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A Synthetic Study on the Preparation of Triarylmethanes

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ABSTRACT

A number of triarylmethanes were prepared, the majority of which are new. One of the aryl groups is a naphthol, 1,3,5-trimethoxybenzene, or resorcinol, or an indole, pyrrole or pyridine ring. Three synthetic routes are described: (1) reaction of a benzhydrol with an electron-rich aromatic compound; (2) direct condensation of benzaldehyde or hydroxybenzaldehydes, with N,N*-dimethylaniline or its derivatives and 2-naphthol; and (3) displacement of benzotriazole in benzotriazolyl derivatives by Grignard reagent according to our recently developed benzotriazole methodology.*

1 INTRODUCTION

Di- and tri-arylmethanes containing electron-donating substituents such as the amino group and the hydroxy group (as well as its conjugate base) in the *ortho* or *para* positions are of considerable importance, as they are leuco dyes which, on hydride abstraction by oxidizing agents, give

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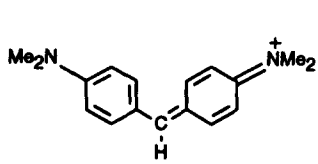
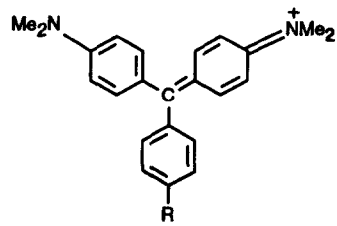


1 Michler's hydrol



2 R = H Malachite Green
3 R = Me_2N Crystal Violet

Scheme 1

colored cations. Some common dyes of this type are Michler's hydrol (**1**) Malachite Green (**2**) and Crystal Violet (**3**).

Heterocycles such as indole and pyridine have also been used in triarylmethane dyes. Diindolylpyridylmethane derivatives yielded dyes upon N-alkylation of the pyridine moiety and treatment with base.[1] Naef[2] has reported the syntheses of trihetaryl dyes in yields of 20 to 85% by treatment of unsymmetrical dihetaryl ketones with 1,2-dimethylindole in the presence of phosphorus oxychloride.

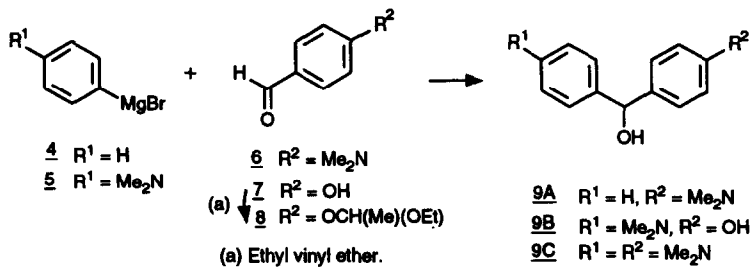
Triarylmethanes are generally prepared by the following methods: (1) treatment of a one carbon electrophilic reagent such as triethyl orthoformate or chloroform, with arene nucleophiles, gives triarylmethanes with three identical aryl groups;[3–6] (2) reaction of an arylaldehyde with arene nucleophiles (usually substituted by hydroxy or amino groups)[4,7–10] affords triarylmethanes which contain at least two identical aryl groups; and (3) condensation of a benzohydrol with aromatic compounds such as toluene[11] and phenols[12,13] provides a general procedure for both symmetrical and unsymmetrical triarylmethanes.

We now report the synthesis of a number of unsymmetrical triarylmethanes, most of which have three different aryl groups. The condensation of a benzhydrol with an arene nucleophile has been intensively investigated. Two new methods have been developed: (1) direct condensation of benzaldehyde and two different nucleophiles, 2-naphthol and *N,N*-dimethylaniline; and (2) displacement of benzotriazole using our recently developed benzotriazole methodology.[14,15]

2 RESULTS AND DISCUSSION

2.1 Condensation of a benzhydrol with electron-rich aromatic compounds

Benzhydrols are usually prepared by the reaction of an aryl organometallic compound with an aryl aldehyde, or by the reduction of the corresponding ketone. Reaction of phenylmagnesium bromide (**4**) with 4-dimethy-



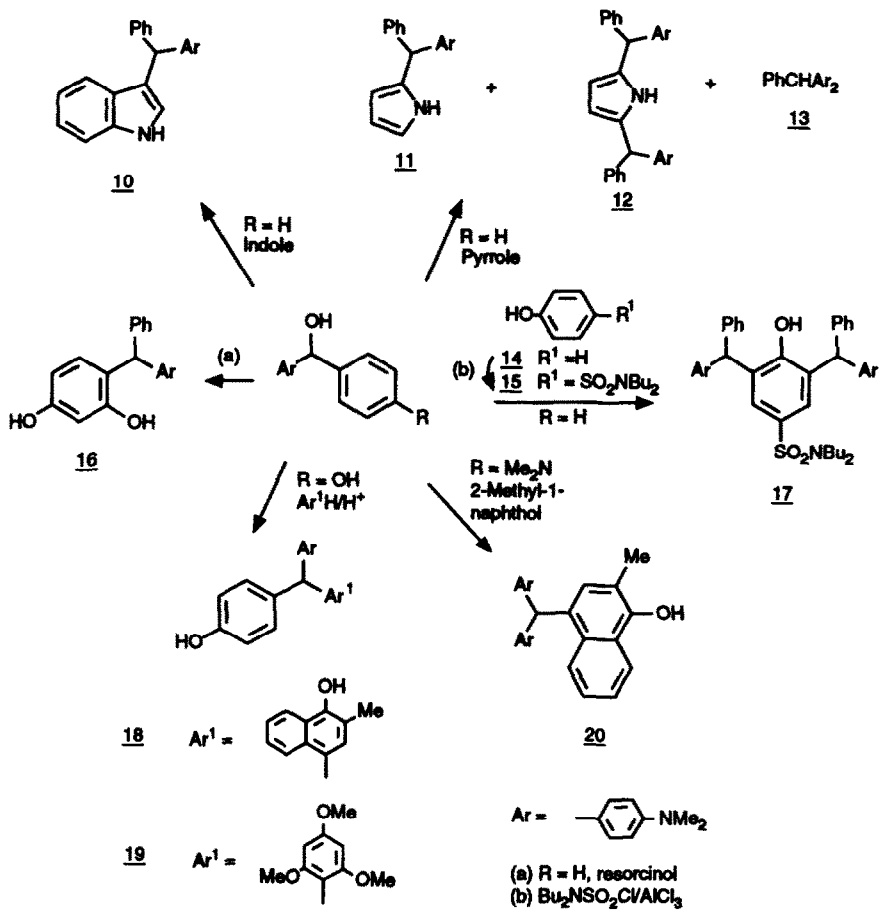
Scheme 2

laminobenzaldehyde (**6**) afforded compound **9A** in 93% yield. This method has an obvious advantage over the reported method of reduction of the corresponding ketone of the readily available starting material.[16]

The benzhydrol **9B** was obtained by a modified literature procedure.[17] The hydroxy group of 4-hydroxybenzaldehyde (**7**) was protected by prior reaction with ethyl vinyl ether to give the acetal **8** in 97% yield. Reaction of **8** with 4-dimethylaminophenylmagnesium bromide (**5**) (instead of the more complicated 4-dimethylaminophenyllithium as reported[17]), followed by acidic work-up gave directly the benzhydrol **9B** in 56% overall yield (Scheme 2). The preparation of 4-dimethylaminophenylmagnesium bromide (**5**) was reported to be tedious and to give divergent results.[18,19] However, we have now developed a modified procedure which reproducibly affords high conversions of 4-bromo-*N,N*-dimethylaniline to the Grignard reagent (see Section 4).

The benzhydrol **29** could be prepared either by the reaction of 4-dimethylaminophenylmagnesium bromide with pyridine-2-carboxaldehyde (Route A of Scheme 5) or by the reaction of pyridine-2-magnesium bromide with 4-dimethylaminobenzaldehyde (Route B of Scheme 5). Pyridyl Grignard reagents have been prepared by the Grignard exchange reactions of the corresponding halides with alkyl or aryl Grignard reagents.[20–23] The preparation of **29** was achieved in only 23% yield using magnesium turnings, ethyl bromide and 2-bromopyridine, and treatment of the resulting Grignard reagent with 4-dimethylaminobenzaldehyde.[20] One report[23] required the transformation of 2-bromopyridine into 2-iodopyridine,[24] followed by the Grignard exchange reaction with ethylmagnesium bromide. We have now developed an efficient method for the preparation of compound **29** in 94% yield by the reaction of 4-dimethylaminophenylmagnesium bromide (**5**) with pyridine-2-carboxaldehyde (Route A of Scheme 5). Our method avoids the complexity in the preparation of the pyridin-2-yl Grignard reagents.

The reactions of the benzhydrols thus obtained, along with the readily available 4,4'-bis(dimethylamino)benzhydrol (**9C**), with various electron-



Scheme 3

rich aromatic compounds under suitable conditions were then examined (Scheme 3). Heating a mixture of the benzhydrol **9A** and indole in refluxing 50% aqueous methanol in the presence of hydrochloric acid afforded compound **10** (Scheme 3) in 97% yield. The product was isolated by filtration and was pure. Compound **10** was previously prepared[25] from the reaction of benzhydrol **9A** with indole in acetic acid in only 32% yield. Our modified conditions provided a much better yield and a simpler work-up procedure; furthermore, no purification was needed. The reaction of the benzhydrol **9A** with pyrrole gave different products, depending on the molar equivalents of pyrrole used. With one equivalent of pyrrole, three products, **11**, **12** and **13** were obtained. Compound **13** was presumably formed by the condensation of the decomposed products from benzhydrol **9A**, benzaldehyde and *N,N*-dimethylaniline. When only

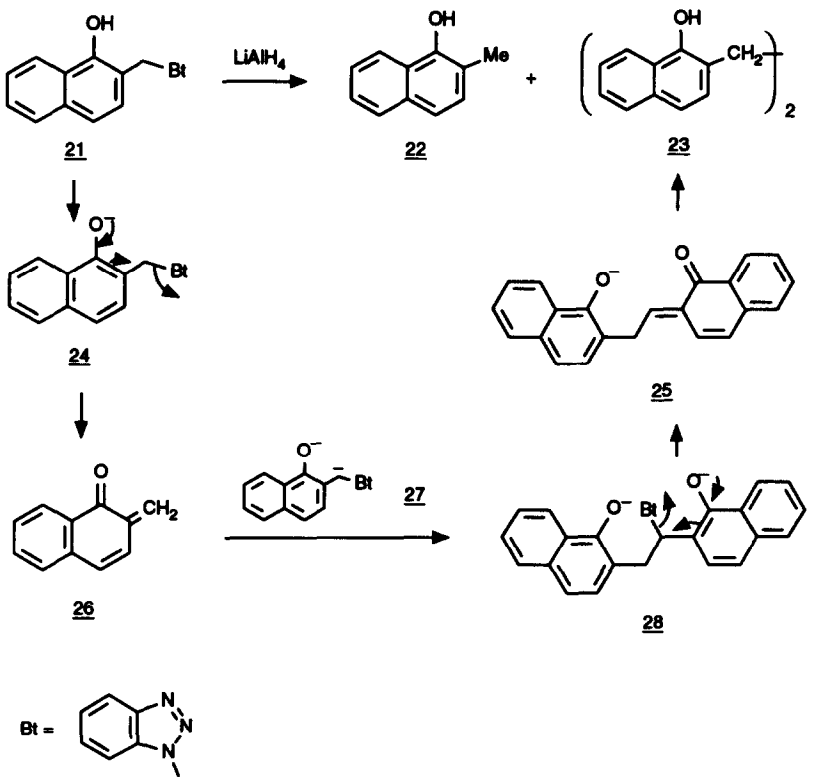
0·5 equivalent of pyrrole was employed, the disubstituted product **12** was formed in 96% yield.

The structures of compounds **10–13** were determined by NMR spectra and comparison with literature data. Indole is known to react with electrophiles at the C-3(β) positions[26] and pyrrole at the α-position.[27–30] We have previously reported similar reactions in our benzotriazole system with indoles and pyrroles[31–33] and we have shown that, for pyrroles, usually the disubstituted products were obtained.

Other reactions of a benzhydrol with resorcinol, 4-(*N,N*-dibutylsulfamoyl)phenol (**15**), 2-methyl-1-naphthol (**22**) and 1,3,5-trimethoxybenzene were also investigated. The phenol **15** is not readily available and the only preparation mentioned in the literature is very complicated,[34] and no physical data were given. It was recently investigated in our laboratory (Scheme 3) and prepared in 67% yield by the reaction of phenol with *N,N*-dibutylsulfamoyl chloride in the presence of aluminum chloride.

2-Methyl-1-naphthol (**22**) was prepared in 70% yield using our previously reported[14] reduction of 2-(benzotriazol-1-ylmethyl)-1-naphthol (**21**) with $LiAlH_4$ (Scheme 4). The simultaneous formation of compound **23** as a by-product could be rationalized as follows. Elimination of benzotriazole from the initially formed phenoxide **24** gave the quinone methide **26**, which was attacked by a dianion **27** to give **28**. Benzotriazole was then eliminated from **28** to give **25**, which was reduced by $LiAlH_4$ to finally give **23**. Formation of a similar dimerized product was also observed recently in our laboratory in the case of *N,N*-dimethylaniline.

Treatment of benzhydrol **9A** with resorcinol in 50% aqueous methanol solution gave the desired product **16** in 30% yield. The reaction of the phenol **15** with the benzhydrol **9A** was found to be successful only in the absence of an acid. In the presence of acid the starting phenol **15** remained unaffected while the benzhydrol **9A** was decomposed, or a by-product was formed. When the reaction was carried out under normal conditions, i.e. in refluxing 50% aqueous methanol in the presence of hydrochloric acid, the phenol **15** was recovered and a product was obtained where the hydroxy group in the benzhydrol **9A** was displaced by a methoxy group. When the reaction was carried out in refluxing acetic acid or in refluxing toluene in the presence of *p*-toluene sulfonic acid, the phenol **15** was completely recovered and **9A** was decomposed. The reaction finally succeeded in refluxing toluene with a Dean–Stark trap without the addition of an acid catalyst, and only the disubstituted product **17** was formed regardless of the number of equivalents of benzhydrol **9A** used. Thus, when a mixture of 2·3 equivalents of the

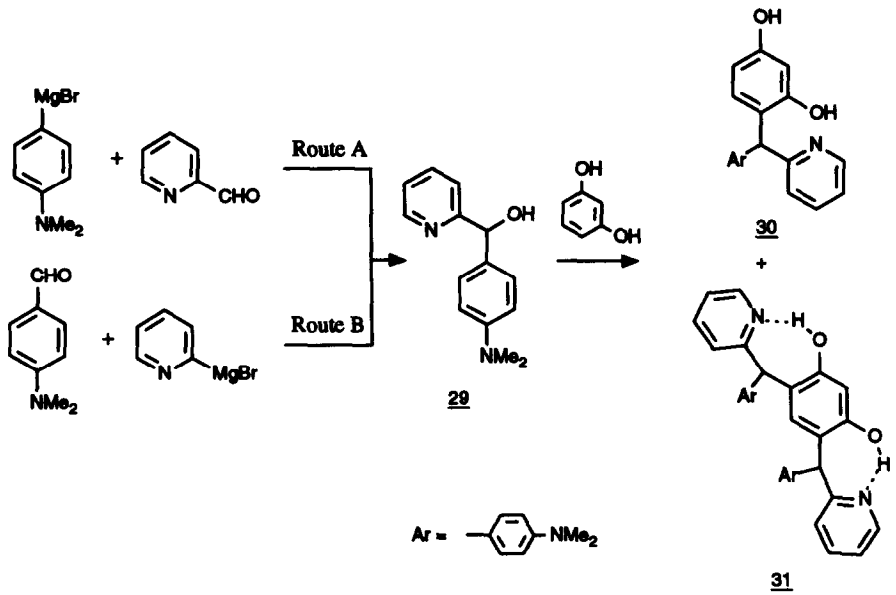


Scheme 4

benzhydrol **9A** and the phenol **15** was heated in toluene under reflux for 48 h, compound **17** was obtained in 73% yield after purification by column chromatography.

The reaction of the naphthol **22** with the benzhydrols **9B** and **9C** in toluene, in the presence of a catalytic amount of *p*-toluenesulfonic acid under reflux, gave the desired products **18** and **20** in 72% and 50% yields, respectively (Scheme 3). However, treatment of benzhydrol **9B** with 1,3,5-tri-methoxybenzene under similar conditions gave the desired **19** in a low yield; major recovery of 1,3,5-trimethoxybenzene was observed, while the benzhydrol was decomposed. Such was the case even when two molar equivalents of the benzhydrol **9B** was utilized. This low reactivity was attributed to steric hindrance.

Reaction of the benzhydrol **29** with resorcinol gave a mixture of the mono- **30** and the disubstituted product **31**. Compound **31** has a high melting point and has poor solubilities in many solvents. Such behavior was attributed to the internal hydrogen bonding, as shown in structure **31** (Scheme 5). The structures of compounds **30** and **31** were identified by

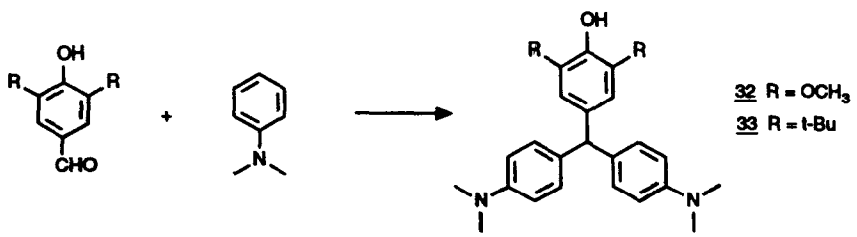


Scheme 5

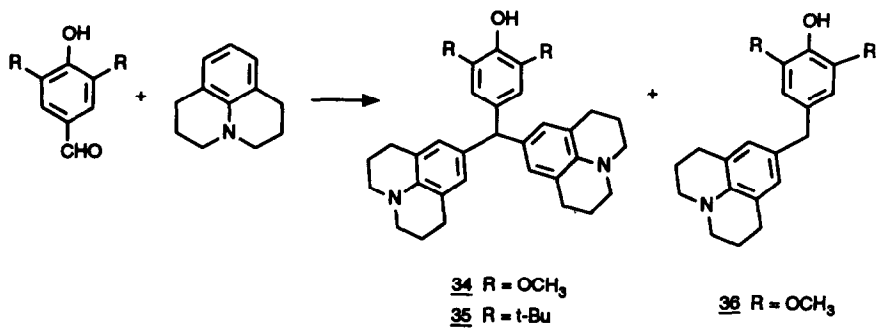
NMR spectra. In the disubstituted product **31**, a symmetrical resorcinol ring was observed as two singlets (6·10 and 6·39 ppm) in the ^{1}H NMR spectra and a total number of 13 carbon resonances in the ^{13}C NMR spectra.

2.2 Direct condensation of 2-naphthol, benzaldehyde and *N,N*-dimethylaniline

The general method for the preparation of triarylmethanes by the reaction of an arylaldehyde with arene nucleophiles uses only one arene nucleophile, and the triarylmethane obtained has two identical aryl groups. Using well established procedures, compounds **32–36** (Schemes 6 and 7) have now been synthesized.



Scheme 6

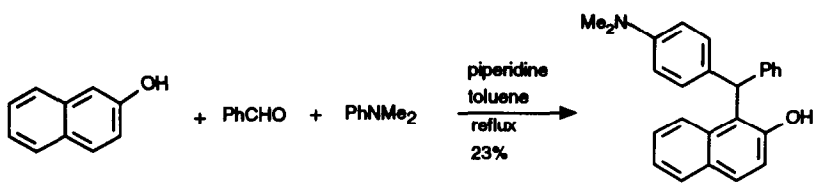


Scheme 7

It is well know that such reactions occur in a stepwise fashion. We thought that if two different arene nucleophiles were employed, an unsymmetrical triarylmethane would be obtained. Thus, heating equal molar amounts of benzaldehyde, 2-naphthol, and *N,N*-dimethylaniline in refluxing toluene in the presence of piperidine afforded 1-[(4-dimethylaminophenyl)benzyl]-2-naphthol (**37**) in 23% yield (Scheme 8). However, similar reactions of 1-naphthol and *N,N*-dimethylaniline with benzaldehyde or with terephthalaldehyde in refluxing toluene or benzene gave only a tar.

2.3 Preparation of triarylmethanes using benzotriazole methodology

We have previously reported a versatile synthesis of substituted phenols by treatment of *o*-(α-benzotriazolylalkyl)phenols with Grignard reagents or $LiAlH_4$.[14] 1-Naphthol was condensed with benzaldehyde and benzotriazole to give compound **39** as reported,[14] but no further displacement of the benzotriazole group was attempted at that time. We now report that the benzotriazole moiety in **38** was successfully displaced by 4-dimethylaminophenylmagnesium bromide (**5**), easily accessible by our improved procedure, in a yield of 90% (Scheme 9).



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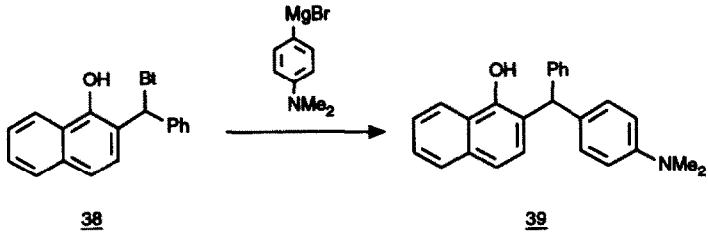
Scheme 8



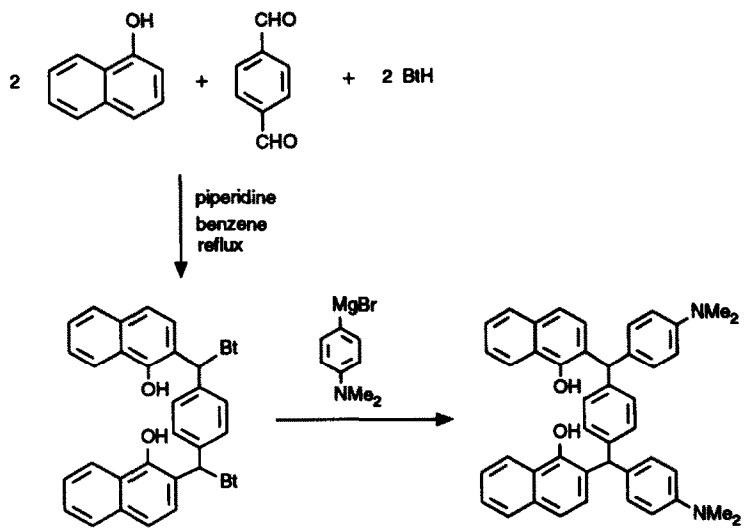
38 39

Scheme 9

We have also found that 1-naphthol condenses with terephthalaldehyde and benzotriazole. Thus, reaction of two equivalents of 1-naphthol and two equivalents of benzotriazole with one equivalent of terephthalaldehyde gave the benzotriazolyl derivative **40** in 40% yield. Compound **40** reacted similarly with the Grignard reagent (**5**) to afford compound **41** in 38% yield (Scheme 10).

3 PRODUCT CHARACTERIZATION

All of the compounds thus prepared were confirmed by NMR spectra along with elemental analysis data or high resolution mass spectroscopic data or by comparison with literature data. The NMR spectra of the



40 41

Scheme 10

triarylmethanes displayed a characteristic methine CH proton as a singlet in the region of 5·00 to 6·39 ppm and the corresponding methine carbon in the region of 43·3 to 56·3 ppm. For the disubstituted products **12**, **17**, **31** and **41**, the proton integral ratio in the ^{1}H NMR spectra, along with the total number of carbon resonances in the ^{13}C NMR spectra, indicated symmetrical patterns of the central aryl ring.

4 EXPERIMENTAL

4.1 General

Dry ether (Et_2O), tetrahydrofuran (THF) and benzene were refluxed in Na/benzophenone immediately prior to use. Melting points were measured in a Thomas–Hoover melting point apparatus and are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C (75 MHz) spectra were measured on a varian VXR-300 spectrometer in $CDCl_3$ solutions unless stated otherwise. For ^{1}H NMR spectra, multiplicity is denoted by s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). Coupling constants are in hertz. Exact mass measurements were performed on a Kratos MS-80-RFA double-focussing spectrometer, using the peak matching technique at a nominal resolution of 5000 (10% valley definition). Elemental analyses (C, H, N) were carried out using a Carbo Erba 1106 elemental analyzer at the University of Florida.

The yields, melting points, molecular formula, elemental analyses or high-resolution mass spectroscopic data and the characteristic methine NMR chemical shifts of the triarylmethanes prepared are summarized in Table 1.

4.2 Preparation of benzhydrols 9A and 9B

4.2.1 4-Dimethylaminophenylmagnesium bromide (5)
To well-ground (in a mortar) magnesium turnings (4·5 g, 190 mmol) and a few crystals of iodine under nitrogen was added a solution of 4-bromo-*N,N*-dimethylaniline (30 g, 150 mmol) in dry THF (150 ml) slowly to keep the mixture in gentle reflux. After addition, the solution was kept at reflux by heating for 1 h and then cooled. It was transferred to a flask and stored in a refrigerator for further use (concentration about 1 M).

4.2.2 1-Ethoxy-1-(4-formylphenoxy)ethane (8)
To 4-hydroxybenzaldehyde (36 g, 0·295 mol) in dry Et_2O (150 ml) under nitrogen was added ethyl vinyl ether (30 g, 0·417 mol) and then *p*-toluenesulfonic acid (0·05 g, 0·3 mmol). The insoluble materials were

TABLE 1
Preparation of Triarylmethanes

Compound	*Yield (%)*	*m.p. (°C)*	*Molecular formula*	*HRMS calc. (found)*			*Methine CH (δ)*	
				C	*H*	*N*	^{1}H	^{13}C
10	97	162–164	$C_{23}H_{22}N_2$	—[a]			5·50	46·6
11	21	Oil	$C_{19}H_{20}N_2$	276·162 6 (276·162 4)			5·31	49·5
12	96 (26[b])	63–65	$C_{34}H_{35}N_3$	84·08 (83·91)	7·26 (7·44)	8·65 (8·59)	5·23	49·6
16	30	186–188	$C_{21}H_{21}NO_2$	78·97 (78·59)	6·63 (6·67)	4·39 (4·23)	5·67	47·7
17	73	68–71	$C_{44}H_{53}N_3O_3S$	75·07 (75·40)	7·59 (7·64)	5·97 (5·79)	5·57	49·9
18	72	132–134	$C_{26}H_{25}NO_2$	81·43 (81·84)	6·57 (6·64)	3·65 (3·47)	5·94	50·0
19	16	*52–56*	$C_{24}H_{27}NO_4$	73·26 (73·12)	6·92 (7·07,	3·56 (3·23)	5·89	43·3
20	50	214–216	$C_{28}H_{30}N_2O$	81·91 (82·09)	7·37 (7·31)	6·82 (6·83)	6·00	50·7
30	52	105–108	$C_{20}H_{20}N_2O_2$	74·98 (74·76)	6·29 (6·41)	8·74 (8·79)	5·21	56·3
31	38	250 (Sintering)	$C_{34}H_{34}N_4O_2$	76·95 (76·57)	6·46 (6·55)	10·56 (10·32)	5·37	54·5
32	87	188–190	$C_{25}H_{30}N_2O_3$	402·225 6 (402·225 6)			5·44	54·5
33	97	136–138	$C_{31}H_{42}N_2O$	458·329 7 (458·329 7)			5·25	54·9
34	27	127–128	$C_{33}H_{38}N_2O_3$	510·288 2 (510·288 2)			5·38	53·3
35	28	210–212	$C_{25}H_{30}N_2O_3$	562·392 4 (562·392 4)			5·00	55·4
36[c]	27	127–128	$C_{21}H_{25}NO_3$	339·103 4 (339·103 4)			6·44	55·17
37	23	187–189[d]	$C_{25}H_{23}NO$	—	—	—	6·39	46·7
38	90	45–51	$C_{25}H_{23}NO$	353·178 0 (353·178 0)			5·68	51·2
41	38	130–132	$C_{44}H_{40}N_2O_2$	628·308 9 (628·309 0)			5·66	50·9

[a] Lit.[25] m.p. 158°C.
[b] Yield when 1 equiv. of pyrrole was used.
[c] Not a triarylmethane.
[d] Lit.[14] m.p. 187–189°C.

dissolved after a few minutes and evolution of heat was observed. It was then heated under reflux for an additional 1 h, cooled, and poured into NaOH solution (10%; 150 ml). The organic phase was separated and dried ($MgSO_4$) and the solvent was evaporated to give the desired product (55·7 g, 97%) as an oil; b.p. 88–90°C/0·3 mm (lit.[17] b.p. 126–128°C/1 mm). ^{1}H NMR: δ 1·20 (t, 3 H, J = 7·1), 1·54 (d, 3 H, J = 5·3), 3·5–3·6 (m, 1 H), 3·7–3·8 (m, 1 H), 5·54 (q, 1 H, J = 5·3), 7·11 (d, 2 H, J = 8·8), 7·83 (d, 2 H, J = 8·8), 9·88 (s, 1 H, CHO); ^{13}C NMR: δ 14·9, 19·6, 60·9, 98·8, 116·6, 130·2, 131·6, 161·9, 190·5.

*4.2.3 4-Dimethylaminobenzhydrol (**9A**)*

To a solution of phenylmagnesium bromide in Et_2O (freshly prepared from magnesium turnings (3·0 g, 120 mmol) and bromobenzene (15·7 g, 100 mmol) in Et_2O (40 ml)) was added a solution of 4-dimethylaminobenzaldehyde (10·0 g, 67 mmol) in a mixture of dry benzene (50 ml) and Et_2O (10 ml). After addition, the mixture was refluxed for 1 h and then poured into aqueous NH_4Cl solution (15%; 70 ml). The solution was extracted with Et_2O (a large emulsion!) (3 × 80 mol) and the combined extracts were dried ($MgSO_4$). Evaporation of the solvent gave the desired product (14·15 g, 93%); m.p. 69–70°C (lit.[16] m.p. 69–70°C). ^{1}H NMR: δ 2·70 (s, 1 H), 2·83 (s, 6 H), 5·62 (s, 1 H), 6·62 (d, 2 H, J = 8·7), 7·12 (d, 2 H, J = 8·7), 7·2–7·4 (m, 5 H). ^{13}C NMR: δ 40·5, 75·6, 112·5, 126·2, 126·9, 127·6, 128·1, 132·1, 144·3, 149·9.

*4.2.4 4-Hydroxy-4'-*N,N*-dimethylaminobenzhydrol (**9B**)*

To a freshly prepared solution of 4-dimethylaminophenylmagnesium bromide in THF (150 mmol; 1·0 M in THF, 150 ml) was added 1-ethoxy-1-(4-formylphenoxy)ethane (29·1 g, 150 mmol) in THF (60 ml). After addition, the mixture was heated under reflux for 2 h and then stirred at room temperature overnight. It was then poured into aqueous HCl solution (20%; 80 ml). The organic layer was separated and the aqueous layer was dropped into dilute ammonia solution. The precipitate was collected and then dissolved in NaOH solution (5%; 800 ml). The well-stirred solution was extracted with $CHCl_3$ (2 × 150 ml) to remove colored impurities. The aqueous solution was neutralized to pH 6–7 with HCl solution (5 N) in the presence of $CHCl_3$. The solids were collected and dried to give the desired product (20·4 g, 56%); m.p. 160–162°C (lit.[17] m.p. 162°C). ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 2·85 (s, 6 H), 5·26 (d, 1 H, J = 3·5), 5·51 (d, 1 H, J = 3·5), 6·62 (d, 2 H, J = 8·4), 6·71 (d, 2 H, J = 8·3), 7·12 (d, 2 H, J = 8·0), 7·15 (d, 2 H, J = 8·3), 8·97 (s, 1 H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ 40·3, 74·1, 111·9, 114·6, 127·0, 127·2, 133·7, 136·4, 149·2, 155·9.

4.3 General procedure for the preparation of compounds 10–13, 16

To a solution of 4-dimethylaminobenzhydrol (0·45 g, 2 mmol) in MeOH (25 ml) under reflux was added a solution of the appropriate aromatic compound (2 mmol) and concentrated HCl (0·8 ml) in H_2O (25 ml). The mixture was then heated under reflux for 90 min. To the solution was added KOH solution (5%; 30 ml) and cooled. The desired product was isolated and purified accordingly.

*4.3.1 3-[α-(4-Dimethylaminophenyl)benzyl]indole (**10**)*
After the solution was cooled, the solids formed were collected and dried to give the desired product (0·63 g, 97%). ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 2·84 (s, 6 H), 5·50 (s, 1 H), 6·55–6·65 (m, 3 H), 6·84 (t, 1 H, J = 7·6), 7·0–7·2 (m, 9 H), 7·31 (d, 1 H, J = 8·1), 10·3 (s, br, 1 H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ 39·2, 46·6, 110·1, 111·1, 117·1, 117·7, 118·1, 119·8, 122·9, 124·5, 125·5, 126·7, 127·4, 128·0, 130·8, 135·6, 143·7, 147·6.

*4.3.2 2-[α-(4-Dimethylaminophenyl)benzyl]pyrrole (**11**)*
The cooled solution was extracted with Et_2O (3 × 30 ml) the extract was dried ($MgSO_4$) and the solvent was evaporated. The residue thus obtained was flash chromatographed with hexane/EtOAc (12:1) to give compounds **11** as oil (0·12 g, 21%), **12** (0·13 g, 26%), and **13** (0·08 g, 24%). For compound **11**, ^{1}H NMR: δ 2·86 (s, 6 H), 5·31 (s, 1 H), 5·75–5·80 (m, 1 H), 6·05–6·15 (m, 1 H), 6·58 (d, 1 H, J = 1·47), 6·64 (d, 2 H, J = 8·8), 7·01 (d, 2 H, J = 8·8), 7·1–7·3 (m, 5 H), 7·75 (s, br, 1 H). ^{13}C NMR: δ 40·6, 49·5, 107·5, 107·9, 112·6, 116·8, 126·3, 128·2, 128·7, 129·4, 131·0, 134·3, 143·8, 149·3.

*4.3.3 2,5-Bis[α-(4-Dimethylaminophenyl)benzyl]pyrrole (**12**)*
This compound was also obtained under similar conditions in 96% yield when 0·5 equivalent of pyrrole was employed. ^{1}H NMR: δ 2·85 (s, 12 H), 5·23 (s, 2 H), 5·5–5·6 (m, 2 H), 6·62 (d, 4 H, J = 8·7), 7·00 (d, 4 H, J = 8·7), 7·1–7·3 (m, 10 H), 7·50 (s, br, 1 H). ^{13}C NMR: δ 40·6, 49·6, 107·5, 112·5, 126·1, 128·1, 128·7, 129·3, 131·2, 133·9, 143·9, 149·2.

*4.3.4 4,4'-Benzylidenebis(*N,N*-dimethylaniline) (**13**)*
Melting point 100–102°C (lit. [35]m.p. 102°C). ^{1}H NMR: δ 2·88 (s, 12 H), 5·37 (s, 1 H), 6·65 (d, 4 H, J = 8·8), 6·97 (d, 4 H, J = 8·8), 7·1–7·3 (m, 5 H). ^{13}C NMR: δ 40·7, 55·0, 112·6, 125·7, 128·0, 129·3, 129·9, 132·9, 145·4, 148·9.

4.3.5 4-[α-(4-Dimethylaminophenyl)benzyl]-1,3-dihydroxybenzene (16)
The cooled solution was extracted with $CHCl_3$ (3 × 40 ml), the extract was dried ($MgSO_4$) and the solvent was evaporated to give a residue. After trituration with CH_2Cl_2, it was stored in a refrigerator overnight. The solids formed were collected and dried to give the desired product (0·19 g, 30%). ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 2·87 (s, 6 H), 5·67 (s, 1 H), 6·23 (dd, 1 H, J = 8·3, 2·4), 6·37 (d, 1 H, J = 2·4), 6·61 (t, 3 H, J = 9·0), 6·94 (d, 2 H, J = 8·7), 7·1–7·3 (m, 5 H), 8·29 (s, 1 H), 8·49 (s, 1 H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ 40·2, 47·7, 102·5, 105·8, 111·9, 122·0, 125·0, 127·3, 128·7, 129·4, 130·1, 131·9, 144·7, 148·3, 154·7, 155·8.

4.4 4-(*N,N*-Dibutylsulfamoyl)phenol (15)

To a solution of phenol (7·57 g, 80 mmol) and dibutylsulfamoyl chloride[36] (18·54 g, 80 mmol) in dry CH_2Cl_2 (150 ml) at −78°C was added anhydrous $AlCl_3$ (21·33 g, 160 mmol) slowly. After addition, it was allowed to warm to room temperature overnight, and poured into ice–water (200 ml). The solution was extracted with $CHCl_3$ (3 × 80 ml), the extract was dried ($MgSO_4$) and the solvent was evaporated. The residue was flash chromatographed with hexane/EtOAc (8:1) to give the desired product (15·3 g, 67%); m.p. 69–71°C (lit.[34] reported no physical data). ^{1}H NMR: δ 0·87 (t, 6 H, J = 7·2), 1·27 (sextet, 4 H, J = 7·1), 1·50 (quintet, 4 H, J = 7·1), 3·09 (t, 4 H, J = 7·1), 6·97 (d, 2 H, J = 8·8), 7·65 (d, 2 H, J = 8·8), 7·81 (s, 1 H). ^{13}C NMR: δ 13·5, 19·7, 30·5, 47·9, 115·8, 129·0, 130·0, 160·3.

$C_{14}H_{23}NO_3S$ (285·4):
Calc. C, 58·92; H, 8·12; N, 4·91
Found C, 59·01; H, 8·19; N, 4·78

4.5 3,5-Bis[α-(4-dimethylaminophenyl)benzyl]-4-hydroxy-*N,N*-dibutylbenzenesulfonamide (17)

A mixture of 4-(*N,N*-dibutylsulfamoyl)phenol (5·70 g, 20 mmol) and 4-dimethylaminobenzhydrol (10·44 g, 46 mmol) in toluene (200 ml) was heated under reflux for 48 h in a Dean–Stark trap. The toluene was evaporated and the residue was chromatographed with gradient eluents (hexane/$CHCl_3$ 3:1 then 3:2) to give the desired product **17** (10·3 g, 73%). ^{1}H NMR: δ 0·84 (t, 6 H, J = 7·3), 1·1–1·2 (m, 4 H), 1·25–1·35 (m, 4 H), 2·80 (t, 4 H, J = 7·2), 2·89 (s, 12 H), 5·35 (s, br, 1 H), 5·57 (s, 2 H), 6·63 (d, 4 H, J = 8·8), 6·9–7·0 (m, 4 H), 7·0–7·1 (m, 4 H), 7·1–7·3 (m, 8 H). ^{13}C NMR: δ 13·6, 19·8, 30·3, 40·3, 47·6, 49·9, 112·6, 126·6, 127·6, 128·5, 129·0, 129·7, 131·1, 132·0, 142·3, 149·4, 154·7.

4.6 4-[(4-Dimethylaminophenyl)(4-hydroxyphenyl)]methyl-2-methyl-1-naphthol (18)

A mixture of 2-methyl-1-naphthol (2·68 g, 17 mmol), 4-dimethylamino-4'-hydroxybenzhydrol (5·42 g, 22·3 mmol) and *p*-toluenesulfonic acid (0·33 g, 1·7 mmol) in toluene (150 ml) was heated under reflux for 12 h in a Dean–Stark trap. The toluene was evaporated and to the residue was added $NaHCO_3$ solution (5%; 40 ml). The solution was extracted with $CHCl_3$ (3 × 80 ml), and the extract was dried ($MgSO_4$). Evaporation of the solvent gave a black residue, which was triturated with hexane/CH_2Cl_2 to give a portion of the desired product **18** (3·29 g). The residue was chromatographed with gradient eluents (hexane/EtOAc; 15:1, 10:1 and then 5:1) to give recovered 2-methyl-1-naphthol (0·5 g, 19%) and another portion of the desired product **18** (1·42 g). The total yield of compound **18** amounted to 4·71 g (72%). ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 2·27 (s, 3 H), 2·84 (s, 6 H), 3·30 (s, br, 1 H), 5·94 (s, 1 H), 6·59 (d, 2 H, J = 8·6), 6·65–6·75 (m, 3 H), 6·85–6·95 (m, 4 H), 7·25 (t, 1 H, J = 7·1), 7·32 (t, 1 H, J = 7·9), 7·88 (d, 1 H, J = 8·3), 8·2–8·3 (m, 2 H), 8·73 (s, br, 1 H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ 16·0, 39·8, 50·0, 111·6, 114·3, 116·2, 121·5, 123·37, 123·39, 124,1, 125·1, 129·1, 129·5, 129·9, 130·5, 131·3, 131·7, 134·7, 147·5, 147·9, 154·5.

4.7 4-[(4-Dimethylaminophenyl)(4-hydroxyphenyl)methyl]-1,3,5-trimethoxybenzene (19)

A mixture of 1,3,5-trimethoxybenzene (3·36 g, 20 mmol), 4-hydroxy-4'-dimethylaminobenzhydrol (9·72 g, 40) mmol) and *p*-toluenesulfonic acid (0·76 g, 4 mmol) in toluene (150 ml) was heated under reflux for 11 h in a Dean–Stark trap. The toluene was evaporated and to the residue was added $NaHCO_3$ solution (5%, 50 ml). The resulting solution was extracted with $CHCl_3$ (3 × 80 ml) and the extract was dried ($MgSO_4$). Evaporation of the solvent gave a residue, which was chromatographed with gradient eluents (hexane/EtOAc, 15:1, 10:1 and then 5:1) to give unreacted 1,3,5-trimethoxybenzene (1·68 g, 50%) and the desired product **19** (1·30 g, 16%). ^{1}H NMR: δ 2·84 (s, 6 H), 3·52 (s, 6 H), 3·74 (s, 3 H), 5·89 (s, 1 H), 6·12 (s, 2 H), 6·51 (d, 2 H, J = 8·5), 6·71 (d, 2 H, J = 8·8), 6·95 (d, 2 H, J = 8·5), 7·10 (d, 2 H, J = 8·6). ^{13}C NMR: δ 41·3, 43·3, 55·1, 55·6, 91·6, 113·5, 114·2, 114·3, 129·67, 129·74, 133·8, 136·4, 148·4, 153·3, 158·9, 159·5.

4.8 4-Bis(4-dimethylaminophenyl)methyl-2-methyl-1-naphthol (20)

A mixture of 2-methyl-1-naphthol (2·21 g, 14 mmol), 4,4'-bis(dimethylamino)benzhydrol (**9C**) (3·78 g, 14 mmol) and *p*-toluenesulfonic acid

(0·27 g, 1·4 mmol) in toluene (150 ml) was heated under reflux for 6·5 h in a Dean–Stark trap. The toluene was evaporated and to the residue was added saturated $NaHCO_3$ solution (30 ml). The resulting solution was extracted with Et_2O (3 × 150 ml), and the extract dried ($MgSO_4$). Evaporation of the solvent gave a residue, which upon trituration with Et_2O gave the desired product (2·88 g, 50%). ^1H NMR: δ 2·24 (s, 3 H), 2·89 (s, 12 H), 5·10 (s, br, 1 H), 6·00 (s, 1 H), 6·64 (d, 4 H, J = 8·7), 6·72 (s, 1 H), 6·96 (d, 4 H, J = 8·6), 7·30–7·45 (m, 2 H), 7·94 (d, 1 H, J = 8·5), 8·13 (d, 1 H, J = 7·8). ^{13}C NMR: δ 15·8, 40·7, 50·7, 112·6, 115·3, 121·3, 124·5, 124·66, 124·72, 125·3, 130·1, 130·3, 131·7, 133·1, 133·3, 147·2, 148·8.

4.9 2-Methyl-1-naphthol (22)

A solution of 2-(benzotriazol-1-ylmethyl)-1-naphthol (**21**)[32] (055 g, 2 mmol) and $LiAlH_4$ (0·4 g, 10 mmol) in dry THF (20 ml) was heated under reflux for 24 h. The solution was cooled, poured into ice–water (30 ml), acidified with HCl (2 N) and extracted with Et_2O (3 × 30 ml). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated to give a residue, which was flash chromatographed with hexane/EtOAc (10:1) to afford the desired product **22** (0·22 g, 70%) and compound **23** (0·11 g, 34%). For compound **22**, m.p. 64–66°C (lit.[37] m.p. 61–63°C). ^1H NMR: δ 2·31 (s, 3 H), 4·70 (s, br, 1 H), 7·1–7·2 (m, 1 H), 7·3–7·5 (m, 3 H), 7·7–7·8 (m, 1 H), 8·05–8·15 (m, 1 H). ^{13}C NMR: δ 15·5, 116·4, 120·1, 120·8, 124·3, 125·2, 125·3, 127·6, 128·9, 133·3, 148·8.

4.10 1,2-Bis(naphthalen-1-ol-2-yl)ethane (23)

Melting point 208–210°C. ^1H NMR: δ 3·08 (s, 4 H), 7·3–7·5 (m, 8 H), 7·73 (dd, 2 H, J = 7·2, 0·8), 8·29 (dd, 2 H, J = 9·2, 1·7), 8·75 (s, br, 2 H). ^{13}C NMR: δ 31·2, 118·8, 121·2, 121·3, 124·0, 124·5, 124·8, 126·6, 128·0, 132·6, 148·7.

$C_{22}H_{18}O_2$ (314·4)
Calc. C, 84·05; H, 5·77
Found C, 83·94; H, 5·86

4.11 α-(Pyridin-2-yl)-4-dimethylaminobenzyl alcohol (29)

To a freshly prepared solution of 4-dimethylaminophenylmagnesium bromide in THF (100 mmol; 1·0, M in THF, 100 ml) was added pyridine-2-carboxaldehyde (10·7 g, 100 mmol) in THF (40 ml). After addition, the mixture was heated under reflux for 4 h and cooled. After decomposing the complex with cold dilute HCl solution (2 N), the acidic (pH 5)

aqueous layer was separated, made alkaline with ammonia solution (pH 9) and then extracted with Et_2O (3 × 200 ml). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated to give the desired product (21·4 g, 94%); m.p. 96–98°C (lit.[20] b.p. 146–152°C/ 0·5 mm). ^1H NMR: δ 2·84 (s, 6 H), 5·30 (s, br, 1 H), 5·66 (s, 1 H), 6·63 (d, 2 H, J = 8·8), 7·0–7·1 (m, 1 H), 7·1–7·2 (m, 3 H), 7·45–7·55 (m, 1 H), 8·43 (d, 1 H, J = 4·9). ^{13}C NMR: δ 40·2, 74·7, 112·2, 120·9, 121·7, 127·7, 131·0, 136·3, 147·4, 149·9, 161·8.

$C_{14}H_{16}N_2O$ (228·3)
Calc. C, 73·66; H, 7·06; N, 12·27
Found C, 73·79; H, 7·17; N, 12·24

4.12 Reaction of α-(Pyridin-2-yl)-4-dimethylaminobenzyl alcohol (29) with resorcinol

To a solution of resorcinol (3·96 g, 36 mmol) and α-(pyridin-2-yl)-4-dimethylaminobenzyl alcohol (**29**) (8·20 g, 36 mmol) in benzene (300 ml) under reflux was added *p*-toluenesulfonic acid (6·86 g, 36 mmol). The mixture was heated under reflux for 12 h. The benzene was evaporated and to the residue was added $NaHCO_3$ solution (6·0 g $NaHCO_3$, 72 mmol in 120 ml H_2O) and MeOH (10 ml). The resulting solution was extracted with $CHCl_3$ (4 × 120 ml) and the extract was dried ($MgSO_4$). The solvent was evaporated and the residue was boiled with methanol. The insoluble material was collected and dried as compound **31** (3·6 g, 38%). Evaporation of the MeOH gave compound **30** (6·0 g, 52%).

4.12.1 4-[(4-Dimethylaminophenyl)(pyridin-2-yl)]methyl-1,3-dihydroxybenzene (30)

^1H NMR: δ 2·76 (s, 6 H), 5·21 (s, 1 H), 6·27 (d, 1 H, J = 8·8), 6·42 (s, 1 H), 6·57 (d, 2 H, J = 8·8), 6·81 (d, 2 H, J = 8·6), 6·90 (d, 1 H, J = 8·2), 7·05 (dd, 1 H, J = 6·4, 5·2), 7·26 (d, 1 H, J = 8·0), 7·58 (dt, 1 H, J = 7·6, 1·3), 8·33 (d, 1 H, J = 4·4). ^{13}C NMR: δ 40·6, 56·3, 105·7, 107·0, 112·8, 119·9, 121·9, 124·0, 128·3, 130·2, 132·1, 138·1, 147·4, 148·9, 156·5, 157·1, 163·1.

4.12.2 2,4-Bis[(4-dimethylaminophenyl)(pyridin-2-yl)]methyl-1,5-dihydroxybenzene (31)

^1H NMR (CF_3CO_2H + DMSO-d_6): δ 2·80 (s, 12 H), 5·37 (s, 2 H), 6·10 (s, 1 H), 6·39 (s, 1 H), 6·86 (d, 4 H, J = 8·1), 7·03 (d, 4 H, J = 8·0), 7·19 (t, 2 H, J = 7·2), 7·35 (t, 2 H, J = 5·5), 7·90 (t, 2 H, J = 7·2), 8·0–8·1

(m, 2 H), 9·40 (s, br, 2 H), ^{13}C NMR (CF_3CO_2H + DMSO-d_6): δ 50·5, 54·5, 108·6, 119·7, 124·4, 129·0, 131·4, 134·8, 137·0, 143·6, 144·7, 145·1, 150·8, 159·4, 160·7.

4.13 4-Bis[4-dimethylaminophenyl]methyl-2,6-dimethoxyphenol (32)

A mixture of syringaldehyde (0·03 mol, 5·46 g); *N*,*N*-dimethylaniline (0·6 mol, 7·26 g), urea (2·7 g), and concentrated sulfuric acid (4·41 g in isopropanol (100 ml), was heated at 90°C under a nitrogen blanket for 24 h. The reaction was monitored by thin-layer chromatography (TLC). The reaction mixture was cooled to room temperature, and 40 ml of water was added, followed by 50% sodium hydroxide until alkaline while the product was separated. The solution was filtered and washed with 200 ml of cold water. The product (slightly blue) was recrystallized from ethanol to give **32** (12·0 g, 97%); m.p. 136–138°C; MS, 406·52; ^{1}H NMR ($CDCl_3$): δ 2·90 (s, 12 H), 3·75 (s, 6 H), 5·30 (s, 1 H), 5·44 (s, 1 H), 6·38 (s, 2 H), 6·66 (d, 6 H), 6·98 (d, 4 H).

4.14 4-Bis[4-dimethylaminophenyl]methyl-2,6-di-*tert* butylphenol (33)

A mixture of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde hemihydrate (0·03 mol, 12·0 g) (**33**); *N*,*N*-dimethylaniline (0·06 mol, 7·26 g), urea (2·7 g) and concentrated sulfuric acid (4·41 g in isopropanol (100 ml)) was heated at 90°C under nitrogen for 20 h. The reaction was monitored by TLC. The reaction mixture was cooled to room temperature, and 20 ml of water, followed by 50% sodium hydroxide was added until alkaline while the product was separated. The precipitate was filtered and washed with 200 ml of cold water. The product was recrystallized from a hot water and isopropanol mixture to give **33**, (12·0 g, 87·2%); m.p. 188–190°C; MS, 458·68; ^{1}H NMR ($CDCl_3$): δ 1·36 (s, 18 H), 2·90 (s, 12 H), 5·02 (s, 1 H), 5·25 (s, 1 H), 6·66 (d, 4 H), 6·97 (dd, 6 H).

4.15 4-Bis[8-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizinyl]methyl-2,6-di-*tert*-butylphenol (35)

A mixture of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde hemihydrate (0·015 mol, 3·85 g), julolidine (0·03 mol, 5·19 g), urea (1·5 g) and concentrated sulfuric acid (1·1 ml) in isopropanol (30 ml) was heated to reflux under a nitrogen blanket for 3 h. The reaction was monitored by TLC. The reaction mixture was cooled to room temperature, and 20 ml of water was added, followed by 50% sodium hydroxide until alkaline (pH 13). The solution was diluted with 200 ml of cold water to separate the

oily product. The oily product was dissolved in ethanol. Removal of solvent gave resinous material. This was chromatographed on silica gel using hexane/ether (5, 10 and 17%) to give the product **35** (2·4 g, 27·9%); m.p. 210–212°C. MS, 562·83; ^{1}H NMR ($CDCl_3$): δ 1·38 (s, 18 H), 1·94 (m, 8 H), 2·66 (m, 8 H), 3·09 (m, 8 H), 5·0 (d, 2 H), 6·55 (s, 4H), 6·95 (s, 2 H).

4.16 4-Bis[8-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizinyl]methyl-2,6-dimethoxyphenol (34) and 4-[8(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]-quinolizinyl]methyl-2,6-dimethoxyphenol (36)

A mixture of syringaldehyde (0·015 mol, 2·73 g), julolidine (0·03 mol, 5·19 g, urea (1·35 g) and concentrated sulfuric acid (1·1 ml) in isopropanol (30 ml) was heated at 90°C under a nitrogen blanket for 5 h. The reaction mixture was cooled to room temperature, and 20 ml of water was added, followed by 50% sodium hydroxide until the reaction mixture was alkaline (pH 12–13) while the product was separated as resinous material. The aqueous layer was decanted and the oily material was washed with 200 ml of cold water. The product (slightly blue) was chromatographed on silica gel using hexane. The first fraction was starting julolidine; the second fraction, which turned green upon oxidation with iodine, could not be characterized due to the paucity of material. The third and fourth fractions were identified as **34** and **36**, respectively.

Compound **34** (1·2 g, 23·5%), m.p. 127–30°C, MS, 339·43; ^{1}H NMR ($CDCl_3$): δ 1·95 (m, 8 H), 2·68 (m, 8 H), 3·10 (m, 8 H), 3·80 (s, 6 H), 5·05 (s, 1 H), 5·38 (s, 1 H), 6·40 (s, 2 H), 6·52 (s, 4 H).

Compound **36** (2·1 g, 27·4%), m.p. 127–128°C, MS, 510·67, ^{1}H NMR ($CDCl_3$): δ 1·95 (m, 4 H), 2·70 (M, 4 H), 3·10 (M, 4 H), 3·73 (s, 2 H), 3·85 (s, 6 H), 5·34 (s, 1 H), 6·44 (s, 2 H), 6·60 (s, 2 H).

4.17 1-[α-(4-Dimethylaminophenyl)benzyl]-2-naphthol (37)

A mixture of benzaldehyde (2·65 g, 25 mmol), 2-naphthol (3·6 g, 25 mmol), *N,N*-dimethylaniline (3·03 g, 25 mmol) and piperidine (0·19 g) in toluene (100 ml) was heated under reflux for 65 h with a Dean–Stark trap. The toluene was evaporated and the residue was triturated with hexane/Et_2O to give the desired product **37** (2·13 g, 24%). Compound **37** thus obtained is identical in all aspects to that reported earlier.[14]

4.18 2-[α-(4-Dimethylaminophenyl)benzyl]-1-naphthol (39)

To a solution of 2-[α-(benzotriazolyl)benzyl]-1-naphthol (**38**) (1·40 g, 4 mmol) in dry THF (30 ml) at −78°C was added a solution of 4-dimethyl-

aminophenylmagnesium bromide (16 mmol; 1·0 M in THF, 16 ml). The cooling bath was then removed and the mixture was warmed to room temperature and stirred overnight. It was poured into water (30 ml), acidified with HCl (2 N) and extracted with Et_2O (3 × 40 ml). The combined extracts were washed with water (40 ml) and dried ($MgSO_4$) and the solvent was evaporated to give a residue which was purified by column chromatography with hexane/CH_2Cl_2 (2:1) to give the desired product **39** (1·26 g, 90%) as a glassy solid. ^{1}H NMR: δ 2·86 (s, 6 H), 5·40 (s, br, 1 H), 5·68 (s, 1 H), 6·64 (d, 2 H, J = 8·6), 6·95–7·05 (m, 3 H), 7·1–7·5 (M, 8 H), 7·7–7·8 (m, 1 H), 8·1–8·2 (m, 1 H). ^{13}C NMR: δ 40·4, 51·2, 112·8, 119·9, 121·7, 123·8, 125·1, 125·8, 126·7, 127·4, 128·0, 128·6, 129·1, 129·3, 129·9, 133·5, 142·7, 148·9, 149·5.

4.19 1,4-Bis[(benzotriazol-1-yl)(1-hydroxy-naphthalen-2-yl)methyl]-benzene (40)

A mixture of 1-naphthol (14·4 g, 0·1 mol), *p*-terephthalaldehyde (6·7 g, 0·05 mol), benzotriazole (11·9 g, 0·1 mol) and piperidine (0·7 g) in benzene (200 ml) was heated under reflux for 3 h. About half of the benzene was evaporated and the remaining solutions was cooled. The solid formed was collected and dried as the desired product **40** (12·6 g, 40%), m.p. 206–208°C. ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 7·18 (d, 2 H, J = 8·8), 7·21 (s, 2 H), 7·3–7·5 (m, 14 H), 7·72–7·76 (m, 2 H), 7·99 (d, 2 H, J = 8·0), 8·02 (s, 2 H), 8·25–8·28 (m, 2 H), 9·60 (s, br, 2 H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ 59·5, 109·6, 118·3, 118·6, 119·0, 121·4, 123·0, 124·3, 124·4, 125·1, 125·6, 126·3, 126·8, 127·4, 132·4, 133·4, 137·4, 144·6, 149·6.

$C_{40}H_{28}N_6O_2$ (624·7)
Calc. C, 76·91; H, 4·52; N, 13·45
Found C, 76·83; H, 4·40; N, 13·13

4.20 1,4-Bis[(4-dimethylaminophenyl)(1-hydroxy-naphthalen-2-yl)-methyl]-benzene (41)

To a solution of 1,4-bis[(benzotriazol-1-yl)(1-hydroxy-naphthalen-2-yl)-methyl]benzene (**40**) (3·74 g, 6 mmol) in dry THF (240 ml) at −78°C was added a solution of 4-dimethylaminophenylmagnesium bromide (60 mmol; 1·0 M in THF, 60 ml). The cooling bath was then removed and the mixture was warmed to room temperature and stirred overnight. It was poured into water (100 ml), acidified with HCl (2 N) and extracted with Et_2O (4 × 100 ml). The combined extracts were washed with water (100 ml) and dried ($MgSO_4$), and the solvent was evaporated to give a

residue which was purified by column chromatography with gradient eluents (hexane/CH_2Cl_2, 4·1, and then CH_2Cl_2) to give the desired product **41** (1·42 g, 38%) as a glassy solid. ^{1}H NMR: δ 2·88 (s, 12 H), 5·40 (s, br, 2 H), 5·66 (s, 2 H), 6·65 (d, 4 H, J = 8·8), 7·03 (t, 6 H, J = 8·0), 7·12 (s, 4 H), 7·3–7·5 (m, 6 H), 7·7–7·8 (m, 2 H), 8·1–8·2 (m, 2 H). ^{13}C NMR; δ 40·5, 50·9, 112·9, 120·0, 121·7, 123·8, 125·1, 125·8, 125·9, 127·4, 128·0, 129·1, 129·6, 129·9, 133·5, 141·0, 148·9, 149·6.

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