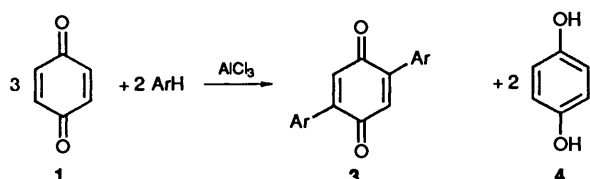


Reinvestigation of the Pummerer Arylation of Quinones: A Selective Approach to 2,2',5'-Trihydroxybiaryls

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A reinvestigation of the Pummerer arylation of quinones in light of the metal-template catalysis has provided a direct and selective route to 2,2',5'-trihydroxybiaryls **7**, a class of compounds useful in the synthesis of polycyclic natural products. Compounds **7** are readily synthesized by mixing dichloroaluminium phenolates **8** with a slurry of the 1:2 adduct formed between *p*-benzoquinone and AlCl₃ in CS₂ (room temp., 4 h).

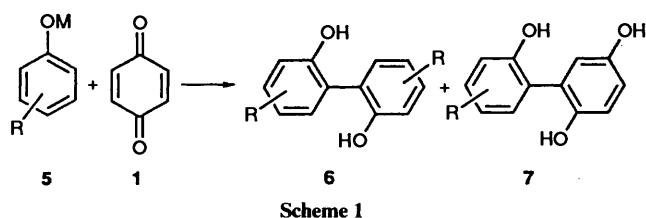
In 1922 Pummerer reported the AlCl₃-promoted reaction of *p*-benzoquinone **1** with aromatic substrates **2** to give 2,5-biaryl-1,4-benzoquinones **3** by a mechanism involving two sequential addition-oxidation steps.¹ Shortly thereafter, examples of the



addition of aromatic and heteroaromatic reagents to quinones appeared in the literature.² This reaction is of continuing interest because of the biological activity and synthetic utility of many arylated and heteroarylated quinones, as reported in recent articles and reviews.³

During our studies aimed at evaluating the factors which control the regio- and chemo-selectivity of the electrophilic as well as the radical arylation of phenols, we have investigated the reaction of oxophilic metal phenolates with quinones and their derivatives. We have recently reported that titanium phenolates react with benzoquinone bis(dimethyl ketals) to afford good yields, with high selectivity, of *ortho*-hydroxyaryl hydroquinone bis(methyl ethers) *via* a 'metal-template process'.⁴

However, our efforts to extend this reaction to *p*-benzoquinone resulted in the production of two biaryls **6** and **7** arising, respectively, from the oxidative coupling of the phenol promoted by the quinone itself⁵ and from the electrophilic arylation of the quinone.



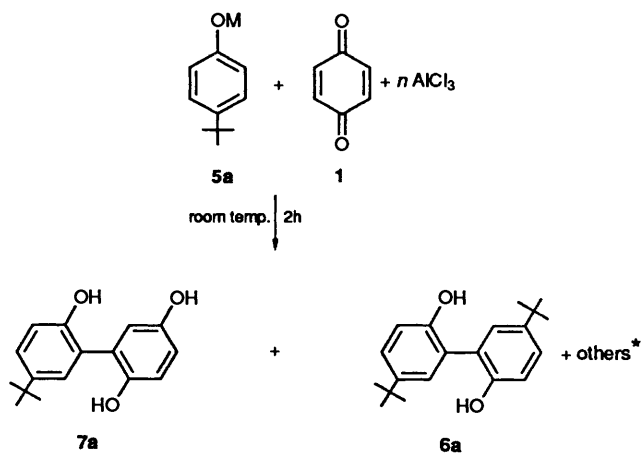
We thus initiated a more detailed investigation of the addition of metal phenolates to quinones with particular interest in the synthesis of monoarylated hydroquinones **7**.

Results and Discussion

We selected *p*-*tert*-butylphenol as the model substrate for our feasibility study. The reaction of different metal *p*-*tert*-butylphenolates **5a** and *p*-benzoquinone **1** (molar ratio 1:1) was examined under varying conditions (see Table 1).

From the analysis of data reported in Table 1, dichloroaluminium *p*-*tert*-butylphenolate proved to be the best promoter of the present reaction. The optimum yield and selectivity was obtained by adding a solution of dichloroaluminium *p*-*tert*-butylphenolate in CS₂ at room temperature to a stirred slurry of the 1:2 adduct formed between *p*-benzoquinone and AlCl₃ in the same solvent at 0 °C. Lower yields were obtained by using *p*-*tert*-butylphenol itself. The use of a large excess of AlCl₃ led to extensive decomposition of the *p*-benzoquinone. Good selectivities were observed with MgBr, Ti^{IV} and K phenolates, but the yields were lower and no reaction occurred at all with Zn^{II} phenolate. Further, the use of the free phenolate anion produced an intractable mixture of polymeric materials.

Table 1 Reaction between metal phenolates and *p*-benzoquinone under different experimental conditions

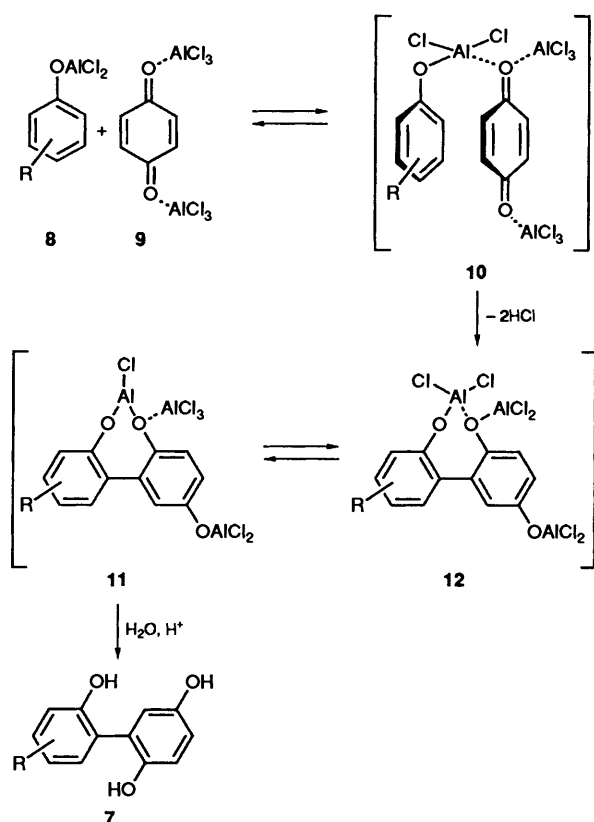


M	<i>n</i>	Solvent	7a yield (%)	6a yield (%)	7a select. (%)
H	1	CS ₂	28	0	86
H	2	CS ₂	38	0	89
H	3	CS ₂	36	0	85
H	5	CS ₂	5	0	60
AlCl ₂	1	CS ₂	55	0	79
AlCl ₂	2	CS ₂	70	0	90
AlCl ₂	2	CH ₃ NO ₂	18	15	50
AlCl ₂	2	CH ₂ Cl ₂	16	19	41
Zn ^{II}	2	CS ₂	0	0	—
MgBr	2	CS ₂	34	5	77
Ti ^{IV}	2	CS ₂	47	0	85
K	2	CS ₂	25	0	60
K/Crown	2	CS ₂	polymeric materials		

* Traces of 2,2',5,5'-tetrahydroxybiphenyl and 5-*tert*-butyl-2,2'-dihydroxybiphenyl were detected.

High yields and good selectivity are crucially dependent on the choice of solvent; for example, the model reaction of dichloroaluminium *p*-*tert*-butylphenolate with *p*-benzoquinone-2AlCl₃ was far more efficient in carbon sulfide (70% yield) than in either nitromethane or methylene dichloride (18 and 16% yield). Although this result is not easily understood, it may be attributed to a change of the redox potential of the complex benzoquinone-AlCl₃, whose reactivity depends upon the solubility and the aggregation number which, obviously, varies when the solvent is changed.

For the general scheme of the reaction, we propose a still speculative metal-template 1,4-reductive addition process mediated by a donor-acceptor complex **10** (see Scheme 2).*



The monoarylated hydroquinone **7** is, in principle, prone to oxidation by a second molecule of the quinone. The nature of the hydroxyaryl substituent introduced will determine, to a great degree, such subsequent chemistry. Our previous results allowed us to suppose that, when the phenolic OH groups are in the two proximate *ortho* positions, the chelates **11** and **12** are obtained, which are relatively stable towards further attack or oxidation.⁵ Consequently, under these experimental conditions, it is possible to stop the reaction at the hydroquinone mono-substituted products **7**.

In contrast, in the general mechanism of Pummerer arylation, the final stage results in the reoxidation of the mono-substituted hydroquinone **7** to the corresponding monoaryl quinone which undergoes further arylation. This behaviour was observed when *p*-benzoquinone reacts with the phenol at the *para* position and, in particular, when the reaction is carried out in highly

Table 2 Oxidation of the product **7a** with *p*-benzoquinone under different experimental conditions

	<i>n</i>	Solvent	13 (%)
	0	CS ₂	50
	1	CS ₂	25
	3	CS ₂	8
	3	THF	30
	3	DMF	40

polar or protic solvents capable of strongly interacting with the Lewis acid, thus disfavoring the formation of chelates such as **11** and **12**.

In order to confirm this hypothesis, we studied the oxidation of the compound **7a** with *p*-benzoquinone in different solvents and in the presence of increasing amounts of AlCl₃.

As the results from Table 2 show, *p*-benzoquinone **1** oxidizes the compound **7a** to the corresponding quinone **13** in 50% yield, but the 1:1 adduct between **7a** and AlCl₃ is more stable toward oxidation (25% yield). Moreover, compound **13** is only produced in 8% yield when the oxidation is performed under the general conditions reported in Scheme 2. Finally, the use of highly solvating media such as THF or DMF has the effect of favouring the oxidation process even in the presence of 3 mol equiv. of AlCl₃.

Attempts to extend the reaction to a variety of phenols and quinones under the optimum conditions of Table 1 gave products **7** in satisfactory yields and with good selectivity (Table 3).

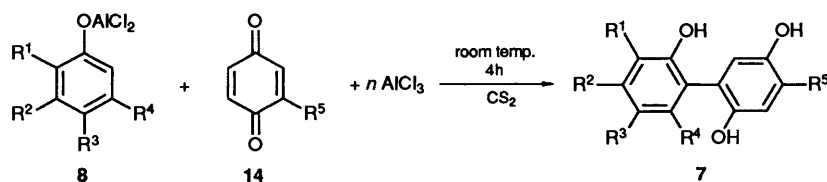
In all cases, only carbon-carbon bond formation was observed. The reaction is extremely sensitive to the electronic effects, and is completely inhibited when phenols bearing electron-withdrawing groups are utilized (*i.e.* *p*-chlorophenol and *p*-ethoxycarbonylphenol). Moreover, the process shows excellent regioselectivity in the reaction with monosubstituted quinones. The less hindered 5-position becomes the sole reaction site of both 2-methyl- and 2-chloro-1,4-benzoquinones, as proved by ¹H NMR spectra of the reaction products (see Experimental section).

In conclusion, a reinvestigation of the Pummerer arylation, in the light of metal-template catalysis, allowed us to open a direct and selective route to the hydroxyaryl hydroquinones **7**, a class of compounds useful in the synthesis of polycyclic natural products.^{3a,6}

Experimental

M.p.s were obtained on an Electrothermal melting point apparatus and are uncorrected. ¹H NMR spectra were recorded 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 TMS as internal standard and *J* values are 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. Chlorine content was determined by combustion in an oxygen-filled flask.⁷

* Dichloroaluminium 2,4-dichlorophenolate and *p*-benzoquinone (molar ratio 1:1) when mixed in CS₂, give immediate formation of a blue colour; the UV-VIS spectrum of the solution shows a large band at 580 nm (log ε 2.44).

Table 3 Reaction between different dichloroaluminium phenolates and various *p*-benzoquinones

Entry	R^1	R^2	R^3	R^4	R^5	n	7 (%)	Selectivity (%)
a	H	H	Bu ^t	H	H	2	70	90
b	H	H	Me	H	H	2	68	85
c	H	H	1,1,3,3-Tetramethylbutyl	H	H	2	64	80
d	H	H	-(O-CH ₂ -O)-	H	H	2	47*	87
e	H	H	-(CH=CH) ₂ -	H	H	1	60	91
f	H	Bu ^t	H	H	H	2	62	85
g	2-OH, 5 Bu ^t Ph	H	Bu ^t	H	H	2	22	91
h	H	H	Bu ^t	H	Me	2	40	83
i	H	H	Bu ^t	H	Cl	2	57	92

* $\text{Al}(\text{ArO})\text{Cl}$ was employed as counterion (see Experimental section).

Zinc *p*-tert-Butylphenolate.—To a stirred solution of *p*-tert-butylphenol (1.5 g, 10 mmol) in CS_2 (30 cm^3) is added under nitrogen a solution of diethylzinc in toluene (1.1 mol dm^{-3} ; 4.5 cm^3 , 5 mmol). The mixture was stirred for 30 min before use.

Dichloroaluminium *p*-tert-Butylphenolate.—To a stirred solution of *p*-tert-butylphenol (1.5 g, 10 mmol) in CS_2 (30 cm^3) was added, under nitrogen, a solution of EtAlCl_2 in hexane (1 mol dm^{-3} ; 10 cm^3 , 10 mmol). The mixture was stirred for 30 min before use. More conveniently AlCl_3 can be utilized instead of EtAlCl_2 as early reported.⁸

All the other phenolates were prepared as previously described.⁹

Hydroxylated Biaryls 7: General Procedure.—A solution of the selected dichloroaluminium phenolate (10 mmol) in CS_2 (20 cm^3) was added at room temperature to a stirred slurry of the 1:2 adduct between *p*-benzoquinone (1.08 g, 10 mmol) and AlCl_3 (2.66 g, 20 mmol) in CS_2 (20 cm^3) at 0 °C under nitrogen. Stirring was continued for 4 h at room temperature. The reaction was quenched with aq. HCl (2 mol dm^{-3} ; 50 cm^3) and the resulting mixture was extracted with methylene dichloride (3 \times 50 cm^3). The organic phase was dried (Na_2SO_4), the methylene dichloride was distilled off and the residue was chromatographed on silica gel plates with 30–50% hexane– EtOAc mixtures to give the products.

2,2',5'-Trihydroxy-4,5-methylenedioxybiphenyl 7d.—To a stirred solution of 3,4-methylenedioxyphenol (1.38 g, 10 mmol) in dry CS_2 (30 cm^3) was added, under nitrogen, a solution of Et_2AlCl in hexane (1 mol dm^{-3} ; 5 cm^3). The mixture was stirred for 30 min and then added to a slurry of *p*-benzoquinone (1.08 g, 10 mmol) and AlCl_3 (2.66 g, 20 mmol) in CS_2 (20 cm^3) at 0 °C under nitrogen. Stirring was continued for 4 h at room temperature after which work-up as described above gave the product **7d** (47%).

Oxidation of the Product 7a: General Procedure.—To a stirred mixture of the product **7a** (1.29 g, 5 mmol) and AlCl_3 (n mol, see Table 2) in the appropriate solvent, a solution of *p*-benzoquinone (0.54 g, 5 mmol) in the same solvent was added under nitrogen. Stirring was continued for 1 h at room temperature after which the reaction was quenched with aq. HCl (2 mol dm^{-3} ; 50 cm^3). The resulting mixture was extracted with

methylene dichloride (3 \times 50 cm^3) and the combined extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel plates with 20% hexane– EtOAc mixture to give the product **13**.

5-tert-Butyl-2,2',5'-trihydroxybiphenyl 7a. A grey solid, m.p. 67 °C (from benzene) (Found: C, 74.45; H, 6.9. $\text{C}_{16}\text{H}_{18}\text{O}_3$ requires C, 74.39; H, 7.02%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3289 (OH); $\delta_{\text{H}}(400 \text{ MHz}, \text{C}_6\text{D}_6, \text{MeOD})$ 1.24 (9 H, s, Bu^t), 7.00 (1 H, dd, J 8.6 and 3.0, 4-H or 4'-H), 7.10 (1 H, d, J 8.6, 3-H or 3'-H), 7.12 (1 H, d, J 8.5, 3'-H or 3-H), 7.21 (1 H, d, J 3.0, 6-H or 6'-H), 7.22 (1 H, dd, J 8.5 and 2.5, 4'-H or 4-H) and 7.54 (1 H, d, J 2.5, 6'-H or 6-H); m/z 258 (M^+ , 58%), 243 (100), 227 (18), 202 (30) and 107 (14).

2,2',5'-Trihydroxy-5-methylbiphenyl 7b. A grey solid, m.p. 146–149 °C (from benzene) (Found: C, 72.1; H, 5.7. $\text{C}_{13}\text{H}_{12}\text{O}_3$ requires C, 72.21; H, 5.59%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3247 (OH); $\delta_{\text{H}}(400 \text{ MHz}, \text{C}_6\text{D}_6, \text{MeOD})$ 2.14 (3 H, s, Me), 6.95 (1 H, dd, J 7.7 and 2.0, 4-H), 7.00 (1 H, dd, J 8.6 and 2.9, 4'-H), 7.08 (1 H, d, J 7.7, 3-H), 7.10 (1 H, d, J 8.6, 3'-H), 7.16 (1 H, d, J 2.9, 6'-H) and 7.21 (1 H, d, J 2.0 Hz, 6-H); m/z 216 (M^+ , 100%), 197 (34), 187 (16), 161 (35) and 134 (30).

2,2',5'-Trihydroxy-5-(1,1,3,3-tetramethylbutyl)biphenyl 7c. A brown solid, m.p. 128–130 °C (from benzene) (Found: C, 76.3; H, 8.3. $\text{C}_{20}\text{H}_{26}\text{O}_3$ requires C, 76.40; H, 8.34%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3293 (OH); $\delta_{\text{H}}(400 \text{ MHz}, \text{C}_6\text{D}_6, \text{MeOD})$ 0.79 (9 H, s, Bu^t), 1.30 (6 H, s, 2Me), 1.66 (2 H, s, CH_2), 7.00 (1 H, d, J 8.6 and 3.0, 4-H, or 4'-H), 7.10 (1 H, d, J 8.6, 3-H or 3'-H), 7.11 (1 H, d, J 8.5, 3'-H or 3-H), 7.20 (1 H, dd, J 8.5 and 2.4, 4'-H or 4-H), 7.24 (1 H, d, J 3.0, 6-H or 6'-H), and 7.54 (1 H, d, J 2.4, 6'-H or 6-H); m/z 314 (M^+ , 71%), 299 (10), 243 (100), 231 (36), 203 (43) and 113 (83).

2,2',5'-Trihydroxy-4,5-methylenedioxybiphenyl 7d. A pale grey solid, m.p. 188–190 °C (from benzene) (Found: C, 63.5; H, 4.0. $\text{C}_{13}\text{H}_{10}\text{O}_5$ requires C, 63.41; H, 4.09%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3401 (OH); $\delta_{\text{H}}(200 \text{ MHz}, \text{C}_6\text{D}_6, \text{MeOD})$ 5.46 (2 H, s, OCH_2O), 6.75 (1 H, s, 3-H or 6-H), 6.90 (1 H, s, 6-H or 3-H), 6.95 (1 H, dd, J 8.6 and 2.9, 4'-H), 7.05 (1 H, d, J 8.6, 3'-H), 7.07 (1 H, d, J 2.9, 6'-H); m/z 246 (M^+ , 100%), 131 (25) and 103 (29).

1-(2',5'-Dihydroxyphenyl)-2-hydroxynaphthalene 7e. A pale brown solid, m.p. 158–160 °C (from benzene) (Found: C, 76.3; H, 4.7. $\text{C}_{16}\text{H}_{12}\text{O}_3$ requires C, 76.18; H, 4.80%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3333 (OH); $\delta_{\text{H}}(400 \text{ MHz}, \text{C}_6\text{D}_6)$ 3.97 (1 H, s, OH), 4.26 (1 H, s, OH), 5.17 (1 H, s, OH), 6.25 (1 H, d, J 3.1, 6'-H), 6.60 (1 H, dd, J 8.7 and 3.1, 4'-H), 6.84 (1 H, d, J 8.7, 3'-H), 7.12–7.16

(2 H, m, ArH), 7.19 (1 H, d, J 8.9, 3-H or 4-H), 7.19 (1 H, d, J 8.9, 4-H or 3-H) and 7.48–7.57 (2 H, m, ArH); m/z 252 (M^+ , 60%), 223 (14), 165 (20), 152 (25), 139 (48), 115 (56), 103 (92) and 88 (100).

4-tert-Butyl-2,2',5'-trihydroxybiphenyl **7f**. A brown foam (Found: C, 74.3; H, 7.1. $C_{16}H_{18}O_3$ requires C, 74.39; H, 7.02%); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3289 (OH); $\delta_{\text{H}}(200 \text{ MHz}, C_6D_6)$ 1.21 (9 H, s, Bu'), 5.2 (3 H, br s, 3 OH), 6.54 (1 H, dd, J 8.5 and 2.9, 5-H or 4'-H), 6.65 (1 H, d, J 2.9, 3-H or 6'-H), 6.72 (1 H, d, J 8.5, 6-H or 3'-H), 6.92 (1 H, dd, J 8.0 and 1.8, 4'-H or 5-H), 7.00 (1 H, d, J 1.8, 6'-H or 3-H) and 7.15 (1 H, d, J 8.0, 3'-H or 6-H); m/z 258 (M^+ , 100%), 243 (78), 215 (18), 202 (49) and 107 (26).

5,5'-di-tert-Butyl-2,2',2'',5''-tetrahydroxy-1,1':3',1''-terphenyl **7g**. A pale brown solid, m.p. 109–114 °C (decomp.) (from benzene) (Found: C, 76.9; H, 7.35. $C_{26}H_{30}O_4$ requires C, 76.82; H, 7.44%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3333 (OH); $\delta_{\text{H}}(400 \text{ MHz}, C_6D_6)$ 1.20 (9 H, s, Bu'), 1.23 (9 H, s, Bu'), 6.55 (1 H, dd, J 8.7 and 3.0, 4-H or 4'-H), 6.76 (1 H, d, J 8.7, 3-H or 3'-H), 6.80 (1 H, d, J 3.0, 6-H or 6'-H), 6.92 (1 H, d, J 8.5, 3'-H or 3-H), 7.15 (1 H, dd, J 8.5 and 2.5, 4''-H or 4-H), 7.42 (1 H, d, J 2.4, 4'-H or 6'-H), 7.46 (1 H, d, J 2.5, 6''-H or 6-H) and 7.49 (1 H, d, J 2.4, 6'-H or 4'-H); m/z 406 (M^+ , 100%), 391 (51), 351 (42), 323 (50) and 295 (96).

5-tert-Butyl-2,2',5'-trihydroxy-4'-methylbiphenyl **7h**. A brown solid, m.p. 175–177 °C (from benzene) (Found: C, 74.9; H, 7.5. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.40%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3333 (OH); $\delta_{\text{H}}(400 \text{ MHz}, C_6D_6, \text{MeOD})$ 1.27 (9 H, s, Bu'), 2.33 (3 H, s, Me), 6.99 (1 H, s, 3'-H or 6'-H), 7.04 (1 H, s, 6'-H or 3'-H), 7.13 (1 H, d, J 8.5, 3-H), 7.21 (1 H, dd, J 8.5 and 2.4, 4-H) and 7.54 (1 H, d, J 2.4, 6-H); m/z 272 (M^+ , 30%), 245 (20) and 217 (100).

5-tert-Butyl-2,2',5'-trihydroxy-4'-chlorobiphenyl **7i**. A brown solid, m.p. 164–166 °C (from benzene) (Found: C, 65.7; H, 5.8; Cl, 12.05. $C_{16}H_{17}ClO_3$ requires C, 65.64; H, 5.85; Cl, 12.11%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3300 (OH); $\delta_{\text{H}}(400 \text{ MHz}, C_6D_6, \text{MeOD})$ 1.22 (9 H, s, Bu'), 7.08 (1 H, d, J 8.5, 3-H), 7.20 (1 H, s, 3'-H or 6'-H), 7.21 (1 H, dd, J 8.5 and 2.5, 4-H), 7.24 (1 H, s, 6'-H or 3'-H) and 7.45 (1 H, d, J 2.5, 6-H); m/z 294 (M^+ , 34%), 292 (M^+ , 100), 277 (38), 265 (35) and 239 (42).

2-(5-tert-Butyl-2-hydroxyphenyl)-1,4-benzoquinone **13**. A brown-red solid, m.p. 122–126 °C (from benzene) (Found: C, 75.1; H, 6.2. $C_{16}H_{16}O_3$ requires C, 74.98; H, 6.29%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3292 (OH) and 1650 (C=O); $\delta_{\text{H}}(400 \text{ MHz}, C_6D_6)$

1.21 (9 H, s, Bu'), 6.00 (1 H, dd, J 10.1 and 2.3, 4-H or 4'-H), 6.03 (1 H, s, OH), 6.04 (1 H, d, J 10.1, 3-H or 3'-H), 6.61 (1 H, d, J 2.3, 6-H or 6'-H), 6.73 (1 H, d, J 8.4, 3'-H or 3-H), 7.10 (1 H, d, J 2.5, 6'-H or 6-H) and 7.14 (1 H, dd, J 8.4 and 2.5, 4'-H or 4-H); m/z 256 (M^+ , 45%), 241 (100) and 213 (16).

5,5'-di-tert-Butyl-2,2'-dihydroxybiphenyl **6a**. A pale yellow solid, m.p. 202 °C (from benzene) (lit.,¹⁰ m.p. 207–208 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3202 (OH); $\delta_{\text{H}}(100 \text{ MHz}, C_6D_6)$ 1.20 (18 H, s, 2 Bu'), 5.5 (br s, 2 H, 2-OH), 6.87 (2 H, d, J 8.5, 3-H and 3'-H), 7.17 (2 H, dd, J 8.5 and 2.5, 4-H and 4'-H) and 7.40 (2 H, d, J 2.5, 6-H and 6'-H); m/z 298 (M^+ , 58%), 283 (100), 227 (75) and 106 (22).

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