

Selective synthesis of unsymmetrical 2,2'-dihydroxylated biaryls via electrophilic arylation of metal phenolates with *p*-benzoquinone monoketals

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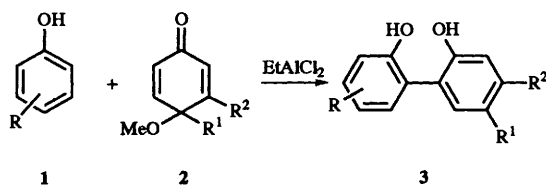
Unsymmetrical 2,2'-dihydroxylated biaryls are obtained by arylation of phenols with *p*-benzoquinone monoketals in the presence of EtAlCl₂. The reaction consists of an unusual and highly selective electrophilic attack at the α -position of the monoketal. A crystal structure determination of biaryl, 1-(2-hydroxy-5-methoxyphenyl)-2-hydroxynaphthalene, **3fx** is presented.

As part of our continuing programme to explore the potential of the 'metal-template' effect for promoting regio- and stereo-selectivity in the functionalisation of phenols, we have reported the efficient synthesis of hydroxylated bi- and poly-aryls via electrophilic arylation and oxidative coupling of convenient metal phenolates.¹

More recently we turned our attention to the preparation of unsymmetrical hydroxylated biaryls² as synthons for the construction of new phenol-based ligands³ and for the preparation of natural products.⁴

Results and discussion

Here we report the efficient synthesis of unsymmetrical biaryls **3** by electrophilic reaction of phenols **1** with monoketals **2** via a selective and unusual attack at the α -position of the reagent **2** promoted by EtAlCl₂ (Scheme 1).



Scheme 1

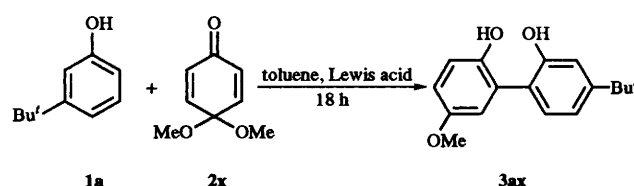
Quinone monoketals are a class of electrophiles which are easily prepared by chemical and electrochemical oxidation of *p*-alkoxyphenols. These compounds have been reported to react with nucleophiles giving 1,2- or 1,4-addition products accompanied by variable amounts of the corresponding phenols by electron-transfer from the nucleophilic reagent.⁵

To our knowledge the direct addition to the α -position of reagents **2** has not been reported with the exception of the α -allylation of 3-bromo-4,4-dimethoxycyclohexa-2,5-dienone which occurs by rearrangement of the aryl allyl ether initially produced.⁶

In order to optimise the reaction conditions, we examined the arylation of 3-*tert*-butylphenol **1a** with benzoquinone mono-(dimethyl ketal) **2x** in the presence of different Lewis acids to produce the biaryl **3ax** (Table 1). 3-*tert*-Butylphenol was chosen as a simple and soluble model in order to verify that compound **2x** reacted at the α -position.

The use of AlCl₃ and SnCl₄ as well as mixtures of SnCl₄ and lithium phenolates as promoters gave the biaryl **3ax** in only

Table 1 Reaction between *m*-(*tert*-butyl)phenol **1a** with *p*-benzoquinone mono(dimethyl ketal) **2x** in the presence of different Lewis acids



Entry	Lewis acid ^a	T/°C	Yield 3ax (%)	Recovered 1a (%)
1	Ti(OPr) ₄	80	5	90
2	EtMgBr	80	25	70
3	AlCl ₃	25	35	52
4	SnCl ₄	25	34	50
5	BuLi, 1/3SnCl ₄	25	23	20
6	EtAlCl ₂	25	55	44

^a Lewis acids react with phenols affording metal phenolates in agreement with published procedures.⁹

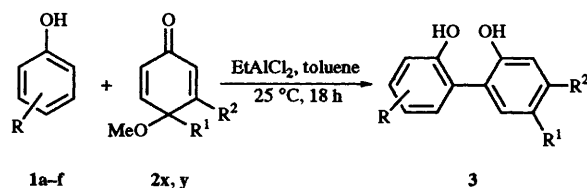
moderate yields since the reagent **2x** is acid-sensitive and **3ax** can react further with **2x** giving polyaryl derivatives in the presence of hard Lewis acids (entries 3, 4 and 5). When titanium tetraisopropoxide was used the product **3ax** was obtained in an unexpectedly low yield compared with that from a similar reaction involving *p*-benzoquinone bis(dimethyl ketal)^{2a} (entry 1). The highest yield of **3ax** was 55% (entry 6) for which the dichloroaluminium 3-*tert*-butylphenolate, directly generated by exchange between EtAlCl₂ and **1a**, was treated with **2x** at 25 °C for 18 h.

The structure of compound **3ax** was assigned from a NOESY experiment in C₆D₆, as in this solvent the aromatic pattern shows well separated signals (Fig. 1).

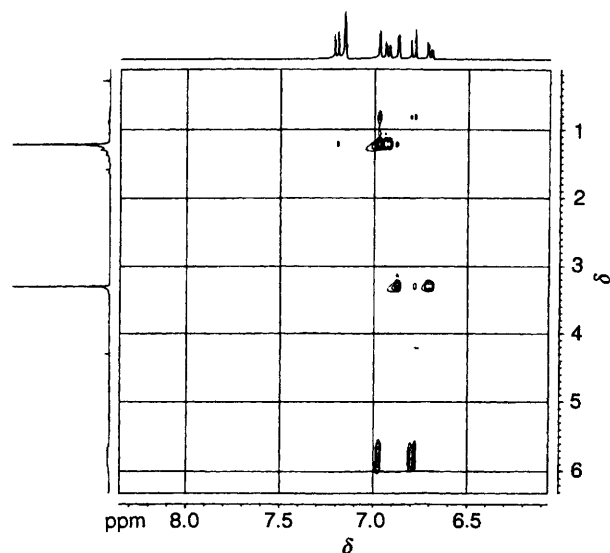
The cross-peak correlations in the 2D spectrum between the aromatic protons and the methoxy or *tert*-butyl group indicate that the higher field signals belong to the methoxylated aromatic ring. The spatial proximity of the two aromatic protons (δ 6.87, d, *J* 3.0 Hz and 6.70, dd, *J* 8.8 and 3.0 Hz) and the methoxy group as well as the proximity of the proton at δ 6.79, d, *J* 8.8 Hz to the hydroxy group, confirm that the reagent **2x** reacted at the α -position.

Next the regioselective arylation of various phenols **1a-f** with two monoketals **2x, y** was similarly attempted. The synthetic results are reported in Table 2.

As is evident from Table 2, the reaction is applicable to highly

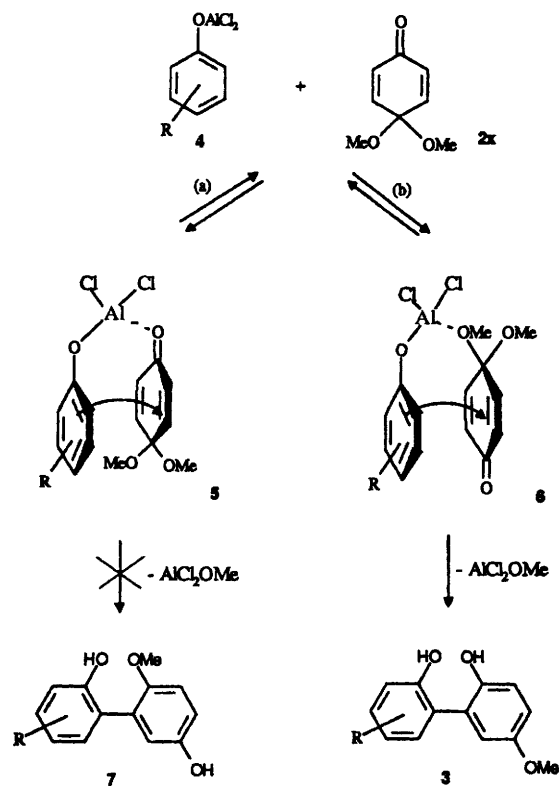
Table 2 Regioselective synthesis of hydroxylated biaryls **3** by the metal-template reaction of phenols **1a-f** with *p*-benzoquinone monoketals **2x, y** in the presence of EtAlCl₂

Entry	Phenol 1 , R	<i>p</i> -Benzoquinone monoketal 2		Biaryl 3	Yield (%)
		R ¹	R ²		
1	1a , 3-Bu'	OMe	H	3ax	53
2	1b , 4-OMe	OMe	H	3bx	52
3	1c , 4-Me	OMe	H	3cx	25
4	1d , 4-Bu'	OMe	H	3dx	30
5	1e , 3,4-(O-CH ₂ -O)	OMe	H	3ex	60
6	1f , 3,4-(CH=CH) ₂	OMe	H	3fx	50
8	1a , 3-Bu'		O-CH ₂ -O	3ay	29
9	1d , 4-Bu'		O-CH ₂ -O	3dy	52

**Fig. 1** Part of the 400 MHz 800 ms NOESY spectrum of compound **3ax**

and moderately activated phenolic substrates, the products **3** being obtained in satisfactory yields and with good selectivities with respect to the phenol. Moreover, the synthetic results are consistent with a typical electrophilic substitution process being favoured with electron rich phenols and completely inhibited when R is an electron withdrawing group such as Cl, COMe and CO₂Et. In addition, the potential coordination of these substituents to the Lewis acid increases their electron withdrawing power.⁷ Interestingly, while the previously reported reactions of **2** with nucleophiles gave exclusively conjugate addition to the enone moiety, the present reaction led to exclusive addition at the α -position of the reagent **2**. This rigorous and unusual regiochemical control can be rationalised on the basis of the purely speculative chelate mechanism shown in the Scheme 2.

In non polar solvents such as toluene the dichloroaluminium phenolates **4** interact with the reagent **2x** affording two geometrically distinct complexes **5** and **6** which can produce two isomeric biaryls **7** and **3** by conjugate addition to the carbonyl or the acetal group [routes (a) and (b), respectively].

**Scheme 2**

Preliminary ¹³C NMR experiments were performed in order to examine the coordination ability of the carbonyl and acetal oxygen atoms. The ¹³C NMR spectrum of a 1:1 complex of 2,4-dichlorophenoxy-magnesium bromide and reagent **2x** showed downfield shifts of the carbonyl signal ($\Delta\delta$ 3 ppm) as well as those of the methyl ($\Delta\delta$ 0.9 ppm) and quaternary carbon ($\Delta\delta$ 0.4 ppm) of the acetal functionality. As the downfield shift of the carbonyl group in the 1:1 adduct of 2,4-dichlorophenoxy-magnesium bromide and cyclohex-2-enone, chosen as a model of carbonyl coordination, is quite large ($\Delta\delta$ 9 ppm), we hypothesise that the metal phenolates are able to coordinate to the oxygen atom of the acetal function as well as to that of the carbonyl group.

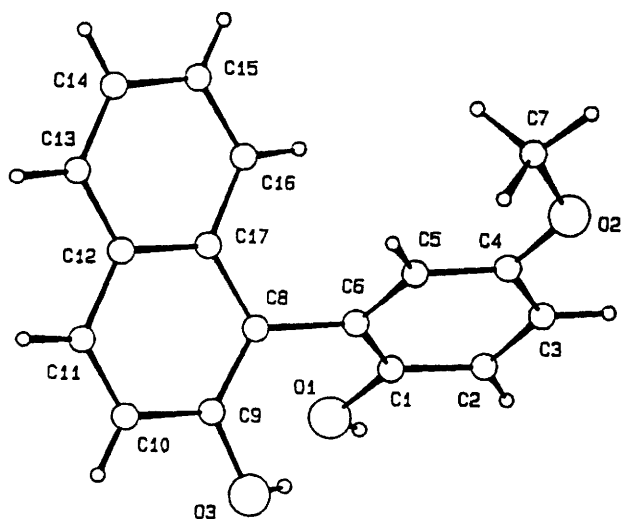


Fig. 2 X-Ray crystal structure of compound 3fx: molecule A with atomic labelling

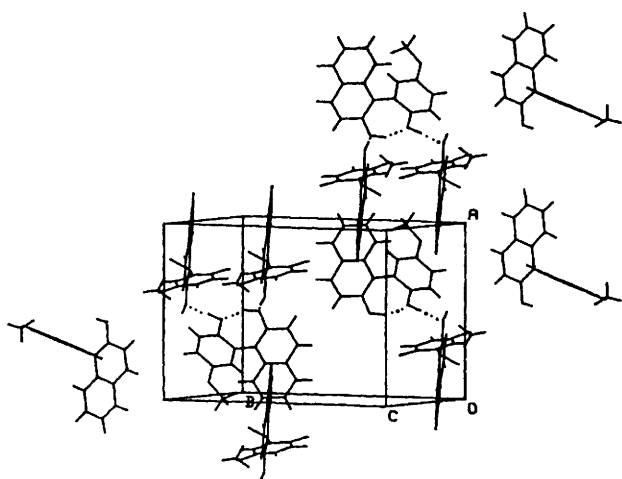


Fig. 3 Packing of the molecules showing some of the intramolecular [H10a...O3b 1.79(3), H30a...O1a 1.71(4)] and intermolecular H-bonds (Å) [H10b...O1c 2.10(4), H30b...O2b 1.87(3), H30c...O2c 2.08(3)]

The outcome of the reaction indicates that complex **6** is the reactive species, since only 2,2'-dihydroxybiaryls **3** were obtained.

In order to estimate the effect of steric hindrance in substrates **1** and **2** in the present process, the reactions of 4,4-dimethoxy-3,5-dimethylcyclohexa-2,5-dienone⁸ with **1a** and of **2x** with 3,5-dimethylphenol were performed, affording reaction mixtures from which biaryl products could not be detected.

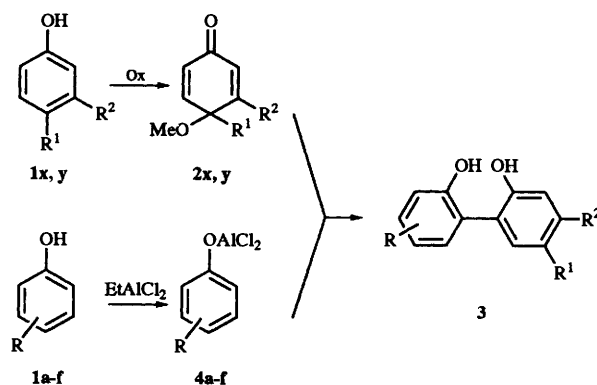
These results indicate that alkyl groups attached at the 3 and 5 positions of the monoketal as well as to the phenol rings provide sufficient steric hindrance to completely inhibit the arylation process probably by disfavoring the formation of the reactive complex **6**.

X-Ray quality crystals of compound **3fx** were obtained from benzene (see Fig. 2). The space group $P\bar{1}$ and the value $Z = 6$ indicate the presence of three independent molecules. The bond distances and angles are as would be expected and are comparable in the three independent molecules. The greatest differences are the reciprocal orientation between aromatic rings in the molecules (Fig. 3).

The naphthalene groups as a whole are not planar and have dihedral angles between the two planar rings of 3.9(1), 1.7(1) and 1.2(1)° in the **A**, **B** and **C** molecules, respectively. The

dihedral angle between the phenyl ring and the mean naphthalene plane in molecule **A** [54.2(1)°] is very different from those in molecules **B** and **C** [75.0(1)° and 76.9(1)°, respectively]. This difference is consistent with the presence of a strong intramolecular hydrogen bond in molecule **A** [$d(\text{O3A}\cdots\text{O1A})$ 2.705(3) Å].

In conclusion, we have described a new and regioselective unsymmetrical coupling of different phenols, compounds **2x**, **y** being obtained from the corresponding phenols **1x**, **y** (Scheme 3).



Scheme 3

Experimental

Melting points were obtained on an Electrothermal melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker CXP200 spectrometer at 200 MHz, on a Bruker AC300 spectrometer at 300 MHz and on a Bruker AMX400 spectrometer at 400 MHz. Chemical shifts are expressed in ppm relative to tetramethylsilane (TMS) as internal standard. *J* Values are given in Hz. The NOESY experiment was performed at 400 MHz in the phase-sensitive mode. 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 the 'E.I. mode'. Microanalyses were carried out by Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica dell'Università di Parma, Italy.

All metal phenolates were prepared as previously reported in the literature.⁹ Compound **2y** was prepared as previously reported in the literature.¹⁰

X-Ray structure determination

The intensity data were collected on a Siemens AED single crystal diffractometer controlled with an IBM compatible personal computer¹¹ using a prismatic specimen of 0.11 × 0.14 × 0.37 mm. Cell parameters were obtained from least-squares of 29 reflections (21.3 < θ < 40.0°) automatically well centred on the diffractometer. Crystallographic data: C₁₇H₁₄O₃, $M_r = 266.30$, triclinic, $P\bar{1}$, $a = 11.596(2)$, $b = 17.481(3)$, $c = 10.121(2)$ Å, $\alpha = 95.27(3)$, $\beta = 91.77(2)$, $\gamma = 89.13(4)$ °, $Z = 6$, $D_x = 1.30$ g cm⁻³, $V = 2041.8(6)$ Å³, Cu-K α , $\lambda = 1.5418$ Å, $\mu = 6.81$ cm⁻¹. A total of 7750 reflections, $\pm h$, $\pm k$, $+l$, were measured at room temperature in the θ range of 3–70° with Cu-K α radiation. One standard reflection was monitored every 100 without indication of misalignment or decomposition. Reflection intensities were corrected for Lorentz and polarisation effects but not for absorption. The structure was obtained through the SIR program¹² using 4237 unique observed reflections with $I \geq 2\sigma(I)$. The refinement was carried out by block-matrix least-squares at the beginning with isotropic thermal parameters and then with anisotropic ones

using SHELX76.¹³ All the hydrogen atoms were located in a difference Fourier map and refined isotropically. The final agreement R and R_w values were 0.039 and 0.048 with $w = 0.562/(\sigma^2 F + 0.013 199 F^2)$. The function minimised was $\Sigma w(\Delta F)^2$; the maximum Δ/σ in the final cycles of refinement was 0.89; $\Delta\rho_{\min/\max} = -0.16/0.19 \text{ e \AA}^{-3}$. The atomic scattering factors were those incorporated in SHELX76. All the calculations were performed on a DELL 466/DE personal computer with CRYSRULER package.¹⁴

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

Synthesis of dihydroxylated biaryls 3

General procedure. To a solution of EtAlCl_2 (0.01 mol) in dry toluene (50 cm³) a solution of the selected phenol 1 (0.01 mol) in dry toluene (50 cm³) was added under nitrogen and the reaction mixture was stirred for 30 min. A solution of the 4,4-dimethoxycyclohexa-2,5-dienone 2 (1.54 g, 0.01 mol, 1.39 cm³) in dry toluene (25 cm³) was added dropwise to the mixture and the reaction was stirred at room temperature for 18 h. The mixture was quenched with aqueous 10% HCl (100 cm³) and then extracted with CH_2Cl_2 (3 × 50 cm³). The organic phase was dried (Na_2SO_4) and the solvent distilled off. The residue was chromatographed on silica gel plates with hexane (90–70%)–ethyl acetate (10–30%) mixtures to give the products.

4'-tert-Butyl-2,2'-dihydroxy-5-methoxybiphenyl 3ax. Pale yellow solid, mp 100.5–102 °C (from benzene) (Found: C, 74.8; H, 7.3. $\text{C}_{17}\text{H}_{20}\text{O}_3$ requires C, 75.0; H, 7.4%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3279 (OH); $\delta_{\text{H}}(400 \text{ MHz}; \text{C}_6\text{D}_6)$ 1.22 [9 H, s, $(\text{CH}_3)_3\text{C}$], 3.30 (3 H, s, OCH_3), 5.7 (1 H, br s, OH), 5.9 (1 H, br s, OH), 6.70 (1 H, dd, 4-H, J 8.8 and 3.0), 6.79 (1 H, d, 3-H, J 8.8), 6.82 (1 H, d, 6-H, J 3.0), 6.93 (1 H, dd, 5'-H, J 8.0 and 1.8), 6.97 (1 H, d, 3'-H, J 1.8) and 7.20 (1 H, d, 6'-H, J 8.0); m/z 272 (M^+ , 15%), 115 (23) and 109 (100).

2,2'-Dihydroxy-5,5'-dimethoxybiphenyl 3bx. White crystals, mp 126–127 °C (from diethyl ether) (lit.,¹⁵ 127–128.5 °C).

2,2'-Dihydroxy-5-methoxy-5'-methylbiphenyl 3cx. Pale yellow solid, mp 108–109 °C (from diethyl ether) (Found: C, 72.9; H, 6.1. $\text{C}_{14}\text{H}_{14}\text{O}_3$ requires C, 73.0; H, 6.1%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3170 (OH); $\delta_{\text{H}}(400 \text{ MHz}; \text{C}_6\text{D}_6\text{-MeOD})$ 2.07 (3 H, s, CH_3), 3.28 (3 H, s, OCH_3), 5.6 (1 H, br s, OH), 5.7 (1 H, br s, OH), 6.72 (1 H, dd, 4-H, J 8.8 and 3.0), 6.78 (1 H, d, 3'-H, J 8.1), 6.80 (1 H, d, 3-H, J 8.8), 6.85 (1 H, d, 6-H, J 3.0), 6.86 (1 H, dd, 4'-H, J 8.1 and 2.8) and 7.00 (1 H, d, 6'-H, J 2.8); m/z 230 (M^+ , 100).

5'-tert-Butyl-2,2'-dihydroxy-5-methoxybiphenyl 3dx. Pale grey solid, mp 49–51 °C (from benzene) (Found: C, 75.0; H, 7.5. $\text{C}_{17}\text{H}_{20}\text{O}_3$ requires C, 75.0; H, 7.4%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3311 (OH); $\delta_{\text{H}}(200 \text{ MHz}; \text{C}_6\text{D}_6)$ 1.19 [9 H, s, $(\text{CH}_3)_3\text{C}$], 3.29 (3 H, s, OCH_3), 5.51 (1 H, s, OH), 5.75 (1 H, s, OH), 6.71 (1 H, dd, 4- or 4'-H, J 8.8 and 2.9), 6.82 (1 H, d, 3- or 3'-H, J 8.8), 6.85 (1 H, d, 3'- or 3-H, J 8.5), 6.92 (1 H, d, 6- or 6'-H, J 2.9), 7.15 (1 H, dd, 4'- or 4-H, J 8.5 and 2.5) and 7.38 (1 H, d, 6'- or 6-H, J 2.5); m/z 272 (M^+ , 85%), 257 (100) and 216 (32).

2,2'-Dihydroxy-5-methoxy-4',5'-methylenedioxybiphenyl 3ex. Pale yellow solid, mp 115–117 °C (from benzene) (Found: C, 64.7; H, 4.6. $\text{C}_{14}\text{H}_{12}\text{O}_5$ requires C, 64.6; H, 4.7%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3215 (OH); $\delta_{\text{H}}(400 \text{ MHz}; \text{C}_6\text{D}_6)$ 3.57 (3 H, s, OCH_3), 3.74 (2 H, br s, 2 OH), 5.40 (2 H, s, CH_2), 6.78 (1 H, dd, 4-H, J 8.8 and 3.0), 6.80 (1 H, s, 3'- or 6'-H), 6.88 (1 H, s, 6'- or 3'-H), 6.91 (1 H, d, 6-H, J 3.0) and 7.06 (1 H, d, 3-H, J 8.8); m/z 260 (M^+ , 100%).

2-Hydroxy-1-(2'-hydroxy-5'-methoxyphenyl)naphthalene 3fx. Pale grey solid, mp 101–102.5 °C (from benzene) (Found: C, 76.8; H, 5.2. $\text{C}_{17}\text{H}_{14}\text{O}_3$ requires C, 76.7; H, 5.3%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3322 (OH); $\delta_{\text{H}}(400 \text{ MHz}; \text{C}_6\text{D}_6)$ 3.18 (3 H, s, OCH_3), 4.33 (1 H, s, OH), 5.21 (1 H, s, OH), 6.62 (1 H, d, 6'-H, J 3.0), 6.79 (1 H, dd, 4'-H, J 8.9 and 3.0), 6.93 (1 H, d, 3'-H, J 8.9), 7.1–7.2 (2 H, m, 5- and 8-H), 7.20 (1 H, d, 3- or 4-H, J 8.9), 7.50 (1 H, d, 4- or 3-H, J 8.9) and 7.5–7.6 (2 H, m, 6- and 7-H); m/z 266 (M^+ , 100%), 251 (10), 233 (12), 205 (15), 165 (23) and 139 (44).

4'-tert-Butyl-2,2'-dihydroxy-4,5-methylenedioxybiphenyl 3ay. Pale grey solid, mp 142–143 °C (from diethyl ether) (Found: C, 71.2; H, 6.2. $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3; H, 6.3%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3175 (OH); $\delta_{\text{H}}(300 \text{ MHz}; \text{C}_6\text{D}_6\text{-CD}_3\text{OD})$ 1.25 (9 H, s, 3 CH_3), 3.36 (2 H, br s, 2 OH), 5.39 (2 H, s, $\text{O-CH}_2\text{-O}$), 6.76 (1 H, s, 3- or 6-H), 6.87 (1 H, s, 6- or 3-H), 6.93 (1 H, dd, 5'-H, J 8.2 and 1.8), 7.21 (1 H, d, 3'-H, J 1.8) and 7.22 (1 H, d, 6'-H, J 8.2); m/z 286 (M^+ , 100%), 259 (14) and 231 (26).

5'-tert-Butyl-2,2'-dihydroxy-4,5-methylenedioxybiphenyl 3dy. White solid, mp 161–162 °C (from benzene) (Found: C, 71.4; H, 6.3. $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3; H, 6.3%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3161 (OH); $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 1.31 [9 H, s, $(\text{CH}_3)_3\text{C}$], 5.52 (2 H, br s, 2 OH), 5.95 (2 H, s, $\text{O-CH}_2\text{-O}$), 6.58 (1 H, s, 3- or 6-H), 6.71 (1 H, s, 6- or 3-H), 6.92 (1 H, d, 3'-H, J 8.5), 7.21 (1 H, d, 6'-H, J 2.4) and 7.31 (1 H, dd, 4'-H, J 8.5 and 2.4); m/z 286 (M^+ , 100%), 259 (60) and 231 (98).

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† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

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