Pergamon

*Tetrahedron*, Vol. 53, No. 40, pp. 13915-13932, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00903-4

# The Chemistry of Novolac Resins. Part 4. The Strategic Synthesis of Model Compounds.

Pauline J. de Bruyn, Linda M. Foo, Audrey S. C. Lim, Mark G. Looney, David H. Solomon*

Polymer Science Group, Department of Chemical Engineering, University of Melbourne, Parkville, Victoria, Australia, 3052

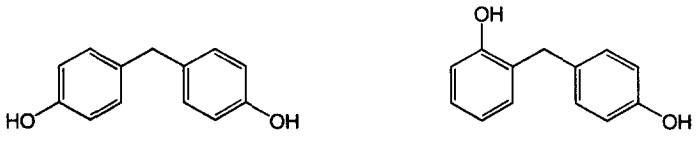
***Abstract:*** An ion assisted *ortho*-specific phenol-formaldehyde condensation process, incorporating selective protecting-deprotecting methodology has been adapted to prepare a range of model novolac compounds which are ideal for studying crosslinking with hexamethylenetetramine. © 1997 Elsevier Science Ltd.

## INTRODUCTION

The commercial importance of phenol-formaldehyde resins has resulted in extensive studies of these systems with the aim of identifying the reaction mechanisms and intermediates that occur during subsequent polymerization processes. However, the complexity of these resins has made a detailed understanding of the subsequent chemical processes and their relationship to the physical properties of the final polymerized product difficult. Many groups have attempted to use model systems[1-5], *i.e.* mono-phenols that resemble residual units of a novolac to simplify the process. However there still exists a great deal of uncertainty with regard to the chemical processes of the commercial systems. The range of suitable higher molecular weight models currently available is limited and it is difficult to extrapolate the chemistry of mono-phenol models to polydispersed resins with molecular weights up to 2000, and doubts exist as to the validity of these small models. This paper further describes the preparation[6] of a series of pure compounds consisting of 4-8 phenol units which will be used to study the chemistry which occurs during crosslinking of novolac resins. The methodology developed during the course of this work has been used to prepare model systems which contain only free *ortho* sites or which contain an *ortho:para* ratio consistent with a statistical commercial novolac resin.

## DISCUSSION

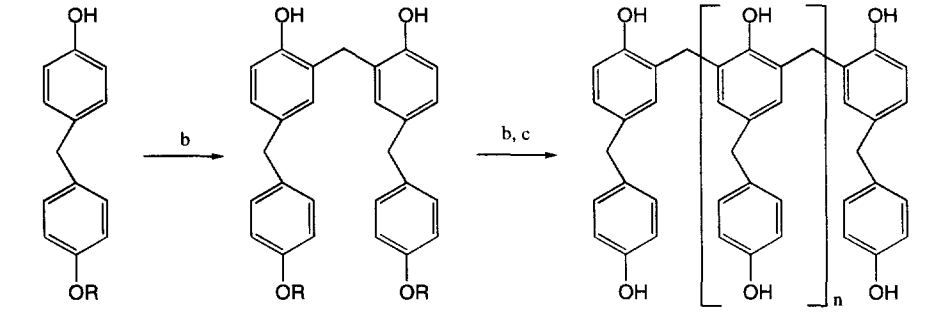
The preparation of the model compounds is based upon selective protection deprotection methodology. In conjunction with an ion assisted *ortho*-specific phenol-formaldehyde coupling procedure[7], the synthesis of higher molecular weight phenols differing in structure and number of reactive *ortho* and *para* positions has been achieved. The precursors for the generation of the two series of model compounds described in this paper are the commercially available bis(hydroxyphenyl)methanes **1** and **2** which incorporate either a *para-para'* or an *ortho-para'* disposed methylene linkage to the final product.




1 2

**Fig. 1.**

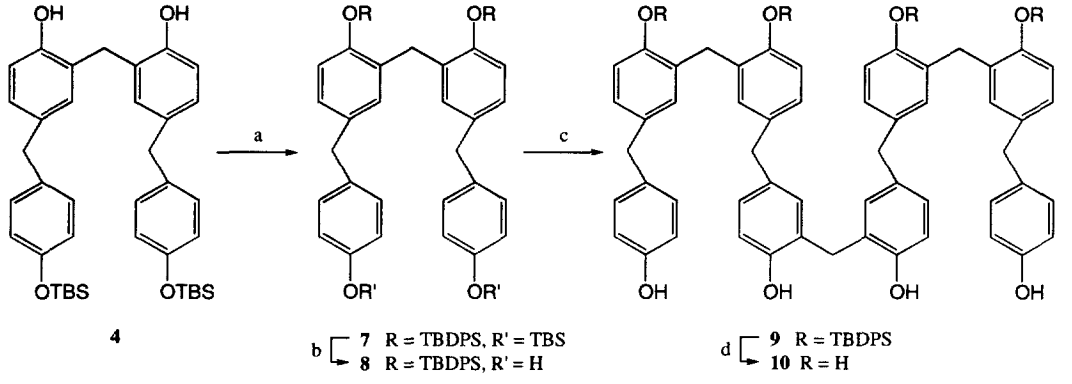
The evaluation of suitable protecting groups included the use of acetate, methyl and benzyl masking moieties. However, the formation of silyl ethers was preferred since the acetate groups were found to be labile; demethylation to the free phenol proved cumbersome; and the separation of benzylated isomers was difficult. The series containing only free *ortho* reactive sites is based on the *para, para'*-linked dimer **1**. Selective silylation[8] using *tert*-butyldimethylsilyl chloride (TBSCl) and imidazole in anhydrous DMF at room temperature afforded after chromatography the mono-protected dimer **3**. Treatment of **3** with ethyl magnesium bromide under standard *ortho-ortho'* coupling conditions[7] induced reaction of the metal phenoxide intermediate with paraformaldehyde in benzene while heated at reflux for 20 h. The desired *ortho-ortho'* linked bis-silylated tetramer **4** was afforded in 72 % yield after chromatography. The selectivity of the *ortho* coupling procedure was confirmed by characteristic $^{13}C$ nuclear magnetic resonance (NMR) signals at 30.9 and 40.1 ppm, indicative of the new *ortho-ortho'* and the original *para-para'* linkages respectively. Deprotection of **4** employing standard TBAF conditions[8] afforded **5**, an ideal model compound suitable for investigating the polymerization of novolacs with only *ortho* reactive sites. Higher molecular weight compounds (octamers) of a linear and branched nature, which also contain only reactive *ortho* positions in their structure were synthesized. To this end, the key intermediate to the synthesis of these larger models in the *para*-linked series was tetramer **4**. The branched octamer was prepared from further coupling of tetramer **4** through the *ortho* site of the more substituted phenol ring bearing the free hydroxyl group and deprotection with TBAF at room temperature afforded the octamer **6** in 90 % yield (Scheme 1).




**Scheme 1.** *Reagents and conditions:* a. TBSCl (1.12 eq), imidazole, DMF, 25° C, 2 h (**3** 45 %); b. EtMgBr (2 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h (**4** 52 %); c. TBAF, THF, 25° C, 6 h (**5** 21 %, **6** 92%).

Preparation of the analogous linear system was more complex, since coupling at the alternate *ortho* position required an additional protection step followed by selective deprotection to unmask the *para* cresol terminal end of **4**. The desired tetramer **7** was generated by treating **4** with *tert*-butyldiphenylsilyl chloride[9] (TBDPSCl), a more robust silyl protecting group. Selective deprotection of the fully protected tetramer **7** was achieved by employing hydrogen fluoride-pyridine[10] or boron trifluoride etherate[11] at 0° C to afford **8**.

Selective coupling of **8** through the *para* cresol terminal afforded octamer **9** and full deprotection with TBAF gave the desired linear octamer **10** (Scheme 2).

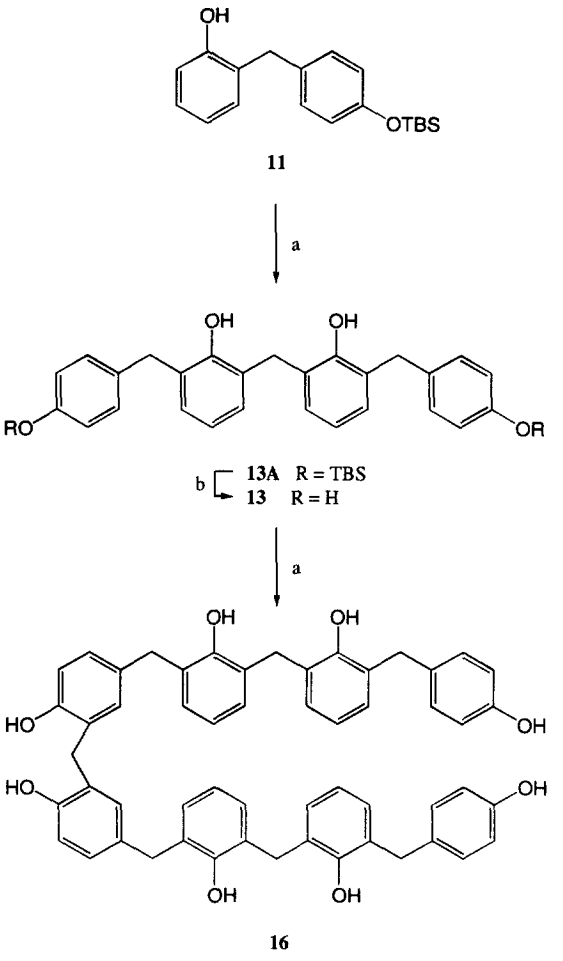



**Scheme 2.** *Reagents and conditions:* a. TBDPSCl (4.5 eq), imidazole (4.5 eq), DMF, 60° C, 10 h (**7** 67 %); b. HF-pyridine, pyridine, THF, 0° C to 25° C, 4.5 h (80 %) or $BF_3Et_2O$, $CHCl_3$, 0° C to 25° C, 3 h (96 %); c. EtMgBr (2 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h (**9** 22 %); d. TBAF, THF, 25° C, 6 h (**10** 97 %).

An *ortho-para'* series containing a ratio of *ortho* and *para* reactive sites was synthesized in order to obtain models that more closely resemble a commercial resin. It was envisaged that this could be achieved by utilizing the same protection, deprotection and coupling methodologies employed in the synthesis of the *para*-linked series. Starting with the commercially available dimer **2**, tetramers **13** and **14** were prepared from coupling of the appropriate precursors generated from **2**.

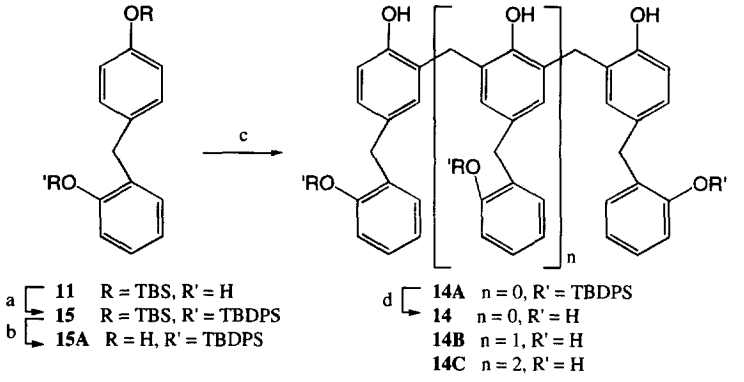

**Fig. 2.**

**2** unlike **1**, is unsymmetrical, and therefore can potentially generate a mixture of mono-protected isomers in addition to the bisilylated species. However, the relative positions of the hydroxyl functionalities resulted in the preferential silylation of the hydroxyl group *para* to the methylene bridge, when treated with TBSCl. Assignment of the major product **11** was tentatively determined by NMR spectroscopy. Furthermore, the coupling of **11** would generate a tetramer with a linear structure. Therefore treatment of **11** with EtMgBr, followed by treatment with TBAF gave the desired tetramer **13**. Characteristic aromatic splitting in the $^1H$ NMR at 6.72 ppm (dd, *J* 7.5, 7.5 Hz), 6.73 (dd, *J* 8.5, 2 Hz), 6.86 (dd, *J* 7.5, 1.5 Hz), 7.03 (dd, *J* 8.5, 2 Hz) and 7.05 (dd, *J* 7.5, 1.5 Hz) was consistent with the protons at H4', H2 and H6, H3', H3 and H5, H5' respectively. These results confirm the structure for tetramer **13** and that of its dimer precursor **11**. Further coupling of **13** through the *ortho* site afforded octamer **16** (Scheme 3).



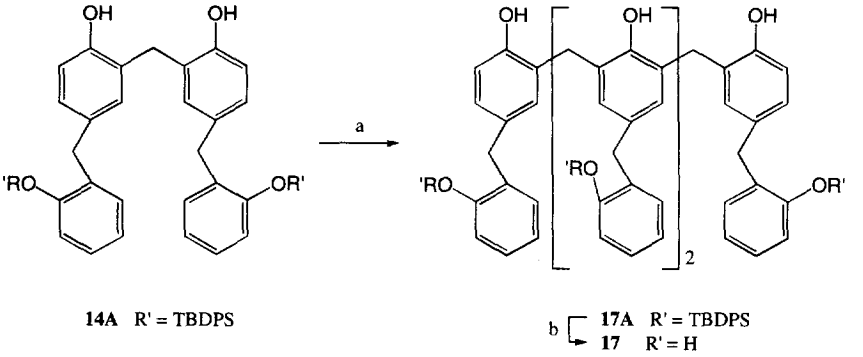

**Scheme 3.** *Reagents and conditions:* a. EtMgBr (1 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h (**13A** 50 %, **16** 15%); b. TBAF, THF, 25° C, 6 h (**13** 71 %).

Synthesis of the homologous tetramer **14** requires *ortho* coupling through the *para*-cresol unit of **12**. However the preferential formation of the mono-protected dimer **11** made additional silylation of **11** with TBDPSCl necessary to produce the precursor **15A**. Purification of **11** by chromatography afforded the fully protected dimer **15**. Selective deprotection[11] of the TBS group was achieved by treatment with boron trifluoride etherate to afford the desired precursor **15A**. Subsequent coupling of **15A** gave tetramer **14A**, from which 14A was produced by treatment with TBAF (Scheme 4). The structure of **14** was confirmed by $^1H$ NMR which showed a doublet at $\delta$ 7.10 ppm with a coupling constant of 1.7 Hz, indicative of the lone proton at C3.




**Scheme 4.** *Reagents and conditions:* a. TBDPSCl (1.1 eq), imidazole (2.4 eq), DMF, 60° C, 10 h (**15** 98 %); b. $BF_3Et_2O$, $CHCl_3$, 0° C to 25° C, 3 h (**15A** 96 %); c. EtMgBr (1 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h (**14A** 73 %); d. TBAF, THF, 25° C, 6 h (**14** 82 %, 17 %)

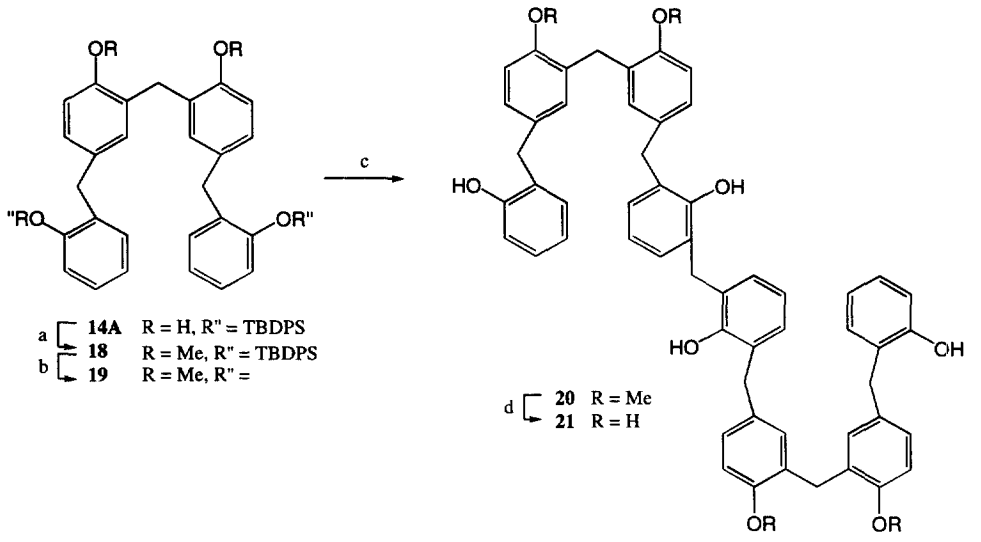
Similar to the *para*-linked series, tetramer **14** can potentially generate two structurally different octamers since **14** has two types of *ortho* sites. Coupling of tetramer **14A** afforded octamer **17A,** from which treatment with TBAF produced **17** (Scheme 5).




**Scheme 5.** *Reagents and conditions:* a. EtMgBr (2 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h (**17A** X %); b. TBAF, THF, 25° C, 6 h (**17** %)

In order to synthesize the homologous octamer **21**, a third type of protecting group was needed to afford coupling through the *ortho* site of the cresol unit in **14A**. For this reason a non-silyl protected group was desired and so **14A** was methylated to give **18**. Treatment of **18** with TBAF cleaved the TBDPS groups to generate the desired precursor **19**. Coupling of **19** gave **20** and demethylation afforded **21** (Scheme 6).

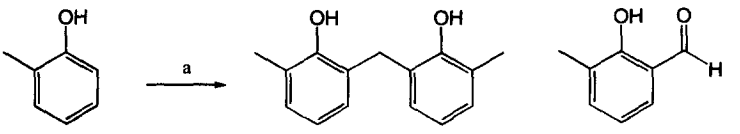
To improve the yield of the intermediate precursors in both the *para-para'* and *ortho-para'* linked series, methylation was utilized instead of TBDPSCl. The TBDPS group, although fairly robust, can still be cleaved during the selective deprotection of the TBS group since the two protecting groups are silyl ethers. Use of a different protecting group that is not affected by silyl deprotection could overcome loss of intermediates during selective desilylation. However methylation did not improve the overall yield of the final tetramers since complete demethylation was difficult to obtain. Therefore, methyl ethers were only used in the synthesis of octamers where the use of a third protecting group was necessary.




**Scheme 6.** *Reagents and conditions:* a. $K_2CO_3$ (eq), $(CH_3)_2SO_4$ (eq), acetone, 68° C, 23.5 h (**18** 58 %); b. TBAF, THF, 25° C, 6 h (**19** 95 %); c. EtMgBr (2 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h; d. $BCl_3$, $CH_2Cl_2$, 26 h.

According to a study of the relationship between the average molecular weight and phenol-formaldehyde ratio used in the preparation of novolacs, recovery of only pure dimer cannot be achieved in a single reaction. This is due to the electrophilic nature of the reaction between phenol and formaldehyde, where a carbonium ion formed from methylene glycol reacts with the phenolic ring. The resulting benzylic derived carbonium ion reacts rapidly with another phenol to form a methylene bridge between two phenol units and this condensation continues until all the formaldehyde has reacted irrespective of molecular size of the phenolic entities. Similarly, this was the case in the regioselective methodology reported in this paper and as a result, the coupling reaction did not terminate after the initial condensation and consequently higher polyphenolic systems were also generated. The distribution of these compounds could be regulated through the ratio of starting dimer to formaldehyde. This was useful since higher molecular weight compounds were desired and manipulation of the coupling ratio allowed the dispersity of products to be controlled. Therefore, in addition to tetramer **5**, separation by chromatography isolated hexamer **6A**, octamer **6**, decamer **6B** and dodecamer **6C** (Scheme 1). This was also the case in the synthesis of the *ortho-para'* series, where the coupling of **2** produced a mixture of compounds containing the desired tetramer **14**, hexamer **14B** and octamer **14C** (Scheme 4).

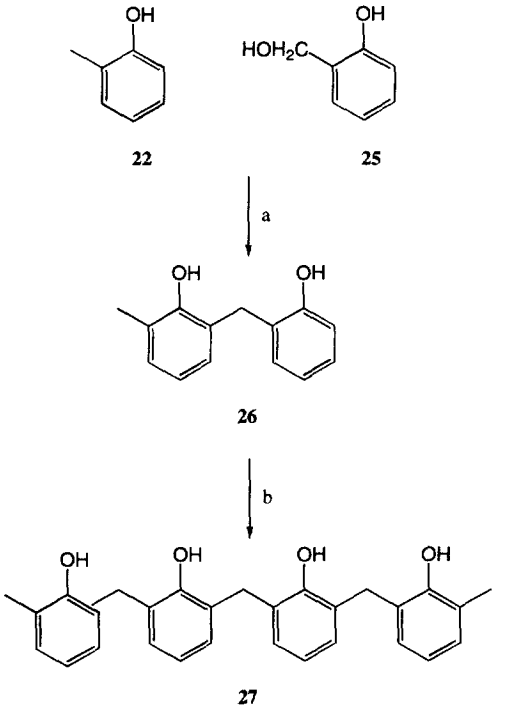
Synthetic methodology was also extended to generate a series of compounds which only contained *para* reactive sites. The *ortho* series predominantly containing *para* reactive sites has been generated[7], but terminal *ortho* reactive sites are also present in the structure. Therefore in order to complement the series of model compounds already described, a homologous model series containing methyl blocked terminal *ortho* sites was synthesized. *Ortho*-cresol **22** was directly coupled to give dimer **23** (Scheme 7). Theoretically, conversion of **22** to **23** requires 0.5 molar equivalents of formaldehyde. When the amount of formaldehyde is increased, trace amounts of an aldehydic product **24** were formed. This was confirmed by characteristic $^1H$ NMR signals at $\delta$ 11.28 and 9.86 ppm indicative of the hydroxyl and aldehydic protons respectively. This result strongly suggests that excess formaldehyde hinders the coupling of two phenolic units due to the complexing nature of formaldehyde with the metal phenoxide intermediate.




22 23 24

**Scheme 7.** *Reagents and conditions:* a. EtMgBr (1 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h (**23** 67 %).

Synthesis of the tetramer homologue **27** was achieved, when an ethereal solution of **22** and salicyl alcohol **25** in a 5:1 molar ratio was slowly added to ethyl magnesium bromide to form the required metal phenoxide intermediates. In this case paraformaldehyde was not required as in the previous cases, since the hydroxybenzyl unit **25** provides the methylene source through the methylol moiety. However in order to prevent self condensation of **25** during *ortho-ortho'* coupling, it was necessary to use an excess of **22** to favour the formation of **26**. Purification by chromatography afforded **26** and coupling of **26** in the presence of formaldehyde gave tetramer **27**, blocked at the terminal *ortho* sites by methyl groups in 25 % yield (Scheme 7).




**Scheme 8.** *Reagents and conditions:* a. EtMgBr (3 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C (**23** 67 %); b. EtMgBr (2 eq), $Et_2O$, 25° C, 30 min, then benzene, 25° C to 80° C, paraformaldehyde (0.5 eq), 20 h (**27** 25 %).

## CONCLUSION

The methodology developed during the course of this work has been used to prepare model systems containing only free *ortho* sites, free *para* sites, or those which contain an *ortho:para* ratio consistent with a statistical commercial novolac resin. The synthesis of the described series of compounds has been achieved and while the yields of the pure compounds are low, it is anticipated that they will provide good examples for modelling and studying commercial novolac systems since they differ structurally and in the ratio of reactive *ortho* and *para* positions. Through the use of these model compounds, work has also been carried out to examine the physical characteristics of novolac resins using gel permeation chromatography (GPC) analysis[12] and the study of adsorption on to activated carbon[13]. Future publications will report on the polymerization of the model tetramers with a crosslinking reagent to determine the importance of structural changes in the polymerization of novolac resins with regard to the final physical properties. It is envisaged that this work will correlate to the more complicated commercial resins and help to explain their complex chemistry.

## EXPERIMENTAL SECTION

### General Procedures

Silylation and coupling reactions were performed in oven-dried or flame-dried glassware under a nitrogen atmosphere. Solvents were distilled: dimethylformamide (DMF) and chloroform from calcium hydride, tetrahydrofuran (THF) from potassium benzophenone ketyl, benzene from sodium metal. Diethyl ether (ether) was dried using sodium wire. The petroleum spirits (petrol) used was 40-60° C. Medium pressure liquid (m.p.l.c) chromatography and flash chromatography were carried out using Merck Silica No. 9175. Thin layer (t.l.c) and preparative layer (p.l.c) chromatography were conducted on plastic sheets and glass plates coated with silica gel 60 $F_{254}$. Melting point determinations (uncorrected) were made using an Electrothermal melting point apparatus. $^1H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were recorded at 300 and 75 MHz repectively using a Varian Unity Spectrometer. Deuterochloroform was used as the solvent with chloroform ($\delta$H 7.26 and $\delta$C 77.0 ppm) as an internal reference, unless otherwise stated. Chemical shifts are quoted on the $\delta$ (ppm) scale followed by multiplicity, assignment and coupling constant(s). Abbreviations used include: s, singlet; d, doublet; m, multiplet; Ar, aromatic. Infrared spectra were recorded on a Bio-Rad FTS-60A spectrometer. For each sample 16 scans were collected in KBr discs and oils on NaCl plates. Absorption maxima, $\nu_{max}$, are quoted in wavenumbers ($cm^{-1}$). Mass spectra were recorded using a V.G Micromass 7070F Spectrometer at 70 eV, or on a Kratos Spectrometer, University of Tasmania as CI (reagent gas ammonia) or LSIMS. The molecular ion, $M^+$ together with fragment ions having intensities 5 % or greater of the base peak are reported with intensities in brackets. Elemental analyses were carried out by Chemical & Micro Analytical Services Pty. Ltd and at the University of Tasmania.

**1-*tert*-butyldimethylsilyloxy-4,4'-methylenediphenol (3).** 4,4'-methylenediphenol **1** (5.00 g, 25 mmol) was dissolved in DMF (20 $cm^3$) under a nitrogen atmosphere. Imidazole (3.40 g, 50 mmol) and *tert*-butyldimethylsilyl chloride (4.15 g, 28 mmol) were added to the mixture and stirred for 2 h at room temperature. The mixture was quenched with water (100 $cm^3$) and the organics were extracted into ether (250 $cm^3$). The combined organic extracts were dried and concentrated *in vacuo*. The crude residue was purified by

m.p.l.c using petrol/ether (7:3) to afford the desired mono silylated diphenol **3** (3.52 g, 45 %). $R_f$ 0.41 (petrol/ether, 7:3). M.p. 54-56° C; $^1$H NMR: δ 0.18 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.98 (s, 9H, SiC(C$\underline{H}_3$)$_3$), 3.84 (s, 2H, $CH_2$), 4.50 (br s, 1H, OH), 6.75 (d, 4H, ArH, J = 8.2), 7.01 (d, 2H, ArH, J = 8), 7.04 (d, 2H, ArH, J = 8); $^{13}$C NMR: δ -4.4 (Si(C$\underline{H}_3$)$_2$), 18.2 (Si$\underline{C}$(CH$_3$)$_3$), 25.7 (SiC(C$\underline{H}_3$)$_3$), 40.2 (C-7), 115.2 (C-2', C-6'), 119.9 (C-2, C-6), 129.7 (C-3, C-5), 130.0 ( C-3', C-5'), 133.9 (C-4'), 134.1 (C-4), 153.7 (C-1'), 153.8 (C-1); IR (KBr) 3284, 2954, 2928, 2896, 2858, 1609, 1508, 1462, 1446, 1375, 1255, 1169, 916, 841, 783 cm$^{-1}$; MS (EI) m/z (relative intensity) 314 ($M^+$, 2 %), 313 ($M^+$-1, 8), 256 (16), 107 (100). Anal. Calcd. for $C_{19}H_{26}SiO_2$: C, 72.61; H, 8.24. Found: C, 72.45; H, 8.41. $C_{19}H_{26}SiO_2$ requires 314.169761. Found $M^+$, 314.1688.

The remaining mixture contained 1,1'-bis(*tert*-butyldimethylsilyloxy)-4,4'-methylenediphenol (3.44 g, 44 %) as the most mobile compound $R_f$ 0.75 (petrol/ether, 7:3), and the starting dimer **1** (0.75 g, 10 %) $R_f$ 0.09 (petrol/ether, 7:3).

**4,4'-bis(4-*t*-butyldimethylsilyloxybenzyl)-2,2'-methylenediphenol (4).** Ethyl magnesium bromide was formed *insitu* in ether (20 cm$^3$) from magnesium (0.22 g, 9.1 mmol) and ethyl bromide (0.7 cm$^3$, 8.8 mmol). 1-*tert*-butyldimethylsilyloxy-4,4'-methylenediphenol **3** (2.78 g, 8.8 mmol) was added dropwise to the ethyl magnesium bromide solution as an ethereal solution (20 cm$^3$). After mixing for 15 min, the bulk of the ether was removed by distillation. Benzene (100 cm$^3$) was added and the remaining ether was removed. Paraformaldehyde (0.13 g, 4.33 mmol) was added to the mixture and boiled for 20 h. The cooled reaction mixture was quenched with 10 % HCl solution (50 cm$^3$) and the organic material was extracted into ether (200 cm$^3$). The combined organic extracts were dried and concentrated *in vacuo*. Purification of the crude material by flash chromatography using petrol/ether (7:3) afforded the desired product **4** (1.47 g, 52 %). $R_f$ 0.71 (petrol/ether, 7:3). M.p. 82-84° C; $^1$H NMR: δ 0.19 (s, 12H, Si(C$\underline{H}_3$)$_2$), 0.99 (s, 18H, SiC(C$\underline{H}_3$)$_3$), 3.82 (s, 4H, $CH_2$), 3.85 (s, 2H, $CH_2$), 6.74 (d, 2H, ArH, J = 8.2), 6.77 (d, 4H, ArH, J = 8.7), 6.87 (dd, 2H, ArH, J = 8.7, 1.9), 7.02 (d, 4H, ArH, J = 8.7), 7.05 (d, 2H, ArH, J = 1.9); $^{13}$C NMR: δ -4.4 (Si(C$\underline{H}_3$)$_2$), 18.2 (Si$\underline{C}$(CH$_3$)$_3$), 25.7 (SiC(C$\underline{H}_3$)$_3$), 31.0 (C-8), 40.2 (C-7), 115.9 (C-6), 119.9 (C-2', C-6'), 126.7 (C-2), 128.3 (C-5), 129.7 (C-3', C-5'), 131.1 ( C-3), 134.0 (C-4), 134.5 (C-4'), 150.7 (C-1), 153.8 (C-1'); IR (KBr) 3245, 3057, 3027, 2955, 2931, 2895, 2859, 1609, 1508, 1469, 1437, 1389, 1361, 1258, 1168, 1109, 1008, 918, 840, 778, 691 cm$^{-1}$; MS (EI) m/z (relative intensity) 641 ($M^+$+1, 9 %), 640 ($M^+$, 22), 639 ($M^+$-1, 40), 582 (43), 466 (2), 374 (4), 221 (34), 107 (38), 73 (100). Anal. Calcd. for $C_{39}H_{52}Si_2O_4$: C, 73.13; H, 8.13. Found: C, 73.00; H, 8.13. $C_{39}H_{52}Si_2O_4$ requires 640.340395. Found $M^+$, 640.3412.

The rest of the crude material contained the starting dimer **3** (0.33 g, 12 %) $R_f$ 0.41 (petrol/ether, 7:3), and the remaining 0.75 g contained higher molecular weight material.

**4,4'-Bis(4-hydroxybenzyl)-2,2'-methylenediphenol (5).** An ethereal solution (15 cm$^3$) of 1-*tert*-butyldimethylsilyloxy-4,4'-methylenediphenol **3** (8.62 g, 27 mmol) was added dropwise to ethyl magnesium bromide (3.6 cm$^3$, 27 mmol) in ether (10 cm$^3$). After 15 min stirring at room temperature, the ether was removed by distillation and replaced with benzene (200 cm$^3$). Paraformaldehyde (0.33 g, 10.9 mmol) was added to the mixture and boiled for 20 h. The reaction mixture was cooled and quenched with 10 % HCl solution (100 cm$^3$) and the organics were extracted in ether (300 cm$^3$), dried and concentrated *in vacuo*. The crude material was dissolved in THF (40 cm$^3$) and treated with tetrabutylammonium fluoride (TBAF) (22 cm$^3$, 76 mmol) for 6 h. The resulting solution was diluted with ethyl acetate (200 cm$^3$) and washed with water (150

$cm^3$). The organic extracts were dried and concentrated *in vacuo*. Purification by m.p.l.c using petrol/ethyl acetate/methanol (70:29:1) afforded the desired tetramer **5** (1.16 g, 21 %). $R_f$ 0.22 (petrol/EtOAc/MeoH, 70:29:1 x 3). M.p. 200-203° C; $^1H$ NMR ($D_6$ acetone): δ 3.72 (s, 4H, $CH_2$), 3.87 (s, 2H, $CH_2$), 6.72 (d, 4H, ArH, J = 8), 6.73 (d, 2H, ArH, J = 8), 6.83 (dd, 2H, ArH, J = 7.8, 2.2), 6.98 (d, 4H, ArH, J = 8), 7.03 (d, 2H, ArH, J = 2.3); $^{13}C$ NMR ($D_6$ acetone): δ 40.8 (C-7), 115.9 (C-2', C-6'), 116.0 (C-6), 128.0 (C-2), 128.2 (C-5), 130.4 (C-3', C-5'), 131.8 ( C-3), 133.7 (C-4'), 134.2 (C-4), 153.4 (C-1), 156.3 (C-1'). IR (KBr) 3438, 3305, 3027, 2917, 1604, 1506, 1440, 1366, 1229, 1107, 821 $cm^{-1}$; MS (EI) m/z (relative intensity) 413 ($M^+$+1, 17 %), 412 ($M^+$, 54), 394 (2), 318 (4), 306 (17), 213 (25), 200 (44), 107 (100). Anal. Calcd. for $C_{27}H_{24}O_4$: C, 78.61; H, 5.88. Found: C, 78.79; H, 5.91. $C_{27}H_{24}NO_4$ requires 430.2018. CI ($NH_3$ reagent gas) found $M^+$+ $NH_4$, 430.2011.

The remaining mixture contained 4,4'-methylenediphenol **1** (1.96 g, 23 %), 6'-(2-hydroxy-5-(4-hydroxybenzyl)-4,4'-bis(4-hydroxybenzyl)-2,2'-methylenediphenol **6A** (0.78 g, 14 %) $R_f$ 0.07 (petrol/EtOAc/MeoH, 70:29:1 x 3), and 6,6'-bis(2-hydroxy-5-(4-hydroxybenzyl)benzyl-4,4'-bis(4-hydroxybenzyl)2,2'-methylenediphenol **6** (0.50 g, 9 %) $R_f$ 0.02 (petrol/EtOAc/MeoH, 70:29:1 x 3).

**6,6'-bis(2-hydroxy-5-(4-hydroxybenzyl)benzyl-4,4'-bis(4-hydroxybenzyl)2,2'-methylenediphenol (6).** 4,4'-bis(4-*t*-butyldimethylsilyloxybenzyl)-2,2'-methylenediphenol **4** (0.20 g, 0.31 mmol) was added dropwise as an ethereal solution (10 $cm^3$) to ethylmagnesium bromide in ether (5 $cm^3$), generated *in situ* from magnesium (15 mg, 0.61 mmol) and ethyl bromide (0.05 cm3, 0.67 mmol). After stirring at room temperture for 15 min, benzene was added (50 $cm^3$) and the ether was removed by distillation. Paraformaldehyde ( 5 mg, 0.15 mmol) was added to the mixture and boiled for 20 h. The mixture was quenched with 10 % HCl and (20 $cm^3$). The organics were extracted into ether (100 $cm^3$) and washed with water (100 $cm^3$). The organic extracts were dried and concentrated *in vacuo*. Purification by p.l.c afforded the desired product **6** (0.18 g, 92 %). $^1H$ NMR ($D_6$-acetone): δ 3.66 (s, 4H, $CH_2$), 3.71 (s, 4H, $CH_2$), 3.83 (s, 2H, $CH_2$), 3.85 (s, 4H, $CH_2$), 6.73 (d, 10H, ArH, J = 8.5), 6.78 (s, 2H, ArH), 6.83 (s, 2H, ArH), 6.88 (d, 4H, ArH, J = 8.5), 6.95 (d, 4H, ArH, J = 8.5), 6.98 (d, 4H, ArH, J = 8.5), 7.04 (s, 2H, ArH), 8.07 (br s, 4H, OH), 8.57 (br s, 4H, OH); $^{13}C$ NMR ($CD_3OH$): δ 31.5 (C-8), 31.8 (C-9), 20.1 (C-7), 20.2 (C-7'), 115.9 (C-6), 116.03 (C-6'), 116.04 (C-2'), 128.4, 128.5, 129.0, 129.1, 129.8, 129.9, 130.7 (C-2', C-6'), 131.9, 113.18, 113.24, 113.9, 135.0, 150.7 (int-C1), 153.0 (ext-C1), 156.2 (int-C1'), 156.3 (ext-C1').

**4,4'-Bis(4-*tert*-butyldimethylsiloxybenzyl)-1,1'-bis-tert-butyldiphenyl-2,2'-methylenediphenol (7).** To a solution of *tert*-butyldiphenylsilyl chloride (0.91 , 3.5 mmol) and imidazole (0.32 g, 0.78 mmol) in DMF (15 $cm^3$) was added tetramer **4** (0.50 g, 0.78 mmol). After 10 h at 60° C the reaction was allowed to cool to room temperature and was quenched with water (50 $cm^3$) and extracted in ether (100 $cm^3$). The organic extracts were dried and concentrated *in vacuo*. The crude mixture was purified by chromatography using petrol/ether (7:3) to give some starting material **4** (0.19 g, 22 %) and the desired fully protected tetramer **7** (0.59 g, 67 %). $R_f$ 0.82 (petrol/ether, 7:3). M.p. 150-153° C; $^1H$ NMR: δ 0.17 (s, 12H, $Si(C\underline{H}_3)_2$), 0.98 (s, 18H, $SiC(C\underline{H}_3)_3$), 1.05 (s, 18 H, $SiPh(C\underline{H}_3)_3$), 3.76 (s, 4H, $CH_2$), 4.36 (s, 2H, $CH_2$), 6.38 (d, 2H, ArH, J = 8.6), 6.57 (dd, 2H, ArH, J = 8.6, 1.9), 6.69 (d, 4H, ArH, J = 8.6), 6.95 (d, 6H, ArH, J = 8.6), 7.37 (dd, 4H, ArH, J = 6.7, 6.7), 7.39 (dd, 4H, ArH, J = 6.7, 6.7), 7.44 (dd, 4H, ArH, J = 6.7, 6.7), 7.76 (d, 8H, ArH, J = 6.7); $^{13}C$ NMR: δ -4.4 ($Si(\underline{C}H_3)_2$), 18.2 ($Si(CH_3)_2\underline{C}(CH_3)_3$), 19.5 ($SiPh_2\underline{C}(CH_3)_3$), 25.7 ($Si(CH_3)_2C(\underline{C}H_3)_3$), 26.5 ($Si\ Ph_2C(\underline{C}H_3)_3$),

31.5 (C-8), 40.3 (C-7), 118.3 (C-6), 119.7 (C-2', C-6'), 126.9 (C-2), 127.7 (C-Ph-2, 6), 129.7 (C-Ph-4), 129.8 (C-3', C-5'), 130.2 (C-5), 130.7 (C-3), 132.9 (C-Ph-1), 133.6 (C-4), 134.2 (C-4'), 135.5 (C-Ph-3, 5), 151.6 (C-1), 153.6 (C-1'); IR (KBr) 2959, 2932, 2889, 2858, 1608, 1507, 1471, 1427, 1257, 1111, 924, 842, 821, 778, 703 $cm^{-1}$; MS (LSIMS) m/z (relative intensity) 1116 ($M^+$, 100 %), 1060, 985, 943, 909, 819, 689. Anal. Calcd. for $C_{71}H_{88}Si_4O_4$: C, 76.3; H, 7.9. Found: C, 76.5; H, 8.1. $C_{71}H_{88}Si_4O_4$ requires 1116.5760. Found $M^+$, 1116.57770.

**4,4'-Bis(4-hydroxybenzyl)-1,1'-bis-*t*-butyldiphenylsilyl-2,2'-methylene diphenol (8).** Selective deprotection of **7** was achieved utilizing two common deprotection prodecedures:-

(A) HF-pyridine (10-11 drops) was added to a solution of tetramer **7** (11.6 mg, 10 mmol) in tetrahydrofuran (3 $cm^3$) under an inert atmosphere, at 0° C and the reaction mixture was allowed to warm to room temperature. After stirring for 4.5 h the mixture was quenched with saturated sodium bicarbonate solution and extracted with ether. The combined organic extracts were washed with aqueous copper sulphate solution, dried and concentrated. The residue was chromatographed using petrol/ether (2:1) to give 4,4'-bis(4-hydroxybenzyl)-1,1'-bis-*t*-butyldiphenylsilyl-2,2'-methylenediphenol **8** (7.3 mg, 80 %). M.p. 150-153° C; $^1H$ NMR: δ 1.03 (s, 18H, $C(C\underline{H}_3)_3$), 3.72 (s, 4H, $CH_2$), 4.33 (s, 2H, $CH_2$), 6.35 (d, ArH, J = 8.3), 6.57 (dd, ArH, J = 8.0, 2.3), 6.64 (d, ArH, J = 8.0), 6.88 (d, ArH, J = 2.0), 6.91 (d, ArH, J = 8.2), 7.33 - 7.55 (m, 20H, Si-ArH); $^{13}C$ NMR: δ 19.5, 26.4, 31.6, 19.2, 113.0, 115.1, 118.3, 126.9, 128.8, 129.8, 130.2, 130.6, 132.8, 133.5, 135.5, 151.7, 153.5.

(B) Tetramer **7** (14.7 mg, 13.1 mmol) was dissolved in chloroform (3 $cm^3$) under a nitrogen atmosphere and boron trifluoroetherate ($BF_3.Et_2O$) (12 drops) was added at 0° C. After 3 h the mixture was diluted with chloroform (5 $cm^3$), washed with water, dried over sodium sulphate and concentrated to give the desired deprotected tetramer **8** as a white solid (112 mg, 96 %) identical to authentic material described earlier.

**4,4'-Bis{4-*t*-butyldiphenylsilyloxy-3-[2-*t*-butyldiphenylsilyloxy-5-(4-hydroxybenzyl)benzyl]benzyl}-2,2'-methylenediphenol (9).** To ethyl magnesium bromide formed *in situ*, an ether solution of tetramer **8** (27 mg, 0.3 mmol) was added. Bulk of the ether was distilled off. Benzene was added so the remaining ether could be removed by distillation. Paraformaldehyde (5 mg, 0.2 mmol) was added with additional benzene and the mixture was boiled for 20 h. The solution was typically worked up and purified by chromatography in petrol/ether (1:1) to afford 4,4'-Bis{4-*t*-butyldiphenylsilyloxy-3-[2-*t*-butyldiphenylsilyloxy-5-(4-hydroxybenzyl)-benzyl]benzyl}-2,2'-methylenediphenol **9** (12 mg, 22 %). $^1H$ NMR: δ 0.99, 1.01, 1.04 (27H, s, s, s, 3 x $C(CH_3)_3$), 3.65, 3.69, 3.72, 3.76 (8H, s, s, s, s, 4 x $CH_2$), 4.07, 4.32, 4.65 (6H, s, s, s, 3 x $CH_2$), 6.32-6.92, 7.29-7.75 (m, 26H, ArH); $^{13}C$ NMR: δ 19.5, 26.5, 30.9, 31.6, 19.2, 64.5, 115.1, 115.2, 116.3, 116.4, 118.3, 118.8, 126.7, 126.9, 127.0, 127.8, 128.1, 128.7, 129.6, 129.7, 123.0, 129.9, 130.1, 130.4, 130.7, 130.9, 132.6, 132.8, 133.2, 133.5, 133.4, 133.8, 113.2, 135.5; IR (KBr) 3404, 2957, 2857, 1603, 1498, 1429, 1259, 1112, 938, 821, 702, 615 $cm^{-1}$.

**4,4'-Bis{4-hydroxy-3-[2-hydroxy-5-(4-hydroxybenzyl)benzyl]-benzyl}-2,2'-methylenediphenol (10).** TBAF (10 drops) was added to a solution of octamer **9** (4.4 mg, 2.8 mmol) in THF (1 $cm^3$) at 0° C. The mixture was then allowed to warm to room temperature. After 2 h the colourless solution was diluted with water and extracted in EtOAc. The combined extracts were dried and concentrated. Purification by p.l.c in

petrol/EtOAc (4:1) afforded the fully deprotected octamer **10** (2.3 mg, 97 %). IR (KBr) 2962, 2934, 2875, 1595, 1512, 1483, 1465, 1382, 1268, 1167, 1113, 882, 823 $cm^{-1}$.

**1-*tert*-butyldimethylsiloxy-2',4 methylene diphenol (11).** 2,4'-Methylene diphenol **2** (5.0 g, 25 mmol) was dissolved in DMF (10 $cm^3$). Imidazole (3.6 g, 53 mmol) and *tert*-butyldimethylsilyl chloride (4.14 g, 27 mmol) was added and the mixture was stirred at room temperature under a nitrogen atmosphere for 1 h. The reaction was quenched with water (20 $cm^3$) and the organics were extracted into ether (100 $cm^3$). The organic phase was washed with water (200 $cm^3$) and the combined extracts were dried and concentrated *in vacuo*. Purification by m.p.l.c using petrol/dichloromethane (2:3) afforded four compounds. The major product was the desired 1-*tert*-butyldimethylsiloxy-2,4'-methylene diphenol **11** (5.11 g, 65 %). $R_f$ 0.34 (pet/dichloromethane, 2:3). M.p. 39-40° C; $^1$H NMR: δ 0.23 (s, 6H, Si($C\underline{H}_3$)$_3$), 1.02 (s, 9H, SiC($C\underline{H}_3$)$_3$), 3.96 (s, 2H, $CH_2$), 4.86 (s, 1H, OH), 6.78 (dd, 2H, ArH, J = 8.4, 1.8), 6.80 (d, 1H, ArH, J = 8.4), 6.89 (dd, 1H, ArH , J = 7.2, 7.2), 7.08 (d, 2H, ArH , J = 8.4), 7.10 (d, 1H, ArH, J = 7.2), 7.13 (ddd, 1H, ArH, J = 7.2, 7.2, 1.8); $^{13}$C NMR: δ -4.4 (Si($\underline{C}H_3$)$_2$), 18.2 (Si$\underline{C}$($CH_3$)$_3$), 25.7 (SiC($\underline{C}H_3$)$_3$), 35.6 (C-7), 115.7 (C-6'), 120.2 (C-2, C-6), 120.8 (C-4'), 127.2 (C-2'), 127.7 (C-5'), 129.6 (C-3, C-5), 130.8 (C-3'), 132.2 (C-4), 153.7 (C-1'), 154.1 (C-1); IR (KBr) 3360, 3028, 2932, 1597, 1505, 1349, 1229, 891, 829, 760 $cm^{-1}$; MS (EI) m/z (relative intensity) 315 ($M^+$ +1, 10 %), 314 ($M^+$, 16), 257 (53), 107 (100). Anal. Calcd. for $C_{19}H_{26}SiO_2$: C, 72.61; H, 8.28. Found: C, 72.42; H, 8.46.

The other compounds isolated were 1,1'-bis(*tert*-butyldimethylsilyloxy)-2,4'-methylene diphenol (2.05 g, 26 %) $R_f$ 0.88 (petrol/dichloromethane, 2:3), 1-*tert*-butyldimethylsilyloxy-2,4'-methylenediphenol **12** (0.28 g, 4 %) $R_f$ 0.19 (petrol/dichloromethane, 2:3), and the starting dimer **2** (0.80 g, 10 %).

**2',4-Bis(1-*tert*-butyldimethylsilyloxybenzyl)-6,6'-methylene diphenol (13A).** 1-*tert*-butyldimethylsiloxy-2,4'-methylene diphenol **11** (1.75 g, 5.6 mmol) was dissolved in ether (20 $cm^3$) and added dropwise to an ethereal solution (5 $cm^3$) containing ethyl magnesium bromide (0.73 $cm^3$, 5.4 mmol). Following the addition, the bulk of the ether was removed by distillation and benzene (100 $cm^3$) was added. Paraformaldehyde (8.4 mg, 2.8 mmol) was added to the mixture and it was boiled for 20 h. The cooled reaction mixture was quenched with 10 % HCl solution (50 $cm^3$) and the organics were extracted into ether (100 $cm^3$) and washed with water (200 $cm^3$). The combined organic extracts were dried and concentrated *in vacuo*. Purification of the crude mixture by flash chromatography using petrol/ ether (9:1) afforded the desired product **13A** (0.49 g, 50 %) as a viscous oil. $^1$H NMR: δ 0.29 (s, 12H, Si($C\underline{H}_3$)$_2$), 1.09 (s, 18H, SiC($C\underline{H}_3$)$_3$), 3.97 (s, 6H, $CH_2$), 6.16 (s, 1H, OH), 6.18 (s, 1H, OH), 6.87 (dd, 4H, ArH, J = 7.5, 1.9), 6.91 (ddd, 2H, ArH, J = 7.5, 7.5, 1.3), 7.03 (ddd, 2H, ArH , J = 7.5, 7.5, 1.3), 7.15 (dd, 4H, ArH , J = 7.5, 1.3), 7.25 (ddd, 2H, ArH, J = 7.5, 7.5, 1.3); $^{13}$C NMR: δ -4.4 (Si($\underline{C}H_3$)$_2$), 18.1 (Si$\underline{C}$($CH_3$)$_3$), 25.7 (SiC($\underline{C}H_3$)$_3$), 30.9 (C-8), 35.9 (C-7), 120.3 (C-2, C-6), 121.0 (C-4'), 127.0 (C-2'), 127.7 (C-6'), 129.0 (C-5'), 129.1 (C-3'), 129.7 (C-3, C-5), 131.9 (C-4), 151.1 (C-1), 154.2 (C-1'); MS (EI) m/z (relative intensity) 620 ($M^+$+1, 3 %), 619 ($M^+$, 7), 618 ($M^+$-1, 13), 582 (6), 221 (16), 164 (7), 313 (16), 256 (36), 128 (21), 107 (100), 73 (27).

The starting dimer **11** (0.50 g, 28 %) was also recovered.

**2',4-Dihydroxybenzyl-6,6'-methylene diphenol (13).** 2',4-Bis(1-*tert*-butyldimethylsilyloxybenzyl)-6,6'-methylene diphenol **13A** (0.72 g, 1.13 mmol) was dissolved in THF (6 $cm^3$) and treated with TBAF (4 $cm^3$, 4.55 mmol). After 6 h the mixture was diluted with ethyl acetate (50 $cm^3$) and washed with water (200 $cm^3$). The organic extracts were dried and concentrated *in vacuo*. Purification by m.p.l.c using petrol/ethyl acetate/methanol (70:29:1) afforded the desired product **13** (0.33 g, 71 %). $R_f$ 0.39 (petrol/EtOAc/MeOH, 70:29:1 x 3). M.p. 158-159° C; $^1H$ NMR ($D_6$-acetone): δ 3.90 (s, 4H, $CH_2$), 3.95 (s, 2H, $CH_2$), 6.72 (dd, 2H, ArH4, J = 7.5, 7.5), 6.73 (dd, 4H, ArH1, J = 8.5, 2), 6.86 (dd, 2H, ArH5, J = 7.5, 1.5), 7.03 (dd, 4H, ArH2, J = 8.5, 2), 7.05 (dd, 2H, ArH3, J = 7.5, 1.5); $^{13}C$ NMR ($D_6$-acetone): δ 31.5 (C-8), 35.6 (C-7), 115.8 (C-2, C-6), 121.1 (C-4'), 128.4 (C-6'), 129.2 (C-3), 129.4 (C-5'), 129.6 (C-2'), 130.6 (C-3, C-5), 132.2 (C-4), 152.4 (C-1'), 156.3 (C-1). IR (KBr) 3132, 3031, 2925,2828, 1612, 1601, 1512, 1227, 1164, 1221, 1192, 1099, 832, 752 $cm^{-1}$; MS (EI) m/z (relative intensity) 413 ($M^+$+1, 2), 412 ($M^+$, 11), 411 ($M^+$-1, 37), 317 (50), 300 (24), 211 (100), 119 (17), 107 (96), 91 (27). Anal. Calcd. for $C_{27}H_{24}O_4$: C, 78.61; H, 5.88. Found: C, 78.39; H, 5.82. $C_{27}H_{28}NO_4$ requires 429.55. CI ($NH_3$ reagent gas) found: $M^+$+$NH_4$, 430.20210.

**Formation of (16).** 2',4-Dihydroxybenzyl-6,6'-methylene diphenol **13** (0.14 g, 0.33 mmol) was dissolved in ether (20 $cm^3$) and added dropwise to an ethereal solution (10 $cm^3$) of ethyl magnesium bromide (0.17 $cm^3$, 1.32 mmol). After 30 min, the bulk of the ether was removed by slow distillation. Benzene was added and the remaining ether removed by further distillation. The volume was adjusted to 100 $cm^3$ with benzene and paraformaldehyde (5 mg, 0.16 mmol) was added. The reaction was boiled for 20 h under nitrogen and the mixture was quenched with 10 % HCl solution (50 $cm^3$), extracted into ether (80 $cm^3$) and washed with water (200 $cm^3$). The organics were dried and concentrated. Purification by chromatography using petrol/ethyl acetate/methanol (70:29:1) afforded the desired product **16** (2 mg, 15 %). $^1H$ NMR ($D_6$-acetone): δ 3.90 (s, 8H, $CH_2$), 3.90 (s, 8H, $CH_2$), 3.96 (s, 4H, $CH_2$), 4.67 (s, 4H, $CH_2$), 4.69 (s, 1H, OH), 6.68 - 6.75 (m, 10H, ArH), 6.87 (m, 4H, ArH), 6.93 (dd, 2H, ArH, J = 8.2, 8.2), 7.01 - 7.10 (m, 10H, ArH), 7.96 (br m, 5H, OH), 8.12 (s, 1H, OH), 8.25 (s, 1H, OH); $^{13}C$ NMR ($D_6$-acetone): δ 31.5, 35.6, 35.7, 115.8, 121.2, 127.9, 128.5, 128.9, 129.1, 129.2, 129.3, 129.4, 129.7, 130.6, 132.2, 152.4, 154.2, 156.3.
Some starting tetramer **13** (0.085 g, 62 %) was also recovered.

**1-*tert*-butyldiphenylsilyloxy-1'-tert-butyldimethylsilyloxy-2,4'-methylene diphenol (15).** 1-*tert*-butyldimethylsiloxy-2,4'-methylene diphenol **11** (2.2 g, 7.01 mmol) was dissolved in DMF (12 $cm^3$). Imidazole (1.14 g, 16.8 mmol) and tert-butyldiphenylsilyl chloride (2.1 $cm^3$, 8.06 mmol) was added and the mixture was stirred under nitrogen for 24 h. The mixture was diluted with ether (100 $cm^3$) and washed with water (300 $cm^3$). The organic layer was extracted, dried and concentrated. Purification by chromatography using petrol/ether (4:1) afforded the desired fully protected product **15** (3.79 g, 98 %). $R_f$ 0.79 (pet/ether, 7:3). $^1H$ NMR: δ 0.17 (s, 6H, $Si(C\underline{H}_3)_2$), 0.97 (s, 9H , $SiPh_2C(C\underline{H}_3)_3$), 1.00 (s, 9H , $SiMe_2C(C\underline{H}_3)_3$), 4.12 (s, 2H , $C\underline{H}_2$), 6.22 (m, 1H , ArH6'), 6.78 (d, 2H, ArH2, 6, J = 8.7), 6.79 (d, 2H, ArH4', 5', J = 8.7), 7.04 (m, 1H, ArH3'), 7.07 (d, 2H, ArH3, 5, J = 8.7), 7.35 (dd, 2H, ArH, J = 7.6, 7.6), 7.17 (dd, 2H, ArH, J = 7.6, 7.6), 7.21 (dd, 2H, ArH, J = 7.6, 7.6), 7.68 (dd, 4H, ArH, J = 7.6, 1.3); $^{13}C$ NMR: δ -4.4 ($Si(\underline{C}H_3)_2$), 18.2 ($SiMe_2\underline{C}(CH_3)_3$), 19.4 ($SiPh_2\underline{C}(CH_3)_3$), 25.7 ($SiMe_2C(\underline{C}H_3)_3$), 26.5 ($SiPh_2C(\underline{C}H_3)_3$), 35.5 (C-7), 118.8 (C-6), 119.9 (C-2', C-6'), 120.8 (C-4), 126.8 (C-5), 127.8 (C-10), 129.7 (C-3', C-5'), 129.8 (C-11), 130.8 (C-3), 131.1 (C-4'), 132.7 (C-8), 133.6 (C-2), 135.4 (C-9), 153.3 (C-1), 153.7 (C-1'); IR 3071, 3052, 2931, 1608, 1508,

1179, 1361, 1255, 1111, 929, 820, 757, 701 $cm^{-1}$; MS (CI, $NH_3$ reagent gas) m/z (relative intensity) 570 ($M^+$+$NH_4$), 552 ($M^+$), 512, 495, 456, 350, 332, 274, 216. Anal. Calcd. for $C_{35}H_{44}Si_2O_2$: C, 76.09; H, 7.97. Found: C, 76.2; H, 8.14. $C_{35}H_{48}Si_2NO_2$ requires 571.02. Found: $M^+$+$NH_4$, 570.30095.

**1-*tert*-butyldiphenylsilyloxy-2,4'-methylene diphenol (15A).** 1-*tert*-butyldiphenylsilyloxy-1'-tert-butyldimethylsilyloxy-2,4'-methylenediphenol **15** (2.28 g, 4.52 mmol) was dissolved in chloroform (10 $cm^3$) which was filtered through a plug of neutral alumina. Boron trifluoroetherate (3.33 $cm^3$, 27.1 mmol) was added dropwise to the mixture at 0° C and the reaction was left to stir under nitrogen for 17 h, slowly warming to room temperature. The mixture was quenched with water (50 $cm^3$), the organics were extracted into ether (100 $cm^3$) and washed further with water (600 $cm^3$). The organic layer was dried and concentrated. Purification by chromatography using petrol/ ether (4:1) afforded the desired product **15A** in excellent yield as a sticky cream solid (1.7 g, 86 %). $R_f$ 0.29 (pet/ether, 7:3). $^1H$ NMR: δ 1.03 (s, 9H, $SiC(C\underline{H}_3)_3$), 4.12 (s, 2H, $CH_2$), 4.64 (br s, 1H, OH), 6.25 (m, 1H, ArH6), 6.78 (d, 2H, ArH2', 6', J = 8.8), 6.80 (d, 2H, ArH4, 5 J = 8.8), 7.03 (m, 1H, ArH3), 7.11 (d, 2H, ArH3', 5', J = 8.8), 7.36 (dd, 2H, ArH, J = 7.0, 7.0), 7.18 (dd, 2H, ArH, J = 7.0, 7.0), 7.21 (ddd, 2H, ArH, J = 7.0, 7.0, 1.8); $^{13}C$ NMR: δ 19.4 ($Si\underline{C}(CH_3)_3$), 26.5 ($SiC(\underline{C}H_3)_3$), 35.3 (C-7), 115.1 (C-2', C-6'), 118.8 (C-6), 120.9 (C-4), 126.8 (C-5), 127.8 (C-10), 129.8 (C-11), 130.0 (C-3', C-5'), 130.7 (C-3), 131.1 (C-4'), 132.7 (C-8), 133.2 (C-2), 135.4 (C-9), 153.2 (C-1), 153.6 (C-1'); MS (EI) m/z (relative intensity) 207 ($M^+$, 0.3 %), 206 ($M^+$-1, 1), 171 (100), 303 (57), 287 (27), 199 (18), 181 (15). Anal. Calcd. for $C_{29}H_{30}SiO_2$: C, 79.45; H, 6.85. Found: C 79.39; H 7.13.

**4,4'-Bis(2-*tert*-butyldiphenylsilyloxybenzyl)-2,2'-methylene diphenol (14A).** 1-*tert*-butyl diphenylsilyloxy-2,4'-methylene diphenol **15A** (1.10 g, 2.50 mmol) was dissolved in ether (20 $cm^3$) and added dropwise to ethyl magnesium bromide (0.4 $cm^3$, 3.07 mmol) in ether (10 $cm^3$). After 30 min the bulk of the ether was removed by slow distillation. Benzene (250 $cm^3$) was added and the residual ether was removed by further distillation. Paraformaldehyde (0.04 g, 1.17 mmol) was added to the mixture and boiled. After 20.5 h, the reaction was quenched with 10% HCl solution, extracted into ether (100 $cm^3$) and washed with water (200 $cm^3$). The organic layer was dried and concentrated. Purification by chromatography using petrol/ ether (4:1) afforded the desired product **14A** (0.82 g, 73 %). $R_f$ 0.12 (petrol/ether, 7:3). M.p. 65° C; $^1H$ NMR: δ 1.05 (s, 18H, $SiC(C\underline{H}_3)_3$), 3.91 (s, 2H, $CH_2$), 4.10 (s, 4H, $CH_2$), 6.28 (m, 2H, ArH), 6.79 (d, 2H, ArH, J = 8.3), 6.80 (d, 4H, ArH, J = 8.3), 6.95 (dd, 2H, ArH, J = 8.3, 1.7), 7.01 (m, 2H, ArH), 7.2 (d, 2H, ArH, J = 1.7), 7.16 (ddd, 4H, ArH, J = 7.5, 7.5, 1.7), 7.18 (dd, 4H, ArH, J = 7.5, 7.5), 7.22 (dd, 4H, ArH, J = 7.5, 7.5), 7.52 (br s, 2H, OH), 7.73 (dd, 8H, ArH, J = 7.5, 1.7); $^{13}C$ NMR: δ 19.24 ($Si\underline{C}(CH_3)_3$), 26.52 ($SiC(\underline{C}H_3)_3$), 31.2 (C-8), 35.4 (C-7), 115.9 (C-6), 118.8 (C-6'), 120.9 (C-4'), 127.8 (Ph-C3, C5), 128.4 (C-2), 129.9 (Ph-C4), 130.6 (C-3'), 131.3 (C-5), 131.4 (C-4), 132.8 (Ph-C1), 133.8 (C-2'), 135.4 (Ph-C2, C6), 150.7 (C-1), 153.2 (C-1'); IR (KBr) 3268, 3071, 3051, 3019, 2959, 2931, 2893, 2568, 1597, 1583, 1280, 1218, 1219, 1256, 1111, 930, 821, 755, 702 $cm^{-1}$; MS (EI) m/z (relative intensity) 889 ($M^+$+1, 1 %), 888 ($M^+$, 1), 887 ($M^+$-1, 0.4), 831 (1), 753 (2), 675 (1), 289 (19), 135 (35), 225 (20), 107 (24), 91 (100). Anal. Calcd. for $C_{59}H_{60}Si_2O_4$: C, 79.67; H, 6.81. Found: C, 79.81; H, 6.83. $C_{59}H_{60}Si_2O_4$ requires 889.37. Found $M^+$, 888.40450.

**4,4'-Bis(2-hydroxybenzyl)-2,2'-methylene diphenol (14).** 4,4'-Bis(2-*tert*-butyldiphenylsilyloxybenzyl)-2,2'-methylene diphenol **14A** (0.05 g, 0.05 mmol) was dissolved in THF (3 $cm^3$) and treated with TBAF (0.3 $cm^3$,

1.0 mmol). After 3 h the mixture was diluted with ethyl acetate (50 $cm^3$) and washed with water (100 $cm^3$). The organics were dried and concentrated. Purification by chromatography using petrol/ethyl acetate/MeOH (60:39:1) afforded the desired product **14** (17.6 mg, 82 %). $R_f$ 0.37 (pet/EtOAc/MeOH, 70:29:1 x 3). M.p. 127-150° C; $^1H$ NMR ($D_6$-acetone): δ 3.80 (s, 4H, $CH_2$), 3.85 (s, 2H, $CH_2$), 6.70 (dd, 2H, ArH, J = 8.1, 8.1), 6.72 (d, 2H, ArH, J = 8.1), 6.82 (d, 2H, ArH, J = 8.1), 6.87 (ddd, 2H, ArH, J = 8.1, 8.1, 2), 6.96 (d, 2H, ArH, J = 7.8), 6.98 (ddd, 2H, ArH, J = 8.1, 8.1, 1.4), 7.10 (d, 2H, ArH, J = 1.7); $^{13}C$ NMR ($D_6$-acetone): δ 30.7 (C-8), 35.3 (C-7), 115.6 (C-6), 115.8 (C-6'), 127.7 (C-5'), 127.8 (C-2), 128.4 (C-5), 129.1 (C-4), 131.0 (C-3'), 132.0 (C-3), 133.2 (C-2'), 153.2 (C-1'), 155.6 (C-1); IR (KBr) 3285, 3017, 2922, 2855, 1608, 1592, 15012, 1257, 1232, 824, 755 $cm^{-1}$; MS (CI, $NH_3$ reagent gas) m/z (relative intensity) 430 ($M^+$+$NH_4$, 100 %), 412 ($M^+$, 24), 319 (5), 213 (19), 107 (27). Anal. Calcd. for $C_{27}H_{24}O_4$: C, 78.62; H, 5.6. Found: C, 78.43; H, 5.66. $C_{27}H_{24}O_4$+$NH_4$ requires 430.56. Found $M^+$+$NH_4$, 430.20107.

**Formation of (17) via (17A).** 4,4'-Bis(2-tert-butyldiphenylsilyloxybenzyl)-2,2'-methylene diphenol **14A** (0.10 g, 0.12 mmol) was dissolved in ether (10 $cm^3$) and added dropwise to an ethereal solution (5 $cm^3$) of ethyl magnesium bromide (0.03 $cm^3$, 0.23 mmol). After 30 mins following the addition, the bulk of the ether was removed by slow distillation. Benzene was added and the remaining ether removed by further distillation. The volume was adjusted to 100 $cm^3$ with benzene and paraformaldehyde (2 mg, 0.06 mmol) was added. The reaction was boiled for 20 h under nitrogen and then the mixture was quenched with 10 % HCl solution (50 $cm^3$), extracted into ether (80 $cm^3$) and washed with water (200 $cm^3$). The organics were dried and concentrated. The crude material was then dissolved in THF (10 $cm^3$) and treated with TBAF (0.4 $cm^3$). After stirring for 4 h, the mixture was diluted with ethyl acetate (30 $cm^3$) and washed with water (200 $cm^3$). The organic extracts were dried and concentrated. Purification by chromatography using ether afforded the desired product **17** (0.026 g, %). $^{13}C$ NMR ($D_6$-acetone): δ 30.71, 32.57, 13.1, 35.3, 115.6, 115.8, 120.2, 127.7, 127.8, 128.4, 128.8, 129.1, 129.5, 131.0, 132.0, 133.2, 153.2.

**4,4'-Bis(2-tert-butyldiphenylsilyloxybenzyl)-2-2'-methylene dimethoxy phenol (18).** 4,4'-Bis(2-*tert*-butyldiphenylsilyloxybenzyl)-2,2'-methylene diphenol **14A** (0.13 g, 0.15 mmol) was dissolved in acetone (10 $cm^3$). Potassium carbonate (0.16 g, 1.2 mmol) and dimethyl sulphate (0.12 $cm^3$, 1.3 mmol) was added and the mixture was boiled. After 23.5 h the mixture was quenched with dichloromethane (50 $cm^3$) and washed with 10 % ammonia solution (10 $cm^3$) and water (100 $cm^3$). The organic layer was dried and concentrated. Purification by chromatography using petrol/ether (4:1) afforded the desired product **18** (0.08 g, 58 %). $R_f$ 0.51 (pet/ether, 4:1). M.p. 56-60° C; $^1H$ NMR: δ 1.01 (s, 18H, $SiC(C\underline{H}_3)_3$), 3.69 (s, 6H, $OCH_3$), 3.93 (s, 2H, $CH_2$), 4.05 (s, 4H, $CH_2$), 6.21 (m, 2H, ArH), 6.72 (dd, 2H, ArH, J = 9.0, 9.0), 6.73 (d, 2H, ArH, J = 8.2), 6.77 (dd, 2H, ArH, J = 8.2, 8.2, 1.7), 6.94 (m, 2H, ArH), 7.01 (dd, 2H, ArH, J = 8.5, 1.7), 7.02 (s, 2H, ArH), 7.13 (dd, 4H, ArH, J = 6.8, 6.8), 7.36 (dd, 4H, ArH, J = 6.8, 6.8), 7.20 (dd, 4H, ArH, J = 6.8, 6.8), 7.70 (dd, 8H, ArH, J = 6.8, 1.7); $^{13}C$ NMR: δ 19.4 ($Si\underline{C}(CH_3)_3$), 26.5 ($SiC(\underline{C}H_3)_3$), 30.2 (C-8), 35.3 (C-7), 55.4 ($OCH_3$), 110.2 (C-6), 118.6 (C-6'), 120.8 (C-4'), 126.5 (C-5'), 127.3 (C-5), 127.7 (Ph-C3, C5), 129.0 (C-2), 129.8 (Ph-C4), 130.5 (C-3'), 131.3 (C-3), 131.6 (C-4), 132.3 (C-2'), 132.8 (Ph-C1), 135.4 (Ph-C2, C6), 153.1 (C-1'), 155.9 (C-1); IR (KBr) 3071, 2955, 2858, 100, 1581, 1282, 1179, 1361, 1253, 1110, 1009, 927, 821, 758, 703 $cm^{-1}$; MS (EI) m/z (relative intensity) 916 ($M^+$, 3), 859 (69), 782 (3), 527 (4), 197 (55), 287 (61), 121 (81), 91 (100). Anal.

Calcd. for $C_{61}H_{64}Si_2O_4$: C, 79.35; H, 7.02. Found: C, 79.85; H, 7.05. $C_{61}H_{64}Si_2O_4$ requires 916.43431. Found $M^+$, 916.43170.

**4,4'-Bis(2-hydroxybenzyl)-2,2'-methylenedimethoxyphenol (19).** 4,4'-Bis(2-tert-butyldiphenylsilyloxybenzyl)-2-2'-methylene dimethoxy phenol **18** (0.06 g, 0.06 mmol) was dissolved in THF (5 $cm^3$) and treated with TBAF (0.3 $cm^3$, 1.0 mmol). After 4 h the mixture was diluted in ethyl acetate (50 cm3) and washed with water (100 $cm^3$). The organics were dried and concentrated. Purification by chromatography using petrol/ethyl acetate (7:3) afforded the desired product **19** (0.03 g, 95 %). $R_f$ 0.08 (petrol/EtOAc, 7:3). M.p. 134° C; $^1H$ NMR: δ 3.70 (s, 6H, $OCH_3$), 3.86 (s, 6H, $CH_2$), 4.90 (s, 2H, OH), 6.75 (d, 2H, ArH, J = 8.5), 6.77 (d, 2H, ArH, J = 8.5), 6.88 (ddd, 2H, ArH, J = 7.3, 7.3, 1.2), 6.92 (d, 2H, ArH, J = 1.8), 7.01 (ddd, 2H, ArH, J = 8.5, 8.5, 1.8), 7.11 (d, 2H, ArH, J = 7.3), 7.12 (ddd, 2H, ArH, J = 7.3, 7.3, 1.2); $^{13}C$ NMR: δ 30.1 (C-8), 35.9 (C-7), 55.3 ($OCH_3$), 110.4 (C-6), 115.8 (C-6'), 120.8 (C-4'), 127.0 (C-5'), 127.4 (C-2), 127.7 (C-5), 129.1 (C-4), 130.7 (C-3'), 130.8 (C-3), 130.9 (C-2'), 153.9 (C-1'), 156.3 (C-1); IR (KBr) 3307, 3003, 2920, 2835, 1608, 1590, 1502, 1257, 1032, 822, 757 $cm^{-1}$; MS (CI, $NH_3$ reagent gas) m/z (relative intensity) 458 ($M^+$+$NH_4$), 440 ($M^+$), 350. Anal. Calcd. for $C_{29}H_{28}O_4$: C, 79.05; H, 6.42. Found: C, 78.65; H, 6.53.

**Formation of (21) via (20).** 4,4'-Bis(2-hydroxy benzyl)-2,2'-methylene dimethoxy phenol **19** (79 mg, 0.18 mmol) was dissolved in ether (10 $cm^3$) and added dropwise to an ethereal solution (10 $cm^3$) of ethyl magnesium bromide (0.10 $cm^3$, 0.36 mmol). 30 min following the addition, the bulk of the ether was removed by slow distillation. Benzene was added and the remaining ether removed by further distillation. The volume was adjusted to 50 $cm^3$ with benzene and paraformaldehyde (3 mg, 0.09 mmol) was added. The reaction was boiled for 20 h under nitrogen and then the mixture was quenched with 10 % HCl solution (50 $cm^3$), extracted into ether (50 $cm^3$) and washed with water (200 $cm^3$). The organics were dried and concentrated. Purification by chromatography using petrol/ether (9:1) afforded the desired octamer **20** (0.010 g, 13 %). $^{13}C$ NMR ($D_6$-acetone): δ 31.6, 35.2, 35.4, 35.6, 55.6, 110.9, 111, 115.6, 115.7, 119.9, 120.1, 121.1, 125.9, 127.7, 128.1, 129.0, 129.1, 129.2, 129.3, 129.33, 129.13, 129.4, 129.5, 129.6, 130.1, 131.1, 131.8, 132.9, 133.4, 133.6, 155.6, 155.7, 156.6, 156.7.

**2,2'-Methylene-6,6'-dimethyl diphenol (23).** An ethereal solution of *ortho*-cresol **22** (10 g, 95.2 mmol) was added dropwise to a solution of ethyl magnesium bromide (12.4 $cm^3$, 95.1 mmol) under nitrogen. After stirring for 30 min the mixture was concentrated by slow distillation of solvent. Benzene was added to the mixture and the remaining ether removed by further distillation until the internal temperature reached 80° C. The volume was adjusted to 500 $cm^3$ with benzene and paraformaldehyde (1.22 g, 47.7 mmol) was added to the mixture and boiled for 20 h. The resulting yellow solution was quenched with 10% HCl, extracted with ether, dried and concentrated. Purification of the yellow crude oil by chromatography using petrol/ether (4:1) yielded the starting *ortho*-cresol **22** and the desired **23** (7.3 g, 67 %). $R_f$ 0.24 (petrol/ether, 4:1).. M.p. 122° C; $^1H$ NMR: δ 2.24 (s, 6H, $CH_3$), 3.93 (s, 2H, $CH_2$), 5.96 (br s, 2H, OH), 6.8 (dd, 2H, ArH, J = 5.9, 5.9), 6.99 (d, 2H, ArH, J = 5.9), 7.13 (dd, 2H, ArH, J = 5.9, 1.2); $^{13}C$ NMR: δ 16.0 (C-8), 31.1 (C-7), 120.0 (C-4), 124.0 (C-6), 126.3 (C-2), 128.4 (C-5), 129.3 (C-3), 151.1 (C-1); IR (KBr) 1351, 3315, 3013, 2925, 2864, 1599, 1471, 1170, 1328,

1201, 1153, 1089, 1008, 935, 813, 756 $cm^{-1}$; MS (EI) m/z (relative intensity) 229 ($M^+$+1, 8), 228 ($M^+$, 50), 121 (100), 108 (24), 91 (26). Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02. Found: C, 78.95; H, 7.12. $C_{15}H_{16}O_2$ requires 228.115023. Found $M^+$, 228.1157.

**2,2'-Methylene-6-methyl diphenol (26).** A mixture of *ortho*-cresol **22** (1.0 g, 9.5 mmol) and salicyl alcohol **25** (1.2 g, 9.6 mmol) in ether (20 $cm^3$) was added dropwise to a solution of ethyl magesium bromide (3.62 $cm^3$, 26.7 mmol) and stirred for 15 min. Concentration of the mixture by slow distillation removed the bulk of the ether. Benzene was added and the remaining ether was removed by further distillation until the internal temperature reached 80° C. The volume was adjusted to 300 $cm^3$ with benzene and the mixture was boiled for 20 h. The resulting pink/brown mixture was quenched with 10% HCl, extracted with ether, dried and concentrated. Purification by chromatography using petrol/ether (7:3) afforded **22** as the most mobile band and the desired dimer product **26** (220.2 mg, 28 %). $R_f$ 0.25 (petrol/ether, 7:3). M.p. 115-117° C; $^1H$ NMR: δ 2.25 (s, 3H, $CH_3$), 3.94 (s, 2H, $CH_2$), 6.47 (s, 2H, OH), 6.79 (dd, 1H, ArH, J = 8.0, 0.7), 6.81 (dd, 1H, ArH, J = 7.3, 7.3), 6.9 (ddd, 1H, ArH, J = 8.0, 8.0, 0.7), 7.01 (d, 1H, ArH, J = 7.3), 7.09 (ddd, 1H, ArH, J = 8.0, 8.0, 1.8), 7.15 (dd, 1H, ArH, J = 7.3, 0.7), 7.28 (dd, 1H, ArH, J = 8.0, 1.8); $^{13}C$ NMR: δ 16.1 (C-8), 30.8 (C-7), 115.8 (C-6'), 120.9 (C-4'), 121.6 (C-4), 124.2 (C-6), 126.3 (C-2'), 126.7 (C-2), 127.9 (C-5'), 128.4 (C-3'), 129.4 (C-3), 130.8 (C-5), 151.1(C-1), 152.4 (C-1'); IR (KBr) 3313, 3018, 2930, 2863, 1598, 1284, 1252, 1359, 1224, 1217, 1097, 904, 817, 751 $cm^{-1}$. Anal. Calcd. for $C_{14}H_{15}O_2$: C, 78.47; H, 6.60. Found: C, 78.22; H, 6.58. $C_{14}H_{15}O_2$ requires 214.099163. Found $M^+$, 214.0989.

**6',6'-Bis (2-hydroxybenzyl)-2,2'-methylene-6,6-bis methyl diphenol (27).** An ethereal solution of 2,2'-methylene-6-methyl diphenol **26** (0.10 g, 0.47 mmol) was added dropwise to a solution of ethyl magnesium bromide (0.12 $cm^3$, 0.92 mmol) under nitrogen. After 15 min the mixture was concentrated by slow distillation of the solvent. Benzene was added to the mixture and the remaining ether was removed by further distillation until the internal temperature reached 80° C. The volume was adjusted to 50 $cm^3$ with benzene and paraformaldehyde (7.0 mg, 0.23 mmol) was added to the mixture and boiled for 20 h. The resulting orange/brown mixture was quenched with 10% HCl, extracted with ether, dried and concentrated. The products were isolated by chromatography using dichloromethane/petrol (2:1) afforded dimer **26** (0.020 g, 19 %) as the most mobile band and the desired tetramer **27** (0.026 g, 25 %) $R_f$ 0.07 (dichloromethane/petrol, 2:1), as a white solid. M.p. 199-201° C; $^1H$ NMR: δ 2.27 (s, 6H, $CH_3$), 3.88 (s, 2H, $CH_2$), 3.91 (s, 4H, $CH_2$), 6.68 (br s, 2H, OH), 6.80 (dd, 2H, ArH, J = 7.5, 7.5), 6.82 (dd, 2H, ArH, J = 6.6, 6.6), 6.99 (d, 2H, ArH, J = 7.2), 7.13 (dd, 6H, ArH, J = 7.5, 1.8), 8.59 (br s, 2H, OH); $^{13}C$ NMR: δ 16.1 (C-8), 31.3 (C-7), 31.6 (C-7'), 121.1 (C-4), 121.8 (C-4'), 124.0 (C-6), 126.5 (C-2), 127.6 (C-2', C6'), 128.5 (C-5), 129.1 (C-3'), 129.2 (C-3), 129.4 (C-5'), 128.7 (C-1), 150.9 (C-1'); IR (KBr) 3213, 3099, 3027, 2925, 1565, 1259, 1220, 1168, 1260, 1211, 1086, 871, 815, 747, 598, 568 $cm^{-1}$; MS (EI) m/z (relative intensity) 210 ($M^+$+1, 23 %), 209 ($M^+$, 69), 314 (31), 221 (27), 226 (100), 211 (27), 121 (73). Anal. Calcd for $C_{29}H_{28}O_4$: C, 79.05; H, 6.42. Found: C, 78.62; H, 6.92. $C_{29}H_{28}O_4$ requires 209.198747. Found $M^+$, 209.1978.

**Acknowledgments**

We thank the Australian Research Council and DITAC for supporting this research and Comalco Aluminium Ltd for financial support. We also thank Daniel J. Naug, Sheela Veluayitham and Ying Huang for technical assistance.

## REFERENCES

1. Zinke, A; Purcher, S. *Monatsh* **1948**, 79, 26.
2. Zinke, A; Ziegler, G. *Ber. Deut. Chem. Ges.* **1944**, 77, 271.
3. Kopf, P. W; Wagner, E. R. *J. Polym. Sci. Polym. Chem. Ed.* **1973**, 11, 939.
4. Megson, N. J. L. *Phenolic Resin Chemistry*, Butterworths, London, 1958.
5. Dargaville, T. R; de Bruyn, P. J; Lim, A. S. C; Looney, M. G.; Potter, A. C; Solomon, D. H; Zhang, X. *J. Polym. Sci. Poly. Chem.* (in press).
6. de Bruyn, P. J; Lim, A. L; Looney, M. G; Solomon, D. H. *Tetrahedron Lett.* **1994**, 35, 4627.
7. Casiraghi, G; Cornia, M; Sartoria, G; Casnati, G; Bocchi, V. *Makromol. Chem.* **1982**, 183, 2611.
8. Corey, E. J; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, 94, 6190.
9. Hanessian, S; Lavallee, P. *Can. J. Chem.* **1975**, 53, 2975.
10. Evans, D. A; Kaldor, S. W; Jones, T. K; Clardy, J; Stout, T. J. *J. Am. Chem. Soc.* **1990**, 112, 7001.
11. Kelly, D. R; Roberts, S. M. *Synth. Commun.* **1979**, 9, 295.
12. Dargaville, T. R; Guerzoni, F. N; Looney, M. G.; Shipp, D. A; Solomon, D. H; Zhang, X. *J. Polym. Sci.*, (in press).
13. Dargaville, T. R; Guerzoni, F. N; Looney, M. G; Solomon, D. H. *J. Coll. Int. Sci.* **1996**, 182, 17.

(*Received in UK* 10 *March* 1997; *revised* 5 *August* 1997; *accepted* 7 *August* 1997)