (2 H, br s, 4-H and 4'-H or 6-H and 6'-H),

6.9 (2 H, br s, 6-H and 6'-H or 4-H and 4'-H), 7.3–7.9 (4 H, m, 2''-H, 4''-H, 5''-H and 6''-H) and 9.92 (1 H, s, CHO); m/z 360 (M^+ , 92%), 267 (12) and 239 (100).

5,5'-Di-tert-butyl-3''-formyl-2,2'-dihydroxytriphenylmethane 11b. A white solid, m.p. 80 °C (from benzene) (Found: C, 80.8; H, 7.8. $C_{28}H_{32}O_3$ requires C, 80.73; H, 7.74%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3400 (OH) and 1690 (C=O); $\delta_{\text{H}}(100 \text{ MHz, CDCl}_3)$ 1.16 (18 H, s, Me_3C), 5.5 (2 H, br s, OH), 6.07 (1 H, s, CH), 6.76 (2 H, d, J 8.3, 3-H and 3'-H), 6.97 (2 H, d, J 2.4, 6-H and 6'-H), 7.16 (2 H, dd, J 8.3 and 2.4, 4-H and 4'-H), 7.3–8.0 (4 H, m, 2''-H, 4''-H, 5''-H and 6''-H) and 9.93 (1 H, s, CHO); m/z 416 (M^+ , 100%), 401 (70), 359 (25) and 267 (90).

1,4-Bis(2,2'-dihydroxy-3'',3'',5'',5''-tetramethyldiphenylmethyl)benzene 7a. A pale yellow solid, m.p. 93–95 °C (from benzene) (Found: C, 81.8; H, 7.3. $C_{40}H_{42}O_4$ requires C, 81.88; H, 7.22%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3496 (OH); $\delta_{\text{H}}(100 \text{ MHz, CDCl}_3)$ 2.16 (12 H, s, CH_3), 2.18 (12 H, s, CH_3), 4.9 (4 H, br s, OH), 5.77 (2 H, s, CH), 6.54 (4 H, d, J 1.7, 3-H and 3'-H), 6.85 (4 H, d, J 1.7, 6-H and 6'-H) and 7.11 (4 H, s, 2-H, 3-H, 5-H and 6-H); m/z 586 (M^+ , 40%), 465 (100) and 255 (40).

1,4-Bis(5'',5''-di-tert-butyl-2'',2''-dihydroxydiphenylmethyl)benzene 7b. A white solid, m.p. 143 °C (from benzene) (Found: C, 82.55; H, 8.3. $C_{48}H_{58}O_4$ requires C, 82.48; H, 8.36%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3350 (OH); $\delta_{\text{H}}(100 \text{ MHz, CDCl}_3)$ 1.17 (36 H, s, Me_3C), 5.4 (4 H, br s, OH), 5.91 (2 H, s, CH), 6.73 (4 H, d, J 8.3, 3'-H and 3''-H) and 6.9–7.3 (12 H, m, 2-H, 3-H, 5-H, 6-H, 4'-H, 4''-H, 6'-H and 6''-H); m/z 698 (M^+ , 30%), 640 (25), 549 (40), 311 (45) and 57 (100).

1,3-Bis(2'',2''-dihydroxy-3'',3'',5'',5''-tetramethyldiphenylmethyl)benzene 12a. A yellow solid, m.p. 70 °C (from benzene) (Found: C, 81.2; H, 7.6. $C_{38}H_{42}O_4$ requires C, 81.10; H, 7.52%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3500 (OH); $\delta_{\text{H}}(100 \text{ MHz, CDCl}_3)$ 2.13 (12 H, s, Me), 2.16 (12 H, s, Me), 4.8 (4 H, br s, OH), 5.70 (2 H, s, CH), 6.48 (4 H, d, J 1.8, 4'-H and 4''-H or 6'-H and 6''-H), 6.82 (4 H, d, J 1.8, 6'-H and 6''-H or 4'-H and 4''-H), 6.9–7.2 (3 H, m, 4-H, 5-H and 6-H) and 7.24 (1 H, s, 2-H); m/z 586 (M^+ , 40%), 465 (100) and 209 (20).

1,3-Bis(5'',5''-di-tert-butyl-2'',2''-dihydroxydiphenylmethyl)benzene 12b. A white solid, m.p. 173 °C (from benzene) (Found: C, 82.55; H, 8.3. $C_{46}H_{58}O_4$ requires C, 82.48; H, 8.36%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3300 (OH); $\delta_{\text{H}}(100 \text{ MHz, CDCl}_3)$ 1.13 (36 H, s, Me_3C), 5.90 (2 H, s, CH), 6.6 (4 H, br s, OH), 6.71 (4 H, d, J 8.3, 3-H and 3'-H) and 6.8–7.3 (12 H, m, 2-H, 4-H, 5-H, 6-H, 4'-H, 4''-H, 6'-H and 6''-H); m/z 698 (M^+ , 85%), 640 (35), 548 (100) and 311 (40).

1,3-Bis(5'-tert-butyl-2'-hydroxyphenyl)-1,3-dihydroisobenzofuran (cis or trans isomer) 15. A pale yellow solid, m.p. 83–86 °C (from benzene) (Found: C, 80.7; H, 7.8. $C_{28}H_{32}O_3$ requires C, 80.73; H, 7.74%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3311 (OH); $\delta_{\text{H}}(300 \text{ MHz, CDCl}_3)$ 1.26 (9 H, s, Me_3C), 6.55 (2 H, s, 1-H and 3-H), 6.84 (2 H, s, J 8.5, 3'-H), 6.92 (2 H, s, OH), 7.12 (2 H, d, J 2.4, 6'-H), 7.26 (2 H, dd, J 8.5 and 2.4, 4'-H), 7.27 (2 H, m, 4-H and 7-H or 5-H and 6-H) and 7.36 (2 H, m, 5-H and 6-H or 4-H and 7-H); m/z 416 (M^+ , 50%), 399 (100), 343 (60) and 267 (96).

1,3-Bis(5'-tert-butyl-2'-hydroxyphenyl)-1,3-dihydroisobenzofuran (trans or cis isomer) 15. A white solid, m.p. 191–193 °C (from benzene) (Found: C, 80.7; H, 7.8. $C_{28}H_{32}O_3$ requires C, 80.73; H, 7.74%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3355 (OH); $\delta_{\text{H}}(400 \text{ MHz, CDCl}_3)$ 1.27 (9 H, s, Me_3C), 6.28 (2 H, s, 1-H and 3-H), 6.55 (2 H, s, OH), 6.74 (2 H, d, J 8.3, 3'-H), 7.12 (2 H, m, 4-H and 7-H or 5-H and 6-H), 7.24 (2 H, dd, J 8.3 and 2.3, 4'-H), 7.26 (2 H, d, J 2.3, 6'-H) and 7.30 (2 H, m, 5-H and 6-H or 4-H and 7-H); m/z 416 (M^+ , 35%), 399 (60), 343 (50) and 267 (100).

1,4-Anthraquinone 17c. A yellow solid, m.p. 210 °C (from toluene) (lit.,¹⁸ m.p. 218 °C).

2-Methyl-1,4-anthraquinone 17d. A yellow–orange solid, m.p. 185 °C (from toluene) (Found: C, 81.0; H, 4.6. $C_{15}H_{10}O_2$ requires C, 81.06; H, 4.54%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1675 (C=O); $\delta_{\text{H}}(100 \text{ MHz, CDCl}_3)$ 2.24 (3 H, d, J 1.5, Me), 6.93 (1 H, q, J 1.5, 3-H), 7.66 (2 H, dd, J 6.2 and 3.3, 6-H and 7-H), 8.04 (2 H, dd, J 6.2 and 3.3, 5-H and 8-H), 8.56 (1 H, s, 9-H or 10-H) and 8.60 (1 H, s, 10-H or 9-H); m/z 222 (M^+ , 100%), 194 (15), 165 (80) and 126 (55).

2-Methoxy-1,4-anthraquinone 17e. A green solid, m.p. 202 °C (from toluene) (lit.,¹⁹ m.p. 217 °C).

2,3-Dimethyl-1,4-anthraquinone 17f. A red solid, m.p. 206 °C (from toluene) (lit.,^{7c} m.p. 218 °C).

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