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Synthesis and characterization of *bis*-(3,5-dimethyl-4-hydroxyphenyl)(aryl)methanes as precursor for three state indicator

Rupam J. Sarma, Jubaraj B. Baruah*

Department of Chemistry, Indian Institute of Technology, Guwahati, 781 039, India

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Abstract

A series of *bis*-(3,5-dimethyl-4-hydroxyphenyl)(aryl)methanes (**1a–i**) (where aryl = phenyl, 4-methyl-phenyl, 4-methoxy-phenyl, 4-hydroxyphenyl, 3,4-dimethoxyphenyl, 3,4,5-trimethoxyphenyl, 2-naphthyl, 4-nitrophenyl, 4-hydroxy-3-methoxyphenyl) are synthesized and characterized. *Bis*-(3,5-dimethyl-4-hydroxyphenyl)(phenyl)methane is a leuco-dye which can be easily oxidized to a quinone, 4-[(3′,5′-dimethyl-4′-hydroxyphenyl)(phenyl)methylene]-2,6-dimethylcyclohexa-2,5-dien-1-one, that exhibits three distinct coloured states in neutral, acidic and basic media/conditions. The single crystal X-ray structure of the quinone shows that it has a non-centrosymetric topology. Whereas the leuco-dye *bis*-(3,5-dimethyl-4-hydroxyphenyl) (phenyl)methane adopts a ''propeller'' conformation having one-dimensional H-bonding interactions along *b*-crystallographic axis.

1. Introduction

The *bis*-phenols are important for their biological and bio-mimetic guest–host chemistry [1] and also for their inherent ability to form polymeric species [2]. Apart from being a basic structural unit of calixarenes and resorcarenes, these *bis*-phenolic compounds have been used in constructing novel macrocylic architectures [1,3] like cyclophanes on the one hand, and as fluorescence probes [4] and dyes [5] on the other. Those *bis*-phenols containing a triarylmethane framework can adopt propeller-like conformations and consequently undergo isomerization through *ring flipping* as well as rotation about the *ipso* carbon atoms [6]. Such conformational mobility would have interesting stereochemical implications. The cation and anion mediated complexation [7] as well as the self-associations [8] has also been realized in the case of preoganised cyclic polyphenols. The supramolecular assemblies of *bis*-phenolic compounds [1a,9] have interesting optical properties [10]. Quinones derived from phenols such as aurine [5] and analogous compounds such as aurones [11] possesses pH dependent chromophores, however incorporation of alkyl or aryl group in the ring would make the such quinone systems nonplanar and unsymmetric. This could result in interesting optical properties. However, the *bis*-phenol precursors for quinones are generally synthesised through the acid catalyzed coupling reaction between an aldehyde and a phenol. This synthetic methodology generally leads to the

* Corresponding author.
E-mail address: juba@iitg.ernt.in (J.B. Baruah).

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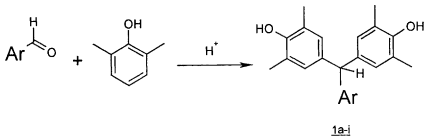
cyclic counterparts if suitably substituted phenols are used [12]. A pioneering study was initiated by Cram et al. on the synthetic precursor for homologation of substituted phenols (i.e. resorcinols) to generate cyclic oligomers (cf. resorcinarenes), yet there are no known systematic approach to such methodology for synthesis of *bis*-phenols [13,14]. A recent report for a specific *bis*-phenol synthesis involving such a methodology based on control of pH is used to achieve selectivity [3]. In this study, we present the synthesis and characterization of a series of prostereogenic *bis*-phenols (which are called as leuco-dyes), based on a triphenylmethane system and derived from 2,6-dimethylphenol. These leuco-dyes serve as precursors for the synthesis of corresponding quinones that has a reversible three-state indicator property.

2. Results and discussions

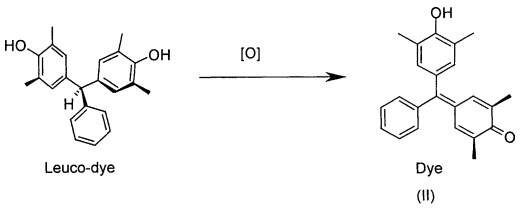
The *bis*-phenols, *bis*-(3,5-dimethyl-4-hydroxyphenyl)(aryl)methanes were prepared by acid catalyzed condensation of 2,6-dimethylphenol with substituted benzaldehydes (Scheme 1). The importance of the reaction is that use of appropriate stoichiometry does not lead to the 1:1 condensed products of phenol and aldehyde but selectively the 2:1 condensation products under milder conditions are formed. This reaction is applicable to a wide variety of aldehydes and the *bis*-phenols (**1a–1i**) could be prepared in near quantitative yield. The side product formation in these reactions is not observed.

However, the *bis*-phenols **1a–1i** are susceptible towards slow aerial oxidation in solution to give corresponding quinines [Eq. (1)]



Ar = phenyl (1a), 4-methyl-phenyl (1b), 4-hydroxy-phenyl (1c), 4-methoxy-phenyl (1d), 3,4-dimethoxy phenyl (1e), 4-hydroxy-3-methhoxyphenyl (1f), 3,4,5-trimethoxy-phenyl (1g), 4-nitrophenyl (1h), 2-naphthyl (1i).

Scheme 1.



(1)

Though they can be preserved under inert atmosphere without appreciable degradation. But the benzoylated derivatives of them are indefinitely stable as observed in the case of **1a**. The corresponding di-benzoylated (**III**) derivative was prepared and characterized.

Most of these bis-phenols have two IR absorptions in the hydroxyl region arising from H-bonded and free O–H stretching in these compounds. For example **1a** has very sharp absorption at 3589 cm^{-1} and a broad but strong absorption band centered at 3467 cm^{-1} in the solid state spectra. This observation is quite striking as we could correlate the H-bonding interactions between the phenolic OH groups. Coincidently this aspect in catechols and naphthalene diols is recently highlighted by Ingold et al. [16] That the IR spectra of the compounds possessing both H-bonded and free OH group shows two sharp peaks of equal intensity separated by 42–138 cm^{-1} which is also found by us in *bis*-phenols reported here.

Indications for the presence of the H-bonding interactions in *bis*-(3,5-dimethyl-4- hydroxyphenyl) (phenyl)methane (**1a**) were also obtained in its UV–visible spectrum (Fig. 1). In methanol, the compound **1a** has two distinct absorptions at 215, 277 nm, respectively at concentrations <132 mM. The absorption at 277 nm is assigned to the π–π^* transition of those fraction of molecules of **1a** that self assembles in solution through H-bonding interactions. It has been also observed that the intensity of absorption at 277 nm in the solution phase UV-spectra of the compound (**1a**) is extremely sensitive to its concentration, whereas the absorbance at 215 nm (assigned to π–π^* transition) shows only a very small change with increase in the concentration (Fig. 1). This concentration dependence of the absorbance at 277 nm and its non-proportional growth compared to the absorption at 215 nm suggesting self-aggregation presumably

through hydrogen bonding [15] was later confirmed by X-ray crystallography of **1a**. The crystal structure with selected bond distances and bond angles is given in Fig. 2.

The concentration dependent ^{1}H NMR of the **1a** in $CDCl_3$ shows the aromatic protons are not significantly affected by the increase in concentration (Fig. 3). However, the NMR studies show a rapid proton exchange phenomena. On concentration change of the **1a** from 0.13 to 1 mM there was a downfield shift in the signal at δ_H1.5 ppm (due to water suspended in $CDCl_3$) indicating a fast proton exchange process and suggesting interaction between the *bis*-phenols and suspended water. This interaction affects the hydrogen-bonded structure and thereby changes in the chemical shift of OH group at 5.28 ppm also. The H-bonded interactions in analogous *bis*-phenols are known to result in the formation of 1:1 adducts with solvent molecules [1c]. The aggregation of phenolic scaffold via H-bonding interactions with bipyridyl group has been demonstrated in a recent study [17].

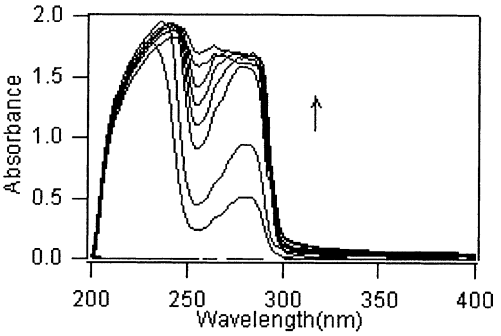


Fig. 1. Concentration dependent spectra of **1a** in methanol at increasing concentrations (0.13, 0.27, 0.4, 0.53, 0.66, 0.8, 0.94 mM). The arrow shows the increment in concentration.

The compound **II** [Eq. (1)], i.e. 4-[(3′,5′-dimethyl-4′-hydroxyphenyl)(phenyl)methylene]-2,6-di-methyl-cyclohexa-2,5-dien-1-one exhibits solvatochromicity possibly due to interaction of the solvent with the carbonyl group of quinone. Accordingly in methanol this compound has absorption at 430 nm whereas in acetonitrile it is at 399 nm (pH 7). The visible absorptions of quinone **II** is sensitive to the change of pH. The addition of acids whose $pK_a < 2$ causes a shift of the absorption with λ_{max} at 430 nm and a new absorption at λ_{max} 524 nm corresponding to the protic state (Fig. 4).

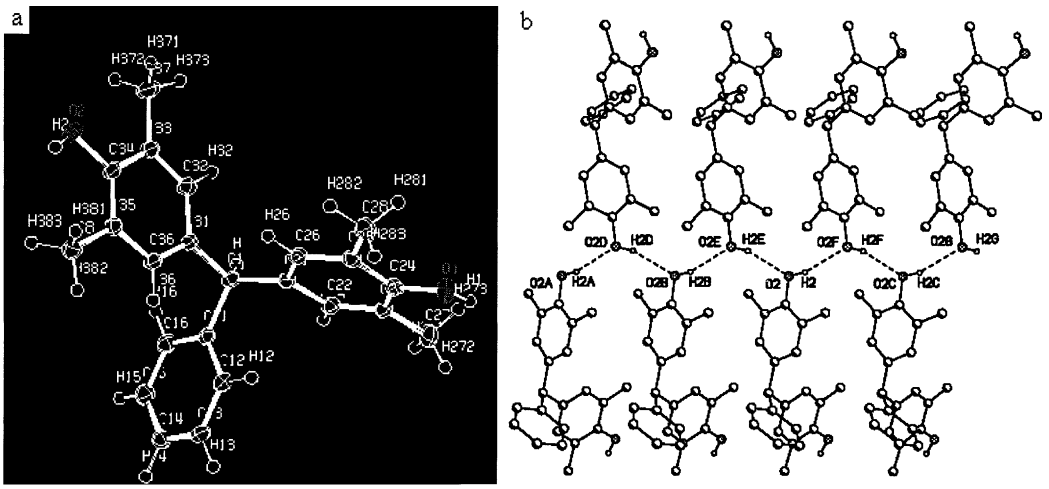


Fig. 2. (a) The single crystal X-ray structure of **1a** (drawn using ORTEP software); selected bond lengths and bond angles are C1–H 0.997 Å, O1–H1 0.867 Å, C24–O1 1.3829 Å, C22–H22 0.982 Å, C1–C11 1.5349 Å, C1– C21 1.5279 Å, C1–C31 1.5255 Å, C(38)–H(381) 1.004 Å, C(38)–H(382) 0.973 Å, C(38)–H(383) 1.027 Å, C(28)–H(281) 0.991 Å, C(28)–H(282) 1.021 Å, C(28)–H(283) 0.988 Å, C(24)–O(1)–H(1) 110.0°, C(34)–O(2)–H(2) 110.1°, C(31)–C(1)–C(21) 113.19°, C(31)–C(1)–C(11) 110.96°, C(21)–C(1)–C(11) 112.42°, C(12)–C(11)–C(1) 122.81°. (b) Packing as viewed parallel to the *b*-axis; intermolecular H-bonding interactions in the solid state leads to a ''chain'' structure' and D–H. . .A bond length for O2–H2..O2F being 3.1922(11) Å.

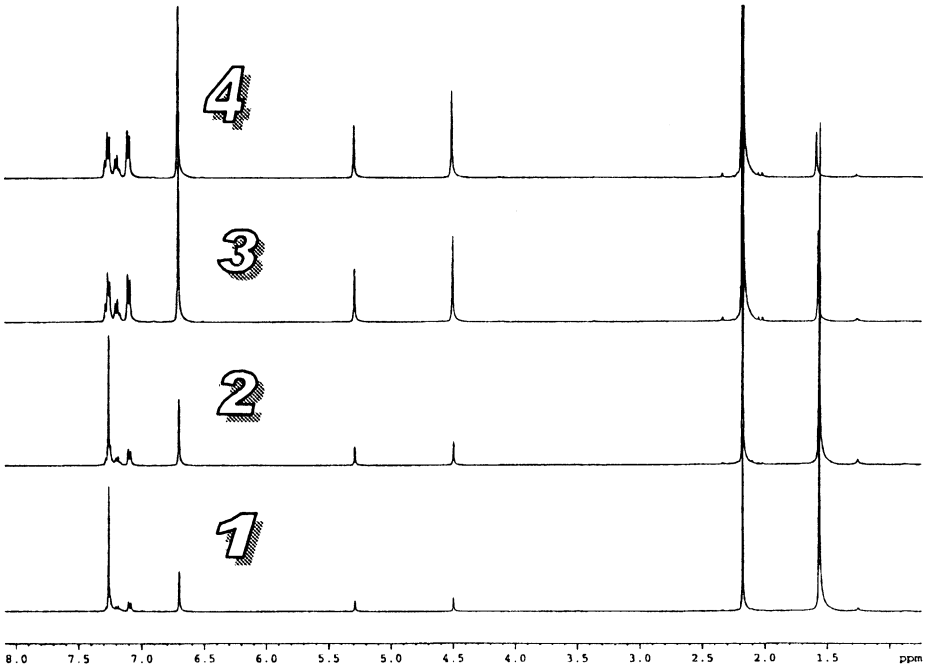


Fig. 3. Concentration dependent ^{1}H NMR spectra of *bis*-(3,5-dimethyl-4-hydroxyphenyl)(phenyl) methane in $CDCl_3$ (1–4 shows the increase in concentration).

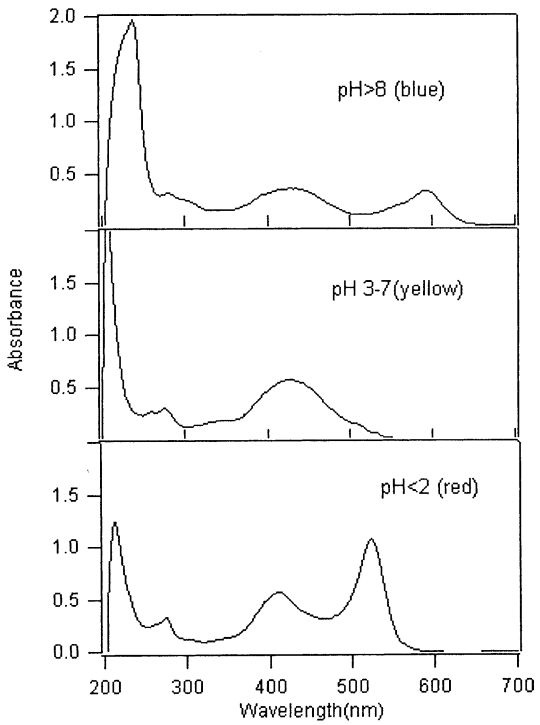


Fig. 4. The UV–visible spectra of **II** in methanol at different pH.

The three distinct well-characterized colored states that occur due to protonation in acid medium and anion formation in basic medium depending on the pH of the solution is a property which is referred here as three state indicator property. Although similar property in aurine indicators [17] are already known, we have a system that has apparently two symmetric aromatic units in the leuco-dye. However, on oxidation the expected planarity is lost due to steric reasons; the solid state 3-D structure of **II** shows it is indeed a non-planar molecule. This compound exists as a non-centrosymmetric H-bonded tetramer in solid state (Fig. 5). The crystal structure with selected bond distances and bond angles is given. The crystal parameters and the refinement data are given in Table 1 in the experimental section. The existence of the different isomeric protonated states (Scheme 2) is revealed in the acid–base titration of the compound.

Upon addition of hydrochloric acid to a solution of **II** in methanol the UV–visible spectra shows a shift in the absorption maxima at 430 nm along with a new absorption at 524 nm;

subsequent addition of triethylamine in methanol to the same solution leads to absorptions 590 nm. The change of color states caused by addition of hydrochloric acid followed by triethylamine to **II** in solution is shown in Fig. 6.

As pointed out in Scheme 2 there are two possible isomeric intermediates in the protic (under different pH conditions) state since the two rings become non-equivalent due to spatial disposition.

These intermediate states are interconvertible in solution as a function of pH. This observation is reflected as two isosbestic points at 424 and 472 nm during acid titration (Fig. 6). The three-state indicator system of the chromophore is sensitive only with alkyl amines and not aromatic amines thereby reflecting the *optically* pH switching nature in solution, however the more likely an indication of the relative pK_a of alkyl and arylamine [18]

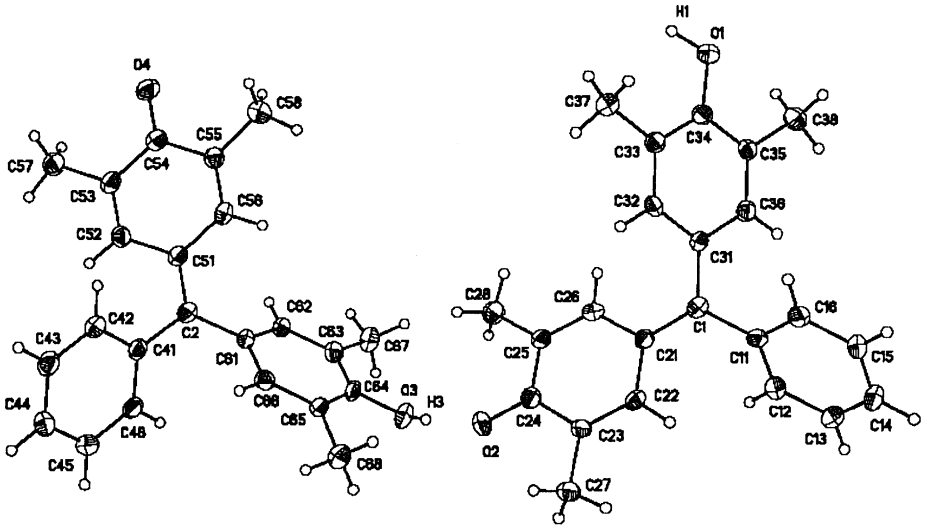
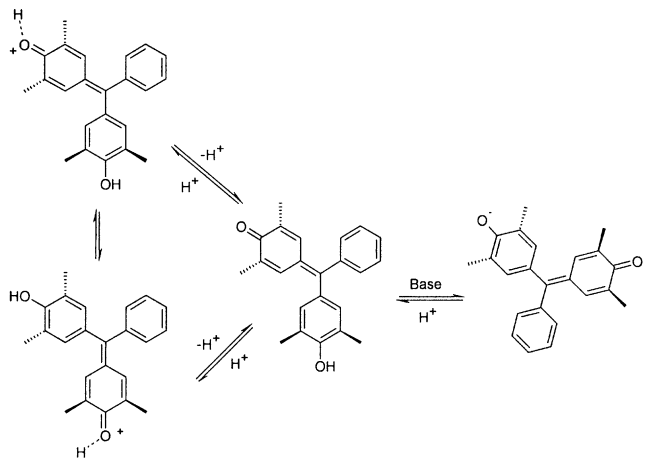


Fig. 5. A view of the structure of **II**. Selected bond distances and bond angles are C(2)–C(51) 1.393 Å; C(2)–C(61) 1.479 Å; C(2)–C(41) 1.487 Å; C(54)–O(4) 1.257 Å; O(3)–C(64) 1.369 Å; C(41)–C(2)–C(61) 116.7°; C(51)–C(2)–C(41) 121.4°; C(51)–C(2)–C(61) 121.9°; C(64)–)(3)–H(3) 109°.



$$Cationic\,(\lambda_{max} = 524nm) \longleftrightarrow Quinone\,(\lambda_{max} = 430nm) \longleftrightarrow Anionic\,(\lambda_{max} = 595nm)$$

Scheme 2.

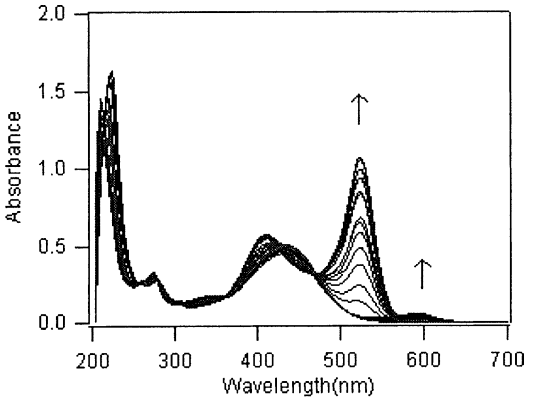


Fig. 6. The UV–visible spectra of **II** (21.5×10^{-6} M) on titration with HCl (−) followed by Et_3N (−) in methanol. HCl (20 μl of 0.1 M) in each aliquot while triethylamine (20 μl of 0.1 M) was added in each aliquot (arrows shows increase in absorbances).

is the key factor for such changes. The color change is also susceptible to other strong alkaline substances such as ammonium hydroxide, alkali metal hydroxides. The compound **II** has a high extinction coefficient ($\varepsilon^{430nm}_{methanol} = 4.6 \times 10^4\ M^{-1}cm^{-1}$).

In conclusion, this study provides a method for synthesis of a few leuco-dye, *bis*-phenols as precursors of quinones of triarylmethanes which show reversible three-state indicator property.

3. Experimental

3.1. Synthesis of bis-(3,5-dimethyl-4-hydroxyphenyl)phenyl methane (1a)

To a 0.1 (M) solution of H_2SO_4 in methanol, benzaldehyde (0.58 g, 5 mmol) and 2,6-dimethyl-

Table 1
Crystal data and structure refinement for **1a** and **II**

	1a	**II**
Empirical formula	$C_{23}H_{24}O_2$	$C_{23}H_{22}O_2$
Formula weight	332.42	330.41
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P 21/c	P-1
Unit cell dimensions	$a = 19.1236(11)$ Å, $\alpha = 90°$.	$a = 10.7663(8)$ Å, $\alpha = 82.261(3)°$
	$b = 5.3707(3)$ Å, $\beta = 116.185(2)°$.	$b = 12.3118(10)$ Å, $\beta = 81.154(3)°$
	$c = 19.2054(12)$ Å, $\gamma = 90°$	$c = 14.6261(10)$ Å, $\gamma = 71.654(3)°$
Volume	1770.10(18) $Å^3$	1810.6(2) $Å^3$
Z	4	4
Density (calculated)	1.247 Mg/m^3	1.212 Mg/m^3
Absorption coefficient	0.078 mm^{-1}	0.076 mm^{-1}
$F(000)$	712	704
Crystal size	$0.42\times0.18\times0.08$ mm^3	$0.28\times0.22\times0.06$ mm^3
Theta range for data collection	1.19 to 30.49°.	1.41 to 30.44°
Index ranges	$-26<=h<=25$, $-7<=k<=7$,	$-14<=h<=14$, $-16<=k<=16$,
	$-27<=l<=26$	$-20<=l<=17$
Reflections collected	20395	13949
Independent reflections	5023 [R(int) = 0.0413]	9645 [R(int) = 0.0562]
Completeness to theta = 30.49°	93.0%	87.7%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5023/0/322	9645/0/467
Goodness-of-fit on F^2	1.042	0.986
Final R indices [$I>2$sigma(I)]	$R1 = 0.0453$, w$R2 = 0.1074$	$R1 = 0.0722$, w$R2 = 0.1286$
R indices (all data)	$R1 = 0.0727$, w$R2 = 0.1175$	$R1 = 0.1809$, w$R2 = 0.1602$
Largest diff. peak and hole	0.314 and −0.182 e.$Å^{-3}$	0.271 and −0.262 e.$Å^{-3}$

phenol (1.24 g, 10.1 mmol) were added and the mixture was refluxed for 10 h with constant stirring. Upon completion of the reaction, the solvent was removed under vacuum and to the residue water (2×25 ml) and then CH_2Cl_2 (50 ml) were added. The organic extract was dried over anhydrous Na_2SO_4 and after removing the solvent the product was purified by column chromatography. (Silica gel 60–120 mesh; EtOAc/hexane =15:85.) The product, **1a** was obtained as a pale yellow solid (mp 158 °C). Yield: 1.19 g (72%). Crystals grown by diffusion of hexane into a solution of **1a** in Et_2O were found suitable for single crystal structure determination. IR (cm^{-1}): 3589 (s), 3467 (s), 2918 (m), 1606 (s), 1505 (s), 1445 (s), 1220 (s), 1009 (m), 890 (m), 839 (m). ^1H NMR ($CDCl_3$): 7.21–7.30 (5H,m) 6.72 (4H,s), 5.3 (1H,s), 4.54 (2H,s), 2.18 (12H,s). ^{13}C NMR ($CDCl_3$): 150.5, 147.4, 144.9, 136.1, 129.5, 129.3, 128.2, 125.9, 122.7, 55.5, 16.0. Mass (*m*/*e*): 332(M^+). Elemental anal. calc. for $C_{23}H_{24}O_2$: C 83.09%, H 7.28% Found: C 83.12%, H 7.25%.

Similar procedures for the compounds (**1b–1i**) were used.

The spectroscopic data for (**1b–1i**) are as follows:

3.1.1. Bis-(3,5-dimethyl-4-hydroxyphenyl)-4-methylphenylmethane (1b)

Light yellow solid (mp 154 °C), Yield: 1.34 g (78%); IR (KBr; cm^{-1}): 3653, 3569, 3123, 3030, 3002, 2970, 1615, 1492, 1461, 1338, 1215, 1184, 1123, 1092, 876. ^1H NMR ($CDCl_3$, 400 MHz): 7.07 (2H, d, J=7.92Hz), 6.98 (2H, d, J=7.97 Hz), 6.71 (4H, s), 5.25 (1H, s), 4.50 (2H, s), 2.32 (3H, s), 2.17 (12H, s). ^{13}C NMR ($CDCl_3$): 150.5, 142.0,136.3, 129.5, 128.2, 126.1, 122.7, 55.5, 55.2, 21.1, 16.1. Mass (*m*/*e*): 346 (M^+) Elemental anal. calc. for $C_{24}H_{26}O_2$: C 83.20%, H 7.56%. Found. C 83.19%, H 7.65%.

3.1.2. Bis-(3,5-dimethyl-4-hydroxyphenyl)-4-hydroxyphenylmethane (1c)

Colorless needles (mp 139 °C). Yield: 1.34 g (77%). IR (KBr; cm^{-1}): 3175 (bs), 2878 (m), 1598 (s), 1449 (s), 1291 (s), 1157 (s), 860 (s), 789 (s). ^1H NMR ($CDCl_3$, 400MHz): δ (ppm) 6.95 (2H, d, J=8.26 Hz), 6.72 (2H, d, J=8.58 Hz), 6.68 (4H, s), 5.22 (1H, s), 4.80 (1H, s), 4.51 (1H, s), 2.17 (12H, s). ^{13}C NMR ($CDCl_3$): δ (ppm) 150.5, 136.4, 130.4, 129.4, 122.7, 115.0, 65.8, 54.6, 15.9,15.2. Mass (*m*/*e*): 348 (M^+). Elemental anal. calc. for $C_{23}H_{24}O_3$: C 79.28%, H 6.94%. Found: C 79.40%, H 7.02%.

3.1.3. Bis-(3,5-dimethyl-4-hydroxyphenyl)-4-methoxyphenylmethane (1d)

Colorless crystals (mp 171 °C). Yield: 1.14 g (63%). IR (KBr; cm^{-1}): 3574 (s), 3513 (s), 2919 (s), 1603 (s), 1458 (s), 1260 (s), 1029 (s), 854 (s). ^1H NMR ($CDCl_3$): δ_H 2.18 (12H, s), 3.79 (3H, s), 4.49 (2H, s), 5.25 (1H, s), 6.81–6.82 (2H, d, J=8.52 Hz), 7.01–7.02 (2H, d, J=8.56 Hz). ^{13}C NMR ($CDCl_3$): 157.8, 150.5, 130.2, 136.4, 137.2, 129.4, 122.7, 113.6, 55.2, 54.7, 52.6, 15.9. Mass (*m*/*e*): 362 (M^+). Elemental anal. calc. for $C_{24}H_{26}O_3$: C 79.53%, H 7.23%. Found: C 79.48%, H 7.23%.

3.1.4. Bis-(3,5-dimethyl-4-hydroxyphenyl)-3,4-dimethoxyphenylmethane (1e)

Colorless crystals (mp 197 °C). Yield: 1.53 g (78%). IR (cm^{-1}): 3494 (s), 3441 (bs), 2934 (w), 2914 (w), 2837 (w), 1593 (s), 1511 (s), 1485 (s), 1326 (s), 1229 (s), 1198 (s), 1029 (s), 886 (s), 825 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.75–6.66 (7H, m), 5.23 (1H, s), 4,57 (2H, s), 3.85 (3H, s), 3.77 (3H, s), 2.17 (12H, s). ^{13}C NMR ($CDCl_3$): δ (ppm) 150.5, 148.7, 147.3, 137.6, 136.3, 129.4, 122.7, 121.4, 112.9, 110.9, 55.9, 55.0, 16.0,10.3. Mass (*m*/*e*): 392 (M^+). Elemental anal. calc. for $C_{25}H_{28}O_4$: C 79.50%, H 7.19%. Found: C 79.36%, H 7.20%.

3.1.5. Bis-(3,5-dimethyl-4-hydroxyphenyl)-4-hydroxy-3-methoxyphenylmethane (1f)

Light pink solid (mp 148 °C). Yield: 1.12 g (59%). IR (KBr; cm^{-1}): 3442 (bs), 2924 (w), 1634 (s), 1598 (s), 1485 (s), 1352 (s), 1270 (s), 1198 (s), 1174 (s), 1075 (s), 876 (s). ^1H NMR ($CDCl_3$, 400MHz): δ (ppm) 6.81 (1H, d, J=8.1Hz), 6.69 (4H, s), 6.63 (1H, d, J=1.63Hz), 6.53 (1H, dd, J=1.6Hz, 8 Hz), 5.51 (1H, s), 5.22 (1H, s), 4.56 (2H, s), 3.77 (3H, s), 2.17 (12H, s). ^{13}C NMR ($CDCl_3$): 150.5, 143.8, 136.9, 136.3, 129.4, 122.7, 122.1, 113.9, 112.1, 60.4, 55.1, 29.7,16.0. Elemental anal. calc. for $C_{24}H_{26}O_4$: C 76.17%, H 6.92%. Found C 76.24%, H 7.01%.

*3.1.6. Bis-(3,5-dimethyl-4-hydroxyphenyl)-2,3,4-trimethoxyphenylmethane (**1g**)*

Pale yellow solid (mp 131 °C) Yield: 1.84 g (88%) IR (KBr; cm^{-1}): 3467 (bs), 2939 (m), 1588 (s), 1490 (s), 1465 (s), 1326 (s), 1193 (s), 1132 (s), 1009 (s), 891 (s), 850 (s), 739 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.70 (4H, s), 6.31 (2H, s), 5.20 (1H, s), 4.51 (2H, s), 3.83 (3H, s), 3.73 (6H, s), 2.19 (12H, s). Elemental anal. calc. for $C_{26}H_{30}O_5$: C 73.91%, H 7.16%. Found: C 73.84%, H 7.20%.

*3.1.7. Bis-(3,5-dimethyl-4-hydroxyphenyl)-4-nitrophenylmethane(**1h**)*

Pale yellow solid. Yield: 1.37 g (73%). IR (KBr, cm^{-1}): 3452 (bs), 2924 (m), 2847 (m), 1634 (s), 1521 (s), 1490 (s), 1347 (s), 1198 (s), 1106 (s), 850 (s), 814 (s), 738 (s). ^1H NMR ($CDCl_3$, 400MHz): δ (ppm) 8.11 (2H, d, $J=8.6$ Hz), 7.26 (2H, d, $J=8.6$Hz), 6.67 (4H, s), 5.35 (1H, s), 4.64 (2H, s), 2.19 (12H, s). ^{13}C NMR ($CDCl_3$): δ (ppm) 152.8, 146.4, 140.1, 134.3, 130.5, 129.4, 127.5, 123.5, 55.3, 16.0. Elemental anal. calc. for: $C_{23}H_{23}O_4N$: C 73.19%, H 6.14%, N 3.17%. Found: C 73.4%, H 6.23%, N 3.34%.

*3.1.8. Bis-(3,5-dimethyl-4-hydroxyphenyl)(2-naphthyl)methane (**1i**)*

Light yellow hygroscopic solid (mp 169 °C). Yield: 1.44 g (76%) IR (KBr, cm^{-1}): 3559 (s), 3413 (s), 2919 (m), 1598 (s), 1486 (s), 1198 (s), 1147 (s), 1024 (s), 825 (s), 743 (s). ^1H NMR ($CDCl_3$, 400MHz): δ (ppm) 7.82 (1H, m), 7.74 (2H, s), 7.45 (3H, m), 6.76 (4H, s), 5.46 (1H, s), 4.53 (2H, s), 2.20 (12H, s). ^{13}C NMR ($CDCl_3$): δ (ppm) 150.6, 142.6, 135.9, 133.5, 132.2, 129.6, 128.3, 127.7, 127.5, 125.5, 125.8, 122.8, 55.7, 15.99. Elemental anal. calc. for $C_{27}H_{26}O_2$: C 84.78%, H 6.85%. Found: C 84.86%, H 6.92%

*3.1.9. Synthesis of 4-[(3′,5′-dimethyl-4′-hydroxyphenyl)(phenyl)methylene]-2,6-dimethylcyclohexa-2,5-dien-1-one (**II**)*

To a solution of **1a** (1.65 g, 5 mmol) in acetonitrile, a solution of ammonium persulphate (1.17 g, 5.2 mmol) in 5 ml of water was added. The mixture was kept at 60 °C for 6 h. The crude mixture on cooling gave 4-[(3′,5′-dimethyl-4′-hydroxyphenyl)(phenyl)methylene]-2,6-dimethyl-cyclohexa-2,5-dien-1-one (**II**) as red crystalline solid. Mp 247-48 °C (decomp); Isolated yield 0.71 g (43%). IR (KBr, cm^{-1}): 3440 (b), 2919 (m), 1567 (s), 1475 (s), 1332 (s), 1198 (s), 1050 (s), 707 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.43(m, 3H), 7.22 (m, 4H), 7.07 (s, 1H), 6.80 (s, 2H), 4.94 (s, 1H), 2.28 (s, 6H), 2.03 (s, 3H), 2.00 (s,3H). Elemental anal. calc. for $C_{22}H_{22}O_2$: C 83.60%, H 7.61%. Found: C 83.58%, H 7.60%.

*3.1.10. Benzoylation of bis-(3,5-dimethyl-4-hydroxyphenyl)phenyl methane (**1a**)*

Benzoylchloride (1.42 g, 10.1 mmol) was dropwise added to a solution of **1a** (1.65 g, 5 mmol) and pyridine (5 ml) in water over 15 min and the reaction mixture was put on a water bath at 80 °C. The reaction was quenched and the excess acid chloride decomposed by adding 50 ml of 10% $NaHCO_3$ solution. The benzoylated derivative *bis*-(4-benzyloxy-3,5-dimethylphenyl)(phenyl)methane (**III**) was obtained as white solid (mp 154 °C). Yield: 2.23 g (92%). IR (KBr; cm^{-1}): 3032 (w), 2919 (m), 2863 (m), 1731 (vs), 1603 (s), 1480 (s), 1270 (s), 1188 (s), 1137 (s), 1081 (s), 1065 (s), 1024 (s), 891 (s), 702 (s). ^1H NMR ($CDCl_3$, 400 MHz): 8.25 (4H, d, $J=7.32$ Hz), 7.65 (2H, t, $J=7.36$ Hz), 7.53 (4H, t, $J=7.66$ Hz), 7.34–7.17 (5H, m), 6.89 (4H, s), 5.46 (1H, s), 2.16 (12H, s). ^{13}C NMR ($CDCl_3$): 164.4, 146.9, 143.9, 141.3, 133.5, 130.2, 130.1, 129.7, 129.6, 128.7, 128.4, 126.3, 55.9, 16.6. Elemental anal. calc. for $C_{37}H_{32}O_4$: C 82.20%, H 5.97%. Found: C 82.19%, H 6.02%.

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