



Polyaromatic amines. Part 3: Synthesis of poly(diarylamino)styrenes and related compounds

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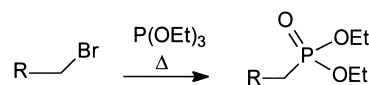
Abstract—The title compounds were synthesised and characterised as part of a study into new aromatic amines for charge transporting materials. Compounds **12–16**, **20–24** and **27–34** are alkene linked triaryl amines, compounds **35–36** are hydrazone derivatives and compounds **38–41** are pyrrole substituted triaryl amines. Each compound was characterised by cyclic voltammetry. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

In previous papers we have reported the synthesis and full spectroscopic characterisation of a series of derivatives of 1,3,5-tris[4-(diarylamino)phenyl]benzene, 1,3,5-tris(diarylamino)benzene, 4,4',4''-tris[*N*-(aryl)-*N*-phenylamino]triphenylamine, *N,N*-bis{4-[*N*-(aryl)-*N*-phenylamino]}-diphenyltolyl amine and *N,N,N',N'*-tetraaryl-*o*-phenylene-diamine derivatives.^{1,2} These and related polyaromatic amines are of interest owing to their potential applications in electrophotography and electroluminescent devices.^{3–5} In these devices positive holes are injected into a thin film of the aromatic amine which is dispersed at high concentration in a binding resin. The charge is transported through the film by positive holes hopping between molecules. Efficient hole transporting ability requires the facile oxidation of aromatic amines to stable radical cations. A good aromatic amine for a charge transport layer should disperse well, form a radical cation that does not decompose and it should form reversibly. Reversible oxidation in solution may be an indicator of radical cation stability for a solid state device and the oxidation potential may indicate the ease with which holes can be injected into the layer. In the search for new potential charge transport materials we have prepared and characterised some further series of aromatic amines in which the amines are linked together by alkenes and hydrazones. The replacement of di- or tri-aryl amines with an electron rich pyrrole group has also been investigated.

2. Results and discussion

Compounds **12–15** were prepared by a Wadsworth–Emmons condensation of the bis-phosphonate **2** with the aromatic aldehydes **8–11**, respectively, using NaH as base.⁶ Phosphonates **1–5** required for stilbene syntheses were prepared by an Arbusov reaction between the appropriate benzylbromide and triethylphosphite^{7,8} (Scheme 1). Benzylic bis-bromide **6** and tris-bromide **7** were prepared by free radical bromination.^{9,10} Aromatic aldehydes **8–11** were prepared by a Vilsmeier formylation reaction of the corresponding triarylamine with DMF and POCl₃¹¹ (Scheme 2). Compounds **12–15** were prepared by a Wadsworth–Emmons condensation of the bis-phosphonate **2** with the aromatic aldehydes **8–11**, respectively using NaH as base⁶ (Scheme 3). The stilbene **16** with a longer biphenyl spacer was prepared by a Wadsworth–Emmons condensation between phosphonate **4** and aldehyde **9**. In each condensation only the thermodynamically favoured *trans* alkene was formed. Stilbene **20** was prepared as a mixture of isomers from a Wittig reaction between phosphonium salt **19** and aldehyde **9**. Treatment of the benzyl alcohol derivative **17** with 48% HBr failed to give the arylbromide **18**. Presumably because of its reactivity, owing to the *para* amino group, the alcohol equilibrates with the bromide so the reaction never goes to completion or



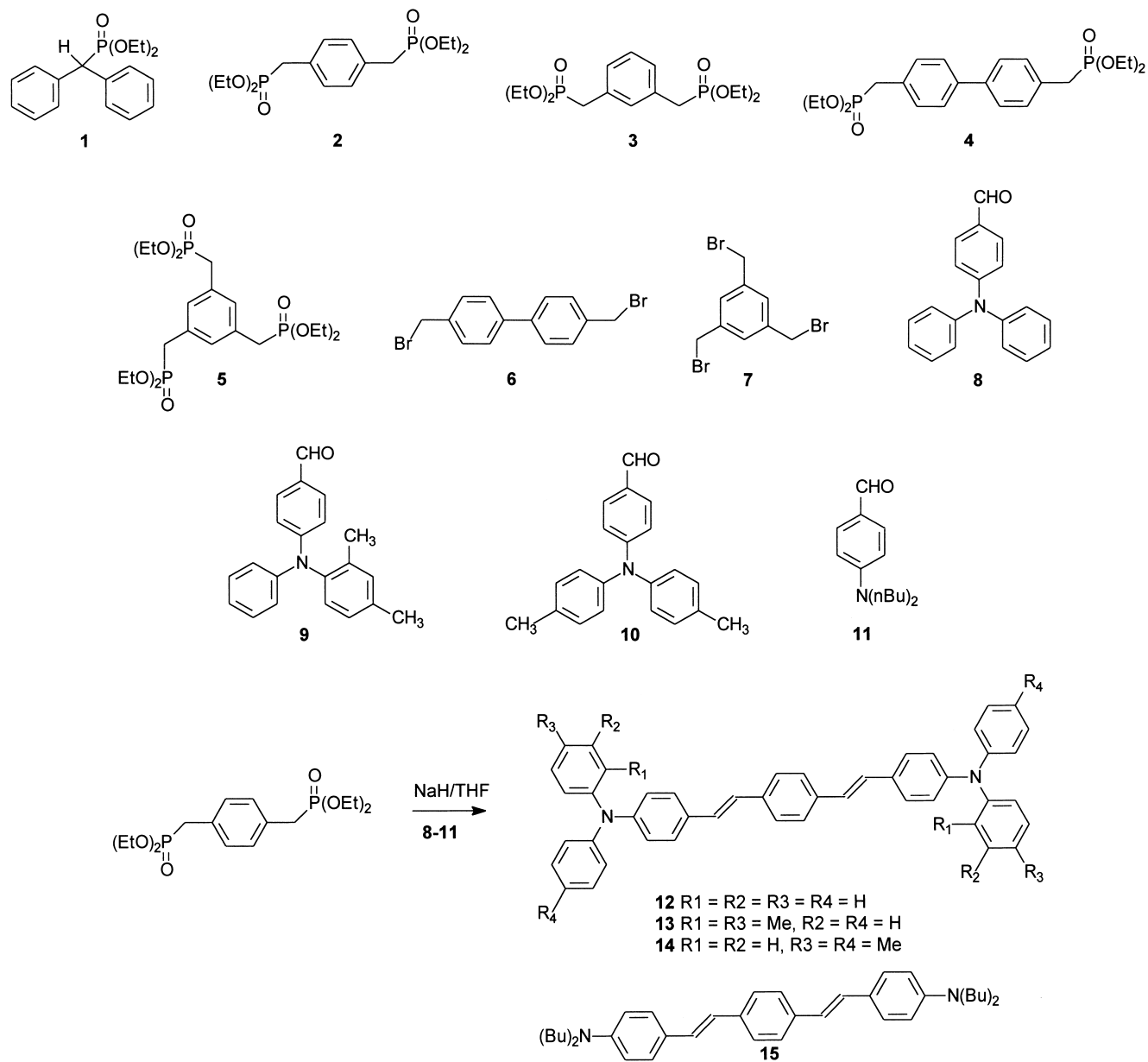
Scheme 1.



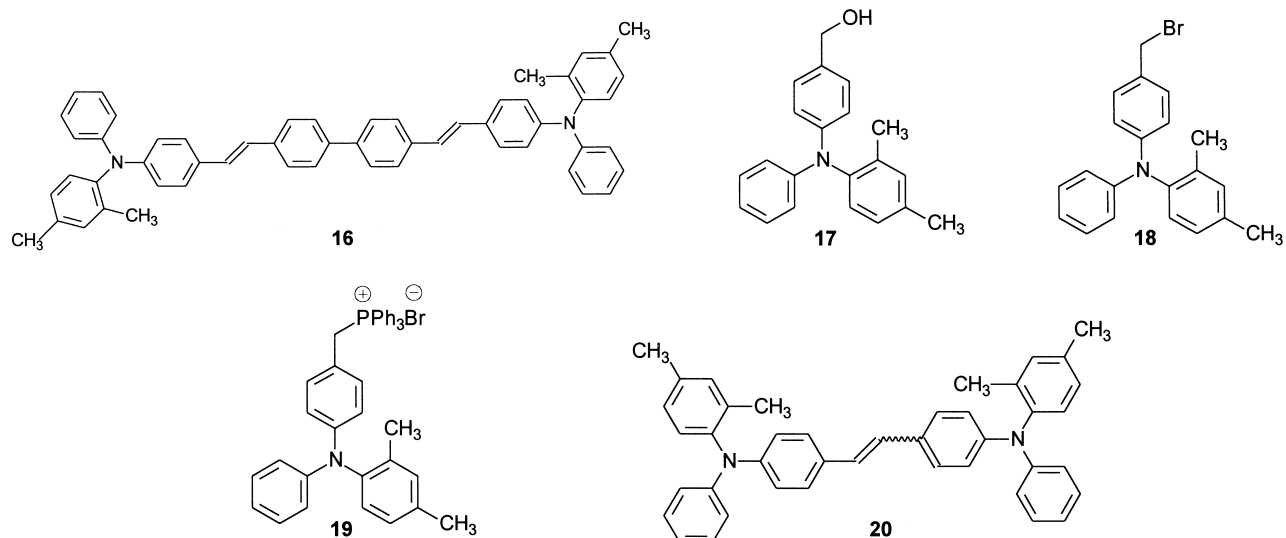
Scheme 2.

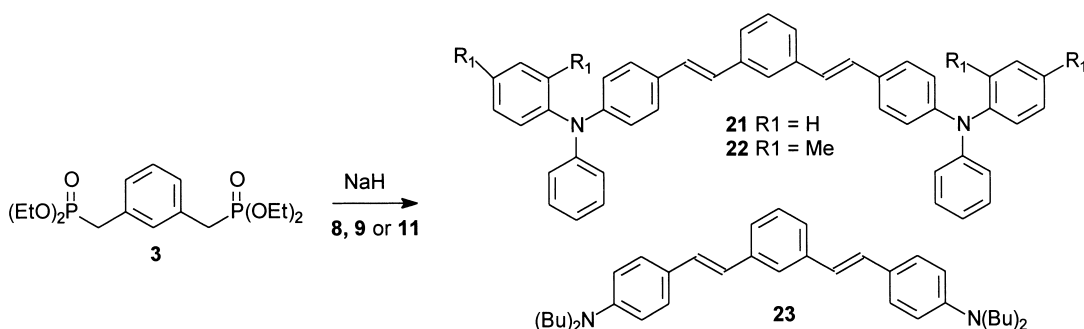
Keywords: polyaromatic amines; benzophenone; recrystallisation.

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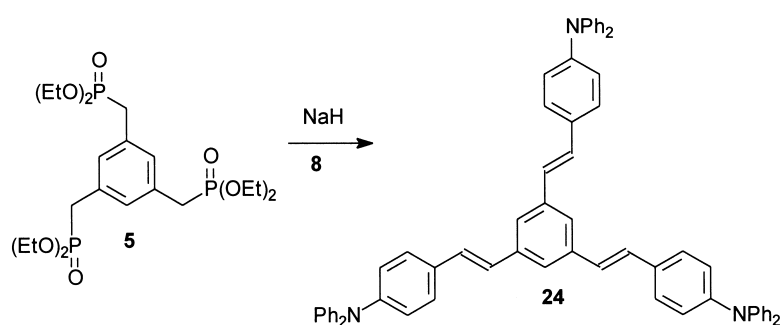


Scheme 3.

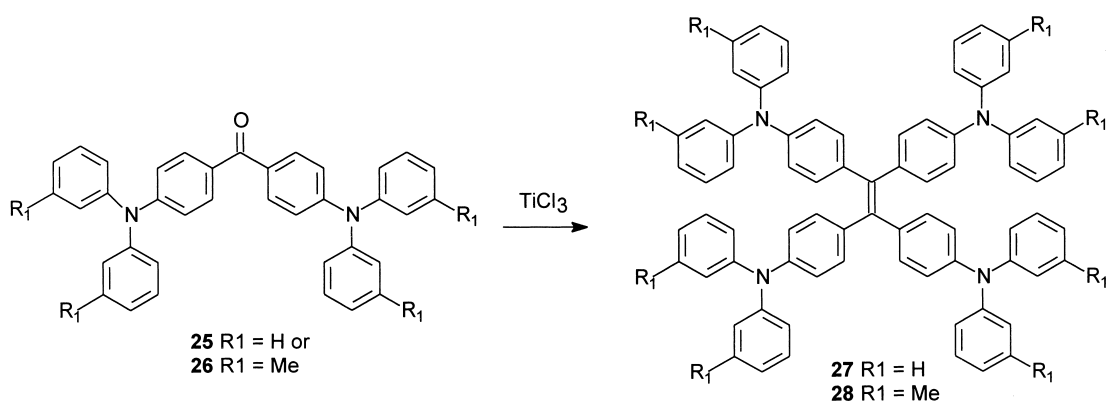




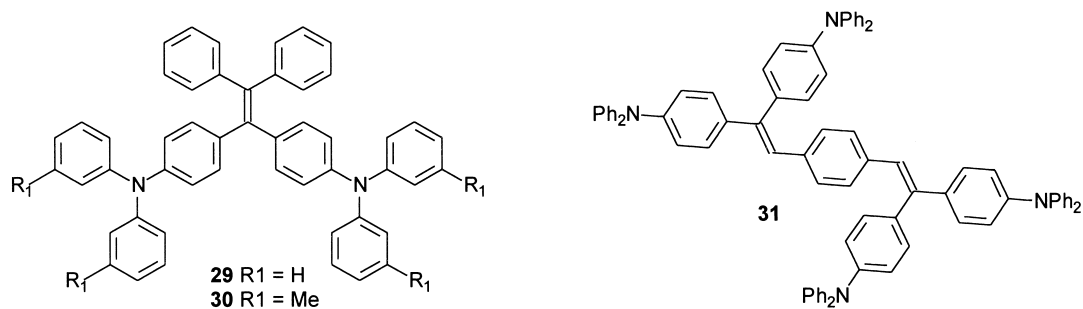
Scheme 4.



Scheme 5.

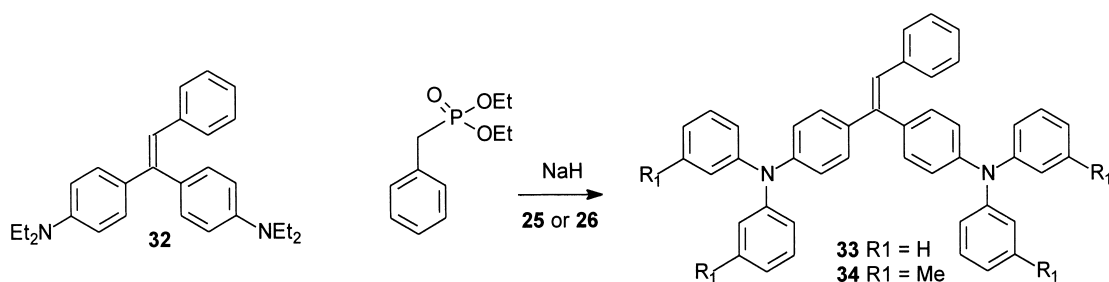


Scheme 6.

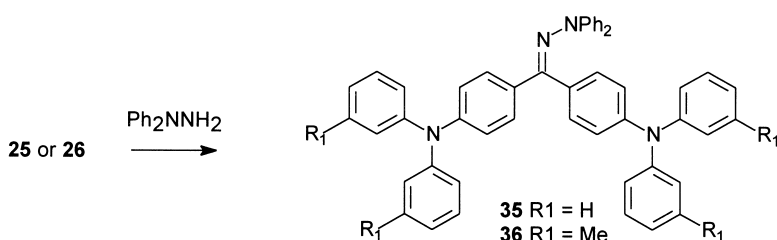


further side reactions occur. To prepare the phosphonium salt **19**, aryl alcohol **17** was heated with PPh₃HBr in CHCl₃. This generates the benzylic bromide **18** in situ which is then intercepted by PPh₃. The *meta* linked stilbenes **21**–**23** were prepared by a Wadsworth–Emmons condensation of bis-phosphonate **3** with aryl aldehydes **8**, **9** and **11**, respectively (Scheme 4). The tris-stilbene **24** was prepared by a Wadsworth–Emmons condensation of tris-phosphonate **5**

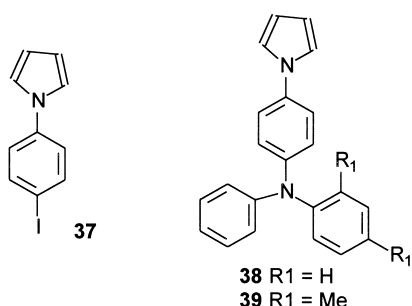
with aryl aldehyde **8** (Scheme 5). The tetra-substituted derivatives **27** and **28** were prepared by a TiCl₃ McMurry cross-coupling reaction between ketones **25** and **26**, respectively^{12,13} (Scheme 6). The ketones were prepared by copper catalysed Ullmann arylations of commercial 4,4'-diaminobenzophenone. The related stilbenes **29** and **30** were prepared by either a mixed McMurray coupling reaction between benzophenone and either ketone **25** or **26** or by the



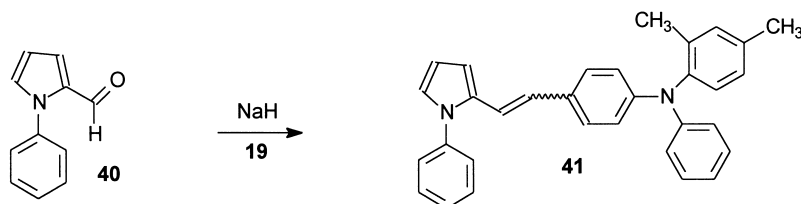
Scheme 7.



Scheme 8.



condensation of benzhydryl magnesium bromide with ketones **25** and **26**. Compound **31** was prepared by a Wadsworth–Emmons condensation between bis-phosphonate **2** and ketone **25**. Compound **32** was prepared by the addition of benzyl magnesium bromide to 4,4'-bis(*N,N*-diethylamino)benzophenone followed by elimination of water with 48% HBr in acetic acid. Compounds **33** and **34** were prepared by a Wadsworth–Emmons condensation between diethylbenzyl phosphonate and ketones **25** or **26** (Scheme 7). Hydrazones **35** and **36** were prepared by the condensation of 1,1-diphenylhydrazine with ketones **25** and **26**, respectively (Scheme 8). Arylpyrroles **38** and **39** were prepared by Ulmann coupling of 4-iodophenylpyrrole **37** with a diarylamine. Arylpyrrole **41** was prepared as a mixture of *cis* and *trans* isomers by condensation of phosphonium salt **19** with the pyrrole aldehyde **40**¹⁴ (Scheme 9). The isomers were separated by flash chromatography.



Scheme 9.

3. Cyclic voltammetry

The methods used have been described previously.² Data is summarised in Table 1. The data for triphenylamine (TPA) and 4,4'-bis[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]biphenyl (TPD) is included for comparison and has been discussed previously.² The stilbene linked amines **12–14** and **16** show a single reversible redox couple. Compound **15**, which possesses two dibutylamino groups, is more easily oxidised but the oxidation is not reversible. Therefore radical cations formed from amines substituted with alkyl groups are less stable than radical cations formed from amines substituted with aryl rings under these conditions. Despite the fact that two oxidisable amines are present in each compound only one redox event is observed. This indicates that after the first oxidation, if the molecule undergoes a second oxidation, it must occur at the same oxidation potential as the first which shows that the two nitrogen centres are isolated from each other. CV of compounds **12–14** also shows the stability conferred upon the radical cations if the aryl rings of the amines are substituted with *para* methyl groups. The unsubstituted derivative **12** shows a reversible redox couple that is stable upon repeated scans if the scan potential is not increased above 1.0 V. Potentials beyond 1.0 V result in a further reversible oxidation at 1.06 V that eventually becomes the predominant redox event. Presumably dimerisation or polymerisation results in a new redox active species. In comparison the methyl substituted derivatives **13** and **14**

Table 1. Summary of electrochemical analyses. Oxidation potentials, E_{pa} , reduction potentials, E_{pc} , and peak current density ratio's i_{pc}/i_{pa} of triarylamines versus SCE

Compound	First redox			Second redox			Third redox		
	E_{pa}	E_{pc}	i_{pc}/i_{pa}	E_{pa}	E_{pc}	i_{pc}/i_{pa}	E_{pa}	E_{pc}	i_{pc}/i_{pa}
TPA	1.21	0.91	0.57						
TPD	0.81	0.70	1.0	1.03	0.93				
12	0.82	0.77	1.0						
13	0.81	0.72	1.0						
14	0.75	0.70	1.0						
15	0.59	0.52	0.49						
16	0.87	0.78	0.85						
20	0.72	0.63	1.0	0.79	0.72	0.97			
21	0.88								
22	0.83								
23	0.60								
24	0.84								
27	0.53	0.48	1.0						
28	0.48	0.44	1.0	1.25	1.16	0.98			
29	0.85	0.78	1.0	1.07	0.95	0.59	1.43		
30	0.82	0.75	0.82	1.03	0.88	0.75	1.41	1.29	0.33
31	0.74	0.70	1.0						
32	0.63			1.11	1.04	1.0			
33	0.92			0.97			1.27		
34	0.88			1.12			1.23		
35	0.76	0.69	1.0						
36	0.76	0.67	1.0						
38	0.99	0.89	1.0						
39	0.96	0.87	1.0						
41	0.66			1.24					

exhibit stable redox couples for scan potentials up to 1.5 V. Stilbene **20**, as a mixture of isomers, in contrast to compounds **12–16**, shows two reversible redox couples. The double bond between the triarylamines keeps the amines in closer proximity so there is greater electronic communication between them. The meta linked amines **21–24** do not show reversible oxidation potentials. This is unusual because even though the amines are not conjugated, single triarylamines such as TPA often display reversible oxidation potentials. The alkenes **27** and **28**, which contain four triarylamine units show particularly low first oxidation potentials of 0.53 and 0.48 V compared to other compounds in Table 1. Compound **28** also has the largest potential gap, we have found between the first and second oxidation states of 770 mV. This compares with the value of 220 mV for TPD. Our previous studies described compounds with values in the range 0–530 mV. High intramolecular charge mobility might form the basis for a good charge transporting material. This suggests that the cation has a good degree of intramolecular charge mobility which is probably a consequence of the close proximity in space of the amines. The aryl rings attached to the central alkene will be twisted out of planarity owing to their steric bulk. This should restrict charge conjugation through the π -system. However, the close proximity in space of the amines might favour charge delocalisation by a ‘through space’ mechanism. A molecule which provides precedent for such a kind of through space conjugation is norbornadiene which has a longer wavelength absorption in the UV which is absent in norbornene. Compounds **29** and **30** which are of similar structure but only possess two triarylamines, show higher first oxidation potentials of 0.85 and 0.82 V and poor reversibility. The higher oxidation potentials provides evidence that through space conjugation lowers the oxidation potentials of compounds **27** and **28**. Compounds

32–34 which possess a trisubstituted alkene show no reversible oxidations. Compound **32** has a low first oxidation potential but this is due to the presence of the diethylamino groups. A possible decomposition pathway might be cyclisation to give a new six membered ring but this might also have occurred for compounds **27–30** so it is difficult to predict the structure of the decomposition products. Compounds **35** and **36** are both hydrazones which display reversible oxidations. The pyrroles **38** and **39** show reversible oxidation states with higher oxidation potentials of 0.99 and 0.96 V. *N,N,N',N'*-Tetra(4-tolyl)-*p*-phenylenediamine has a first oxidation potential of 0.51 V.² Replacement of the pyrrole moiety with a diarylamine almost doubles the oxidation potential. However the *trans* isomer of the stilbene type pyrrole **41** shows a low first oxidation state at 0.66 V but at higher potentials decomposition occurs. This compares with a value of 0.72 mV for compound **20** in which the *N*-phenylpyrrole group has been replaced with a triarylamine. Pyrrole is an electron rich π -excessive compound and when conjugated via the π -system can serve as a replacement for a triarylamine in terms of producing a compound with a low oxidation potential.

In conclusion a series of new aromatic amines of different structural types have been prepared and characterised by cyclic voltammetry. Compound **28** shows a large potential gap of 770 mV indicating good intramolecular charge mobility.

4. Experimental

4.1. General

For general details see part 1 of this series.¹

4.1.1. Diethoxydiphenylmethylphosphonate 1. Benzhydryl bromide (24.5 g, 99.0 mmol) and triethyl phosphite (25 mL, 150 mmol) were heated to reflux at 185°C for 3 h with stirring. The resulting clear brown oil was then distilled under reduced pressure. Excess triethyl phosphite was collected at 69°C (1.5 mm Hg) and a further fraction of mixed boiling points up to 150°C (1.5 mm Hg). The major fraction was collected as a colourless oil at 185°C (1.5 mm Hg). Column chromatography, eluting with dichloromethane/light petroleum (10:90), gave a clear viscous oil. Recrystallisation from hexane yielded the title compound (9.72 g, 35%) as a colourless solid, mp 42–44°C. (lit. 40–41°C)⁸ (Found: C, 67.0, H, 7.0. C₁₇H₂₁PO₃ requires C, 66.9, H, 6.9%); ν_{\max} (KBr)/cm⁻¹ 3064m, 2982s, 2907m, 1597m, 1495m, 1452m, 1395m, 1240s, 1054s, 1027s, 967s, 744m and 700s; δ_{H} (250 MHz; CDCl₃) 1.04–1.10 (6H, t, $J=7.1$ Hz, CH₃), 3.88–3.92 (4H, m, CH₂), 4.36–4.44 (1H, d, $J=24.1$ Hz, PCH), 7.15–7.30 (6H, m, Ar) and 7.50–7.54 (4H, d, $J=8.2$ Hz, Ar); δ_{C} (62.9 MHz; CDCl₃) 16.2 (d, $J_{\text{PC}}=5.9$ Hz), 52.4–50.3 (d, $J_{\text{PC}}=137.7$ Hz), 62.6 (d, $J_{\text{PC}}=6.8$ Hz), 127.2, 128.6, 129.5 (d, $J_{\text{PC}}=4.9$ Hz) and 136.9 (d, $J_{\text{PC}}=7.8$ Hz); δ_{P} (101 MHz, CDCl₃) 25.4; m/z 304 (M⁺, 50%).

4.1.2. 1,4-Bis(diethoxyphosphinylmethyl)benzene 2. General procedure as for **1** α,α' -dibromo-*p*-xylyl (12.0 g, 45.5 mmol) and triethyl phosphite (22.7 g, 137.0 mmol) were refluxed at 185°C for 6 h. Yield 97%; white crystalline solid, mp 74–75°C (from cooling colourless oil obtained from distillation), (lit. 70–72°C)⁷ (Found: C, 50.9; H, 7.25. C₁₆H₂₈O₆P₂ requires C, 50.8; H, 7.5%); ν_{\max} (KBr)/cm⁻¹ 2983s, 2952m, 2909m, 1514m, 1480w, 1439m, 1391m, 1368w, 1242s, 1161w, 1100m, 1033s, 962s, 863m, 801m, 743m, 708m, 655w and 560m; δ_{H} (250 MHz; CDCl₃) 1.16–1.22 (12H, t, $J=7.2$ Hz, CH₃), 3.04–3.12 (4H, d, $J=22.4$ Hz, P–CH₂), 3.90–4.01 (8H, dq, $J=7.2, 8.3$ Hz, CH₂) and 7.06–7.23 (4H, s, Ar); δ_{C} (62.9 MHz; CDCl₃) 16.3, 34.5–32.2 (d, $J_{\text{PC}}=138.7$ Hz), 62.0 (d, $J_{\text{PC}}=5.9$ Hz) and 129.9, 130.4; δ_{P} (101 MHz; CDCl₃) 26.6; m/z 378 (M⁺, 15%).

4.1.3. 1,3-Bis(diethoxyphosphinylmethyl)benzene 3. General procedure as for **1** α,α' -dibromo-*m*-xylyl (12.0 g, 45.5 mmol) and triethyl phosphite (22.7 g, 137 mmol) were refluxed at 185°C with stirring for 6 h. Yield 87%; colourless oil (230°C, 1.5 mm Hg) (Found: C, 48.2; H, 7.6. C₁₆H₂₈O₆P₂ requires C, 50.8; H, 7.6%) (There was a 2.6% error in the carbon analysis); ν_{\max} (NaCl)/cm⁻¹ 2981m, 2908m, 1606m, 1488m, 1392m, 1247s, 1052s, 1024s, 996s, 844m, 781m and 696m; δ_{H} (250 MHz; CDCl₃) 1.12–1.19 (12H, t, $J=7.2$ Hz, CH₃), 3.03–3.13 (4H, d, $J=22.2$ Hz, P–CH₂), 3.95–4.06 (8H, dq, $J=7.2, 8$ Hz, CH₂) and 7.08–7.22 (4H, m, Ar); δ_{C} (62.9 MHz; CDCl₃) 16.4 (d, $J_{\text{PC}}=2.9$ Hz), 34.7–32.5 (d, $J_{\text{PC}}=138.7$ Hz), 62.2 (d, $J_{\text{PC}}=5.5$ Hz), 128.6 (d, $J_{\text{PC}}=5.5$ Hz), 128.7, 131.2 (d, $J_{\text{PC}}=7.1$ Hz) and 131.9 (d, $J_{\text{PC}}=5.8$ Hz); δ_{P} (101 MHz; CDCl₃): 26.6; m/z 378 (M⁺, 35%).

4.1.4. 4,4'-Bis(diethoxyphosphinylmethyl)-1,1'-biphenyl 4. General procedure as for **1** 4,4'-bis(bromomethyl)-1,1'-biphenyl **6** (2.00 g, 5.92 mmol) and triethyl phosphite (6.0 g, 36.0 mmol) were refluxed at 185°C for 6 h. Yield 93%; yellow crystalline solid, mp 100–103°C (crystallised

on cooling of distillation residues) (lit. 109–110°C)⁷ (Found: C, 57.3, H, 7.1. C₂₂H₃₂O₆P₂ requires C, 58.15, H, 7.1%); ν_{\max} (KBr)/cm⁻¹ 2982m, 2905m, 2867w, 1604w, 1560w, 1503m, 1443w, 1390m, 1368w, 1239s, 1162m, 1098m, 1059s, 1023s, 959s, 859m, 822m, 765m and 728m; δ_{H} (250 MHz; CDCl₃) 1.25–1.19 (12H, t, $J=7.2$ Hz, CH₃), 3.19–3.10 (4H, d, $J=21.7$ Hz, P–CH₂), 4.06–4.00 (8H, dq, $J=7.2, 8.1$ Hz, CH₂), 7.33–7.30 (4H, d, $J=7.5$ Hz) and 7.51–7.48 (4H, d, $J=7.5$ Hz); δ_{C} (62.9 MHz; CDCl₃) 16.3 (d, $J_{\text{PC}}=5.9$ Hz), 34.5–32.3 (d, $J_{\text{PC}}=138.7$ Hz), 62.1 (d, $J_{\text{PC}}=6.9$ Hz), 127.1, 130.2 (d, $J_{\text{PC}}=6.8$ Hz), 130.7 (d, $J_{\text{PC}}=9.8$ Hz) and 139.3 (d, $J_{\text{PC}}=2.0$ Hz); δ_{P} (101 MHz; CDCl₃) 26.6; m/z 454 (M⁺, 100%).

4.1.5. 1,3,5-Tris(diethoxyphosphinylmethyl)benzene 5. General procedure as for **1** 1,3,5-trisbromomesitylene **7** (3.00 g, 8.47 mmol) and triethyl phosphite (6.33 g, 38.1 mmol) were refluxed at 185°C for 6 h. Yield 84%; light yellow oil. ν_{\max} (NaCl)/cm⁻¹ 2982s, 2909s, 2819w, 1602m, 1478w, 1457m, 1368w, 1253s, 1164m, 1097m, 1060s, 963s, 885m and 781m; δ_{H} (250 MHz; CDCl₃) 1.16–1.22 (18H, t, $J=7.1$ Hz, CH₃), 3.18–3.10 (6H, d, $J=22.3$ Hz, P–CH₂), 3.93–4.04 (12H, dq, $J=7.1, 8.2$ Hz, CH₂) and 7.1 (3H, d, $J=7.0$ Hz, Ar); δ_{C} (62.9 MHz; CDCl₃) 16.4 (d, $J_{\text{PC}}=5.3$ Hz), 34.6–32.4 (d, $J_{\text{PC}}=137.7$ Hz), 62.2 (d, $J_{\text{PC}}=6.8$ Hz), 129.9 (d, $J_{\text{PC}}=10.7$ Hz) and 132.2 (d, $J_{\text{PC}}=7.8$ Hz); δ_{P} (101 MHz, CDCl₃): 26.4; m/z 528 (M⁺, 40%).

4.1.6. 4,4'-Bis(bromomethyl)-1,1'-biphenyl 6. 4,4'-Bis-methyl-1,1'-biphenyl (5.00 g, 27.4 mmol), *N*-bromosuccinimide (9.75 g, 54.8 mmol) and α,α' -azoisobutyronitrile (50 mg, as initiator) were heated to reflux at 76°C in dry CCl₄ (100 mL) with stirring for 18 h in the presence of bright light. With two spots predominant by tlc the reaction was ceased and the mixture filtered to remove the succinimide and the filtrate washed (×3) with distilled H₂O and dried over MgSO₄. The solvent was removed under reduced pressure. Solids were recrystallised seven times from hot dichloromethane/hexane to give the title compound as white crystalline flakes (2.32 g, 22%), mp 167–169°C (lit. 171–173°C)¹⁰ δ_{H} (250 MHz; CDCl₃) 4.54 (4H, s, CH₂) and 7.57–7.44 (8H, dd, $J=7.5, 22.8$ Hz, Ar), δ_{C} (62.9 MHz; CDCl₃) 33.3, 127.5, 129.6, 137.2 and 140.6; m/z 339.9 (M⁺, 100%).

4.1.7. 1,3,5-Tris-bromomesitylene 7. Mesitylene (20.0 g, 166 mmol), *N*-bromosuccinimide (90.0 g, 514 mmol) and α,α' -azoisobutyronitrile (50 mg, as initiator) were heated to reflux at 76°C in dry CCl₄ (250 mL) with stirring for 24 h. With two spots predominant on tlc the reaction was ceased and the mixture filtered to remove the succinimide and the filtrate washed with distilled H₂O (×3) and dried over MgSO₄. The solvents were removed under reduced pressure. The resulting yellow oil was dissolved in boiling light petroleum and left to stand in the fridge overnight. The mother liquor was decanted and the white crystalline solid remaining was recrystallised ten times until one spot was isolated by tlc. The title compound (3.72 g, 7%), was obtained as white crystalline needles, mp 104–105°C (from light petroleum), (lit. 101–105°C).⁹ ν_{\max} (KBr)/cm⁻¹ 3023m, 2971w, 1456m, 1434m, 1211s, 1166m, 1120m, 892m, 856w, 703s and 580s; δ_{H} (250 MHz; CDCl₃) 4.44

(6H, s, CH₂) and 7.34 (3H, s, Ar); δ_{C} (62.9 MHz; CDCl₃) 32.2, 129.6 and 139.1; m/z 356 (M⁺, 100%).

4.1.8. 4-[[N-(2,4-Dimethylphenyl)-N-phenylamino]benzaldehyde 9. *N,N*-Diphenyl-(2,4-dimethyl)phenylamine (10.0 g, 36.6 mmol) was dissolved in DMF (16.0 g, 219.0 mmol). Phosphorus oxychloride (5.61 g, 36.6 mmol) was added dropwise and the mixture was then heated at 100°C for 3 h. After cooling the mixture was dissolved in CH₂Cl₂ and washed with a dilute sodium hydrogen bicarbonate solution and then with distilled H₂O (×2). Column chromatography, eluting with dichloromethane gave the title compound (8.0 g, 73%) as light yellow crystals, mp 104–105°C (from dichloromethane/hexane) (Found: C, 83.1; H, 6.2; N, 4.5. C₂₁H₁₉NO requires C, 83.6; H, 6.4; N, 4.65%); ν_{max} (KBr)/cm⁻¹ 3051w, 3007w, 2948w, 2916w, 2810w, 2732m, 1908m, 1683s, 1584s, 1558s, 1505s, 1488s, 1433m, 1378w, 1316s, 1221s, 1161s, 1073m, 1028m, 875w, 821s, 768s, 730s, 701s, 558s and 474m. δ_{H} (250 MHz; CDCl₃) 2.03 (3H, s, Me), 2.35 (3H, s, Me), 6.85–6.88 (2H, d, *J*=9.1 Hz, Ar), 7.04–7.15 (6H, m, Ar), 7.25–7.32 (2H, m, Ar), 7.63–7.67 (2H, d, *J*=9.0 Hz, Ar) and 9.77 (1H, s, CHO). δ_{C} (100.5 MHz; CDCl₃) 19.3, 22.1, 118.4, 125.3, 125.5, 129.4, 129.5, 130.5, 132.5, 133.7, 137.3, 138.2, 142.3, 146.4, 154.1 and 191.4 (one overlapping peak); m/z 301 (M⁺, 100%).

4.1.9. 4-[N,N-Di(4-tolyl)amino]benzaldehyde 10. General procedure as for **9** *N,N*-di(4-tolyl)aniline (1.80 g, 6.59 mmol) was dissolved in DMF (2.89 g, 39.5 mmol). Phosphorus oxychloride (1.01 g, 6.59 mmol) was added dropwise. The mixture was then heated at 100°C for 3 h. Yield 61%; yellow crystalline solid, mp 112–113°C (from hexane) (Found: C, 83.4; H, 6.1; N, 4.5. C₂₁H₁₉NO requires C, 83.7; H, 6.4; N, 4.65%); ν_{max} (KBr)/cm⁻¹ 3028w, 2920w, 2833w, 2817w, 2747w, 1683s, 1589s, 1561m, 1504s, 1435m, 1326s, 1296s, 1266m, 1225s, 1160s, 1117m, 916w, 815s, 795m and 677m; δ_{H} (250 MHz; CDCl₃) 2.34 (6H, s, Me), 6.91–6.96 (2H, d, *J*=8.5 Hz, Ar), 7.04–7.07 (4H, d, *J*=8.5 Hz, Ar), 7.12–7.15 (4H, d, *J*=8.5 Hz, Ar), 7.61–7.65 (2H, d, *J*=8.5 Hz, Ar) and 9.77 (1H, s, CHO); δ_{C} (100.5 MHz; CDCl₃) 21.0, 118.2, 126.4, 128.4, 130.4, 131.4, 135.1, 143.5, 153.7 and 190.4; m/z 301 (M⁺, 100%).

4.1.10. 4-(N,N-Dibutylamino)benzaldehyde 11. *N,N*-Dibutylaniline (20.0 g, 97.4 mmol) was dissolved in DMF (42.72 g, 584 mmol). Cooling to -4°C with a salt ice bath and with continuous stirring phosphorus oxychloride (14.9 g, 97.4 mmol) was added dropwise, while not allowing the temperature to rise above 10°C, resulting in a green solution. The mixture was then heated at 100°C for 3 h until a brown colour had formed. After cooling the mixture was dissolved in CH₂Cl₂ and washed with a dilute sodium hydrogen bicarbonate solution and then with distilled H₂O (×2). Column chromatography, eluting with dichloromethane gave a yellow oil which was distilled under reduced pressure to give the title compound as a yellow oil (16.8 g, 74%), (180°C/0.7 mm Hg) (lit. 176–179°C, 1.5 Torr).¹¹ ν_{max} (KBr)/cm⁻¹ 2956s, 2932s, 2871s, 2803m, 2729m, 2676m, 1685s, 1669s, 1596s, 1554s, 1525s, 1465m, 1436m, 1406m, 1367m, 1314m, 1290m, 1241m, 1224m, 1168s, 1110m, 998w, 926w, 814s, 743w, 639w and 608m. δ_{H} (250 MHz; CDCl₃) 0.93–0.99 (6H, t,

J=7.1 Hz, CH₃), 1.28–1.43 (4H, m, *J*=7.1 Hz, CH₂), 1.52–1.72 (4H, q, *J*=7.2 Hz, CH₂), 3.30–3.36 (4H, t, *J*=8.3 Hz, CH₂), 6.59–6.64 (2H, d, *J*=8.9 Hz, Ar), 7.66–7.70 (2H, d, *J*=9.1 Hz, Ar) and 9.68 (1H, s, CHO). δ_{C} (62.9 MHz; CDCl₃) 13.9, 20.3, 29.3, 50.9, 110.7, 124.6, 132.2, 152.7 and 189.9; m/z 233 (M⁺, 20%).

4.1.11. 1,4-Bis[4-(N,N-diphenylamino)styryl]benzene 12. To 1,4-bis(diethoxyphosphinylmethyl)benzene **2** (0.50 g, 1.30 mmol) in dry THF (20 mL) was added NaH (0.07 g, 3.00 mmol). After initial effervescence the suspension was stirred for 1 h at 50°C under nitrogen. To this diphenylaminobenzaldehyde **8**, (0.70 g, 2.60 mmol) in dry THF (10 mL) was added dropwise and the mixture heated to reflux at 66°C for 2 h. The mixture was cooled and quenched with EtOH. All solvents were then removed under reduced pressure, solids dissolved in CH₂Cl₂, washed in distilled H₂O (×2) and dried over MgSO₄. Column chromatography, eluting with dichloromethane/light petroleum (30:70) yielded a yellow solid. Recrystallisation from dichloromethane/methanol yielded the title compound (0.52 g, 66%) as a yellow crystalline solid, mp 210–211°C (lit. 209–211°C).⁶ λ_{max} (CH₂Cl₂)/nm 305 (log ϵ 5.61) and 409 (6.41); ν_{max} (KBr)/cm⁻¹ 3055w, 3022m, 1589s, 1513m, 1492s, 1422w, 1325m, 1283s, 1174m, 1075w, 961m, 835m, 750s, 695s, 619w and 547m; δ_{H} (250 MHz; CDCl₃) 7.00–7.13 (19H, m), 7.23–7.29 (9H, m), 7.37–7.40 (4H, d, *J*=8.5 Hz, Ar) and 7.46 (4H, s, Ar); δ_{C} (100.6 MHz; CDCl₃) 124.1, 124.6, 125.5, 127.6, 127.7, 128.4, 128.9, 130.3, 132.6, 137.7, 148.4 and 148.6; m/z 616 (M⁺, 16%). Accurate mass: calculated 616.2878, found 616.2872.

4.1.12. 1,4-Bis[4-[N-(2,4-dimethylphenyl)-N-phenylamino]styryl]benzene 13. General procedure as for **12** to 1,4-bis(diethoxyphosphinylmethyl)benzene **2** (1.26 g, 3.40 mmol) in dry THF (20 mL) was added NaH (0.17 g, 7.00 mmol). To this was added 4-(*N*-(2,4-dimethylphenyl)-*N*-phenylamino)benzaldehyde **9** (2.00 g, 6.64 mmol) in dry THF (30 mL) and refluxed at 66°C for 2 h. Yield 66%; yellow crystalline solid, mp 233–234°C (from dichloromethane/hexane) (Found: C, 89.1; H, 6.65; N, 3.9. C₅₀H₄₄N₂ requires C, 89.2; H, 6.6; N, 4.2%); λ_{max} (CH₂Cl₂)/nm 411 (log ϵ 5.79); ν_{max} (KBr)/cm⁻¹ 3054w, 3025m, 2942w, 2914w, 2853w, 1589s, 1511s, 1488s, 1377w, 1307s, 1277s, 1230m, 1174m, 1122w, 1028w, 963s, 832s, 746s, 692s, 615m, 542s, 509w and 474w. δ_{H} (400 MHz; CDCl₃) 2.03 (6H, s, Me), 2.34 (6H, s, Me), 6.87–6.92 (8H, m), 6.96–7.01 (9H, m), 7.02–7.06 (3H, m), 7.16–7.22 (4H, m), 7.29–7.33 (4H, d, *J*=8.9 Hz, Ar) and 7.42 (4H, s, Ar). δ_{C} (100.5 MHz; CDCl₃) 19.5, 22.1, 121.9, 122.7, 122.9, 127.1, 127.5, 128.3, 129.0, 129.2, 130.1, 130.5, 131.2, 133.4, 137.0, 137.3, 137.7, 143.4, 148.1 and 148.2; m/z 672 (M⁺, 20%).

4.1.13. 1,4-Bis[4-[N,N-di(4-tolyl)amino]styryl]benzene 14. General procedure as for **12** to 1,4-bis(diethoxyphosphinylmethyl)benzene **2** (0.69 g, 1.83 mmol) in dry THF (20 mL) was added NaH (0.09 g, 3.65 mmol). To this was added 4-(*N,N*-di(4-tolyl)amino)benzaldehyde **10** (1.10 g, 3.65 mmol) in dry THF (30 mL) and refluxed at 66°C for 2 h. Yield 81%; bright yellow crystalline solid, mp 231–232°C (from dichloromethane/hexane), (lit. 231–233°C)⁶ (Found: C, 88.9; H, 6.2; N, 4.0. C₅₀H₄₄N₂ requires

C, 89.2; H, 6.6; N, 4.2%); λ_{\max} (CH₂Cl₂)/nm: 306 (log ϵ 4.68) and 417 (5.06); ν_{\max} (KBr)/cm⁻¹ 3023m, 2948w, 2918m, 2858w, 1598s, 1504s, 1415w, 1377w, 1320s, 1276s, 1177m, 1108m, 1037w, 958m, 816s and 715m; δ_{H} (250 MHz; CDCl₃) 2.32 (12H, s, Me), 6.91–7.09 (24H, m), 7.33–7.36 (4H, d, $J=8.0$ Hz, Ar) and 7.45 (4H, s, Ar); δ_{C} (62.9 MHz; CDCl₃) 20.9, 122.4, 124.8, 126.2, 126.6, 127.2, 128.0, 129.9, 130.7, 132.8, 136.7, 145.1 and 147.8; m/z 672 (M⁺, 50%).

4.1.14. 1,4-Bis{4-[*N,N*-(dibutylamino)styryl]}benzene 15.

General procedure as for **12** to 1,4-bis(diethoxyphosphinylmethyl)benzene **2** (3.0 g, 7.94 mmol) in dry THF (50 mL) was added NaH (0.48 g, 20.0 mmol). To this was added 4-(*N,N*-dibutylamino)benzaldehyde **11** (3.70 g, 15.6 mmol) in dry THF (50 mL) and refluxed at 66°C for 2 h. Yield 77%; bright yellow crystalline solid gave, mp 138–139°C (from dichloromethane/hexane) (Found: C, 84.6; H, 9.55; N, 5.0. C₃₈H₅₂N₂ requires C, 85.0; H, 9.8; N, 5.2%); λ_{\max} (CH₂Cl₂)/nm 415 (log ϵ 6.62); ν_{\max} (KBr)/cm⁻¹ 3072w, 3017m, 2951s, 2929s, 2869s, 1602s, 1554w, 1519s, 1462m, 1397m, 1365s, 1285m, 1220s, 1186s, 1143s, 1108m, 961s, 923m, 865w, 822s and 545m. δ_{H} (250 MHz; CDCl₃) 0.93–0.99 (12H, t, $J=7.1$ Hz, CH₃), 1.28–1.43 (8H, m, CH₂), 1.52–1.72 (8H, m, CH₂), 3.26–3.32 (8H, t, $J=7.1$ Hz, CH₂), 6.61–6.64 (4H, d, $J=8.9$ Hz, Ar), 6.83–6.89 (2H, d, $J=16.3$ Hz, vinyl), 6.89–7.06 (2H, d, $J=16.4$ Hz, Ar), 7.35–7.39 (4H, d, $J=9.0$ Hz, Ar) and 7.42 (4H, s, Ar). δ_{C} (62.9 MHz; CDCl₃) 14.1, 20.4, 29.5, 50.8, 111.7, 123.5, 124.7, 126.2, 127.7, 128.2, 136.7 and 147.8; m/z 536 (M⁺, 100%).

4.1.15. 4,4'-Bis{4-[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]styryl}-1,1'-biphenyl 16.

General procedure as for **12** to 4,4'-bis(diethoxyphosphinylmethyl)biphenyl **4** (0.60 g, 1.32 mmol) in dry THF (20 mL) was added NaH (0.08 g, 3.00 mmol). To this was added 4-(*N*-(2,4-dimethylphenyl)-*N*-phenylamino)benzaldehyde **9** (0.79 g, 2.64 mmol) in dry THF (30 mL), refluxed at 66°C for 2 h. Yield 25%; yellow crystalline solid, mp 142–143°C (from dichloromethane/hexane) (Found: C, 89.8; H, 6.3; N, 3.5. C₅₆H₄₈N₂ requires C, 89.8; H, 6.5; N, 3.7%); λ_{\max} (CH₂Cl₂)/nm 402 (log ϵ 4.89); ν_{\max} (KBr)/cm⁻¹ 3023m, 2950w, 2917w, 2867w, 1590s, 1541w, 1506s, 1492s, 1456w, 1311s, 1289m, 1273m, 1231w, 1175w, 1123w, 962m, 872w, 824m, 752m, 695m, 569w and 535m. δ_{H} (400 MHz; CDCl₃) 2.03 (6H, s, Me), 2.34 (6H, s, Me), 6.88–6.94 (7H, m), 6.97–7.01 (9H, m), 7.03–7.08 (4H, m), 7.16–7.22 (4H, m), 7.32–7.35 (4H, d, $J=9.1$ Hz, Ar), 7.50–7.53 (4H, d, $J=8.8$ Hz, Ar) and 7.55–7.59 (4H, d, $J=8.7$ Hz, Ar). δ_{C} (100.5 MHz; CDCl₃) 19.4, 22.1, 121.8, 122.7, 122.9, 126.8, 127.7, 128.0, 128.3, 129.2, 129.4, 130.1, 130.5, 131.1, 133.5, 137.0, 137.3, 137.9, 140.3, 143.4, 148.2 and 148.2; m/z 648 (M⁺, 20%).

4.1.16. 4-[*N*-(2,4-Dimethylphenyl)-*N*-phenylamino]benzyl alcohol 17.

4-[*N*-(2,4-Dimethylphenyl)-*N*-phenylamino]benzaldehyde **9** (2.0 g, 6.64 mmol) and NaBH₄ (1.0 g, 26.6 mmol) were refluxed at 78°C in EtOH (50 mL) for 3 h. The mixture was poured into ice cold H₂O and extracted with diethyl ether. The organic layer was dried over MgSO₄ and then filtered through silica. Solvents were removed under reduced pressure to leave the title compound (1.89 g, 93%) as a viscous, opaque oil (Found: C,

83.3; H, 6.8; N, 4.3. C₅₆H₄₈N₂ requires C, 83.1; H, 7.0; N, 4.6%); ν_{\max} (KBr)/cm⁻¹ 3059m, 2975s, 2921s, 2865m, 2732w, 2607m, 1898w, 1594s, 1508s, 1496s, 1454s, 1380s, 1315s, 1274s, 1175s, 1010s, 1028s, 938w, 879w, 817m, 752s and 695s. δ_{H} (250 MHz; CDCl₃) 1.61 (1H, s, OH), 2.00 (3H, s, Me), 2.34 (3H, s, Me), 4.59 (2H, s, CH₂) and 6.87–7.20 (12H, m, Ar). δ_{C} (62.9 MHz; CDCl₃) 18.4, 21.0, 65.2, 121.1, 121.4, 121.5, 128.1, 128.2, 129.0, 129.5, 132.4, 133.4, 135.9, 136.3, 142.6, 147.2 and 147.4; m/z 303 (M⁺, 100%).

4.2. 4-Bromomethyl-*N*-(2,4-dimethylphenyl)-*N*-phenylaminobenzene 18

4-[*N*-(2,4-Dimethylphenyl)-*N*-phenylamino]benzyl alcohol **17** (1.0 g, 3.3 mmol) in CH₂Cl₂ (50 mL) was agitated vigorously with 48% HBr in acetic acid (10 mL) for 1/2 h until no more of **17** remained. The mixture was washed (×2) with distilled H₂O and dried over MgSO₄. The organic solvents were removed under reduced pressure to give a colourless solid which revealed a mixture of components by tlc. No mass peak for the title compound was found.

4.2.1. 4-[*N*-(2,4-Dimethylphenyl)-*N*-phenylamino]benzyl(triphenyl)phosphonium bromide 19.

To a 0.2 mol dm⁻³ solution of 4-[*N*-(2,4-methylphenyl)-*N*-phenylamino]benzyl alcohol (3.50 g, 11.6 mmol) **17** in CHCl₃ (58 mL) was added triphenylphosphonium hydrogen bromide (3.91 g, 11.4 mmol). The mixture was refluxed at 61°C for 2 h and then the solvent distilled off to dryness. Further CHCl₃ was added (30 mL) to dissolve the crude product and the solution washed with saturated K₂CO_{3(aq)} and then distilled H₂O (×2). The organic extract was dried over MgSO₄ and concentrated under reduced pressure before precipitating in dry diethyl ether. The title compound (7.24 g, 98%) was obtained as a colourless solid, mp 149–150°C. ν_{\max} (KBr)/cm⁻¹ 3053w, 3006w, 2859m, 2781w, 1590m, 1537w, 1507s, 1491s, 1436s, 1376w, 1326m, 1304m, 1272m, 1231m, 1181w, 1111s, 995w, 839w, 747s, 719m, 689s, 602w and 512m. δ_{H} (400 MHz; CDCl₃) 1.89 (3H, s, Me), 2.26 (3H, s, Me), 5.17–5.20 (2H, d, $J=13.7$ Hz, CH₂), 6.60–6.62 (2H, d, $J=8.2$ Hz, Ar), 6.79–6.87 (6H, m, Ar), 6.91–6.97 (2H, m, Ar), 7.09–7.13 (2H, t, $J=7.9$ Hz, Ar), 7.55–7.59 (6H, m, Ar) and 7.64–7.72 (9H, m, Ar). δ_{C} (100.6 MHz; CDCl₃): 19.3, 22.0, 31.2–31.7 (d, $J_{\text{PC}}=137.3$ Hz), 118.7, 119.1–119.2 (d, $J_{\text{PC}}=12.5$ Hz), 119.5, 121.4 (d, $J_{\text{PC}}=4.3$ Hz), 123.1 (d, $J_{\text{PC}}=5.2$ Hz), 129.2, 130.1, 130.3, 131.1–131.2 (d, $J_{\text{PC}}=12.5$ Hz), 133.1 (d, $J_{\text{PC}}=7.3$ Hz), 133.4, 135.4 (d, $J_{\text{PC}}=12.7$ Hz), 136.0 (d, $J_{\text{PC}}=4.6$ Hz), 137.0, 137.2, 143.1, 147.8 and 148.7 (d, $J_{\text{PC}}=5.5$ Hz). δ_{C} (101.3 MHz; CDCl₃): 22.36; m/z 548 (M⁺–Br⁻, 25%).

4.2.2. *N,N'*-Di(2,4-dimethyl)-*N,N'*-(diphenyl)-4,4'-diamino stilbene 20.

To a stirred suspension of 4-[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]benzyltriphenylphosphonium bromide **19** (1.50 g, 2.33 mmol) in dry THF (20 mL) under nitrogen was added NaH (0.08 g, 3.33 mmol) resulting in a deep orange coloration. After 30 min 4-[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]benzaldehyde **9** (0.70 g, 2.33 mmol) in dry THF (10 mL) was added dropwise and the mixture refluxed at 66°C for 2 h. After cooling the reaction mixture was poured into distilled H₂O

(100 mL) and extracted with CH_2Cl_2 ($\times 2$). The extract was then dried over MgSO_4 and the solvents were removed under reduced pressure. Column chromatography, eluting with dichloromethane/light petroleum (15:85), yielded the title compound (0.57 g, 43%) as a light yellow oil that formed a yellow solid on complete removal of solvent under high vacuum, mp 82–83°C (Found: C, 88.1; H, 6.9; N, 4.55. $\text{C}_{42}\text{H}_{38}\text{N}_2$ requires C, 88.4; H, 6.7; N, 4.9%); λ_{max} (CH_2Cl_2)/nm 305 (log ϵ 4.94) and 386 (5.68); ν_{max} (KBr)/ cm^{-1} 3058w, 3024m, 2950m, 2916m, 2861m, 1591s, 1508s, 1377w, 1312s, 1288s, 1231m, 1175m, 1123w, 1076w, 1028w, 959m, 873w, 825m, 751s, 694s, 599w, 571m and 533m; δ_{H} (250 MHz; CDCl_3): 2.01 (6H, s, Me), 2.34 (6H, s, Me), 6.78–6.82 (1H, d, $J=8.8$ Hz), 6.89–7.07 (15H, m), 7.13–7.24 (8H, m) and 7.29–7.33 (2H, d, $J=8.5$ Hz); δ_{C} (62.9 MHz; CDCl_3): 18.4, 21.1, 120.4, 121.1, 121.5, 121.6, 121.7, 126.1, 127.0, 128.2, 129.1, 129.5, 129.6, 130.7, 132.4, 135.9, 136.3, 142.5, 146.7 and 147.3 (14 overlapping peaks for a mixture of *cis* and *trans* isomers); m/z 570 (M^+ , 90%).

4.2.3. 1,3-Bis{[4-(*N,N*-diphenylamino)styryl]}benzene 21. General procedure as for **12** to 1,3-bis(diethoxyphosphinylmethyl)benzene **3** (0.50 g, 1.30 mmol) in dry THF (20 mL) was added NaH (0.07 g, 2.60 mmol). To this diphenylaminobenzaldehyde **8** (0.70 g, 2.60 mmol) in dry THF (10 mL) was added and refluxed at 66°C for 2 h. Yield 52%; light yellow crystalline solid, mp 108–110°C (from dichloromethane/methanol) (Found: C, 89.15; H 5.9; N, 4.55. $\text{C}_{46}\text{H}_{36}\text{N}_2$ requires C, 89.5; H, 5.9; N, 4.5%); λ_{max} (CH_2Cl_2)/nm 298 (log ϵ 5.76) and 376 (6.29); ν_{max} (KBr)/ cm^{-1} 3057w, 3023m, 1588s, 1514s, 1491s, 1420w, 1327m, 1313m, 1278s, 1175w, 1074w, 1027w, 958w, 815w, 752m, 695s and 619w; δ_{H} (250 MHz; CDCl_3): 6.97–7.14 (19H, m), 7.23–7.42 (16H, m) and 7.60 (1H, s, Ar); δ_{C} (62.9 MHz; CDCl_3): 123.1, 123.6, 124.4, 124.6, 125.2, 126.9, 127.4, 128.4, 128.9, 129.3, 131.5, 138.0, 147.4 and 147.6; m/z 616 (M^+ , 80%).

4.2.4. 1,4-Bis{4-[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]styryl}benzene 22. General procedure as for **12** to 1,3-bis(diethoxyphosphinylmethyl)benzene **3** (0.84 g, 2.21 mmol) in dry THF (20 mL) was added NaH (0.11 g, 4.50 mmol). To this 4-(*N,N*-(2,4-diphenylamino))benzaldehyde **9** (1.30 g, 4.32 mmol) in dry THF (10 mL) was added and refluxed at 66°C for 2 h. Yield 58%; light yellow crystalline solid, mp 200–201°C (from dichloromethane/methanol) (Found: C, 89.5; H, 6.5; N, 4.0. $\text{C}_{50}\text{H}_{44}\text{N}_2$ requires C, 89.2; H, 6.6; N, 4.2%); λ_{max} (CH_2Cl_2)/nm 297 (log ϵ 4.84) and 378 (5.15); ν_{max} (KBr)/ cm^{-1} 3028m, 3014w, 2921w, 1589s, 1492s, 1376w, 1309s, 1288m, 1272m, 1232m, 1176m, 956m, 814m, 748m, 693m and 633w; δ_{H} (250 MHz; CDCl_3): 2.02 (6H, s, Me), 2.36 (6H, s, Me), 6.91–7.12 (20H, m), 7.18–7.38 (11H, m) and 7.58 (1H, s, Ar); δ_{C} (62.9 MHz; CDCl_3): 18.4, 21.1, 120.8, 121.7, 121.9, 124.3, 125.0, 126.3, 127.3, 128.2, 128.6, 128.9, 129.1, 129.5, 130.1, 132.4, 136.0, 136.3, 138.1, 142.4 and 147.2 (one overlapping peak); m/z 672 (M^+ , 40%).

4.2.5. 1,3-Bis{4-[*N,N*-(dibutylamino)styryl]}benzene 23. General procedure as for **12** to 1,3-bis(diethoxyphosphinylmethyl)benzene **3** (3.00 g, 7.94 mmol) in dry THF (50 mL) was added NaH (0.48 g, 20.0 mol). To this was

added 4-(*N,N*-dibutylamino)benzaldehyde **11** (3.70 g, 15.6 mmol) in dry THF (50 mL) and refluxed at 66°C for 2 h. Yield 25%; waxy yellow solid (from viscous yellow oil) (Found: C, 84.7; H, 9.4; N, 5.1. $\text{C}_{38}\text{H}_{52}\text{N}_2$ requires C, 85.0; H, 9.7; N, 5.0%); λ_{max} (CH_2Cl_2)/nm 375 (log ϵ 6.00); ν_{max} (KBr)/ cm^{-1} 3019m, 2954s, 2930s, 2860s, 1605s, 1585s, 1518s, 1461m, 1395m, 1365s, 1283m, 1217m, 1186s, 1108m, 960s, 927m, 897w, 841w, 773s, 718w, 689m and 519m. δ_{H} (250 MHz; CDCl_3): 0.96 (12H, t, $J=7.1$ Hz, CH_3), 1.28–1.43 (8H, m, CH_2), 1.52–1.68 (8H, m, CH_2), 3.29 (8H, t, $J=7.1$ Hz, CH_2), 6.61–6.64 (4H, d, $J=8.8$ Hz, Ar), 6.85–6.91 (2H, d, $J=16.2$ Hz, vinyl), 7.03–7.09 (2H, d, $J=16.3$ Hz, vinyl), 7.27–7.33 (3H, m, Ar), 7.37–7.40 (4H, d, $J=9.1$ Hz, Ar) and 7.55 (1H, s, Ar). δ_{C} (62.9 MHz; CDCl_3): 14.0, 20.4, 29.5, 50.8, 111.7, 123.8, 124.2, 124.6, 127.8, 128.8, 128.9, 138.6 and 147.8 (one overlapping peak); m/z 536 (M^+ , 100%).

4.2.6. 1,3,5-Tris{4-(*N,N*-diphenylamino)styryl}stilbene 24. General procedure as for **12** to 1,3,5-tris(diethoxyphosphinylmethyl)benzene **5** (1.00 g, 1.89 mmol) in dry THF (20 mL) was added NaH (0.15 g, 6.00 mmol). To this diphenylaminobenzaldehyde **8** (1.49 g, 5.50 mmol) in dry THF (20 mL) was added and the mixture refluxed at 66°C for 2 h. Yield 27%; light yellow crystalline solid, mp 286–288°C (from dichloromethane/methanol) (Found: C, 89.0; H 5.85; N, 4.7. $\text{C}_{66}\text{H}_{51}\text{N}_3$ requires C, 89.4; H, 5.8; N, 4.7%); λ_{max} (CH_2Cl_2)/nm 300 (log ϵ 5.65) and 381 (6.17); ν_{max} (KBr)/ cm^{-1} 3057w, 3021m, 1584s, 1506s, 1491s, 1420w, 1326s, 1278s, 1174m, 956m, 754m, 695m and 617w; δ_{H} (250 MHz; CDCl_3): 6.99–7.18 (30H, m), 7.24–7.30 (12H, m), 7.41 (6H, d, $J=8.5$ Hz) and 7.49 (3H, s, Ar); δ_{C} (62.9 MHz; CDCl_3): 123.1, 123.3, 123.6, 124.6, 126.8, 127.5, 128.6, 129.3, 131.4, 138.3, 147.5 and 147.6; m/z 886 (M^+ , 100%).

4.2.7. 4,4'-Bis(*N,N*-diphenylamino)benzophenone 25. 4,4'-Bis(amino)benzophenone (8.50 g, 40.0 mmol), copper powder (15.12 g, 240 mmol), K_2CO_3 (66.3 g, 480 mmol), iodobenzene (163.2 g, 800 mmol) and 18-crown-6 (1.00 g) were heated to reflux at 188°C under nitrogen with stirring for 7 h. The mixture was then cooled, slurried with CH_2Cl_2 and filtered. The filtrate was then washed with distilled H_2O ($\times 2$), dried over MgSO_4 and solvents removed under reduced pressure. Column chromatography, eluting with dichloromethane, produced yellow oil that crystallised on standing. Recrystallisation from ethanol to yield the title compound (19.4 g, 94% yield) as a yellow crystalline solid, mp 188–189°C. (lit. 189°C)¹² (Found: C, 85.4, H, 5.2, N, 5.4. $\text{C}_{37}\text{H}_{28}\text{N}_2\text{O}$ requires C, 85.7, H, 5.5, N, 5.6%); λ_{max} (CH_2Cl_2)/nm 292 (log ϵ 5.61) and 377 (6.27); ν_{max} (KBr)/ cm^{-1} 3060m, 3035m, 1650s, 1583s, 1488s, 1308s, 1274s, 1170s, 924m, 848m, 750s and 696s; δ_{H} (250 MHz; CDCl_3): 6.71 (4H, d, $J=8.8$ Hz, Ar), 7.17 (10H, m, Ar), 7.27 (10H, m, Ar) and 7.66–7.69 (4H, d, $J=8.8$ Hz, Ar); δ_{C} (62.9 MHz; CDCl_3): 120.0, 124.4, 125.8, 129.6, 130.6, 131.6, 146.7, 151.4 and 194.0; m/z 516 (M^+ , 100%).

4.2.8. 4,4'-Bis[*N,N*-(3,3-dimethyldiphenylamino)]benzophenone 26. General procedure as for **25** 4,4'-bis(amino)benzophenone (15.0 g, 71.0 mmol), copper powder (26.8 g, 426 mmol), K_2CO_3 (118 g, 852 mmol), 3-iodotoluene (300.0 g, 1.38 mol) and 18-crown-6 (1.00 g) were heated at 190°C for 12 h. Yield 80%; yellow crystalline solid, mp

138–139°C (from dichloromethane/hexane) (Found: C, 86.15; H, 6.1; N, 5.0. C₄₁H₃₆N₂O requires C, 86.0; H, 6.3; N, 4.9%); λ_{\max} (CH₂Cl₂)/nm 293 (log ϵ 6.15) and 380 (6.99); ν_{\max} (KBr)/cm⁻¹ 3033m, 2915m, 2859w, 1641s, 1579s, 1506s, 1486s, 1451m, 1377w, 1310s, 1272s, 1175s, 1088w, 927s, 838m, 772s, 706m, 695s and 563m; δ_{H} (250 MHz; CDCl₃) 2.29 (12H, s, Me), 6.92–7.00 (16H, m, Ar), 7.16–7.25 (4H, m, Ar) and 7.65–7.70 (4H, d, $J=8.5$ Hz, Ar); δ_{C} (62.9 MHz; CDCl₃) 21.4, 119.7, 123.1, 125.3, 126.5, 129.3, 130.3, 131.6, 139.5, 146.7, 151.6 and 194.0; m/z 572 (M⁺, 100%).

4.2.9. Tetra[4-(*N,N*-diphenylamino)]phenylethene 27.

Zinc dust (0.33 g, 5.0 mmol) was slurried with TiCl₃ (2.5 mL, 2.50 mmol, 1.0 M in dichloromethane/THF (2:1)) in dry THF (40 mL) to which 4,4'-bis(*N,N*-diphenylamino)-benzophenone **25** (0.50 g, 0.97 mmol) in dry THF (10 mL) was added. The mixture was heated to reflux at 66°C under nitrogen with stirring for 5 h. The mixture was slurried with hot THF and filtered. The filtrate was concentrated in vacuo to leave dark brown solids. Column chromatography, eluting with dichloromethane, gave a bright yellow solid recrystallised from methanol/dichloromethane to yield the title compound, (0.31 g, 60%), as a bright yellow crystalline solid, mp 293–295°C. (lit. 296–297°C).¹³ λ_{\max} (CH₂Cl₂)/nm 309 (log ϵ 6.18); ν_{\max} (KBr)/cm⁻¹ 3056m, 3031m, 1590s, 1504s, 1324s, 1275s, 1176m, 832m, 749s, 695s and 533m; δ_{H} (250 MHz; CDCl₃) 6.82–7.20 (56H, m, Ar); δ_{C} (62.9 MHz; C₆D₆) 123.6, 125.3, 126.3, 130.1, 133.3, 139.2, 147.1 and 148.7 (one overlapping peak); m/z 1000 (M⁺, 100%). Accurate mass: calculated 1000.4504, found 1000.4466.

4.2.10. Tetra[4-[*N,N*-(3,3-dimethyldiphenylamino)]phenylethene 28.

General procedure as for **27**; zinc dust (3.00 g, 52.4 mmol) was slurried with TiCl₃ (26.0 mL, 26.2 mmol; 1.0 M in dichloromethane/THF (2:1)) in dry THF (50 mL) to which 4,4'-bis[*N,N*-(3-dimethyldiphenyl)]-benzophenone **26** (5.0 g, 8.74 mmol) in dry THF (20 mL) was added. Refluxed at 66°C for 3 h. Yield 64%; bright yellow crystalline solid (from dichloromethane/light petroleum), mp 238–239°C (Found: C, 88.5; H, 6.5; N, 4.8. C₈₂H₇₂N₄ requires C, 88.45; H, 6.5; N, 5.0%); λ_{\max} (CH₂Cl₂)/nm 311 (log ϵ 6.75); ν_{\max} (KBr)/cm⁻¹ 3027m, 2953w, 2918m, 2861w, 1597s, 1582s, 1505s, 1487s, 1457m, 1372w, 1314s, 1276s, 1232w, 1180m, 839m, 771s, 695s and 635w; δ_{H} (250 MHz; CDCl₃) 2.21 (24H, s, Me), 6.77–6.87 (33H, m, Ar), 6.94–6.98 (7H, m, Ar) and 7.06–7.13 (8H, m, Ar); δ_{C} (100.5 MHz; CDCl₃) 21.5, 121.5, 122.8, 123.5, 125.0, 128.9, 132.4, 138.1, 139.0, 146.1 and 147.8; m/z 1112 (M⁺, 100%).

4.2.11. 4,4'-(2-Diphenylvinyl)-*N,N'*-(diphenyl)phenylamine 29.

Method A. Zinc dust (0.78 g, 12.0 mmol) was slurried with TiCl₃ (6 mL, 6.0 mmol; 1.0 M in dichloromethane/THF (2:1)) in dry THF (30 mL) to which benzophenone (0.91 g, 5.00 mmol) and 4,4'-bis(*N,N*-diphenylamino)benzophenone **25** (0.50 g, 1.00 mmol) in dry THF (10 mL) were added. The mixture was heated to reflux at 66°C under nitrogen with stirring for 3 h. The mixture was slurried in hot THF and filtered. The filtrate was concentrated in vacuo to leave dark brown solids. Column chromatography, eluting with dichloromethane/light petroleum (30:70), separated the product of middle polarity

which was recrystallised from dichloromethane/methanol to yield the title compound (0.13 g, 30%) as a pale yellow crystalline solid mp 224–225°C (Found: C, 90.0, H, 5.4, N, 3.9. C₅₀H₃₈N₂ requires C, 90.0, H, 5.7, N, 4.2%); λ_{\max} (CH₂Cl₂)/nm 306 (log ϵ 6.01) and 337 (5.86); ν_{\max} (KBr)/cm⁻¹ 3057m, 3022m, 1589s, 1490s, 1442m, 1312s, 1290s, 1177m, 1028m, 836m, 751s, 695s, 630m and 518m; δ_{H} (250 MHz; CDCl₃) 6.82–7.41 (38H, m, Ar); δ_{C} (62.9 MHz; CDCl₃) 147.6, 146.0, 144.2, 140.5, 137.8, 132.3, 131.5, 129.2, 128.5, 127.6, 126.3, 124.3, 122.9 and 122.7; m/z 666 (M⁺, 100%).

Method B. In a dry round bottomed flask Mg turnings (0.18 g, 7.31 mmol) were activated with a few small crystals of iodine and benzhydryl bromide (1.82 g, 73.0 mmol) in dry diethyl ether (10 mL) was added dropwise resulting in effervescence. The mixture was then heated to reflux under nitrogen with stirring for 1 h to give a pale yellow solution. 4,4'-Bis(*N,N*-diphenylamino)benzophenone **25** (2.50 g, 5.00 mmol) in dry THF (10 mL) was added dropwise to give a dark red/orange solution which was refluxed at 66°C for 3 h. The solvents were removed under reduced pressure and a 48% solution of HBr in acetic acid (5 mL) was added to produce a deep purple precipitate. This was washed with H₂O (×2) and extracted with CH₂Cl₂. The organic solvents were subsequently removed under reduced pressure. Column chromatography, eluting with dichloromethane, and recrystallisation from dichloromethane/methanol yielded the title compound (1.10 g, 31%) as a pale yellow crystalline solid, mp 224–225°C. Spectroscopic properties were identical to those obtained for Method A.

4.2.12. 4,4'-(2-Diphenylvinyl)-*N,N'*-(3,3-dimethyldiphenyl)phenylamine 30.

General procedure as for **29** (Method B). Mg turnings (0.48 g, 20.0 mmol), activated with iodine, benzhydryl bromide (4.32 g, 17.5 mmol), 4,4'-bis[*N,N*-(3-dimethyldiphenyl)]benzophenone **26** (5.00 g, 8.74 mmol) in dry THF (100 mL) were refluxed at 66°C for 3 h. Yield 59%; yellow crystalline solid (from dichloromethane/light petroleum), mp 224–226°C (Found: C, 89.6; H, 6.3; N, 3.65. C₅₄H₄₆N₂ requires C, 89.7; H, 6.4; N, 3.9%); λ_{\max} (CH₂Cl₂)/nm 308 (log ϵ 5.70) and 339 (5.52); ν_{\max} (KBr)/cm⁻¹ 3030m, 2951w, 2916m, 2861w, 1597s, 1583s, 1505s, 1486s, 1441m, 1378w, 1319s, 1277s, 1232w, 1179m, 1089w, 835m, 767s, 702s and 635w; δ_{H} (400 MHz; CDCl₃): 2.22 (12H, s, Me), 6.74–6.82 (16H, m, Ar), 6.88 (4H, d, $J=8.5$ Hz, Ar) and 7.02–7.13 (14H, m, Ar); δ_{C} (100.5 MHz; CDCl₃) 22.5, 122.5, 123.8, 124.5, 126.0, 127.2, 128.6, 129.9, 132.5, 133.3, 138.5, 139.9, 140.9, 141.7, 145.3, 147.3 and 148.7; m/z 722 (M⁺, 100%).

4.2.13. 1,4-Bis{2,2-di[4-(*N,N*-diphenylamino)]phenylvinyl}benzene 31.

To 1,4-bis(diethoxyphosphinylmethyl)benzene **2** (1.0 g, 2.65 mmol) in dry THF (20 mL) was added NaH (0.15 g, 6.25 mmol) with stirring under nitrogen. After initial effervescence subsided the white slurry was refluxed at 66°C for 1 h forming a brown suspension. To this 4,4'-bis(diphenylamino)benzophenone **25** (2.50 g, 4.84 mmol) in dry THF (20 mL) was added and the mixture refluxed at 66°C for 24 h. The reaction mixture was cooled and quenched in dry EtOH. Solvents were removed under reduced pressure, solids dissolved with CH₂Cl₂ and the solution washed twice with distilled H₂O, dried over

MgSO₄ and the CH₂Cl₂ removed under reduced pressure. Column chromatography, eluting with dichloromethane/methanol (3%) removed impurities and the silica was slurried with boiling cyclohexane. The yellow solution was filtered, concentrated and allowed to cool resulting in the title compound (0.51 g, 17%) crystallising as yellow solid, mp 295–298°C (from cyclohexane) (Found: C, 89.7, H, 5.5, N, 5.0. C₈₂H₆₂N₄ requires C, 89.3, H, 5.7, N, 5.1%); λ_{max} (CH₂Cl₂)/nm 303 (log ε 6.86) and 407 (6.16); ν_{max} (KBr)/cm⁻¹ 3057w, 3031m, 1588s, 1507s, 1492s, 1421w, 1382w, 1314s, 1275s, 1176m, 1074w, 1027w, 893w, 836m, 751s, 695s and 622w; δ_H (400 MHz; CDCl₃) 6.78 (2H, s, vinyl), 6.84 (4H, s, Ar), 7.02–6.92 (16H, m, Ar), 7.12–7.03 (20H, m, Ar) and 7.33–7.15 (20H, m, Ar); δ_C (100.5 MHz; CDCl₃): 123.9, 124.0, 124.1, 124.8, 125.4, 125.6, 129.3, 130.1, 130.3, 132.3, 135.5, 137.1, 138.2, 142.6, 148.1, 148.3, 148.6 and 148.7 (two overlapping peaks); *m/z* 1103 (M⁺, 100%).

4.2.14. 4,4'-(2-Vinylphenyl)-N,N'-(diethyl)phenylamine 32. General procedure as for **29** (Method B). Benzyl magnesium chloride (2.25 mL, 4.50 mmol) was added to 4,4'-bis(*N,N*-diethylamino)benzophenone (0.50 g, 1.54 mmol) in dry THF (15 mL). Refluxed at 66°C for 2 h. Yield 65%; viscous yellow oil (Found: C, 84.75; H, 8.8; N, 6.45. C₂₈H₃₄N₂ requires C, 84.4; H, 8.6; N, 7.0%); λ_{max} (CH₂Cl₂)/nm 331 (log ε 5.15); ν_{max} (NaCl)/cm⁻¹ 2985s, 2915m, 2877m, 1612m, 1594m, 1548w, 1527m, 1493m, 1465m, 1446m, 1369m, 1255m, 1199m, 1149m, 1076m, 1012w, 809m, 746w and 696m; δ_H (250 MHz; CDCl₃) 1.13–1.21 (12H, m, CH₃), 3.32–3.40 (8H, q, *J*=7 Hz, CH₂), 6.58–6.64 (4H, d, *J*=8.8 Hz, Ar), 6.70 (1H, s, vinyl), 7.02–7.15 (5H, m, Ar) and 7.22–7.26 (4H, d, *J*=8.8 Hz, Ar); δ_C (62.9 MHz; CDCl₃) 12.8, 44.3, 44.4, 111.1, 111.7, 123.1, 125.5, 127.5, 127.8, 129.0, 129.3, 131.3, 131.6, 139.0, 143.0, 147.1 and 147.3 (one overlapping peak at δ 12.8); *m/z* 398 (M⁺, 100%).

4.2.15. 4,4'-(2-Vinylphenyl)-N,N'-(diphenyl)phenylamine 33. Diethyl benzylphosphonate (2.05 g, 9.00 mmol) in dry THF (10 mL) was cooled to -77°C in an acetone/dry ice bath. With stirring under nitrogen, *n*-BuLi (0.75 mL, 1.2 mmol; 1.6 M in hexane) was added dropwise to give a yellow solution which was left to stir for 1 h. To this 4,4'-bis(*N,N*-diphenylamino)benzophenone **25** (0.50 g, 1.00 mmol) in dry THF (5 mL) was added dropwise. The mixture was allowed to warm to room temperature and left to stir for 3 h. Column chromatography, eluting with dichloromethane/light petroleum (30:70), and recrystallisation from methanol/dichloromethane yielded the title compound (1.10 g, 59%) as a yellow crystalline solid, mp 154–156°C. (lit. 153°C)¹³ (Found: C, 89.2; H, 5.7; N, 4.6. C₄₇H₄₃N₃ requires C, 89.45; H, 5.8; N, 4.7%); λ_{max} (CH₂Cl₂)/nm 302 (log ε 6.05) and 342 (5.81); ν_{max} (KBr)/cm⁻¹ 3058m, 3032m, 1585s, 1490s, 1444m, 1321s, 1275s, 827m, 750s, 694s, 623m and 500m; δ_H (250 MHz; CDCl₃) 6.95 (1H, s, vinyl), 7.05–7.17 (23H, m, Ar) and 7.28–7.35 (10H, m, Ar); δ_C (62.9 MHz; CDCl₃) 122.9, 123.0, 123.1, 123.8, 124.4, 124.5, 126.4, 126.5, 127.9, 128.3, 129.2, 129.3, 129.5, 131.4, 134.3, 137.1, 137.9, 141.8, 147.0, 147.3, 147.6 and 147.7; *m/z* 590 (M⁺, 100%).

4.2.16. 4,4'-(2-Vinylphenyl)-N,N'-(3,3-dimethyldiphenyl)phenylamine 34. General procedure as for **33**

diethyl benzylphosphonate (4.00 g, 17.5 mmol) was dissolved in dry THF (100 mL) and heated at 40°C for 1 h. 4,4'-Bis[*N*-(3-dimethylphenyl)-*N*-phenylamino]benzophenone **26** (5.00 g, 8.74 mmol) in dry THF (50 mL) was added and the mixture refluxed at 66°C for 3 h. Yield 83%; yellow crystalline solid, mp 97–98°C (from dichloromethane/methanol) (Found: C, 88.8; H, 6.6; N, 4.2. C₄₈H₄₂N₂ requires C, 89.1; H, 6.55; N, 4.3%); λ_{max} (CH₂Cl₂)/nm 303 (log ε 6.26) and 345 (6.04); ν_{max} (KBr)/cm⁻¹ 3023m, 2951w, 2916w, 2861w, 1597s, 1582s, 1506s, 1486s, 1444m, 1376w, 1317s, 1275s, 1232w, 1179m, 835w, 772m, 693s and 630w; δ_H (250 MHz; CDCl₃) 2.28 (12H, s, Me) and 6.82–7.29 (30H, m, Ar); δ_C (100.5 MHz; CDCl₃) 22.5, 22.6, 122.6, 122.9, 123.8, 124.7, 124.8, 124.9, 126.1, 126.3, 127.3, 127.4, 128.9, 129.3, 130.0, 130.1, 130.6, 132.3, 135.1, 137.7, 139.0, 140.1, 140.2, 143.0, 148.2, 148.6, 148.7, 148.8; *m/z* 646 (M⁺, 100%).

4.2.17. 4,4'-Bis(*N,N*-diphenylamino)benzophenone diphenylhydrazone 35. 4,4'-Bis(*N,N*-diphenylamino)benzophenone **25** (1.00 g, 1.94 mmol) and *N,N*-diphenylhydrazine (0.43 g, 1.94 mmol) were heated to reflux at 78°C in EtOH (150 mL) for 36 h. The mixture was allowed to cool and EtOH removed under reduced pressure. Residual solids were dissolved in CH₂Cl₂ and washed (×2) in distilled H₂O. CH₂Cl₂ was removed under reduced pressure and column chromatography, eluting with dichloromethane/light petroleum (30:70), gave a yellow solid. Recrystallisation from dichloromethane/methanol yielded the title compound (0.35 g, 27%) as a yellow crystalline solid, mp 209–210°C (Found: C, 85.95; H, 5.5; N, 8.05. C₄₀H₃₈N₄ requires C, 85.9; H, 5.7; N, 8.35%); λ_{max} (CH₂Cl₂)/nm 303 (log ε 5.24) and 343 (5.35); ν_{max} (KBr)/cm⁻¹ 3056w, 3033m, 1590s, 1488s, 1320m, 1272s, 1207m, 1175m, 1048m, 826m, 751s, 695s, 623w and 511w. δ_H (250 MHz; CDCl₃) 6.78–6.87 (4H, m, Ar), 6.97–7.02 (15H, m, Ar), 7.04–7.31 (17H, m, Ar) and 7.57–7.61 (2H, d, *J*=8.9 Hz, Ar). δ_C (100.5 MHz; CDCl₃) 122.5, 122.9, 123.6, 124.0, 124.1, 124.6, 125.3, 126.1, 129.8, 130.2, 130.4, 130.6, 132.2, 132.9, 148.3, 148.5, 149.1, 150.5 and 164.6 (two overlapping peaks); *m/z* 682 (M⁺, 100%).

4.2.18. 4,4'-Bis(*N,N*-(3,3-dimethyldiphenylamino))-benzophenone-diphenylhydrazone 36. General procedure as for **35** 4,4'-bis(*N,N*-(3,3-dimethyldiphenylamino))benzophenone **26** (0.50 g, 87.4 mmol) and *N,N*-diphenylhydrazine (0.19 g, 87.4 mmol) were refluxed at 78°C in EtOH (150 mL) for 36 h. Yield 55%; yellow crystalline solid, mp 118–119°C (from aqueous ethanol) (Found: C, 85.75; H, 6.2; N, 7.4. C₅₃H₄₆N₄ requires C, 86.15; H, 6.3; N, 7.6%); λ_{max} (CH₂Cl₂)/nm 305 (log ε 6.06) and 346 (5.84); ν_{max} (KBr)/cm⁻¹ 3030m, 2916m, 2858m, 1597s, 1487s, 1451m, 1377w, 1318s, 1274s, 1208m, 1177m, 1085w, 1038m, 839m, 772m, 694s and 442w. δ_H (250 MHz; CDCl₃) 2.28 (12H, s, Me), 6.79–6.99 (24H, m, Ar), 7.10–7.25 (8H, m, Ar) and 7.56–7.60 (2H, d, *J*=8.8 Hz, Ar). δ_C (100.5 MHz; CDCl₃) 22.4, 22.5, 122.5, 122.6, 122.7, 123.4, 123.5, 123.6, 124.9, 125.5, 126.1, 126.8, 129.8, 130.0, 130.2, 130.4, 131.7, 132.5, 140.0, 140.3, 148.3, 148.5, 148.7, 149.2, 150.7 and 165.3 (one overlapping peak); *m/z* 738 (M⁺, 10%).

4.2.19. *N*-(4-Iodophenyl)pyrrole 37. In glacial acetic acid (100 mL) 4-iodoaniline (10.0 g, 45.9 mmol) and

dimethoxytetrahydrofuran (6.00 g, 45.9 mmol) were heated to reflux at 116°C for 2 h. The mixture was cooled, poured into H₂O (100 mL) and extracted with CH₂Cl₂. Polar impurities were removed by filtering through silica and the solvent was removed under reduced pressure. Recrystallization from dichloromethane/hexane yielded the title compound (7.95 g, 65%) as a yellow/orange crystalline solid. Sublimation of a small quantity gave a white crystalline solid, mp 128–129°C. (lit. 131–133°C) (Found: C, 44.8; H, 3.0; N, 5.2. C₁₀H₈Nl requires C, 44.6; H, 3.0; N, 5.2%); ν_{\max} (KBr)/cm⁻¹ 3148w, 3128m, 3101w, 3064w, 1885w, 1586s, 1496s, 1407m, 1330s, 1247m, 1188m, 1120m, 1078m, 999m, 918m, 815s, 725s, and 608m; δ_{H} (250 MHz; CDCl₃) 6.35 (2H, t, $J=2.3$ Hz, Ar), 7.05 (2H, t, $J=2.14$ Hz, Ar), 7.15 (2H, d, $J=8.7$ Hz, Ar) and 7.72 (2H, d, $J=8.6$ Hz, Ar); δ_{C} (62.9 MHz; CDCl₃) 89.4, 111.0, 119.1, 122.2, 128.6 and 140.4; m/z 269.1 (M⁺, 10%).

4.2.20. *N*-[4-(*N,N'*-Diphenylamino)]phenylpyrrole 38.

N-(4-Iodophenyl)pyrrole 37 (1.00 g, 3.72 mmol), *N,N*-diphenylamine (0.63 g, 3.72 mmol), copper powder (0.23 g, 3.72 mmol), K₂CO₃ (1.03 g, 7.40 mmol), 18-crown-6 (0.20 g) and *o*-dichlorobenzene (100 mL) were heated to 180°C for 90 h. The mixture was allowed to cool and slurried with CH₂Cl₂ and filtered. The filtrate was washed with distilled H₂O (×2) and dried over MgSO₄. Solvents were removed under reduced pressure to leave a yellow/brown solid. Column chromatography, eluting with dichloromethane/light petroleum (10:90), yielded an off white solid. Recrystallisation from dichloromethane/light petroleum gave the title compound (253 mg, 22%), as a colourless solid, mp 116–117°C (from hexane) (Found: C, 85.0; H, 5.8; N, 9.0. C₂₂H₁₈N₂ requires C, 85.1; H, 5.8; N, 9.0%); λ_{\max} (CH₂Cl₂)/nm 308 (log ϵ 5.13); ν_{\max} (KBr)/cm⁻¹ 3123m, 3099m, 3055m, 3035m, 1934w, 1910w, 1590s, 1483s, 1449m, 1385w, 1327s, 1314s, 1278s, 1245m, 1172m, 1114m, 1070s, 1020m, 922m, 844m, 824m, 754s, 733s, 696s and 612m; δ_{H} (250 MHz; CDCl₃) 6.32–6.33 (2H, t, $J=2.14$ Hz, Ar), 6.99–7.05 (4H, m, Ar), 7.08–7.15 (6H, m, $J=8.5$ Hz, Ar) and 7.22–7.29 (6H, m, Ar); δ_{C} (62.9 MHz; CDCl₃) 110.1, 119.4, 121.6, 122.9, 124.2, 124.9, 129.4, 135.8, 145.7 and 147.7; m/z 310 (M⁺, 100%).

4.2.21. *N*-{4-[*N'*-(2,4-Dimethylphenyl)]-*N'*-phenylamino}phenylpyrrole 39.

General procedure as for 38 *N*-(4-iodophenyl)pyrrole 37 (5.00 g, 1.90 mmol), *N*-(2,4-dimethylphenyl)-*N*-phenylamine (3.94 g, 20.0 mmol), copper powder (1.15 g, 18.0 mmol), K₂CO₃ (5.15 g, 37.0 mmol), 18-crown-6 (0.50 g) and *o*-dichlorobenzene (100 mL) were heated to 180°C for 90 h. Yield 48%; yellow/orange glass (after sublimation of unreacted starting materials) (Found: C, 84.9; H, 6.5; N, 7.8. C₂₄H₂₂N₂ requires C, 85.2; H, 6.55; N, 8.2%). λ_{\max} (CH₂Cl₂)/nm 307 (log ϵ 5.71); ν_{\max} (KBr)/cm⁻¹ 3100w, 3036m, 2917m, 2856w, 1594s, 1513s, 1493s, 1339w, 1326s, 1271s, 1230m, 1116w, 1070s, 1019m, 923m, 821m, 753m, 722s, 693s and 552m; δ_{H} (250 MHz; CDCl₃): 2.02 (3H, s, Me), 2.34 (3H, s, Me), 6.30–6.32 (2H, t, $J=2.14$ Hz, Ar), 6.88–7.03 (9H, m, Ar), 7.08 (1H, bs, Ar) and 7.17–7.25 (4H, m, Ar); δ_{C} (62.9 MHz; CDCl₃) 18.5, 21.1, 109.9, 119.5, 121.3, 121.4, 121.5, 122.0, 128.2, 129.1, 129.4, 132.5, 134.6, 136.0, 136.2, 142.5, 145.6 and 147.4; m/z 338 (M⁺, 100%).

4.2.22. *N*-Phenylpyrrole-2-carboxaldehyde 40. To DMF (3.06 g, 41.9 mmol) cooled in an salt–ice bath was added dropwise phosphorus oxychloride (6.42 g, 41.9 mmol). A solution of *N*-phenylpyrrole (5.0 g, 34.9 mmol) in 1,2-dichloroethane (100 mL) was added and the mixture warmed to room temperature and then heated with stirring at 100°C for 3 h. The mixture was washed with concentrated aqueous Na₂(CO₃)₂ solution and then distilled H₂O (×2). The organic extract dried over MgSO₄ and the solvents removed under reduced pressure. Column chromatography, eluting with dichloromethane, yielded a brown/yellow non-viscous oil which crystallised on standing in the cool to give the title compound (5.1 g, 84%) as a white crystalline solid, mp 26–27°C. (lit. 27–30°C)¹⁴ (Found: C, 77.6; H, 5.3; N, 8.1. C₁₁H₉NO requires C, 77.2; H, 5.3; N, 8.2%); ν_{\max} (KBr)/cm⁻¹ 3113w, 3055m, 2985w, 2842w, 2800m, 2782w, 1673s, 1597s, 1525s, 1499s, 1452s, 1415s, 1391s, 1367s, 1329s, 1201w, 1167w, 1063m, 1039s, 888w, 181s, 741s, 699s, 671m and 602m. δ_{H} (250 MHz, CDCl₃) 6.40–6.42 (1H, dd, $J=2.5$, 6.4 Hz), 7.06–7.08 (1H, t, $J=2.4$ Hz), 7.15–7.17 (1H, dd, $J=1.5$, 5.5 Hz), 7.31–7.50 (5H, m, Ar) and 9.57 (1H, s, CHO). δ_{C} (62.9 MHz, CDCl₃) 110.9, 122.0, 126.1, 128.3, 129.1, 131.1, 132.6, 138.8 and 179.1; m/z 171 (M⁺, 10%).

4.2.23. *N*-Phenyl-2-[*N*-(2,4-dimethylphenyl)phenyl-*N*-phenyl-4-(ethenyl)phenylamine]pyrrole 41.

In a dry flask a slurry of 4-(*N*-(2,4-dimethylphenyl)-*N*-phenylamino)benzyltriphenylphosphonium bromide 19 (2.50 g, 3.97 mmol) and NaH (0.10 g, 3.97 mmol) in dry THF (40 mL) was stirred under nitrogen. After 1 h *N*-phenylpyrrole-2-carboxaldehyde 40 (0.70 g, 3.97 mmol) in dry THF (10 mL) was added dropwise and the reaction then left to stir at room temperature for 2 h. The mixture was subsequently quenched in H₂O and extracted with CH₂Cl₂, dried over MgSO₄ and the solvents removed under reduced pressure to give a viscous brown oil. Column chromatography, eluting with dichloromethane/light petroleum mixture (25:75) yielded two yellow viscous oils. Complete removal of solvent gave the two isomers of the title compound (0.56 g, 31%) as two yellow solids which proved to be *cis*, mp 50–51°C, and *trans*, mp 70–71°C, respectively. *cis* λ_{\max} (CH₂Cl₂)/nm 300 (log ϵ 5.52) and 359 (5.67); δ_{H} (250 MHz; CDCl₃) 2.01 (3H, s, Me), 2.34 (3H, s, Me), 6.04 (1H, d, $J=12.2$ Hz, vinyl), 6.20 (1H, t, $J=2.5$ Hz, Ar), 6.25 (1H, d, $J=12.2$ Hz, vinyl), 6.42 (1H, dd, $J=1.5$, 2.4 Hz, Ar), 6.82–7.06 (8H, m, Ar) and 7.16–7.44 (10H, m, Ar). δ_{C} (62.9 MHz; CDCl₃) 18.5, 21.0, 109.1, 110.2, 118.3, 120.4, 121.4, 121.7, 122.1, 125.8, 126.8, 128.0, 128.1, 128.9, 129.0, 129.4, 129.5, 130.0, 130.3, 132.4, 135.9, 136.3, 139.9, 142.5, 146.4 and 147.3; m/z 440 (M⁺, 100%). *trans* (Found: C, 87.3; H, 6.5; N, 6.1. C₃₂H₂₈N₂ requires C, 87.2; H, 6.4; N, 6.4%); λ_{\max} (CH₂Cl₂)/nm 302 (log ϵ 5.49) and 373 (6.32); ν_{\max} (KBr)/cm⁻¹ 3058w, 3028m, 2916m, 2852w, 1600w, 1591s, 1499s, 1457s, 1414w, 1376w, 1323s, 1289s, 1273s, 1231m, 1175w, 1146w, 1096w, 1036w, 955m, 854w, 813m, 752m, 696s, 672w, 610w; δ_{H} (250 MHz; CDCl₃) 1.99 (3H, s, Me), 2.33 (3H, s, Me), 6.31 (1H, t, $J=3.4$ Hz, Ar), 6.60 (1H, dd, $J=1.5$, 2.1 Hz, Ar), 6.63–6.69 (1H, d, $J=16.2$ Hz, vinyl), 6.81 (1H, d, $J=16.2$ Hz, vinyl), 6.85–7.04 (9H, m, Ar), 7.14–7.21 (4H, m, Ar) and 7.33–7.49 (5H, m, Ar). δ_{C} (62.9 MHz; CDCl₃) 18.4, 21.0, 106.8, 109.6, 115.9, 121.0, 121.4, 121.5,

123.1, 126.1, 126.2, 126.7, 127.2, 128.1, 129.0, 129.2, 129.5, 130.7, 132.4, 132.7, 135.9, 136.3, 139.8, 142.4, 146.5 and 147.2; m/z 440 (M^+ , 30%).

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