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Oxidative Coupling of Dichloroaluminium Phenolates: Highly Selective Synthesis of Hydroxylated Bi- and Tetraaryls

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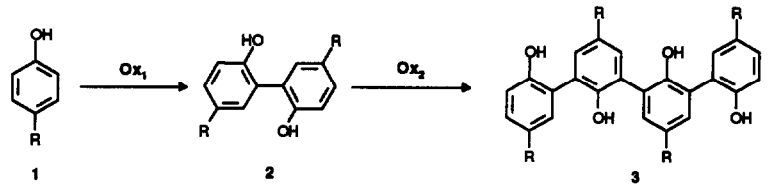
Abstract: Dichloroaluminium phenolates **4** undergo highly selective $FeCl_3$-promoted oxidative coupling. Variously substituted symmetric 2,2'-dihydroxy biaryls **2** are obtained in good yields and excellent selectivities. The chelation control in the final reaction products **7** promotes the chemoselectivity of the process.

Introduction

Oxidative coupling of phenols is a fundamental method for the synthesis of hydroxylated biaryls[1]. Nature makes extensive use of this reaction for the selective construction of more complex compounds from simple phenolic starting materials[1,2]. On the contrary, the numerous attempts to duplicate this process in the laboratory usually showed poor selectivity and complicated mixtures of dimeric, polymeric and quinonoid compounds have been obtained[3]. Although a number of methods have proven to be useful in overcoming such difficulties, these methods are limited in the generality of the reaction since only substrates showing intrinsic selectivity due to the particular substitution pattern of the aromatic ring are used (e.i. 2,4-disubstituted phenols or 2,3-dihydroxynaphthalenes)[4]. Nevertheless, the reaction can be used for the synthesis of hydroxylated bi- and triaryls because the complex reaction mixtures can now be separated by efficient chromatographic techniques.

In a previous communication we reported that, by using highly coordinating metal phenolates instead of the corresponding phenols, the oxidative coupling was performed with an excellent level of regiochemical

control[5]. We now present a detailed synthetic study of the $FeCl_3$-promoted oxidative coupling of dichloroaluminium phenolates together with preliminary but informative experiments which indicate that the process involves a radical insertion mechanism. We also show the broad utility of the reaction and the possibility of extending this strategy to different phenolic substrates with particular interest in the stepwise polyphenol synthesis 1-->2-->3 (Scheme 1).

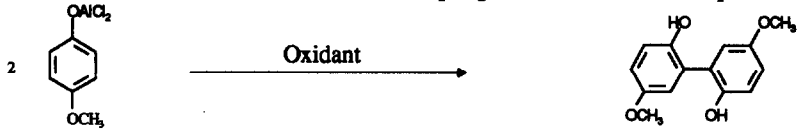


Scheme 1

Results and Discussion

At first, series of experiments were effected with various solvents and oxidizing reagents which are synthetically useful or have potential for the synthetic use in the laboratory.

Table 1. Oxidant and Solvent Effect for the Oxidative Coupling of Dichloroaluminium p-Methoxyphenolate*



Entry	Oxidant#	Phenol/Ox	Solvent (DN§)	Physical State	Yield (%)	Selectivity (%)
a	p-benzoq.	1 : 0.5	CH_3NO_2 (2.7)	homog.	64	80
b	MnO_2	1 : 1	"	heterog.	39	70
c	$VOCl_3$	1 : 1	"	homog.	52	88
d	$CuBr_2$	1 : 1	"	heterog.	11	55
e	$FeCl_3$	1 : 1	"	homog.	78	98
f	"	1 : 0.5	"	"	38	92
g	$FeCl_3 + O_2$	1 : 0.5	"	"	40	90
h	$FeCl_3$	1 : 1	CH_2Cl_2 (0)	heterog.	73	91
i	"	1 : 1	MeOH (19)	"	18	86
l	"	1 : 1	THF (20)	"	15	88
m	"	1 : 1	DMF (26.6)	homog.	0	
n	Anodic Oxid. (Pt electrode)		CH_3NO_2	"	55	90

* All the reactions were carried out at 25°C for 5 hours under normal laboratory light. Similar results were obtained by carrying out the reactions in the dark.

The use of $FeCl_3$ alone promotes the oxidative coupling of p-methoxy phenol in lower yield (35%) and nitromethane does not bring about coupling of p-methoxy phenol without $FeCl_3$.

§ See reference 7.

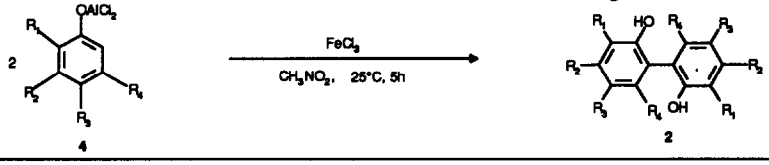
Both homogeneous and heterogeneous oxidants were employed covering a range of oxidation potentials. Dichloroaluminium p-methoxyphenolate utilized as model substrate was simply prepared by reacting p-methoxyphenol and $EtAlCl_2$ in dry ethyl ether[6] then replaced by the selected reaction solvent. Results are summarized in Table 1.

Although various oxidizing reagents were found to work in most of the experiments, the optimum yield and selectivity were achieved by using anhydrous $FeCl_3$, being the biaryl **2a** obtained as the sole reaction product in 78% yield (Table 1, Entry e). The reaction requires a stoichiometric amount of $FeCl_3$ and the product **2a** was only obtained in 38% yield when the molar ratio phenol/$FeCl_3$ was 2/1. The same result was obtained by bubbling oxygen in the reaction mixture (Table 1, Entries f and g).

Heterogeneous reagents such as MnO_2 and $CuBr_2$ were shown to be less efficient (Table 1, Entries b and d).

As indicated in Table 1, the efficiency of this reaction is highly dependent upon the nature of the solvent, being particularly favoured by using solvents with a low donor number[7], such as nitromethane and methylene chloride (Table 1, Entries e and h). For example, the conversion **4a--->2a** is sluggish in THF (Table 1, Entry l) but is completely inhibited in DMF (Table 1, Entry m).

Table 2. Reaction between Different Dichloroaluminium Phenolates and $FeCl_3$.



4 2

Entry	R_1	R_2	R_3	R_4	Recovered Phenol	Yield (%)	Selectivity (%)
a	H	H	OCH_3	H	20	80	98
b	H	H	CH_3	H	52	40	83
c	H	H	Cl	H	70	25	83
d	H	H	$C(CH_3)_3$	H	68	30	94
e	H	H	OH	H	45	50	91
f	H	H	(4-OH)-C_6H_5	H	60	32	80
g	H	H	-$(CH=CH)_2$-		20	77	96
h	H	-$(O-CH_2-O)$-		H	12	80[a]	91
i	$C(CH_3)_3$	H	$C(CH_3)_3$	H	48	40[b]	77
l	CH_3	H	CH_3	H	52	37	77
m	CH_3	H	$C(CH_3)_3$	H	55	33	73
n	OH	H	-$(CH=CH)_2$-		60	28[b]	70

[a] Al(OAr)Cl was employed as counterion (see ref. 9).

[b] MgBr was employed as counterion (see ref. 10).

For a synthetic purpose, the active dichloroaluminium phenolate was more conveniently prepared by reacting the selected phenol with a stoichiometric amount of $AlCl_3$ in nitromethane as early reported in the

literature[8]. Thus freshly sublimed $AlCl_3$ and p-methoxyphenol (molar ratio 1/1) were reacted in dry nitromethane under nitrogen. The addition of one equivalent of anhydrous $FeCl_3$ in nitromethane afforded the desired product **2a** in 80% yield after 5 hours at 25°C.

The oxidative coupling of various phenols in the presence of $AlCl_3$-$FeCl_3$ couple was then tried and it was found that the process was of general applicability with respect to the p-substituted phenolic substrate (Table 2).

The reaction shows good chemo- and regioselectivity: various functionalized phenols can be used and only carbon-carbon bond formation occurs, affording biaryls **2** in satisfactory yields and excellent selectivities. There is also evidence that electronwithdrawing substituents on the phenol ring reduce the reactivity of the substrate (Table 2, Entry c). Moreover, the reaction is highly sensitive to the bulk of the substituent (Table 2, Entries d, f, i and m).

We succeeded in crystallizing the biaryl **2a** and in characterizing it by X-ray analysis. Indeed **2a** (R = 4-OCH_3) crystallized out as white needles from ethyl ether.

A picture of the molecule **2a** is shown in Fig. 1. The molecule conformation is characterized by a mutual rotation of the two aromatic units that show a dihedral angle of 53.7°. The hydrogen atoms of the OH groups point toward opposite directions. The two OH groups show the following distances: O...O = 2.91 Å, O-H...O = 2.58 Å, O-H...H-O = 2.47 Å.

The molecule package is depicted in Fig. 2.

Concerning the mechanistic pathway there is no warranty that all phenol coupling processes proceed by one and the same mechanism[1,3]. However, our results suggest that the sequence of steps outlined in Scheme 2 could play a significative role in the present reaction.

Fig. 1. X-Ray molecular structure of **2a** showing crystallographic numbering.

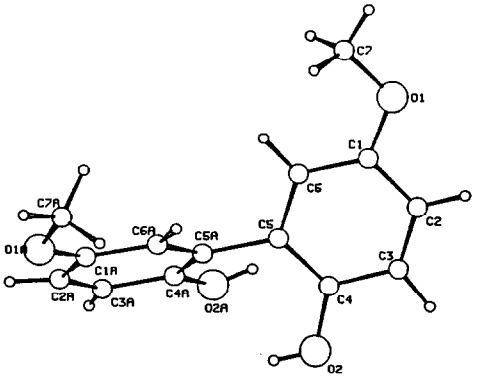
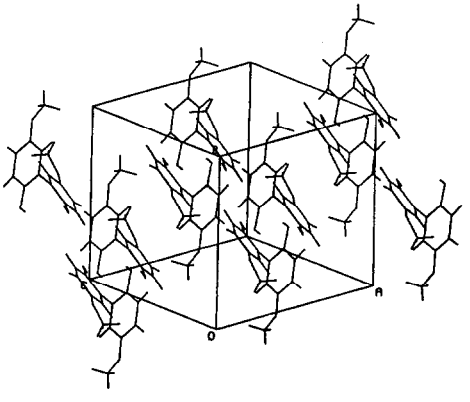
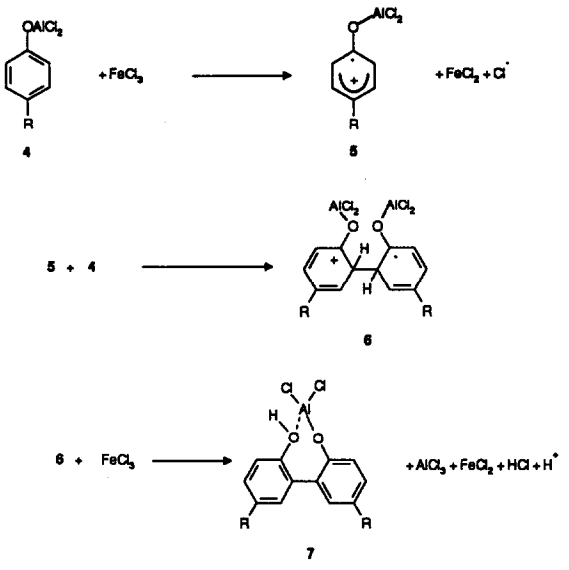


Fig. 2. The unit cell packing for **2a**.





Scheme 2

It is reasonable to suppose that the aryloxy radical **5**, formed by "one-electron transfer" from the phenolate **4** to $FeCl_3$, is inserted into a second molecule of the substrate **4**, present in high concentration, producing the new radical **6** which, after a second "one-electron transfer" to $FeCl_3$ and rearomatization leads to the dichloroaluminum chelate biaryl **7**. Electrochemical studies were performed on the model phenolate **4a**. Two chemically irreversible oxidations appear near 0.96 V and 1.07 V on the cyclic voltammogram obtained at a platinum electrode from a solution of **4a** in nitromethane (Fig. 3). After the analysis the compound **2a** was recovered in the solution as the sole reaction product according to the mechanism showed in the Scheme 2[11].

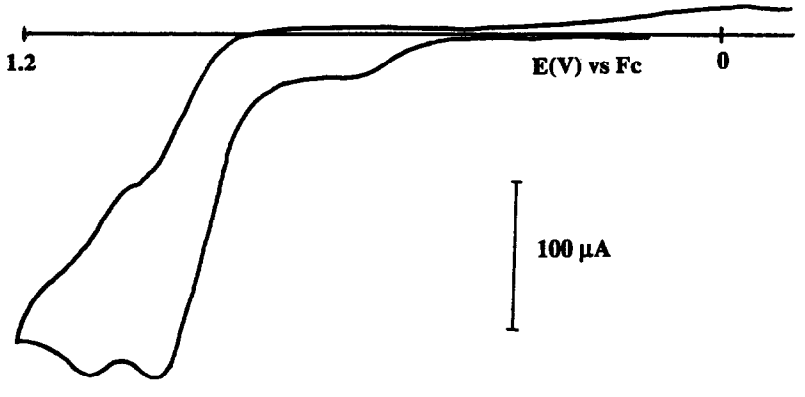
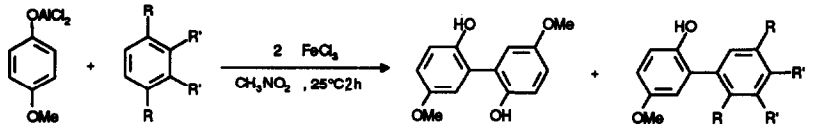


Fig. 3. Cyclic voltammogram of dichloroaluminum p-Methoxyphenolate **2a** 0.001M in 0.1M TBAEFP nitromethane. Working electrode Pt sphere A=10.1 mm^2, Reference: KCl (3M in agar agar) AgCl/Ag separated from the organic solution by a 1M TBAEFP in nitromethane salt bridge. Scan rate 50 mV/sec.

Further evidence for a radical insertion mechanism is indicated by the formation of the crossed products **9** accompanied by the expected biaryl **2a** by reacting the model dichloroaluminium p-Methoxyphenolate **4a** with activated aromatic substrates **8** in the presence of $FeCl_3$.

Table 3. Reaction between Dichloroaluminium p-Methoxyphenolates and Different Aromatic Substrates.



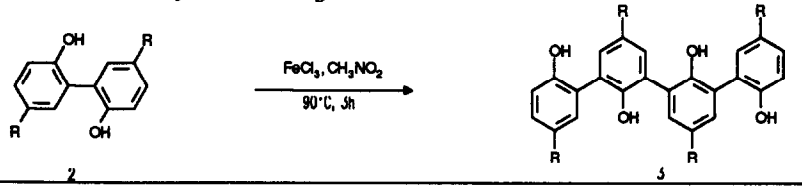
4a 8 2a 9

Entry	R	R'	2a Yield (%)	9 Yield (%)
a	OMe	H	43	46
b	OMe	Me	51	10

We successively turned our attention to the use of biaryls **2** as building blocks for the stepwise synthesis of hydroxylated polyaryls due to the current interest in the preparation of new polyphenol ligands[12].

In our previous communication, we ascribed the high selectivity of the oxidative coupling of dichloroaluminium phenolates to the formation of stable chelates **7** involving the dimeric product and the oxygenophilic Lewis acid[5]. Thus our attempts to achieve oxidative coupling of compound **2b** under the general experimental conditions reported in Table 2 led to almost total recovery of starting material because the tetrameric product **3** was obtained in only 5% yield. On the other hand, the substrate **1f**, a biaryl having the two hydroxy groups in the para position, underwent dimerization affording the product **2f** in 32% yield (Table 2, Entry f).

Table 4. Reaction between Biaryls **2** and $FeCl_3$



2 3

Entry	R	Lewis Acid	Yield (%)	Selectivity (%)
b	CH_3	$AlCl_3$	5	92
b'	CH_3	--	37	98
d	$C(CH_3)$	--	20	90

These results prompted us to investigate the oxidative coupling of compounds **2** without addition of $AlCl_3$. Thus the dimeric product **2b** was directly oxidized with $FeCl_3$ in nitromethane leading to the expected tetrameric product **3b** in 37% yield and 98% selectivity (Table 4, Entry b').

We attempted to expand this reaction to different compounds **2**.

Some synthetic results listed in Table 4 indicate that the present oxidation process can be applyed to the stepwise synthesis of more complex polyphenols **3** *via* C-C selective coupling of simple phenolic starting materials. Our efforts to extend the reaction to biphenyl **2a** (R=4-OCH_3) resulted in the production of a mixture of isomeric tetraaryls.

The ready availability of suitable catalysts and reagents and the simplicity of the experimental procedures make this approach a convenient method for the preparation of bi-and tetraaryls **2** and **3**, which are useful intermediates in the synthesis of macrocyclic oxygenated ligands[12a]. The optimization of the yields as well as the extention of the present methodology to the selective synthesis of various hydroxylated polyaryls are in progress.

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Experimental

Melting points were obtained on an Electrothermal melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC100 spectrometer at 100 MHz, on a Bruker CXP 200 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. Mass spectra were obtained in "E.I. mode" on a Finnigan SSQ 710 instrument at 70 eV. Microanalyses were carried out at the Istituto di Chimica Farmaceutica dell'Università degli Studi di Parma, Italy. TLC analyses were performed on Stratocrom SIF silica gel plates (Carlo Erba) developed with hexane-ethyl acetate mixtures. X-ray structure determination: a specimen of 0.3x0.4x0.7 mm was mounted on a Siemens AED single crystal diffractometer controlled by an IBM PS2/30 personal computer. Lattice parameters were obtained from least-squares of 30 reflections with $25.5<\Theta<44.9°$ automatically well centred. Intensity data, measured at room temperature in 3-70° Θ range with Cu-Kα radiation resulted in 2559 reflections with *h,k,l* range = -13/13, 0/14, 0/10. The units cell constants are: a = 11.029(2), b = 11.716(2), c = 9.816(3) Å; β = 107.28(2)°. The structure was solved in the monoclinic space group *C2/c* by direct methods with SHELXS86 using the 972 unique (R_{int} = 0.04) observed reflections with $I \geq 2\sigma(I)$. The hydrogen atoms were located in a difference Fourier map. The refinement was performed by full-matrix anisotropic least-squares [function minimized $\Sigma w(\Delta F)^2$ with isotropic thermal parameters for H atoms] using

SHELXS76 to a final R = 0.049. All the calculations were performed on an IBM PS2/80 personal computer with the CRYSRULER package.

Table 5 and Table 6 contain selected geometrical parameters.

Table 5. Bond Lengths (Å) of **2a**

O1 - C1	1.361(2)	C1 - C6	1.397(3)	C5 - C6	1.393(2)
O1 - C7	1.421(3)	C2 - C3	1.360(3)	C5- C5'	1.496(1)
O2 - C4	1.366(2)	C3 - C4	1.396(3)		
C1 - C2	1.390(3)	C4 - C5	1.401(2)		

Table 6. Bond Angles (°) of **2a**

C1 - O1 - C7	117.8(1)	O1 - C1 - C6	124.6(1)	O1 - C1 - C2	116.0(1)
C2 - C1 - C6	119.4(1)	C1 - C2 - C3	120.5(1)	C2 - C3 - C4	121.0(2)
O2 - C4 - C3	116.7(1)	C3 - C4 - C5	119.5(1)	O2 - C4 - C5	123.8(1)
C4 - C5 - C5'	121.8(1)	C4 - C5 - C6	119.1(1)	C6 - C5 - C5'	119.1(1)
C1 - C6 - C5	120.5(1)				

Final atomic coordinates of heavy atoms and equivalent isotropic temperature factors are in Table 7.

Table 7. Atomic Fractional Coordinates ($x10^4$) and Ueq ($x10^4 Å^2$) of **2a**

	X/A	Y/B	Z/C	Ueq
O1	-2140(1)	4611(1)	-6221(1)	617(6)
O2	681(1)	928(1)	-3563(2)	648(6)
C1	-1430(1)	3743(1)	-5465(2)	466(6)
C2	-1191(2)	2837(2)	-6263(2)	541(7)
C3	-509(2)	1919(2)	-5606(2)	531(6)
C4	-19(2)	1871(1)	-4122(2)	546(6)
C5	-257(1)	2770(1)	-3296(1)	394(6)
C6	-962(1)	3704(1)	-3978(2)	432(6)
C7	-2246(2)	5626(2)	-5472(2)	636(8)

Electrochemical experimental section: the nitromethane was dried with molecular sieves 4Å. The potentiostat used for cyclic voltammetry was a three electrodes Metrohm E506 equipped with a Metrohm E612 voltage scanner. The voltammograms were recorded on a XY recorder Linseis LY8200. The working electrode was a 1.8 mm diameter Platinum sphere. The reference was KCl (3M in agar agar) AgCl/Ag

separated from the organic solution by a 1M TBAEFP in nitromethane salt bridge. The working region of the cell was separated from the Counter and Reference ones by porous frits.

Synthesis of Hydroxylated Biaryls (2). General Procedure. A solution of the selected phenol (0.01 mol) in dry nitromethane (20 ml) was added to a stirred solution of $AlCl_3$ (0.01 mol) in dry nitromethane (20 ml) under nitrogen. After 30 min, a solution of anhydrous $FeCl_3$ (0.01 mol) in dry nitromethane (20 ml) was added and the mixing was continued for 5 h at room temperature. The reaction was quenched with 2N HCl (60 ml) and the resulting mixture was extracted with methylene chloride (3 x 50 ml). The organic phase was dried (Na_2SO_4), the methylene chloride was distilled off and the residue was chromatographed on silica gel column with 20-40% hexane-EtOAc mixtures to give the products.

Synthesis of Hydroxylated Tetraaryls (3). General Procedure. A solution of anhydrous $FeCl_3$ (0.005 mol) in dry nitromethane (15 ml) was added to a solution of selected biaryl (0.005 mol) in dry nitromethane (15 ml) and mixed for 3 h at room temperature. The reaction was quenched with 2N HCl (30 ml) and the resulting mixture was extracted with methylene chloride (2 x 50 ml) and EtOAc (1 x 50 ml). The organic phase was dried (Na_2SO_4) and distilled off; the residue was chromatographed on silica gel column with 40-50% hexane-EtOAc mixtures to give the products.

Synthesis of Hydroxylated Asymmetric Biaryls (9) General Procedure. A solution of selected aromatic substrate (0.01 mol) in dry nitromethane (20 ml) and a solution of $FeCl_3$ (0.02 mol) in dry nitromethane (20 ml) was successively added to a solution of dichloroaluminum p-Methoxyphenolate (0.01 mol) in dry nitromethane (0.01 mol) under nitrogen and the mixing was continued for 2 h at room temperature. The reaction was quenched with 2N HCl (50 ml) and the resulting mixture was extracted with methylene chloride (3 x 50 ml). The organic phase was dried (Na_2SO_4), the methylene chloride was distilled off and the residue was chromatographed on silica gel column with 10-20% hexane-EtOAc mixtures to give the products.

2,2'-Dihydroxy-5,5'-dimethoxybiphenyl (**2a**). White cristals (Et_2O), m.p. 126-7°C (lit.[13] m.p. 127-8.5°C); ^1H NMR (C_6D_6, 200 MHz), δ (ppm) 3.29 (s, 6H, 2 OCH_3), 6.71 (dd, 2H, H-4 and H-4', J=8.8 and 3.0 Hz), 6.8 (br s, 2H, 2 OH), 6.89 (d, 2H, H-3 and H-3', J=8.8 Hz), 6.91 (d, 2H, H-6 and H-6', J=3.0 Hz); IR (KBr) 3424, 1615, 1468, 1226, 1010, 813 cm^{-1}; MS *m/z* 246 (M^+, 100%), 231 (35), 213 (18), 115 (18).

2,2'-Dihydroxy-5,5'-dimethylbiphenyl (**2b**). Pale brown solid, m.p. 153-4°C (lit.[14] m.p. 154°C); ^1H NMR (C_6D_6, 400 MHz), δ (ppm) 2.08 (s, 6H, 2 CH_3), 5.80 (s, 2H, 2 OH), 6.80 (d, 2H, H-3 and H-3', J=8.2 Hz), 6.86 (dd, 2H, H-4 and H-4', J=8.2 and 2.2 Hz), 6.97 (d, 2H, H-6 and H-6', J=2.2 Hz); IR (KBr) 3058, 1492, 1234, 1121, 813, 772 cm^{-1}; MS *m/z* 214 (M^+, 100%), 197 (17), 171 (26), 106 (19).

2,2'-Dihydroxy-5,5'-dichlorobiphenyl (**2c**). Gray solid, m.p. 156-8°C (lit.[15] m.p. 170°C); ^1H NMR (C_6D_6-MeOD, 400 MHz), δ (ppm) 6.96 (d, 2H, H-3 and H-3', J=8.6 Hz), 7.07 (dd, 2H, H-4 and H-4', J=8.6

and 2.6 Hz), 7.17 (d, 2H, H-6 and H-6', J=2.6 Hz); IR (KBr) 3164, 1639, 1398, 1219, 819 cm^{-1}; MS *m/z* 256 (M+2, 70%), 254 (M^+, 100), 219 (53), 184 (45), 127 (34).

2,2'-Dihydroxy-5,5'-ditertbutylbiphenyl (**2d**). Pale yellow solid, m.p. 202°C (lit.[16] m.p. 207-8°C); ^1H NMR (C_6D_6, 100 MHz), δ (ppm) 1.20 (s, 18H, 2 $C(CH_3)_3$), 5.5 (br s, 2H, 2 OH), 6.87 (d, 2H, H-3 and H-3', J=8.5 Hz), 7.17 (dd, 2H, H-4 and H-4', J=8.5 and 2.5 Hz), 7.40 (d, 2H, H-6 and H-6', J=2.5 Hz); IR (KBr) 3205, 1605, 1136, 900, 833 cm^{-1}; MS *m/z* 298 (M^+, 58%), 283 (100), 227 (75), 106 (22).

2,2',5,5'-Tetrahydroxybiphenyl (**2e**). White solid, m.p. 239-40°C (lit.[17] m.p. 240°C dec.); ^1H NMR (C_6D_6-MeOD, 400 MHz), δ (ppm) 6.94 (dd, 2H, H-4 and H-4', J=8.6 and 3.0 Hz), 7.04 (d, 2H, H-3 and H-3', J=8.6 Hz), 7.14 (d, 2H, H-6 and H-6', J=3.0 Hz); IR (KBr) 3425, 1639, 1136, 735 cm^{-1}; MS *m/z* 218 (M^+, 100%), 163 (15), 147 (18), 115 (14).

2",4,4',4"'-Tetrahydroxy-1,1':3',1":5",1"'-tetraphenyl (**2f**). Pale brown solid, dec. before melting (Found: C, 77.93; H, 4.81. Calc. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%); ^1H NMR (C_6D_6-MeOD, 400 MHz), δ (ppm) 7.05 (d, 4H, H-2, H-6, H-2"' and H-6"' or H-3, H-5, H-3"' and H-5"', J=8.7 Hz), 7.22 (d, 2H, H-5' and H-3", J=8.4 Hz), 7.41 (d, 4H, H-3, H-5, H-3"' and H-5"' or H-2, H-6, H-2"' and H-6"', J=8.7 Hz), 7.46 (dd, 2H, H-6' and H-4", J=8.4 and 2.4 Hz), 7.66 (d, 2H, H-2' and H-6", J=2.4 Hz); IR (KBr) 3378, 2937, 1623, 1510, 1282, 1053, 825 cm^{-1}; MS *m/z* 370 (M^+, 100%), 326 (5), 277 (6).

2,2'-Dihydroxybinaphthyl (**2g**). Pale yellow solid, m.p. 212-4°C (lit.[18] m.p. 218°C); ^1H NMR (C_6D_6-MeOD, 200 MHz), δ (ppm) 7.01 (ddd, 2H, H-6 and H-6' or H-7 and H-7', J=8.2, 8.1 and 1.3 Hz), 7.14 (ddd, 2H, H-7 and H-7' or H-6 and H-6', J=8.2, 8.1 and 1.3 Hz), 7.31 (dd, 2H, H-5 and H-5' or H-8 and H-8', J=8.2 and 1.3 Hz), 7.44 (d, 2H, H-3 and H-3' or H-4 and H-4', J=8.8 Hz), 7.71 (dd, 2H, H-8 and H-8' or H-5 and H-5', J=8.1 and 1.3 Hz), 7.75 (d, 2H, H-4 and H-4' or H-3 and H-3', J=8.8 Hz); IR (KBr) 3496, 1631, 1524, 1388, 833, 754 cm^{-1}; MS *m/z* 286 (M^+, 100%), 258 (15), 228 (14), 120 (19).

2,2'-Dihydroxy-4,5,4',5'-dimethylendioxybiphenyl (**2h**). Pale brown solid, m.p. 200-1°C (Found: C, 61.25; H, 3.77. Calc. for $C_{14}H_{10}O_6$: C, 61.32; H, 3.68%); ^1H NMR (C_6D_6-MeOD, 100 MHz), δ (ppm) 5.48 (s, 4H, 2 -O-CH_2-O-), 6.75 (s, 2H, H-3 and H-3' or H-6 and H-6'), 6.76 (s, 2H, H-6 and H-6' or H-3 and H-3'); IR (KBr) 3257, 2915, 1639, 1123, 781 cm^{-1}; MS *m/z* 274 (M^+, 100%), 243 (11), 215 (10), 175 (28).

2,2'-Dihydroxy-3,3',5,5'-tetratertbutylbiphenyl (**2i**). Pale yellow solid, m.p. 198°C (lit.[16] m.p. 200-2°C); ^1H NMR (C_6D_6, 100 MHz), δ (ppm) 1.23 (s, 18H, 2 $C(CH_3)_3$), 1.56 (s, 18H, 2 $C(CH_3)_3$), 5.18 (s, 2H, 2 OH), 7.20 (d, 2H, H-4 and H-4' or H-6 and H-6', J=2.5 Hz), 7.58 (d, 2H, H-6 and H-6' or H-4 and H-4', J=2.5 Hz); IR (KBr) 3484, 2915, 1416, 1219, 869, 755, 637 cm^{-1}; MS *m/z* 410 (M^+, 100%), 395 (43), 339 (18), 57 (17).

2,2'-Dihydroxy-3,3',5,5'-tetramethylbiphenyl (**2l**). White solid, m.p. 134-5°C (lit.[19] m.p. 137-8°C); ^{1}H NMR (C_6D_6, 100 MHz), δ (ppm) 2.07 (s, 6H, 2 CH_3), 2.23 (s, 6H, 2 CH_3), 5.05 (s, 2H, 2 OH), 6.78 (s, 4H, H-4, H-4', H-6 and H-6'); IR (KBr) 3506, 2941, 1486, 1126, 855, 794 cm^{-1}; MS *m/z* 242 (M^+, 100%).

2,2'-Dihydroxy-3,3'-dimethyl-5,5'-ditertbutylbiphenyl (**2m**). Pale brown solid, m.p. 101-3°C (Found: C, 83.70; H, 6.19. Calc. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%); ^{1}H NMR (C_6D_6, 100 MHz), δ (ppm) 1.21 (s, 18H, 2 $C(CH_3)_3$), 2.30 (s, 6H, 2 CH_3), 5.16 (s, 2H, 2 OH), 7.19 (s, 2H, H-4 and H-4' or H-6 and H-6'), 7.20 (s, 2H, H-6 and H-6' or H-4 and H-4'); IR (NaCl) 3546, 2890, 1605, 1488, 1117, 877, 826, 766 cm^{-1}; MS *m/z* 326 (M^+, 68%), 311 (100), 270 (15), 255 (96), 148 (19).

2,2',3,3'-Tetrahydroxybinaphthyl (**2n**). Brown solid, dec. before melting (lit.[20] m.p. 275°C with dec.); ^{1}H NMR (C_6D_6-MeOD, 400 MHz), δ (ppm) 6.93 (td, 2H, H-6 and H-6' or H-7 and H-7', J=7.5 and 1.2 Hz), 7.17 (td, 2H, H-7 and H-7' or H-6 and H-6', J=7.5 and 1.2 Hz), 7.19 (d, 2H, H-5 and H-5' or H-8 and H-8', J=7.5 Hz), 7.49 (s, 2H, H-4 and H-4'), 7.67 (d, 2H, H-8 and H-8' or H-5 and H-5', J=7.5 Hz); IR (KBr) 3472, 1600, 1519, 1458, 1250, 943, 746 cm^{-1}; MS *m/z* 318 (M^+, 100%).

2'-Hydroxy-2,5,5'-trimethoxybiphenyl (**9a**). Pale brown solid, m.p. 90-91°C (lit.[21] m.p. 91-93°C).

2'-Hydroxy-3,4-dimethyl-2,5,5'-trimethoxybiphenyl (**9b**). Pale brown solid, m.p. 101-2°C (Found: C, 70.70; H, 7.08. Calc. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99); ^{1}H NMR (C_6D_6, 100 MHz), δ (ppm) 1.99 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 3.13 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 6.58 (s, 1H, H-6), 6.78 (dd, 1H, H-4', J=8.8 and 3.1 Hz), 7.14 (d, 1H, H-6', J=3.1 Hz), 7.28 (d, 1H, H-3', J=8.8 Hz), 7.48 (s, 1H, OH); IR (KBr) 3337, 1572, 1493, 1465, 1188, 787 cm^{-1}; MS *m/z* 288 (M^+, 100%), 273 (8), 257 (27).

2,2',2'',2'''-Tetrahydroxy-3,5',5'',5'''-tetramethyl-1,1':3',1'':3'',1'''-tetraphenyl (**3b**). Pale yellow solid, dec before melting (Found: C, 78.93; H, 6.21. Calc. for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14); ^{1}H NMR (C_6D_6-MeOD, 400 MHz), δ (ppm) 2.16 (s, 6H, 2 CH_3), 2.17 (s, 6H, 2 CH_3), 6.95 (dd, 2H, H-4 and H-4''', J=8.1 and 1.9 Hz), 7.04 (d, 2H, H-3 and H-3''', J=8.1 Hz), 7.11 (d, 2H, H-6' and H-4'' or H-4' and H-6'', J=2.3 Hz), 7.13 (d, 2H, H-4' and H-6'' or H-6' and H-4'', J=2.3 Hz), 7.14 (d, 2H, H-6 and H-6''', J=1.9 Hz); IR (KBr) 3380, 1499, 1223, 811 cm^{-1}; MS *m/z* 426 (M^+, 100%), 297 (10), 285 (16), 257 (99).

2,2',2'',2'''-Tetrahydroxy-3,5',5'',5'''-tetratertbutyl-1,1':3',1'':3'',1'''-tetraphenyl (**3d**). Pale yellow solid, dec. before melting (Found: C, 80.69; H, 8.38. Calc. for $C_{40}H_{50}O_4$: C, 80.77; H, 8.47); ^{1}H NMR (C_6D_6, 400 MHz), δ (ppm) 1.23 (s, 18H, 2 $(CH_3)_3C$), 1.24 (s, 18H, 2 $(CH_3)_3C$), 6.88 (d, 2H, H-3 and H-3''', J=8.4 Hz), 7.10 (dd, 2H, H-4 and H-4''', J=8.4 and 2.1 Hz), 7.50 (d, 2H, H-6 and H-6''', J=2.1 Hz), 7.52 (d, 2H, H-4' and H-6'' or H-6' and H-4'', J=2.3 Hz), 7.56 (d, 2H, H-6' and H-4'' or H-4' and H-6'', J=2.3 Hz); IR (KBr) 3367, 1559, 1501, 1465, 1228, 822 cm^{-1}; MS *m/z* 594 (M^+, 100%), 579 (33), 539 (22), 483 (43), 427 (30).

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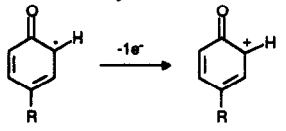

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