PERKIN 1

Synthesis of 1,3,5-tris[4-(diarylamino)phenyl]benzene and 1,3,5-tris(diarylamino)benzene derivatives

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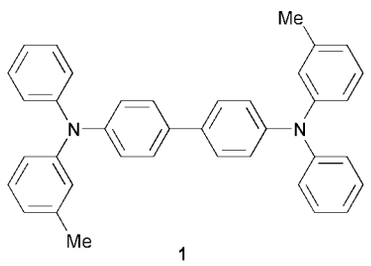
The title compounds were prepared by the copper catalysed Ullmann coupling of aromatic amines with aromatic aryl iodides. Full spectroscopic details are reported. Solutions of 1,3,5-tris(diarylamino)benzene derivatives in deuterated chloroform undergo hydrogen–deuterium exchange on the central ring and readily turn green owing to partial oxidation by traces of dissolved oxygen. The green colour is quenched by the addition of ascorbic acid. The solutions are more stable in chloroform that has been filtered through basic alumina to remove traces of acid. *N*-Arylbenzenesulfonamides can be converted to diarylamines by treatment with the sodium salt of an aniline.

Introduction

4,4′-Bis[(3-methylphenyl)phenylamino]biphenyl **1** was patented in 1976 as a positive hole transporting material for electrophotographic devices such as photocopiers and laser printers.[1] Electrophotography is the world's largest reprographics technology and not surprisingly this compound and related polyaromatic amines have been intensively studied. There are over 500 electrophotography patents which include 4,4′-bis-[(3-methylphenyl)phenylamino]biphenyl **1**[2a,b] and over 6000 electrophotography patents on polyaromatic amines in general. Polyaromatic amines are also of interest as hole transporting materials[3] for electroluminescent devices,[4] for their ability to form amorphous glassy phases and different polymorphs upon melting and cooling[5] and for their facile oxidation to stable high spin radical cations.[6] A standard method for preparing triarylamines was developed by the Xerox Corporation[7] which has been widely exploited in different laboratories. This involves heating a diarylamine and an iodoaromatic with copper powder and KOH in a solvent such as decalin, soltrol or *n*-decane under a nitrogen atmosphere. The methodology is similar to the processes pioneered by Ullmann,[8] Goldberg and Nimerovsky[9] and Nelson and Adams[10] for the synthesis of triarylamines which involve heating the arylamine reactants in no solvent, in nitrobenzene[11] or using the iodoaromatic as solvent[12] with copper powder or copper bronze and K_2CO_3. The diarylamine can also be deprotonated with nBuLi or NaH and coupled with an iodoaromatic in Ph_2O with CuI.[6b,f,13]



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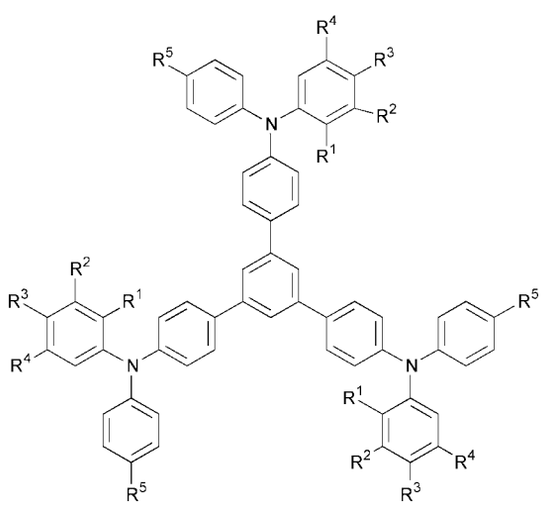
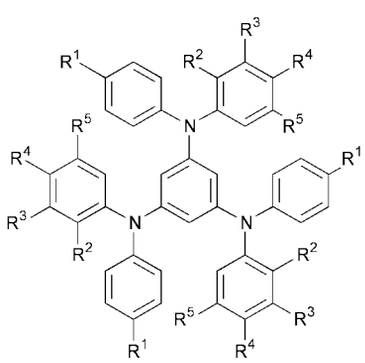


2a-f

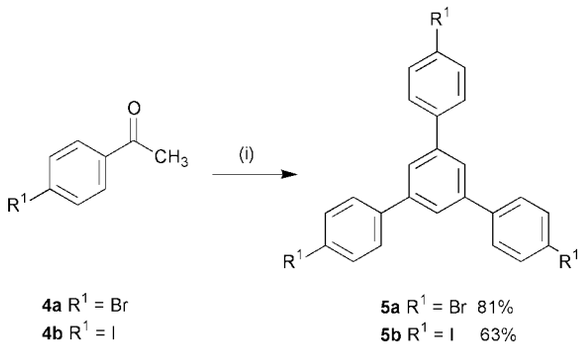


3a-h

Results and discussion

In this paper we report the synthesis and full spectroscopic characterisation of 1,3,5-tris[4-(diarylamino)phenyl]benzene **2a**–**f** and 1,3,5-tris(diarylamino)benzene derivatives **3a**–**h**. 1,3,5-Tris(4-iodophenyl)benzene **5b** was used as a building block for trimer series **2a**–**f**. It was prepared by the cyclotrimerisation of 4-iodoacetophenone **4b** with $SiCl_4$ in EtOH[14] or by using $HC(OMe)_3$ in dry EtOH saturated with dry HCl gas (Scheme 1).[15] It was coupled with diarylamines **6a**–**f** by heating with copper bronze and KOH in an inert solvent at 180 °C (Scheme 2 and Table 1). The tribromo derivative **5b** was not sufficiently reactive to undergo the coupling reactions. The use of copper iodide as catalyst in place of copper bronze was unsatisfactory and gave mixtures of mono-, di- and tri-substituted products after extended reaction times.

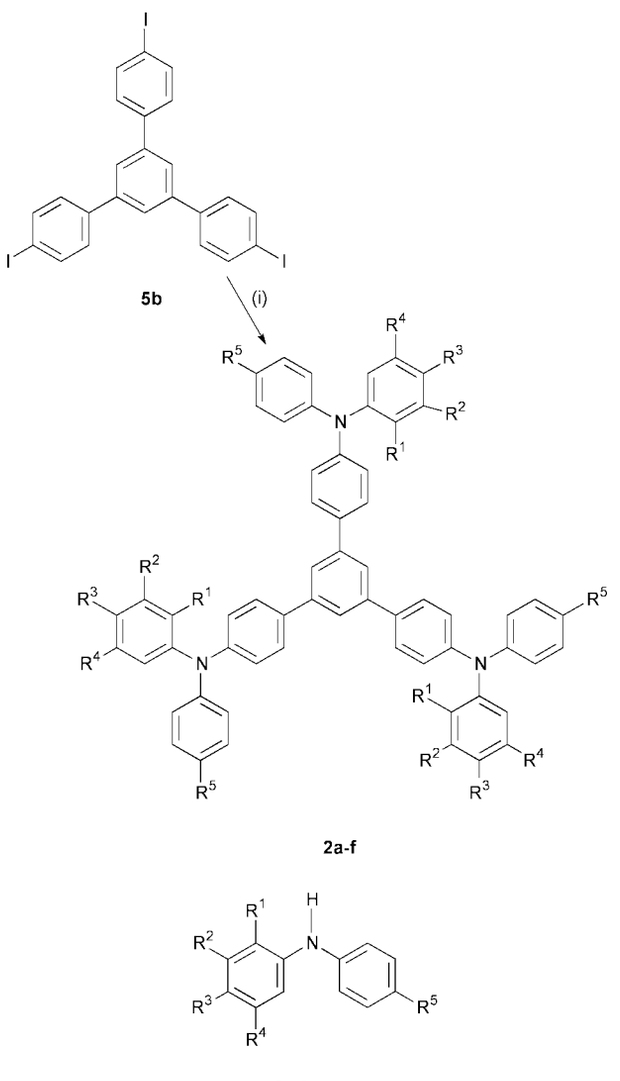
Diarylamines are typically prepared by the copper catalysed arylation of an acetanilide[16] followed by deacetylation or by the



4a R^1 = Br
4b R^1 = I

5a R^1 = Br 81%
5b R^1 = I 63%

Scheme 1 *Reagents and conditions*: (i) $SiCl_4$–EtOH, rt.

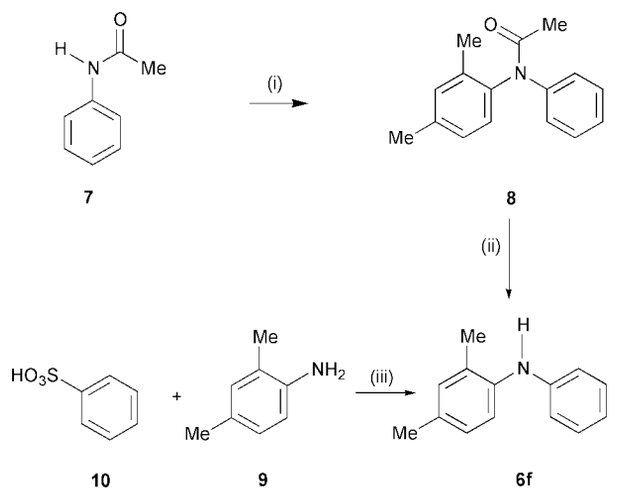


Scheme 2 *Reagents and conditions*: (i) diarylamine **6a**–**f**, KOH, Cu, *n*-decane, Δ, 48 h.

condensation of an aniline with a sulfonic acid with sodium amide as base.[17] The latter reaction is accelerated by the presence of KCl. *N*-(2,4-Dimethylphenyl)aniline was prepared by both methods (Scheme 3). The latter is an interesting example of a nucleophilic substitution reaction because, in the absence of a metal catalyst, nucleophilic displacement of aromatic substituents which are not activated with electron withdrawing groups usually proceed by either benzyne intermediates or by free radical initiated chain processes. Neither of these mechanisms seems likely here because no cine-substitution, characteristic of a benzyne mechanism, is observed and no free radical initiators are present. The reaction bears resemblance to the

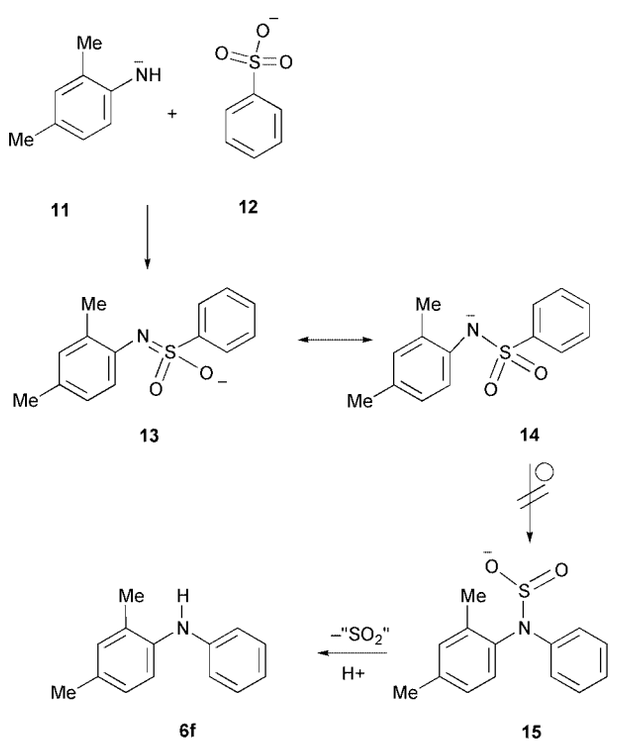
Table 1 Yields of compounds **2a**–**f** after coupling of diarylamines **6a**–**f** with copper bronze and KOH in an inert solvent at 180 °C

Diaryl-amine	R^1	R^2	R^3	R^4	R^5	Product Yield (%)
6a	H	H	H	H	H	**2a** (65)
6b	H	Me	H	H	H	**2b** (64)
6c	H	Me	Me	H	H	**2c** (60)
6d	H	Me	H	Me	H	**2d** (58)
6e	H	H	Me	H	Me	**2e** (48)
6f	Me	H	Me	H	H	**2f** (15)



Scheme 3 *Reagents and conditions*: (i) PhI, Cu, K_2CO_3, *p*-iodoxylene, *o*-dichlorobenzene, rt, Δ; (ii) KOH, EtOH, Δ; (iii) $NaNH_2$, KCl, *n*-decane, Δ.

formation of phenols by the fusion of sulfonic acids with alkali.[18] Treatment of the aniline **9** with sodium amide generates the sodium anilinide **11** and gives off ammonia. An excess of the anilinide salt is used so that the sulfonic acid is deprotonated. One possible mechanism is shown which involves the initial formation of a sulfonamide **13/14** which might rearrange to the product **6f** *via* intermediate **15** (Scheme 4).



Scheme 4

Table 2 Preparation of **3a**–**h** by copper catalysed arylation of **17a** or **17b**

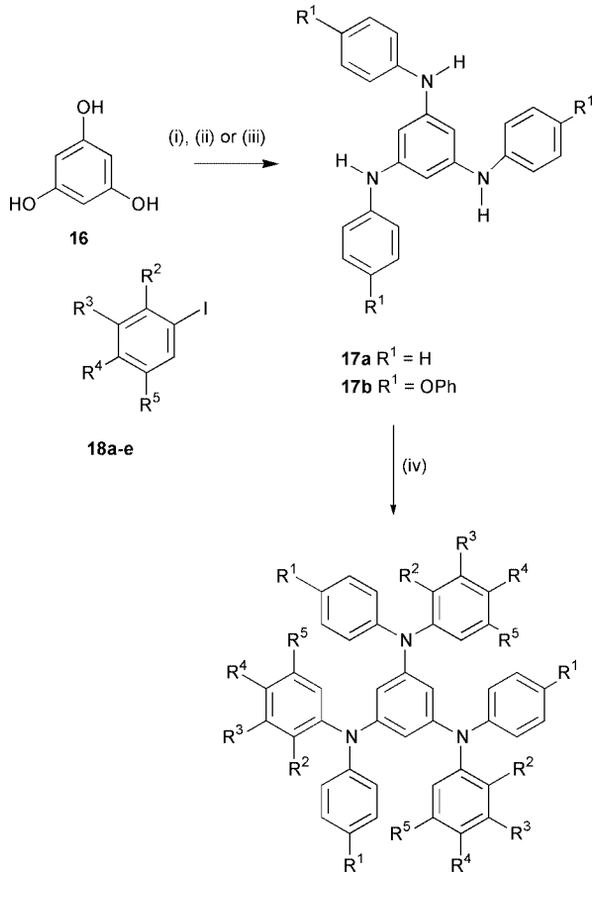
R^1	R^2	R^3	R^4	R^5	1,3,5-Tris(diarylamino)-benzenes Yield (%)
H	H	H	H	H	**3a** (68)
H	H	Me	H	H	**3b** (72)
H	H	H	Me	H	**3c** (49)
H	H	Me	Me	H	**3d** (71)
H	H	Me	H	Me	**3e** (69)
H	Me	H	Me	H	**3f** (53)
H	H	Cl	H	H	**3g** (30)
PhO	H	Me	H	H	**3h** (51)

Table 3 Preparation of **17a** and **17b**, see Scheme 5

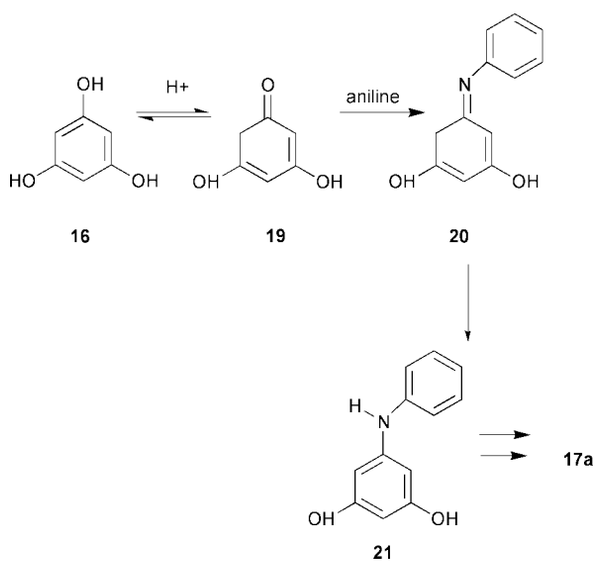
Conditions	Product Yield (%)	R^1
(i)	**17a** (75)	H
(ii)	**17a** (90	H
(iii)	**17b** (57)	PhO

This mechanism is supported by the fact that only primary arylamines undergo the reaction and not secondary arylamines. To investigate this hypothesis a sample of *N*-phenylbenzenesulfonamide was treated under the same reaction conditions with the sodium salt of 3-methylaniline. The product obtained was 3-methylphenyl(phenyl)amine **6b** which showed that although the reaction had proceeded no evidence for an intramolecular rearrangement of *N*-phenylbenzenesulfonamide was provided. The sulfonic acid to diarylamine reaction could therefore proceed *via* an *N*-arylbenzenesulfonamide intermediate although this may not necessarily form in the reaction or could be a minor reaction pathway. A further attempt to rearrange *N*-phenylbenzenesulfonamide to diphenylamine by treating with one equivalent of sodium amide in *N*-methylpyrrolidine and heating at 200 °C was also unsuccessful.

The second series of compounds 1,3,5-tris(diarylamino)-benzene derivatives **3a**–**h** were prepared by copper catalysed arylation of either 1,3,5-tris(phenylamino)benzene **17a** or 1,3,5-tris(4-phenoxyphenylamino)benzene **17b** (Table 2). Compound **17a** can be prepared by the literature method which involves the condensation of aniline with phloroglucinol with a catalytic quantity of iodine (Scheme 5 and Table 3).[19,20] The iodine presumably reacts with some aniline or phloroglucinol to generate HI which catalyses the reaction. A keto tautomeric form of phloroglucinol **19** condenses with aniline to form an imine **20** which tautomerises re-aromatising the central aromatic ring (Scheme 6). Two more condensations lead to the product **17a**. We have shown that the reaction can also be conveniently catalysed by hydrochloric acid which avoids the potential formation of iodinated by-products. If the compounds **3a**–**h** are left standing in $CDCl_3$ then the central aromatic protons exchange for deuterium as shown by the disappearance of this signal in the ^1H NMR spectrum and the absence of a signal in the ^{13}C DEPT spectrum. Traces of acid in $CDCl_3$ presumably catalyse the process. Although the three attached nitrogens are both diaryl substituted, which is expected to decrease their electron density, they must still help stabilise the positive charge of the Wheland intermediate that forms upon protonation of the central ring. The compounds produce coloured solutions on standing in $CDCl_3$ presumably due to the above Wheland intermediate or owing to the formation of some radical cations which can make the collection of NMR data problematic. The coloured chromophore(s) may also act as sensitizers in daylight causing accelerated decomposition of the $CDCl_3$, increasing the acidity and rate of exchange of the central aromatic protons. The coloured solutions are quenched by the addition of the anti-oxidant ascorbic acid. The stability of the amines **3a**–**h** is



Scheme 5 *Reagents and conditions*: (i) aniline, I_2, Δ; (ii) aniline, cHCl, Δ; (iii) *p*-phenoxyaniline, I_2, Δ; (iv) aryl iodide, Cu, KOH, *n*-decane, Δ.

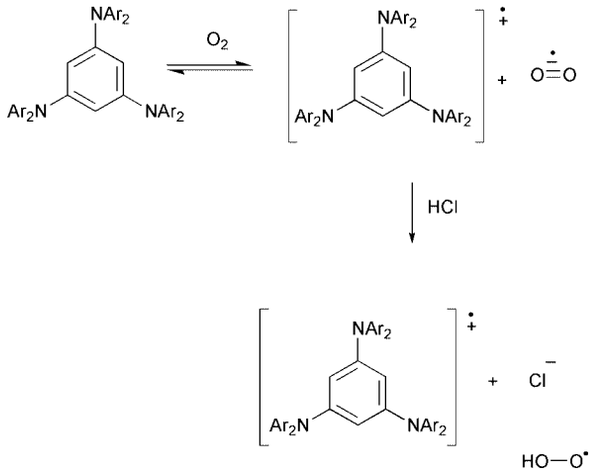


Scheme 6

enhanced in $CDCl_3$ filtered through basic alumina to remove traces of acid. The presence of chloride counterions may drive the equilibrium shown in Scheme 7 to the right increasing the concentration of free radicals formed by traces of dissolved oxygen.

Experimental

NMR spectra were recorded on a Bruker 250 MHz instrument. *J* values are given in Hz. Infrared spectra were recorded on a ATI Mattson spectrometer with samples prepared as KBr discs.



Scheme 7

UV spectra were recorded on a Perkin-Elmer Lambda 15 UV-VIS spectrophotometer using chloroform as solvent. Mass spectra were obtained with a VG Quattro II triple quadrupole mass spectrometer. Melting points were measured using a Kofler hot-stage microscope and are uncorrected. Flash column chromatography was conducted using Kieselgel 60 (Merck). Light petroleum refers to the fraction with bp 40–60 °C. Diarylamines **6a**–**e** are commercially available.

1,3,5-Tris(4-halophenylbenzenes) 5a and 5b

These were prepared in a similar manner to literature procedures using either $SiCl_4$ or $HC(OMe)_3$ in EtOH. Purification was difficult on a large scale (~10 g starting material) but was acceptable on a smaller scale.

General procedure: 1,3,5-tris(4-bromophenylbenzene) 5a. 4-Bromoacetophenone (1.0 g, 5 mmol) in dry EtOH (20 ml) was slowly treated with $SiCl_4$ (1.72 ml, 15 mmol) by syringe under a nitrogen atmosphere. After stirring at room temperature for up to 80 h the reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$, concentrated *in vacuo* and purified by flash chromatography on silica gel. Light petroleum–dichloromethane (90:10) eluted the *title compound* (0.73 g, 81%) as colourless needles, mp 266–267 °C (lit.,[14] 262 °C) (from dichloromethane–light petroleum) (Found: C, 52.7; H, 2.6; Br, 43.8. $C_{24}H_{15}Br_3$ requires C, 53.1; H, 2.8; Br, 44.1%); $\lambda_{max}(HCCl_3)$/nm 288 (log ε 4.21); ν_{max} (KBr)/cm^{-1} 3064m, 3037m, 1593s, 1487s, 1439s, 1377s, 1355m, 1301m, 1243m, 1189w, 1071s, 1024w, 1001s, 886m, 808s, 697m, 637w and 605s; δ_H (250 MHz; $CDCl_3$) 7.50 (6H, dd, *J* 8.6 and 2.0, H4), 7.59 (6H, dd, *J* 8.6 and 2.0, H5) and 7.66 (3H, s, H1); δ_C (62.9 MHz; $CDCl_3$) 121.9, 124.8, 128.7, 131.9, 139.6 and 141.4.

1,3,5-Tris(4-iodophenylbenzene) 5b. Yield 63%; pale yellow needles, mp 270–271 °C (from dichloromethane–light petroleum) (Found: C, 42.2; H, 2.0; I, 54.8. $C_{24}H_{15}I_3$ requires C, 42.1; H, 2.2; I, 55.7%); $\lambda_{max}(HCCl_3)$/nm 291 (log ε 4.44); ν_{max} (KBr)/cm^{-1} 3060w, 3033w, 1590m, 1483s, 1436m, 1373m, 1344w, 1301w, 1242m, 1060m, 998s, 963w, 886w, 809s, 698m and 604w; δ_H (250 MHz; $CDCl_3$) 7.39 (6H, dd, *J* 2.0 and 8.4, H4), 7.67 (3H, s, H1) and 7.80 (6H, dd, *J* 2.0 and 8.4, H5); δ_C (62.9 MHz; $CDCl_3$) 93.5, 124.8, 129.0, 137.9, 140.1 and 141.5.

General procedure: 1,3,5-tris[4-(diphenylamino)phenyl]benzene 2a

1,3,5-Tris(4-iodophenyl)benzene (1.40 g, 2.06 mmol), diphenylamine (2.08 g, 12 mmol), KOH pellets (2.07 g, 37 mmol), copper bronze (1.23 g), and *n*-decane (8 ml) were placed in a two necked flask equipped with a water condenser and nitrogen supply. The reaction mixture was refluxed with a sand bath for 48 h or until only one product spot could be detected by TLC. The reaction mixture was then allowed to cool followed by the addition of methanol (50 cm^3) which precipitated the crude product. The solid was filtered off, dissolved in CH_2Cl_2 and filtered to remove inorganic residues. The product was purified by flash chromatography on silica gel. Light petroleum–dichloromethane (90:10) eluted the *title compound* (1.07 g, 65%) as colourless needles, mp 272–273 °C (lit.,[5b] 269 °C) (from dichloromethane–methanol) (Found: C, 88.6; H, 5.1; N, 5.2. $C_{60}H_{45}N_3$ requires C, 89.2; H, 5.6; N, 5.2%); $\lambda_{max}(HCCl_3)$/nm 341 (log ε 4.81); ν_{max} (KBr)/cm^{-1} 3058m, 3031m, 1587s, 1503s, 1484s, 1443s, 1399m, 1364w, 1330s, 1320s, 1279s, 1175s, 1114m, 1075m, 1048w, 1026m, 956w, 919m, 887m and 822s; δ_H (250 MHz; $CDCl_3$) 7.01 (6H, t, *J* 7.2, H10), 7.12 (12H, d, *J* 8.0, H8), 7.14 (6H, d, *J* 8.5, H5), 7.25 (12H, dd, *J* 7.3 and 8.2, H9), 7.56 (6H, d, *J* 8.5, H4) and 7.68 (3H, s, H1); δ_C (62.9 MHz; $CDCl_3$) 122.8, 123.7, 123.8, 124.3, 127.8, 129.1, 135.2, 141.6, 147.3 and 147.7; *m*/*z* 808 (M^+ + H, 100%).

1,3,5-Tris{4-[(3-methylphenyl)phenylamino]phenyl}benzene2b. Yield 64%; colourless needles, mp 235–236 °C (lit.,[5b] 231 °C) (from dichloromethane–methanol) (Found: C, 88.9; H, 5.8; N, 4.6. $C_{63}H_{51}N_3$ requires C, 89.0; H, 6.1; N, 4.9%); $\lambda_{max}(HCCl_3)$/nm 344 (log ε 4.87); ν_{max} (KBr)/cm^{-1} 3029m, 2949w, 2917s, 2859m, 1592s, 1505s, 1487s, 1445s, 1400w, 1316s, 1278s, 1215m, 1179m, 1115w, 1081w, 1023w, 881w, 834m, 808m, 777m, 753s, 697s and 636m; δ_H (250 MHz; $CDCl_3$) 2.26 (9H, s, Me), 6.83–7.17 (27H, m, Ar), 7.24 (6H, dd, *J* 7.7 and 8.5), 7.54 (6H, d, *J* 8.5) and 7.68 (3H, s); δ_C (62.9 MHz; $CDCl_3$) 21.1, 121.7, 122.7, 123.6, 123.7, 123.8, 124.3, 125.1, 127.7, 128.9, 129.0, 135.1, 139.0, 141.6, 147.4, 147.6 and 147.8; *m*/*z* 850 (M^+ + H, 100%).

1,3,5-Tris{4-[(3,4-dimethylphenyl)phenylamino]phenyl}-benzene 2c. Yield 60%; colourless needles, mp 232–233 °C (from dichloromethane–methanol) (Found: C, 89.2; H, 6.2; N, 4.6. $C_{66}H_{57}N_3$ requires C, 88.9; H, 6.4; N, 4.7%); $\lambda_{max}(HCCl_3)$/nm 346 (log ε 4.88); ν_{max} (KBr)/cm^{-1} 3027w, 2964w, 2919w, 2854w, 1594s, 1507s, 1494s, 1442m, 1409w, 1313m, 1294m, 1275s, 1221m, 1180w, 1154w, 1116w, 1077w, 1014w, 823m, 809m, 753m, 709w and 696m; δ_H (250 MHz; $CDCl_3$) 2.19 (9H, s, Me), 2.24 (9H, s, Me), 6.89–7.14 (24H, m, Ar), 7.25 (6H, dd, *J* 7.3 and 8.5, H9), 7.54 (6H, d, *J* 7.5, H4) and 7.68 (3H, s, H1); δ_C (62.9 MHz; $CDCl_3$) 19.1, 19.8, 122.3, 122.7, 123.1, 123.6, 123.8, 126.4, 127.7, 129.0, 130.4, 131.8, 134.5, 137.6, 141.6 (C2), 145.2, 147.4 and 147.8; *m*/*z* 892 (M^+ + H, 100%).

1,3,5-Tris{4-[(3,5-dimethylphenyl)phenylamino]phenyl}-benzene 2d. Yield 58%; colourless needles, mp >285 °C (from dichloromethane–methanol) (Found: C, 89.2; H, 6.4; N, 4.6. $C_{66}H_{57}N_3$ requires C, 88.9; H, 6.4; N, 4.7%); $\lambda_{max}(HCCl_3)$/nm 345 (log ε 4.84); ν_{max} (KBr)/cm^{-1} 3029m, 2944w, 2916m, 2858w, 1592s, 1504s, 1443m, 1398w, 1380w, 1329s, 1302s, 1273m, 1230m, 1182m, 1154w, 1111w, 1035w, 962w, 836m, 784w, 750m, 697s, 635w and 606w; δ_H (250 MHz; $CDCl_3$) 2.24 (18H, s, Me), 6.70 (3H, s, H14), 6.76 (6H, s, H12), 7.00 (3H, t, *J* 7.3, H10), 7.11–7.14 (12H, m, H5 and H8), 7.25 (6H, dd, *J* 7.3 and 7.9, H9), 7.56 (6H, d, *J* 7.9, H4) and 7.70 (3H, s, H1); δ_C (62.9 MHz; $CDCl_3$) 21.2, 122.4, 122.7, 123.7, 123.8, 124.3, 125.1, 127.8, 129.1, 135.1, 138.9, 141.8, 147.6, 147.6 and 148.0; *m*/*z* 892 (M^+ + H, 100%).

1,3,5-Tris{4-[bis(4-methylphenyl)amino]phenyl}benzene 2e

Yield 48%; colourless needles, mp 272–273 °C (from dichloromethane–methanol) (Found: C, 89.2; H, 6.2; N, 4.8. $C_{66}H_{57}N_3$ requires C, 88.9; H, 6.4; N, 4.7%); $\lambda_{max}(HCCl_3)$/nm 345 (log ε 4.85); ν_{max} (KBr)/cm^{-1} 3026m, 2917m, 2859m, 1602s, 1503s, 1444s, 1320s, 1275s, 1183m, 1111m, 1038w, 1017w, 916w, 881w,

817s, 736w, 711m and 638w; δ_H (250 MHz; $CDCl_3$) 2.33 (18H, s, Me), 7.03–7.21 (30H, m, Ar), 7.53 (6H, d, *J* 8.5, H4) and 7.67 (3H, s, H1); δ_C (62.9 MHz; $CDCl_3$) 20.9 (Me), 122.7, 123.6, 124.7, 127.8, 130.0, 132.6, 134.3, 141.8, 145.3 and 147.8; *m*/*z* 892 (M^+ + H, 100%).

1,3,5-Tris{4-[(2,4-dimethylphenyl)phenylamino]phenyl}benzene 2f

Yield 15%; colourless solid, mp 146–147 °C (from THF–methanol); $\lambda_{max}(HCCl_3)$/nm 339 (log ε 4.83); ν_{max} (KBr)/cm^{-1} 3030m, 2916m, 2855m, 1592s, 1506s, 1492s, 1440m, 1314s, 1290s, 1274s, 1231m, 1179, 821s, 751s, 694s and 547w; δ_H (250 MHz; $CDCl_3$) 2.03 (9H, s, Me), 2.32 (9H, s, Me), 6.89–6.95 (3H, t, *J* 7), 7.00–7.07 (19H, t, *J* 8), 7.18–7.25 (5H, d, *J* 7.5), 7.48–7.52 (5H, d, *J* 8.5) and 7.63 (3H, s); δ_C (62.9 MHz; $CDCl_3$) 18.5, 21.1, 121.1, 121.5, 121.7, 123.4, 127.8, 129.1, 129.6, 132.4, 133.8, 136.0, 136.6, 141.7, 142.5, 147.0, 147.3; *m*/*z* 892 (M^+ + H, 100%); accurate mass: calculated 891.4553, found 891.4527.

N-(2,4-Dimethylphenyl)aniline 6f

KCl (400 g, 5.36 mol), $NaNH_2$ (207 g, 5.36 mol) and 2,4-dimethylaniline (1078 g, 8.90 mol) were heated to 55 °C and stirred under a nitrogen atmosphere for 2 h until all ammonia had been evolved. Benzenesulfonic acid (247 g, 1.56 mol) was then added slowly over a period of 10 min *via* a pressure equalised dropping funnel. The mixture was then heated to 195 °C and stirred for 4 h, cooled to room temperature and a sulfonic acid solution (75.5 g H_2SO_4, 1.00 l H_2O) added and left to stir for 12 h. The mixture was filtered and excess aniline removed under reduced pressure. Reduced pressure distillation (138 °C, 0.20 mmHg) yielded an orange–yellow oil. Recrystallisation from hexane gave the *title compound* (259 g, 74%) as a white crystalline solid, mp 43–44 °C (Found: C, 85.56, H, 7.57; N, 7.1. $C_{14}H_{15}N$ requires C, 85.2; H, 7.7; N, 7.1%); $\lambda_{max}(HCCl_3)$/nm 295 (log ε 4.81); ν_{max} (KBr)/cm^{-1} 3407s, 3046w, 2967w, 2915m, 2854w, 1597s, 1508s, 1496s, 1416m, 1310s, 1215m, 1174m, 1027w, 820m, 746s, 691s and 445m; δ_H (250 MHz; $CDCl_3$) 2.27 (3H, s, Me), 2.36 (3H, s, Me), 5.31 (1H, s, NH), 6.90–7.05 (4H, m, Ar), 7.10 (1H, s, Ar), 7.20–7.40 (3H, m, Ar); δ_C (62.9 MHz; $CDCl_3$) 17.9, 20.8, 116.3, 119.7, 120.9, 127.4, 129.4, 129.9, 131.8, 132.4, 138.3 and 145.0; *m*/*z* 197 (M^+ + H, 100%).

N-Acetyl-*N*-(2,4-dimethylphenyl)aniline 8

Acetanilide (2.00 g, 0.015 mol), 2,4-dimethyliodobenzene (6.96 g, 0.03 mol), copper powder (1.89 g, 0.03 mol), potassium carbonate (8.28 g, 0.06 mol), 18-crown-6 (0.50 g) and *o*-dichlorobenzene (100 ml) were refluxed with stirring in a nitrogen atmosphere for 90 h. The mixture was cooled, filtered and washed twice with deionized water. Dichlorobenzene was removed under reduced pressure. Column chromatography, eluting with CH_2Cl_2 yielded a light yellow oil. Trituration with hexane gave the *title compound* (2.4 g, 67%) as a light brown crystalline solid, mp 115–116 °C (Found: C, 80.3; H, 7.0; N, 5.8. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.2; N, 5.85%); $\lambda_{max}(HCCl_3)$/nm 298 (log ε 3.9); ν_{max} (KBr)/cm^{-1} 3421s, 3208s, 2878m, 2813w, 1685m, 1596m, 1497w, 1475s, 1414m, 1331s, 1304s, 1221m, 1154s, 1092s, 928s, 905m, 753s, 725m, 580s and 551s; δ_H (250 MHz; $CDCl_3$, 223 K) 1.97 (2H, s, Me), 2.15 (2H, s, Me), 2.17 (1H, s, Me), 2.28 (1H, s, Me), 2.30 (1H, s, Me), 2.34 (2H, s, Me) and 7.02–7.35 (8H, m, Ar) (two conformers are present in a 2 : 1 ratio); δ_C (62.9 MHz; $CDCl_3$, 223 K) 18.4, 18.8, 21.5, 23.6, 24.5, 125.7, 125.9, 127.4, 127.6, 128.0, 128.1, 128.2, 129.0, 129.5, 129.8, 132.2, 132.7, 135.2, 135.7, 138.0, 138.0, 138.8, 141.0, 143.1, 171.2 and 171.5 (two overlapping peaks are present); δ_H (250 MHz; $CDCl_3$, 293 K) 1.92 (3H, s, Me), 2.18 (3H, s, Me), 2.37 (3H, s, Me), 7.05 (4H, s, Ar) and 7.31 (4H, s, Ar); *m*/*z* 239 (M^+ + H, 100%).

Deprotection to *N*-(2,4-dimethylphenyl)aniline 6f

N-Acetyl-*N*-(2,4-dimethylphenyl)aniline **8** (2.40 g, 0.01 mol) was refluxed in 40% ethanolic potassium hydroxide solution for 48 h. The mixture was extracted with CH_2Cl_2 and concentrated *in vacuo*. Purification by chromatography on silica (20 : 80 dichloromethane–light petroleum) yielded a yellow oil that recrystallized from hexane to give the *title compound* (0.99 g, 50%) as a white crystalline solid with identical spectroscopic properties to the previous sample.

(3-Methylphenyl)phenylamine 6b

Compound **6b** was prepared from *N*-phenylbenzenesulfonamide. Method A. KCl (1.24 g, 0.021 mol), $NaNH_2$ (0.81 g, 0.021 mol) and 3-methylaniline (20 g, 0.19 mol) were heated to 50 °C under a nitrogen atmosphere and stirred for 2 h until all ammonia had been evolved. Benzenesulfonamide (0.5 g, 2.15 mmol) was added to the reaction mixture which was then heated at 200 °C for 4 h. After cooling the mixture was dissolved in dichloromethane and washed with an aqueous hydrochloric acid solution (1 M) followed by deionized water. Purification by chromatography on silica (30 : 70 dichloromethane–light petroleum), yielded the *title compound* as a colourless crystalline solid (0.23 g, 54%) mp 30–31 °C; δ_H (250 MHz; $CDCl_3$) 2.32 (3H, s, Me), 5.65 (1H, br s, NH), 6.74–6.78 (1H, d, *J* 7.5, Ar), 6.87–6.96 (3H, m, Ar), 7.04–7.10 (2H, m, Ar), 7.13–7.19 (1H, m, Ar) and 7.23–7.31 (2H, m, Ar); δ_C (62.9 MHz; $CDCl_3$) 21.6, 115.0, 117.9, 118.5, 120.9, 121.9, 129.2, 129.4, 139.3, 143.1 and 143.3.

Attempted rearrangement of *N*-phenylbenzenesulfonamide

N-Phenylbenzenesulfonamide (0.50 g, 2.15 mmol), $NaNH_2$ (0.08 g, 2.15 mmol) and 1-methylpyrrolidin-2-one (25 g, 0.25 mol) were heated at 200 °C for 6 h with stirring under a nitrogen atmosphere. After cooling the reaction mixture was diluted with CH_2Cl_2, extracted with aqueous hydrochloric acid solution (1 M) followed by deionized water. Column chromatography eluting with dichloromethane yielded the *starting material* (0.39 g, 78%) with identical spectroscopic properties.

1,3,5-Tris(arylamino)benzenes

1,3,5-Tris(phenylamino)benzene 17a. Method A. This was prepared in an analogous manner to the literature procedure with some modifications. Anhydrous phloroglucinol (5.0 g, 40 mmol), aniline (16.6 g, 178 mmol) and iodine (0.2 g, 2%) were placed in a flask and connected to a distillation apparatus. The mixture was heated at 190 °C with a sand bath for 8 h to drive off water. The mixture was then allowed to cool and was diluted with methanol which precipitated the crude product. Excess aniline was removed by washing with methanol until the filtrate was virtually clear. The *title compound* (10.5 g, 75%) was obtained as pale brown needles, mp 200–201 °C (from dichloromethane–methanol) (Found: C, 82.3; H, 5.8; N, 11.9. $C_{24}H_{21}N_3$ requires C, 82.0; H, 6.0; N, 12.0%); $\lambda_{max}(HCCl_3)$/nm 298 (log ε 4.38); ν_{max} (KBr)/cm^{-1} 3384s, 3374s, 3033m, 1615w, 1601w, 1578s, 1491s, 1462s, 1433m, 1407s, 1299s, 1248s, 1192w, 1170s, 1073w, 992m, 958w, 895m, 826w, 753s, 722m, 699w, 637w and 612w; δ_H (250 MHz; $CDCl_3$) 5.61 (3H, s, NH), 6.33 (3H, s, H1), 6.92 (3H, t, *J* 7.2, H6), 7.08 (6H, d, *J* 8.1, H5) and 7.25 (6H, dd, *J* 7.3 and 8.1, H5); δ_C (62.9 MHz; $CDCl_3$) 99.5, 118.7, 121.2, 129.1, 142.9 and 145.5; *m*/*z* 351 (100%).

Method B. Anhydrous phloroglucinol (5.0 g, 40 mmol) was mixed with aniline (16.6 g, 178 mmol) and concentrated HCl (2 ml). The reaction mixture was stirred at rt for 1 h and then refluxed at 190 °C for 1 h. After being allowed to cool the reaction was treated with concentrated HCl (10 ml) which solidified the mixture. The solid was slurried several times with MeOH to remove excess aniline. The *title compound* (12.5 g, 90%)

was obtained as long colourless needles, mp 201 °C (from dichloromethane–light petroleum) with identical spectroscopic properties to the above material.

1,3,5-Tris(4-phenoxyphenylamino)benzene 17b. Anhydrous phloroglucinol (3.0 g, 24 mmol), 4-phenoxyaniline (19.8 g, 108 mmol), iodine (0.10 g) and decalin were placed in a flask and connected to a distillation apparatus. The reaction mixture was heated with a sand bath at 190 °C for 8 h to drive off water. After being allowed to cool the product was precipitated with methanol and purified by flash chromatography on silica gel. Ethyl acetate–light petroleum (20 : 80) eluted the *title compound* (8.5 g, 57%) as purple flakes, mp 174–175 °C (from dichloromethane–methanol) (Found: C, 80.7, H, 5.0; N, 6.7. $C_{42}H_{33}N_3O_3$ requires C, 80.4; H, 5.3; N, 6.7%); $\lambda_{max}(HCCl_3)$/nm 299 (log ε 4.63); ν_{max} (KBr)/cm^{-1} 3382m, 3356m, 3035w, 1594s, 1503s, 1452m, 1392w, 1278m, 1228s, 1162m, 1106m, 1069w, 1017w, 868w, 852w, 816m, 794m, 747m and 692m; δ_H (250 MHz; $CDCl_3$) 5.53 (3H, s, NH), 6.16 (3H, s, H1), 6.91–7.09 (21H, m, Ar) and 7.33 (6H, dd, *J* 7.3 and 8.5, H9); δ_C (62.9 MHz; $CDCl_3$) 96.7, 118.0, 120.4, 121.4, 122.8, 129.7, 138.3, 146.4, 151.5 and 158.1; *m*/*z* 627 (100%).

General procedure: 1,3,5-tris(diphenylamino)benzene 3a

A method similar to that reported previously was used but with the following modifications and improvements: 1,3,5-tris-(phenylamino)benzene (2.0 g, 6.0 mmol), iodobenzene (6.97 g, 34 mmol), crushed KOH pellets (3.83 g, 68 mmol), copper bronze (2.6 g) and *n*-decane as solvent were added to a two necked flask equipped with a water condenser and nitrogen supply. The reaction mixture was refluxed with a sand bath for 24 h or until only one product spot could be detected by TLC. The reaction mixture was then allowed to cool followed by the addition of methanol (50 cm^3) which precipitated the crude product. The solid was filtered off, dissolved in CH_2Cl_2 and filtered to remove inorganic residues. The product was purified by flash chromatography on silica gel. Light petroleum–dichloromethane (85 : 15) eluted the *title compound* (2.25 g, 68%) as colourless needles, mp 259–260 °C (lit.,[5a] 257 °C) (from dichloromethane–methanol) (Found: C, 86.8; H, 5.5; N, 7.2. $C_{42}H_{33}N_3$ requires C, 87.0; H, 5.7, N, 7.3%); $\lambda_{max}(HCCl_3)$/nm 304 (log ε 4.75); ν_{max} (KBr)/cm^{-1} 3057w, 3029w, 1577s, 1490s, 1464s, 1437m, 1318m, 1286m, 1243s, 1171m, 1148m, 1074w, 1036w, 830w, 754m, 695s, 631m and 620m; δ_H (250 MHz; $CDCl_3$) 6.42 (3H, s, H1), 6.91 (6H, tt, *J* 1.3 and 7.1, H6), 7.03 (12H, dd, *J* 1.2 and 8.3, H4) and 7.16 (12H, m, H5); δ_C (62.9 MHz; $CDCl_3$) 114.5, 122.6, 124.0, 129.0, 147.4 and 149.1; *m*/*z* 579 (M$^+$, 100%).

1,3,5-Tris[(3-methylphenyl)phenylamino]benzene 3b. Yield 72%; colourless solid, mp 183–184 °C (lit.,[5a] 183 °C) (from dichloromethane–methanol) (Found: C, 86.9; H, 6.3; N, 6.5. $C_{45}H_{39}N_3$ requires C, 86.9; H, 6.3; N, 6.8%); $\lambda_{max}(HCCl_3)$/nm 304 (log ε 4.74); ν_{max} (KBr)/cm^{-1} 3060w, 3030m, 2949w, 2919w, 2858w, 1579s, 1489s, 1461s, 1294s, 1254s, 1189m, 1170m, 1043w, 893w, 801w, 778m, 757m, 723w, 694s, 651w and 627w; δ_H (250 MHz; $CDCl_3$) 2.22 (9H, s, Me), 6.43 (3H, s, H1), 6.73–7.20 (27H, m, Ar); δ_C (62.9 MHz; $CDCl_3$) 21.5, 114.6, 121.2, 122.4, 123.5, 123.9, 124.5, 128.9, 129.0, 138.8, 147.2, 147.4 and 149.0; *m*/*z* 621 (M$^+$, 100%).

1,3,5-Tris[(4-methylphenyl)phenylamino]benzene 3c. Yield 49%; colourless needles, mp 214–215 °C (lit.,[5a] 198 °C) (from dichloromethane–methanol) (Found: C, 87.4; H, 6.2; N, 6.6. $C_{45}H_{39}N_3$ requires C, 86.9; H, 6.3; N, 6.8%); $\lambda_{max}(HCCl_3)$/nm 304 (log ε 4.74); ν_{max} (KBr)/cm^{-1} 3060w, 3030w, 2920w, 2858w, 1579s, 1507s, 1464m, 1444m, 1315m, 1287s, 1247s, 1176w, 1146w, 1112w, 1037w, 816m, 722m, 694m and 614w; δ_H (250 MHz; $CDCl_3$) 2.29 (9H, s, Me), 6.41 (3H, s, H1), 6.89 (3H, t, *J* 7.1, H6), 6.92–7.04 (18H, m, Ar) and 7.16 (6H, dd, *J* 7.3 and 8.5, H5); δ_C (62.9 MHz; $CDCl_3$) 20.8, 113.8, 121.9, 123.1, 124.6, 128.9, 129.7, 132.5, 144.7, 147.5 and 149.0; *m*/*z* 621 (M$^+$, 100%).

1,3,5-Tris[(3,4-dimethylphenyl)phenylamino]benzene 3d. Yield 71%; colourless needles, mp 232–233 °C (from dichloromethane–methanol) (Found: C, 87.2; H, 6.8; N, 6.2. $C_{48}H_{45}N_3$ requires C, 86.8; H, 6.8; N, 6.3%); $\lambda_{max}(HCCl_3)$/nm 306 (log ε 4.79); ν_{max} (KBr)/cm^{-1} 3059w, 3014m, 2966m, 2916m, 2856m, 1578s, 1495s, 1461s, 1447s, 1298s, 1252s, 1210s, 1177m, 1145m, 1075w, 1045w, 1018w, 1000w, 902w, 813m, 764m, 715m, 692s and 626m; δ_H (250 MHz; $CDCl_3$) 2.16 (9H, s, Me), 2.20 (9H, s, Me), 6.41 (3H, s, H1), 6.80 (3H, dd, *J* 2.2 and 8.1), 6.85–6.99 (9H, m, Ar), 7.02 (6H, dd, *J* 1.1 and 8.4, H4), 7.15 (6H, tt, *J* 7.3 and 8.5, H5); δ_C (62.9 MHz; $CDCl_3$) 19.1, 19.9, 113.9, 121.7, 122.2, 123.2, 125.8, 128.8, 130.2, 131.2, 137.2, 145.0, 147.7 and 148.9; *m*/*z* 663 (M$^+$, 24%).

1,3,5-Tris[(3,5-dimethylphenyl)phenylamino]benzene 3e. Yield 69%; colourless solid, mp 208–209 °C (from dichloromethane–light petroleum) (Found: C, 86.9; H, 6.6; N, 6.3. $C_{48}H_{45}N_3$ requires C, 86.8; H, 6.8; N, 6.3%); $\lambda_{max}(HCCl_3)$/nm 306 (log ε 4.79); ν_{max} (KBr)/cm^{-1} 3032m, 2950m, 2915m, 2858m, 1576s, 1489s, 1465s, 1440s, 1379m, 1329s, 1273m, 1245s, 1203s, 1155m, 1072m, 1029m, 870w, 838w, 804w, 766m, 729w and 701s; δ_H (250 MHz; $CDCl_3$) 2.19 (18H, s, Me), 6.42 (3H, s, H1), 6.58 (3H, s, H10), 6.65 (6H, s, H8), 6.91 (3H, t, *J* 7.3, H6), 7.02 (6H, d, *J* 8.6, H4) and 7.16 (6H, dd, *J* 7.3 and 8.5, H5); δ_C (62.9 MHz; $CDCl_3$) 21.4, 114.8, 121.8, 122.2, 123.7, 124.5, 128.9, 138.5, 147.1, 147.6 and 148.9; *m*/*z* 663 (M$^+$, 100%).

1,3,5-Tris[(2,4-dimethylphenyl)phenylamino]benzene 3f. Yield 53%; colourless solid, mp 87 °C (from dichloromethane–methanol) (Found: C, 87.0; H, 6.6; N, 6.3. $C_{48}H_{45}N_3$ requires C, 86.8; H, 6.8; N, 6.3%); $\lambda_{max}(HCCl_3)$/nm 301 (log ε 4.97); ν_{max} (KBr)/cm^{-1} 3033m, 1583s, 1493s, 1464s, 1442s, 1294s, 1253s, 1228s, 1159w, 739m and 692s; δ_H (250 MHz; $CDCl_3$) 1.91 (9H, s, Me), 2.28 (9H, s, Me), 6.12 (3H, s, Ar), 6.82–6.91 (18H, m, Ar) and 7.03–7.09 (6H, t, *J* 7.5 and 7.5); δ_C (62.9 MHz; $CDCl_3$) 18.3, 21.0, 109.2, 120.3, 127.8, 128.6, 129.2, 132.0, 135.5, 136.1, 142.4, 147.2 and 148.1; *m*/*z* 663 (M$^+$, 100%).

1,3,5-Tris[(3-chlorophenyl)phenylamino]benzene 3g. Yield 30%; colourless solid, mp 176–177 °C (from dichloromethane–light petroleum) (Found: C, 73.04; H, 4.25; N, 6.22. $C_{42}H_{30}N_3Cl_3$ requires C, 73.9; H, 4.4; N, 6.2%); $\lambda_{max}(HCCl_3)$/nm 302 (log ε 4.93); ν_{max} (KBr)/cm^{-1} 3057m, 3035m, 1583s, 1565s, 1493s, 1473s, 1423m, 1283s, 1239s, 1150m, 1076m, 947w, 759s and 701s; δ_H (250 MHz; $CDCl_3$) 6.37 (3H, s), 6.85–6.88 (6H, d, *J* 7.5), 6.95–7.10 (15H, m) and 7.19–7.25 (6H, t, *J* 7.5 and 7.5); δ_C (62.9 MHz; $CDCl_3$) 114.6, 121.2, 122.4, 123.0, 123.8, 124.8, 129.4, 130.0, 134.6, 146.4, 148.6 and 148.7; *m*/*z* 682 (M$^+$, 100%).

1,3,5-Tris[(3-methylphenyl)(4-phenoxyphenyl)amino]benzene 3h. The same general procedure above was followed but 1,3,5-tris(4-phenoxyphenylamino)benzene **17b** was used in place of 1,3,5-tris(phenylamino)benzene **17a**. Yield 51%; colourless needles, mp 153–154 °C (from dichloromethane–methanol) (Found: C, 84.0; H, 5.4; N, 4.7. $C_{63}H_{51}N_3O_3$ requires C, 84.3; H, 5.7; N, 4.7%); $\lambda_{max}(HCCl_3)$/nm 307 (log ε 4.84); ν_{max} (KBr)/cm^{-1} 3037m, 2918w, 2861w, 1588s, 1573s, 1501s, 1487s, 1462s, 1306m, 1290m, 1259s, 1228s, 1191s, 1163m, 870m, 837m, 780m, 749m, 729m and 691s; δ_H (250 MHz; $CDCl_3$) 2.22 (9H, s, Me), 6.33 (3H, s, H1), 6.73 (3H, d, *J* 7.0), 6.86–7.10 (30H, m, Ar) and 7.32 (6H, dd, *J* 7.5 and 8.3); δ_C (62.9 MHz; $CDCl_3$) 21.6, 112.3, 118.4, 119.8, 120.6, 123.0, 124.0, 126.3, 128.8, 129.7, 138.7, 143.0, 147.3, 149.1, 152.5 and 157.7 (one overlapping resonance); *m*/*z* 663 (M$^+$, 100%).

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