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Intramolecular Addition of Aryl Radicals to Carbon-Nitrogen Double Bonds♦

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Abstract: Cyclisation of radicals **6a,b** is highly regioselective towards a 5-exo process; 6-endo ring closure is a minor route and their ratio depends on the substituents. No ring expansion of the five-membered radical intermediates **7a,b** was observed. Radicals **27a,b** give rise to 5-exo cyclisation regiospecifically. A competitive 1,5-hydrogen shift leading to imidoyl radicals was noticed. An analogous behaviour is also exhibited by vinyl radicals when allowed to add to carbon-nitrogen double bonds.

INTRODUCTION

In the last decades a lot of examples involving intramolecular addition of free radicals to carbon-carbon multiple bonds have been reported.[1] Recently, some papers dealing with an analogous addition to carbon-heteroatom[2] and heteroatom-heteroatom[3] multiple bonds have appeared as well.

As far as aryl radical cyclisations onto double bonds are concerned, we have studied the 5-exo ring closure of 2'-arylazobiphenyl-2-yl- to (9H-carbazol-9-yl)arylaminyl radicals; these intermediates afford 9-(arylamino)-9H-carbazoles by hydrogen abstraction;[4] in some cases, when the aryl group has an acyloxy substituent in the *ortho* position, we have also observed a novel rearrangement of the acyl moiety from the oxygen to the nitrogen atom.[5]

Unexpectedly, much less attention has been paid to inter-[6] and intramolecular[7] radical addition to the carbon-nitrogen double bond. In particular, Roberts et al.[6b] have observed a regioselective addition of alkyl and silyl radicals to the methylenic carbon of N-methylene-*tert*-butylamine; on the contrary, addition of silyl[6c] or stannyl[6d] radicals to 1,2-disubstituted imines leads to α-aminoalkyl radicals, exclusively. Very recently, Warkentin et al.[8] have studied the intramolecular addition of aryl radicals to aldimines. In this case, the radicals give rise to a fast 6-endo ring closure onto the carbon atom, affording tetrahydroisoquinolines; in addition, the reaction yields minor amounts of dihydroindoles through 5-exo cyclisation.

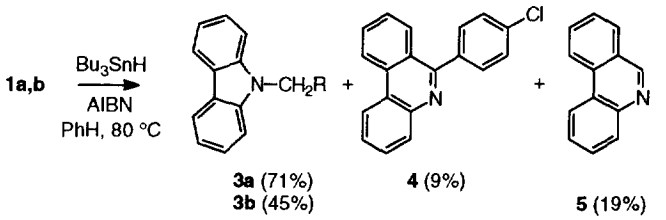
To get some more insight into the intramolecular addition of aryl radicals to the imine double bond, we studied the reaction of 2-alkylidenamino-2'-iodobiphenyls **1** and N-[(2'-bromobiphenyl-2-yl)methylene]amines **2** with stannyl radicals (Figure 1); in particular, we aimed at investigating the regiochemistry of the cyclisation of the corresponding aryl radicals.

Figure 1.

♦ This paper is dedicated to Professor Antonio Tundo on the occasion of his 70th birthday.

RESULTS AND DISCUSSION

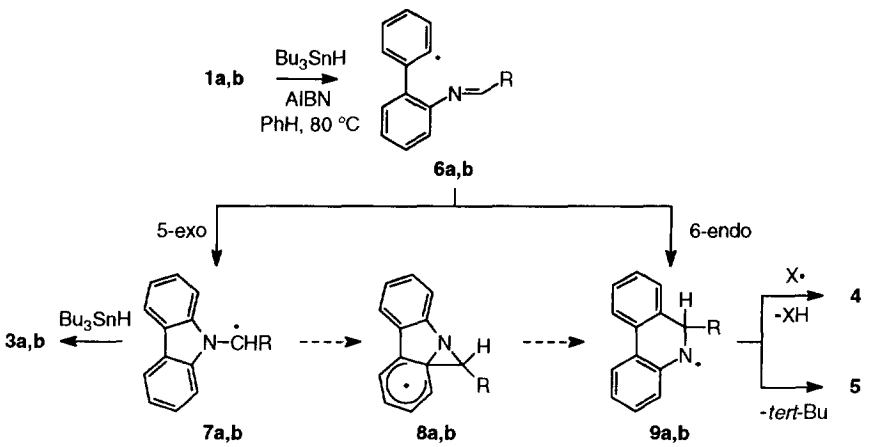
When the imines **1a,b** were allowed to react with tri-*n*-butyltin hydride (1.2 equiv) in the presence of α,α'-azo-bis-*iso*-butyronitrile (AIBN) (0.3 equiv) in boiling benzene they afforded mixtures of 9-alkylcarbazoles **3a,b** and phenanthridines **4** and **5** (Scheme 1).



Scheme 1. Reaction of imines **1a,b** with tri-*n*-butyltin hydride and AIBN.

Imine **1a** gave only **3a** and phenanthridine **4** with no traces of **5**, whereas **1b** afforded only **3b** and phenanthridine **5** and no trace amounts of the corresponding *tert*-butyl derivative were observed. In the case of **1a**, besides the compounds reported in Scheme 1, we also noticed the presence of trace amounts of some products which looked like dimeric derivatives and coupling compounds between **7** (or **9**) and the α-cyano-*iso*-propyl radical (Scheme 2).

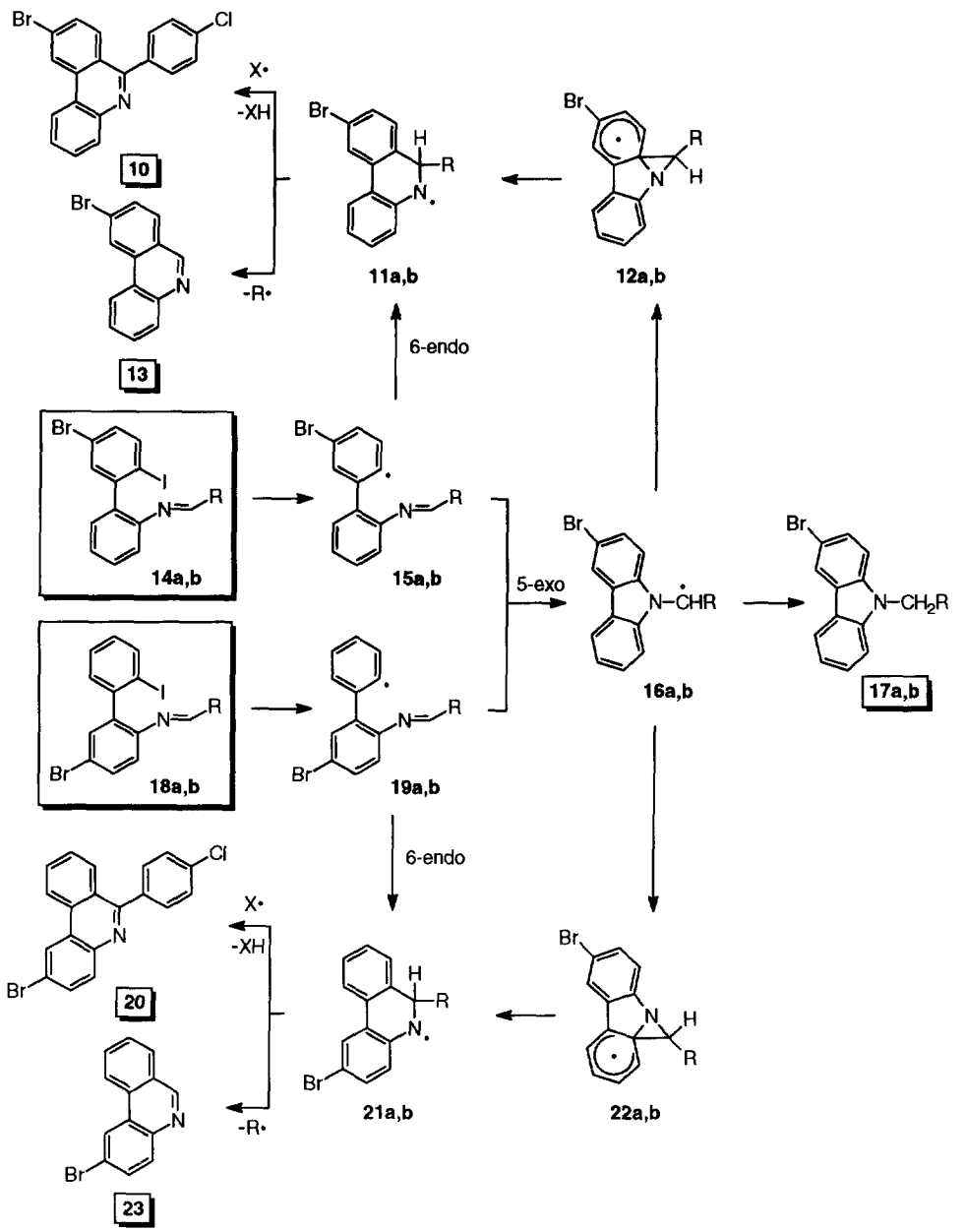
The biphenyl-2-yl radicals **6a,b** obtained from the imines **1a,b** by iodine-atom abstraction by means of stannyl radicals can give rise to a 5-exo cyclisation through attack on the imine nitrogen; the resulting (9H-carbazol-9-yl)alkyl radicals **7a,b** lead to carbazoles **3a,b** by hydrogen abstraction from tri-*n*-butyltin hydride. Meanwhile, the same radicals **6a,b** can also give a 6-endo ring closure on the imine carbon; the corresponding nitrogen-centred radicals **9a,b** afford 6-(4-chlorophenyl)phenanthridine (**4**) by hydrogen loss — in the case of **1a** — and the unsubstituted phenanthridine (**5**) by β-fragmentation with loss of *tert*-butyl radical — in the case of **1b** (Scheme 2).



Scheme 2. Reaction mechanism for imines **1a,b**.

It is worth to point out that phenanthridines (**4** and **5**) might originate from radicals **7a,b** *via* a ring-expansion process through the radical intermediates **8a,b**. Many examples of rearrangement concerning nitrogen-[9] and carbon-centred[10] radicals have been reported in the literature. Very recently, McNab et al.[11] have described the ring expansion of (N-heteroaryl)methyl radicals, which are very similar to our radicals **7a,b**, generated from the corresponding N-(4-chlorophenoxy)methyl derivatives by flash vacuum pyrolysis (FVP).

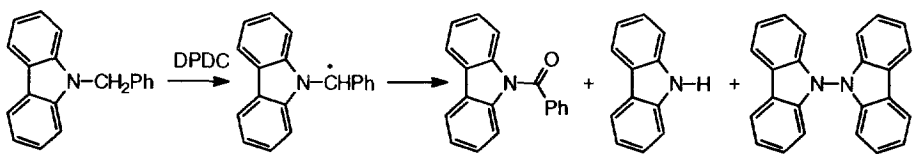
In our case the possibility of this rearrangement was excluded from the results obtained with the imines **14a,b** and **18a,b**. As one can see in Scheme 3, in our conditions these imines generate the same intermediate **16** *via* 5-exo cyclisation of **15** and **19**. Radical **16** can abstract a hydrogen atom to give the corresponding carbazole **17** or expand on either of the two different benzenic rings affording the nitrogen-centred radicals **11** and **21**. These last two intermediates are the same as those formed by direct 6-endo cyclisation of **15** and **19**.



Scheme 3. Reaction mechanism for imines **14a,b** and **18a,b**.

If the phenanthridines were formed by exclusive 6-endo ring closure, imines **14a,b** should give **10** or **13** only, whereas **20** or **23** should be obtained from **18a,b**. On the contrary, if a ring-expansion mechanism were involved, imines **14a,b** and **18a,b** should lead to two different couples of isomeric phenanthridines, *i.e.* **10** and **20** when R = 4-chlorophenyl, **13** and **23** when R = *tert*-butyl. An accurate GC analysis of the products obtained from the reactions of **14a,b** and **18a,b** showed that each imine produced only the phenanthridine expected from a 6-endo cyclisation. These results proved that, in our experimental conditions, the ring-expansion process must be excluded.

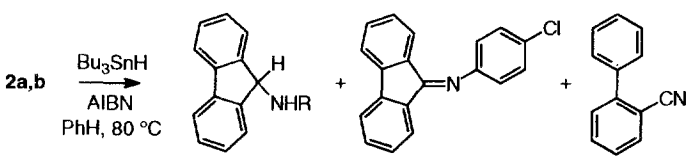
A further support to our assumption that (9H-carbazol-9-yl)alkyl radicals in solution cannot undergo ring enlargement was found in the previously reported decarbonylation of (9H-carbazol-9-yl)acetyl radicals[12] and was furnished by the reaction of 9-benzyl-9H-carbazole with di-*iso*-propyl peroxydicarbonate (DPDC). In these conditions the only products we got were carbazole derivatives, proving once more that (9H-carbazol-9-yl)-substituted alkyl radicals do not expand on the heterocyclic ring (Scheme 4). The mechanism of formation of the compounds obtained from this reaction has no relation to our study, therefore it was not investigated.



Scheme 4. Reaction products obtained by hydrogen abstraction from 9-benzyl-9H-carbazole.

On the basis of our results, one can see that cyclisation of **6a** is highly regioselective, the 5-exo/6-endo ratio being greatly in favour of the 5-membered ring closure; in the case of **6b** this regioselectivity is lowered, probably due to the lower stability of radical **7b** with respect to the substituted benzyl radical **7a**. On the other hand, if the facile loss of *tert*-butyl radical from **9b** by β-scission could affect the 5-exo/6-endo ratio, it would lead us to postulate a mechanism involving the reversibility of cyclisation of **6**, that is inconceivable. The regioselectivity of our aryl radicals is completely different from that reported by Warkentin et al.,[8] who observed a large 6-endo preference.

When we allowed the imines **2a,b** to react under the same experimental conditions, the products reported in Scheme 5 were obtained.

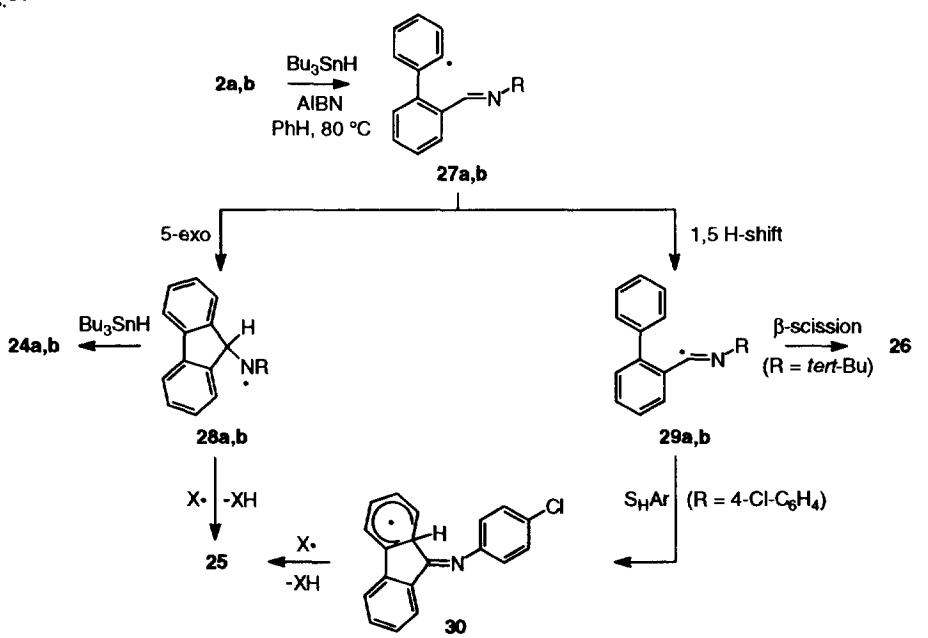


Scheme 5. Reaction of imines **2a,b** with tri-*n*-butyltin hydride and AIBN.

Imine **2a** gave only **24a** and fluorenonimine **25** with no traces of **26**, whereas **2b** afforded only **24b** and 2-cyanobiphenyl **26** and no trace amounts of the *tert*-butyl analogue of **25** were observed. In addition, **2a** also yielded small amounts of a compound whose structure was not investigated but, on the basis of its highly symmetric ^{1}H-NMR spectrum, appears to be a dimer of radical **28a** (Scheme 6).

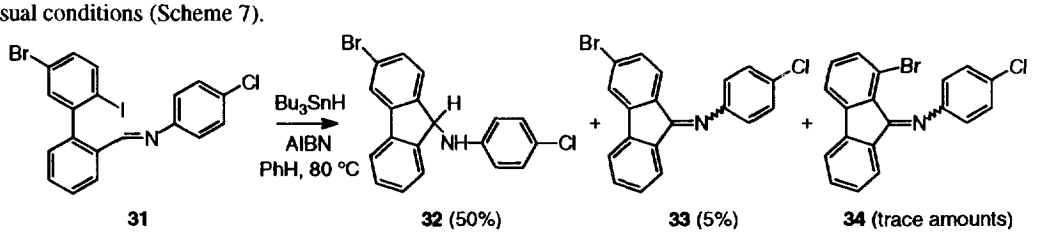
The biphenyl-2-yl radicals **27a,b** obtained from **2a,b** by bromine abstraction can attack the carbon atom of the imine double bond giving rise to the radical intermediates **28a,b**, which lead to 9-aminofluorenes **24a,b** by hydrogen atom abstraction. Alternatively, **27a,b** can rearrange to the imidoyl radicals **29a,b** through 1,5-hydrogen shift; **29b** leads to **26** by β-fragmentation with loss of *tert*-butyl radical: this kind of process is a peculiarity of N-alkyl substituted imidoyl radicals.[13]

As far as the formation of fluorenonimine **25** is concerned, we can envisage two different pathways, *i.e.* loss of hydrogen from **28a** or homolytic aromatic substitution of imidoyl radical **29a**, which is a well known process.[14]



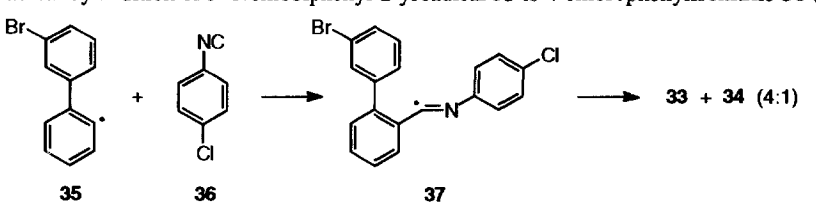
Scheme 6. Reaction mechanism for imines **2a,b**.

With the aim of understanding the real route to **25**, we carried out the reaction of imine **31** under the usual conditions (Scheme 7).



Scheme 7. Reaction of imine **31** with tri-*n*-butyltin hydride and AIBN.

As is shown in Scheme 7, the reaction afforded only trace amounts of **34**, which we detected only by means of a very careful GC analysis. If the fluorenonimine were produced *via* cyclisation of the imidoyl radical **37**, we should expect to obtain **33** and **34** in a 4:1 ratio, which is the ratio we observed when we generated the same imidoyl radical by addition of 3'-bromobiphenyl-2-yl radical **35** to 4-chlorophenylisonitrile **36** (Scheme 8).

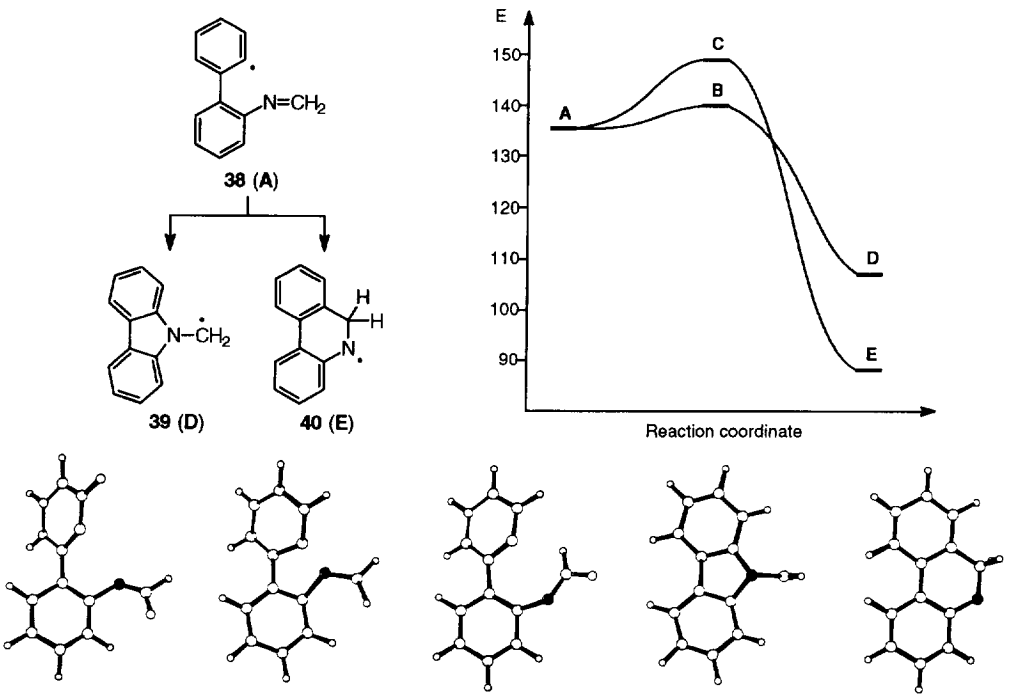


Scheme 8. Reaction of radical **35** with 4-chlorophenylisonitrile.

On the basis of these results we suggest that the fluorenonimines are obtained from the 5-exo-cyclisation-intermediate **28** by assisted hydrogen loss and the 1,5-hydrogen shift is only a minor process. The virtual absence of hydrogen shift in the case of radical **27a** could be ascribed to a faster 5-exo ring closure of **27a** with respect to **27b**, probably due to a higher stability of **28a** in comparison with **28b**. It is worth to point out that cyclisation of radicals **27a,b** is a regiospecific process which leads to the formation of 5-membered rings, exclusively.

In conclusion we can say that aryl radicals **6a,b** and **27a,b** show a remarkable preference towards a 5-exo cyclisation, as it has been observed in the ring closure of aryl radicals onto alkenes.[15] The presence of small quantities of products due to 6-endo ring closure in the case of radicals **6a,b** is probably the result of the formation of a strong carbon-carbon bond.[16]

To obtain some theoretical confirmation for our experimental data, AM1 semiempirical calculations were performed on the parent radical of our series, i.e. the N-methylene-2'-aminobiphenyl-2-yl radical (**38**). The estimated heats of formation of **38** and its 5-exo- and 6-endo-cyclisation intermediates **39** and **40** were determined as 134.8, 107.7, and 88.9 kcal mol^{-1}, respectively. The activation energies were calculated as 5.5 kcal mol^{-1} — for the 5-exo ring closure — and 14.7 kcal mol^{-1} — for the 6-endo process (Figure 2).



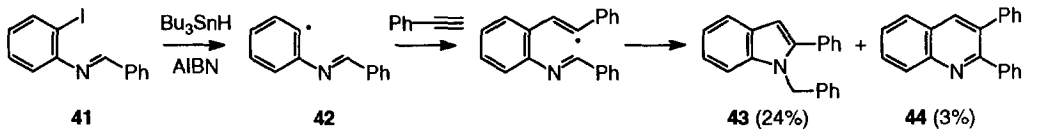
A (134.8 kcal mol^{-1}) **B** (140.3 kcal mol^{-1}) **C** (149.5 kcal mol^{-1}) **D** (107.7 kcal mol^{-1}) **E** (88.9 kcal mol^{-1})

Figure 2. Reaction profile for the cyclisation of radical **38**.

These data indicate that, for radical **38**, 5-exo- and 6-endo cyclisation modes are competitive but that the 5-exo ring closure is the remarkably preferred pathway. The heats of formation of the *tert*-butyl-substituted radicals **6b**, **7b**, and **9b** were estimated as 113.4, 84.0, and 78.4 kcal mol^{-1}, respectively. For these radicals, transition state computations were extremely time-consuming, due to the presence of nearly degenerate conformational isomers. This notwithstanding, it is of interest to observe that the calculated energy difference between the two cyclisation intermediates (5.6 kcal mol^{-1}) is appreciably lower than that computed for the unsubstituted radicals (18.8 kcal mol^{-1}). An identical difference was also calculated for the two intermediates

(**7c**, 128.5 kcal mol^{-1} and **9c**, 122.9 kcal mol^{-1}) arising from cyclisation of the phenyl-substituted radical **6c** (R = Ph). This might also be reflected in the transition state energies.

The same preference towards a 5-membered ring closure was exhibited by vinyl radicals **42** in the novel annulation we accomplished when imine **41** was allowed to react with stannyl radicals in the presence of an excess of phenylacetylene; the reaction afforded indole **43** and quinoline **44** in a 8:1 ratio (Scheme 9).



41 **42** **43** (24%) **44** (3%)

Scheme 9. Reaction of imine **41** with stannyl radicals and phenylacetylene.

Studies on the reactivity of vinyl radicals towards carbon-nitrogen multiple bonds are still underway.

EXPERIMENTAL SECTION

General Procedures.

Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^{1}H-NMR spectra were recorded in deuterochloroform (unless otherwise stated) on Varian EM 360L (60 MHz) or Varian Gemini 200 (200 MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra and high resolution mass spectra (HRMS) were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. IR spectra were recorded in chloroform on a Perkin-Elmer 257 spectrophotometer. GC-MS analyses were carried out on a Carlo Erba AUTO/HRGC/MS-QMD 1000 instrument equipped with a Quadrex capillary column (007, 25 m x 0.25 mm I.D.) and a NIST/NBS library. HPLC was performed on a Varian 5000 liquid chromatograph equipped with a C-18 column (Supelcosil LC-18, 5 μ, 25 cm x 4.6 mm I.D.) and a Varian 2050 variable λ detector operating at 254 nm, using acetonitrile/water mixtures as eluant. GC was performed on a Varian Star 3400 CX gas chromatograph equipped with a FID and the same column described for GC-MS analyses. Column chromatography was carried out on silica gel (ICN Silica, 63-200, 60 A), using light petroleum (40-70 °C) and a light petroleum/diethyl ether gradient (from 0 up to 100% diethyl ether) as eluant. Previously reported reaction products were identified by spectral comparison and mixed mp determination with authentic specimens.

Semiempirical AM1 (1, 2, 3) calculations[17] were carried out with the use of the MOPAC package (4) running on a RS/6000 250 IBM workstation. Starting geometries were obtained from standard bond lengths and angles. Unconstrained geometry optimisation was performed in Cartesian coordinates using BFGS minimiser with the PRECISE and GNORM=0.0 options turned on. Transition state localisation and optimisation was performed with the SADDLE option.

Starting Materials.

All reactions were carried out in benzene (J. T. Baker). Azo-bis-*iso*-butyronitrile (AIBN), di-*tert*-butyl peroxide (DTBP) (Fluka), tri-*n*-butyltin hydride, 4-chlorobenzoyl chloride, 4-chlorobenzaldehyde, trimethylacetaldehyde, 4-chlorobenzenamine, *tert*-butylamine, phenanthridine, and phenylacetylene (Aldrich) were commercially available; AIBN was purified by being dissolved in chloroform and reprecipitated with methanol. 2-Amino-2'-nitrobiphenyl,[18] 2-amino-2'-iodobiphenyl,[19] 2-amino-3'-bromobiphenyl,[20] 2-amino-5-bromobiphenyl,[21] 2-bromophenanthridine,[22] 9-bromophenanthridine,[23] 9-benzylcarbazole,[24] 2,2'-dibromobiphenyl,[25] 2-amino-2'-methylbiphenyl,[26] 2'-bromobiphenyl-2-ylcarboxaldehyde,[26] 4-chlorophenylisonitrile,[27] 3-bromo-9H-fluoren-9-one,[28] N-phenylmethylene-2-iodobenzenamine,[29] N-(phenylmethylene)benzenamine,[30] 1-benzyl-2-phenylindole,[31] 2,3-diphenylquinoline,[32] and di-*iso*-propyl peroxydicarbonate (DPDC)[33] were prepared according to the literature. DPDC was stored at 5 °C as a benzene solution and the peroxide content was determined by iodometric titration.[34]

2-Amino-5-bromo-2'-nitrobiphenyl. A solution of bromine (16.00 g, 100 mmol) in glacial acetic acid (35 mL) was added dropwise at 13-14 °C to a stirred solution of 2-amino-2'-nitrobiphenyl (21.40 g, 100 mmol) in acetic acid (100 mL). The reaction mixture was kept under stirring at r.t. for 4 h. Half of the solvent was evaporated and the residue diluted with cold water. The solution was extracted with diethyl ether and the organic layer washed with an aqueous solution (3%) of sodium carbonate and then with water. The ethereal phase was dried over sodium sulfate, the solvent evaporated, and the residue chromatographed to give 20.13 g (69%) of the title compound, mp = 133-134.5 °C (from 2-propanol); 60 MHz ^{1}H-NMR δ 3.47 (2 H, bs, -N*H*$_2$), 6.53 (1 H, d, *J* = 8.4 Hz, Ar-*H*), 6.97-8.20 (6 H, m, Ar-*H*); MS *m/e* (rel inten) 294 (M^+ + 2, 100), 292 (M^+, 97), 277 (35), 275 (34), 247 (14), 245 (18), 232 (9), 230 (6), 167 (91), 139 (32); HRMS calcd for $C_{12}H_9BrN_2O_2$ 291.98473, found 291.98456. Anal. calcd for $C_{12}H_9BrN_2O_2$: C, 49.17; H, 3.09; Br, 27.26; N, 9.56. Found: C, 49.40; H, 3.08; Br, 27.19; N, 9.52.

5-Bromo-2-iodo-2'-nitrobiphenyl. Following the procedure previously reported for 2-iodo-2'-nitrobiphenyl,[19] a mixture of 2-amino-5-bromo-2'-nitrobiphenyl (22.00 g, 75 mmol), water (1040 mL), and conc. hydrochloric acid (200 mL) was warmed at 60-70 °C until a clear solution was obtained. The amine was then diazotised, following the standard procedure, with an aqueous solution of sodium nitrite (8.50 g, 123 mmol). After 30 min of stirring, a solution of potassium iodide (39.60 g, 238 mmol) in the minimum amount of water was rapidly added (CAUTION: explosion hazard!) and the mixture was cautiously warmed up to its boiling point. After cooling, the solution was extracted with diethyl ether, the organic phase was washed with an aqueous solution (5%) of sodium hydroxide and then with water. After drying over sodium hydroxide pellets, the solvent was evaporated and the residue chromatographed to give the title compound (17.54 g, 58%), mp = 168-170 °C (from ethanol/benzene); 60 MHz ^{1}H-NMR δ (acetone-d_6) 7.10-7.47 (3 H, m), 7.53-7.87 (3 H, m), 7.93-8.20 (1 H, m); MS *m/e* (rel inten) 405 (M^+ + 2, 6), 403 (M^+, 5), 278 (100), 276 (90), 248 (20), 246 (19), 232 (9), 230 (7), 169 (43); HRMS calcd for $C_{12}H_7BrINO_2$ 402.87049, found 402.87075. Anal. calcd for $C_{12}H_7BrINO_2$: C, 35.68; H, 1.75; Br, 19.78; I, 31.41; N, 3.47. Found: C, 35.59; H, 1.75; Br, 19.82; I, 31.57; N, 3.48.

2-Amino-5'-bromo-2'-iodobiphenyl. A mixture of 5-bromo-2-iodo-2'-nitrobiphenyl (17.54 g, 43.4 mmol), anhydrous tin (II) chloride (31.80 g, 169 mmol), and conc. hydrochloric acid (31.80 mL, 169 mmol) in absolute ethanol (140 mL) was refluxed for 7 h. The solvent was evaporated and the residue neutralised under stirring with an aqueous solution (330 mL) of sodium hydroxide (39.74 g). The mixture was extracted with diethyl ether, the organic phase dried over sodium sulfate and the solvent evaporated to give the title amine (8.12 g, 50%), mp = 109-111 °C (from 2-propanol); 60 MHz ^{1}H-NMR δ 3.23 (2 H, bs, -N*H*$_2$), 6.50-7.43 (6 H, m, Ar-*H*), 7.68 (1 H, d, *J* = 8.2 Hz, Ar-*H*); MS *m/e* (rel inten) 375 (M^+ + 2, 22), 373 (M^+, 25), 248 (23), 246 (21), 167 (100), 166 (16), 139 (16); HRMS calcd for $C_{12}H_9BrIN$ 372.89631, found 372.89658. Anal. calcd for $C_{12}H_9BrIN$: C, 38.54; H, 2.43; Br, 21.36; I, 33.93; N, 3.74. Found: C, 38.37; H, 2.44; Br, 21.40; I, 34.03; N, 3.76.

2-Amino-5-bromo-2'-iodobiphenyl. Following the procedure previously described for 2-amino-5-bromo-2'-nitrobiphenyl, 2-amino-2'-iodobiphenyl (14.75 g, 50 mmol) gave 13.98 g (75%) of the title compound, oil; 60 MHz ^{1}H-NMR δ 3.33 (2 H, bs, -N*H*$_2$), 6.40 (1 H, d, *J* = 8.2 Hz, Ar-*H*), 6.57-7.47 (5 H, m, Ar-*H*), 7.80 (1 H, dd, J_1 = 8.0 Hz, J_2 = 0.5 Hz, Ar-*H*); MS *m/e* (rel inten) 375 (M^+ + 2, 31), 373 (M^+, 32), 248 (15), 247 (8), 246 (15), 245 (6), 167 (100), 166 (18); HRMS calcd for $C_{12}H_9BrIN$ 372.89631, found 372.89653. Anal. calcd for $C_{12}H_9BrIN$: C, 38.54; H, 2.43; Br, 21.36; I, 33.93; N, 3.74. Found: C, 38.38; H, 2.43; Br, 21.43; I, 34.04; N, 3.72.

N-(3'-Bromobiphenyl-2-yl)-4-chlorobenzamide. A benzene solution of 4-chlorobenzoyl chloride (3.83 g, 22 mmol) was added dropwise at r.t. to a stirred benzene solution of 2-amino-3'-bromobiphenyl (5.43 g, 22 mmol) and triethylamine (2.53 g, 25 mmol). The mixture was then refluxed for 90 min and filtered; the solvent

was removed under vacuum and the residue recrystallised from ethanol to give 4.25 g (50%) of the amide, mp = 104-106 °C; 60 MHz ^{1}H-NMR δ 7.00-8.33 (13 H, m, Ar-*H* + -N*H*-); MS *m/e* (rel inten) 389 (M^+ + 4, 8), 387 (M^+ + 2, 30), 385 (M^+, 24), 167 (8), 166 (4), 141 (43), 139 (100), 113 (9), 111 (28); HRMS calcd for $C_{19}H_{13}BrClNO$ 384.98690, found 384.98711. Anal. calcd for $C_{19}H_{13}BrClNO$: C, 59.02; H, 3.39; Br, 20.67; Cl, 9.17; N, 3.62. Found: C, 59.21; H, 3.37; Br, 20.55; Cl, 9.21; N, 3.61.

*9-Bromo-6-(4-chlorophenyl)phenanthridine (**10**).* Phosphorus pentoxide (49.29 g) was added portionwise at 185 °C to 85% phosphoric acid (15.30 mL). After stirring for 50 min, N-(3'-bromobiphenyl-2-yl)-4-chlorobenzamide (2.00 g, 5.2 mmol) was added and the reaction vessel kept at 185 °C for 2 h. After cooling, the mixture was poured into water, neutralised with aqueous ammonia, and extracted with diethyl ether; the organic phase was dried over sodium sulfate, the solvent removed, and the residue chromatographed to give 1.05 g (55%) of **10**, mp = 213-215 °C (from light petroleum/benzene) [200 MHz ^{1}H-NMR δ 7.54 (2 H, A part of AA'BB', *J* = 8.5 Hz), 7.63-7.84 (5 H, m + B part of AA'BB', *J* = 8.5 Hz), 7.92 (1 H, d, *J* = 8.7 Hz), 8.22 (1 H, dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz), 8.52 (1 H, dd, J_1 = 7.9 Hz, J_2 = 1.5 Hz), 8.82 (1 H, d, *J* = 1.7 Hz); MS *m/e* (rel inten) 371 (M^+ + 4, 27), 370 (M^+ + 3, 37), 369 (M^+ + 2, 100), 368 (M^+ + 1, 91), 367 (M^+, 75), 366 (56), 334 (40), 332 (37), 290 (26), 289 (29), 288 (84), 287 (31), 253 (32), 252 (25), 251 (26), 226 (7), 225 (8), 224 (6), 144 (27), 126 (46); HRMS calcd for $C_{19}H_{11}BrClN$ 366.97633, found 366.97616. Anal. calcd for $C_{19}H_{11}BrClN$: C, 61.90; H, 3.01; Br, 21.67; Cl, 9.62; N, 3.80. Found: C, 61.75; H, 3.02; Br, 21.75; Cl, 9.67; N, 3.81] together with 0.29 g (15%) of 7-bromo-6-(4-chlorophenyl)phenanthridine, mp = 159-162 °C (from light petroleum/benzene) [200 MHz ^{1}H-NMR δ 7.48 (4 H, s), 7.61-7.83 (3 H, m), 7.95 (1 H, bd, *J* = 7.8 Hz), 8.20 (1 H, dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz), 8.56 (1 H, bd, *J* = 8.0 Hz), 8.72 (1 H, bd, *J* = 8.3 Hz); MS *m/e* (rel inten) 371 (M^+ + 4, 11), 370 (M^+ + 3, 19), 369 (M^+ + 2, 39), 368 (M^+ + 1, 44), 367 (M^+, 35), 366 (27), 334 (27), 332 (27), 290 (34), 289 (30), 288 (100), 287 (36), 253 (67), 252 (63), 251 (66), 226 (20), 225 (24), 224 (22), 150 (35), 126 (23); HRMS calcd for $C_{19}H_{11}BrClN$ 366.97633, found 366.97610. Anal. calcd for $C_{19}H_{11}BrClN$: C, 61.90; H, 3.01; Br, 21.67; Cl, 9.62; N, 3.80. Found: C, 61.75; H, 3.02; Br, 21.76; Cl, 9.65; N, 3.82].

2-Amino-5-bromo-2'-methylbiphenyl. Following the procedure previously described for 2-amino-5-bromo-2'-nitrobiphenyl, 2-amino-2'-methylbiphenyl (23.00 g, 125 mmol) gave 19.22 g (60%) of the title compound, bp (1 mbar) = 154-156 °C, mp = 42-43 °C; 200 MHz ^{1}H-NMR δ 2.18 (3 H, s, Me), 3.48 (2 H, bs, -NH_2), 6.65 (1 H, d, *J* = 8.2 Hz, Ar-*H*), 7.12-7.33 (6 H, m, Ar-*H*); MS *m/e* (rel inten) 263 (M^+ + 2, 94), 261 (M^+, 100), 183 (19), 182 (20), 181 (31), 180 (25), 167 (50), 165 (58), 91 (16), 90 (25); HRMS calcd for $C_{13}H_{12}BrN$ 261.01531, found 261.01528. Anal. calcd for $C_{13}H_{12}BrN$: C, 59.56, H, 4.61; Br, 30.48; N, 5.35. Found: C, 59.41; H, 4.63; Br, 30.59; N, 5.37.

5-Bromo-2-iodo-2'-methylbiphenyl. Following the procedure previously described for 5-bromo-2-iodo-2'-nitrobiphenyl, 2-amino-5-bromo-2'-methylbiphenyl (19.22 g, 73.4 mmol) yielded 20 g (73%) of the title iodide, mp = 72.5-73 °C (from light petroleum); 200 MHz ^{1}H-NMR δ 2.10 (3 H, s, Me), 7.05 (1 H, bd, *J* = 7.1 Hz, Ar-*H*), 7.15-7.40 (5 H, m, Ar-*H*), 7.78 (1 H, d, *J* = 8.5 Hz, Ar-*H*); MS *m/e* (rel inten) 374 (M^+ + 2, 36), 372 (M^+, 41), 166 (100), 165 (58), 83 (17); HRMS calcd for $C_{13}H_{10}BrI$ 371.90106, found 371.90065. Anal. calcd for $C_{13}H_{10}BrI$: C, 41.86; H, 2.70; Br, 21.42; I, 34.02. Found: C, 41.70; H, 2.71; Br, 21.47; I, 34.12.

5-Bromo-2'-(bromomethyl)-2-iodobiphenyl. A mixture of 5-bromo-2-iodo-2'-methylbiphenyl (17.54 g, 47 mmol) and N-bromosuccinimide (8.36 g, 47 mmol) in tetrachloromethane (100 mL) was refluxed for 18 h in the presence of catalytic amounts of dibenzoyl peroxide. The mixture was cooled and filtered and the filtrate chromatographed to give the title bromide (18.00 g, 85%), mp = 83-84 °C (from light petroleum); 200 MHz ^{1}H-NMR δ 4.13 (1 H, A part of AB, *J* = 9.7 Hz, -CH_2Br), 4.40 (1 H, B part of AB, *J* = 9.7 Hz, -CH_2Br), 7.10 (1 H, dd, J_1 = 6.8 Hz, J_2= 2.0 Hz, Ar-*H*), 7.25 (1 H, dd, J_1 = 8.5 Hz, J_2= 2.2 Hz, Ar-*H*), 7.33-7.58 (4 H, m,

Ar-*H*), 7.80 (1 H, d, J = 8.5 Hz, Ar-*H*); MS *m/e* (rel inten) 454 (M^+ + 4, 7), 452 (M^+ + 2, 10), 450 (M^+, 7), 373 (3), 246 (44), 244 (41), 165 (100), 164 (19), 163 (16); HRMS calcd for $C_{13}H_9Br_2I$ 449.81156, found 449.81127. Anal. calcd for $C_{13}H_9Br_2I$: C, 34.55; H, 2.01; Br, 35.36; I, 28.08. Found: C, 34.42; H, 2.02; Br, 35.44; I, 28.12.

5-Bromo-2-iodobiphenyl-2'-ylmethanol. A mixture of 5-bromo-2'-(bromomethyl)-2-iodobiphenyl (16.17 g, 35.7 mmol), dioxane (10 mL), and 10% aqueous solution of sodium carbonate (80.8 mL) was refluxed for 24 h. The mixture was then extracted with diethyl ether, the organic phase dried over sodium sulfate, the solvent removed, and the residue chromatographed to give the title alcohol (12.2 g, 88%), mp = 117-118.5 °C; 200 MHz ^{1}H-NMR δ 1.50-1.70 (1 H, m, -CH_2OH, disappearing by adding D_2O), 4.30-4.53 (2 H, m, -CH_2OH, collapsing to an AB system, J = 12.4 Hz, by adding D_2O), 7.08 (1 H, dd, J_1 = 7.4 Hz, J_2 = 1.5 Hz, Ar-*H*), 7.21 (1 H, dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, Ar-*H*), 7.31-7.51 (3 H, m, Ar-*H*), 7.55-7.63 (1 H, m, Ar-*H*), 7.77 (1 H, d, J = 8.5 Hz, Ar-*H*); MS *m/e* (rel inten) 390 (M^+ + 2, 6), 388 (M^+, 6), 263 (6), 261 (7), 245 (8), 243 (8), 182 (100), 181 (27), 165 (6), 154 (9), 153 (11), 152 (22), 151 (9); HRMS calcd for $C_{13}H_{10}BrIO$ 387.89597, found 387.89581. Anal. calcd for $C_{13}H_{10}BrIO$: C, 40.14; H, 2.59; Br, 20.54; I, 32.62. Found: C, 40.01; H, 2.60; Br, 20.59; I, 32.70.

5-Bromo-2-iodobiphenyl-2'-ylcarboxaldehyde. A solution of 5-bromo-2-iodobiphenyl-2'-ylmethanol (12.20 g, 31.4 mmol) in dichloromethane (62.7 mL) was added dropwise at 25 °C to a stirred mixture of chromic anhydride (18.82 g, 188 mmol), pyridine (28.8 g, 365 mmol), and dichloromethane (470 mL). After 24 h the mixture was filtered on silica gel, the solvent was evaporated, and the residue crystallised to give the title aldehyde (7.50 g, 60%), mp = 101-102 °C (from 2-propanol); 200 MHz ^{1}H-NMR δ 7.22-7.30 (2 H, m, Ar-*H*), 7.47 (1 H, d, J = 2.0 Hz, Ar-*H*), 7.58 (1 H, dddd, $J_1 = J_2$ = 7.2 Hz, J_3 = 1.5 Hz, J_4 = 0.8 Hz, Ar-*H*), 7.69 (1 H, ddd, $J_1 = J_2$ = 7.2 Hz, J_3 = 1.5 Hz, Ar-*H*), 7.81 (1 H, d, J = 8.3 Hz, Ar-*H*), 8.04 (1 H, dd, J_1 = 7.2 Hz, J_2 = 1.5 Hz, Ar-*H*), 9.80 (1 H, d, J = 0.8 Hz, -C*H*O); MS *m/e* (rel inten) 261 (M^+ + 2 - 127, 100), 259 (M^+ - 127, 100), 180 (25), 152 (40), 151 (22), 150 (13), 76 (19). Anal. calcd for $C_{13}H_8BrIO$: C, 40.35; H, 2.08; Br, 20.65; I, 32.79. Found: C, 40.25; H, 2.09; Br, 20.68; I, 32.85.

3-Bromo-2'-iodobiphenyl. Following the procedure previously described for 5-bromo-2-iodo-2'-nitrobiphenyl, 2-amino-3'-bromobiphenyl (13.00 g, 52.6 mmol) yielded the title compound (17.40 g, 92%), reddish oil, bp (0.3 mmHg) = 145-147 °C; 200 MHz ^{1}H-NMR δ 7.07 (1 H, ddd, J_1 = 7.9 Hz, J_2 = 7.9 Hz, J_3 = 1.7 Hz), 7.26-7.46 (4 H, m), 7.50-7.58 (2 H, m), 7.98 (1 H, dd, J_1 = 7.9 Hz, J_2 = 0.9 Hz); MS *m/e* (rel inten) 360 (M^+ + 2, 66), 358 (M^+, 66), 152 (100), 151 (16), 127 (6), 76 (18). HRMS calcd for $C_{12}H_8BrI$ 357.88541, found 357.88520. Anal. calcd for $C_{12}H_8BrI$: C, 40.15; H, 2.25; Br, 22.25; I, 35.35. Found: C, 40.02; H, 2.26; Br, 22.29; I, 35.43.

Synthesis of the imines.

General procedure. A benzene (100 mL) solution of the amine (50 mmol) and 4-chlorobenzaldehyde (50 mmol) or trimethylacetaldehyde (100 mmol) was refluxed with azeotropic removal of water in the presence of catalytic amounts of *p*-toluenesulfonic acid (0.1 g). The solvent was evaporated and the residue crystallised; in some cases the reaction yielded oily products which could not be distilled and were used in the subsequent reactions without further purification. Microanalyses of these oily compounds were not performed, but their ^{1}H-NMR spectra are in accordance with a very good sample homogeneity. Their identity was confirmed by HRMS analysis. The following imines were prepared according to this general procedure.

5-Bromo-N-[(4-chlorophenyl)methylene]-2-aminobiphenyl, yield = 75%, mp = 162-164 °C (from light petroleum/benzene); 60 MHz ^{1}H-NMR δ 6.85 (1 H, d, J = 8.0 Hz, Ar-*H*), 7.10-7.77 (11 H, m, Ar-*H*), 8.30 (1 H, s, -N=C*H*-); MS *m/e* (rel inten) 373 (M^+ + 4, 7), 372 (M^+ + 3, 7), 371 (M^+ + 2, 20), 370 (M^+ + 1, 18), 369 (M^+, 16), 368 (15), 292 (7), 290 (25), 288 (18), 260 (97), 258 (100), 179 (20), 152 (35); HRMS calcd for

$C_{19}H_{13}BrClN$ 368.99198, found 368.99218. Anal. calcd for $C_{19}H_{13}BrClN$: C, 61.57; H, 3.53; Br, 21.56; Cl, 9.56; N, 3.78. Found: C, 61.40; H, 3.55; Br, 21.64; Cl, 9.61; N, 3.80.

*N-[(4-Chlorophenyl)methylene]-2'-iodo-2-aminobiphenyl (**1a**)*, oil, 60 MHz ^{1}H-NMR δ 6.50-7.83 (12 H, m, Ar-*H*), 8.24 (1 H, s, -N=C*H*-); MS *m/e* (rel inten) 419 (M^+ + 2, 3), 417 (M^+, 8), 292 (38), 290 (100), 255 (41); HRMS calcd for $C_{19}H_{13}ClIN$ 416.97813, found 416.97783.

*N-(tert-Butylmethylene)-2'-iodo-2-aminobiphenyl (**1b**)*, oil, 60 MHz ^{1}H-NMR δ 0.93 (9 H, s, *tert*-Bu), 6.63-7-40 (7 H, m, Ar-*H*), 7.47 (1 H, s, -N=C*H*-), 7.75 (1 H, d, *J* = 8.0 Hz, Ar-*H*); MS *m/e* (rel inten) 363 (M^+, 70), 348 (60), 306 (5), 236 (100), 180 (85), 179 (100), 168 (65), 166 (60), 152 (85), 151 (80), 150 (40); HRMS calcd for $C_{17}H_{18}IN$ 363.04840, found 363.04808.

*5'-Bromo-N-[(4-chlorophenyl)methylene]-2'-iodo-2-aminobiphenyl (**14a**)*, yield = 40%, mp = 110-112 °C (from 2-propanol); 60 MHz ^{1}H-NMR δ 6.83-7.67 (11 H, m, Ar-*H*), 8.26 (1 H, s, -N=C*H*-); MS *m/e* (rel inten) 499 (M^+ + 4, 2), 497 (M^+ + 2, 5), 495 (M^+, 4), 372 (26), 370 (100), 368 (82), 334 (5), 332 (5), 290 (11), 288 (28), 253 (10), 177 (13), 151 (14), 127 (28); HRMS calcd for $C_{19}H_{12}BrClIN$ 494.88864, found 494.88888. Anal. Calcd for $C_{19}H_{12}BrClIN$: C, 45.95; H, 2.44; Br, 16.09; Cl, 7.14; I, 25.56; N, 2.82. Found: C, 45.80; H, 2.43; Br, 16.14; Cl, 7.16; I, 25.63; N, 2.84.

*5'-Bromo-N-(tert-butylmethylene)-2'-iodo-2-aminobiphenyl (**14b**)*, yield = 20% after column chromatography on basic aluminium oxide, oil; 60 MHz ^{1}H-NMR δ 0.98 (9 H, s, *tert*-Bu), 6.63-7.70 (8 H, m, Ar-*H* + -N=C*H*-); MS *m/e* (rel inten) 443 (M^+ + 2, 36), 441 (M^+, 32), 428 (13), 426 (14), 316 (32), 314 (36), 259 (100), 257 (100), 235 (80), 178 (27), 151 (66); HRMS calcd for $C_{17}H_{17}BrIN$ 440.95891, found 440.95752.

*5-Bromo-N-[(4-chlorophenyl)methylene]-2'-iodo-2-aminobiphenyl (**18a**)*, oil; 60 MHz ^{1}H-NMR δ 6.57-7.93 (11 H, m, Ar-*H*); 8.21 (1 H, s, -N=C*H*-); MS *m/e* (rel inten) 499 (M^+ + 4, 3), 497 (M^+ + 2, 13), 495 (M^+, 10), 372 (27), 370 (100), 368 (77), 334 (3), 332 (3), 290 (27), 288 (27), 253 (7), 177 (13), 151 (13), 127 (33); HRMS calcd for $C_{19}H_{12}BrClIN$ 494.88864, found 494.88842.

*5-Bromo-N-(tert-butylmethylene)-2'-iodo-2-aminobiphenyl (**18b**)*, oil; 60 MHz ^{1}H-NMR δ 0.90 (9 H, s, *tert*-Bu), 6.50-8.00 (8 H, m, Ar-*H* + -N=C*H*-); MS *m/e* (rel inten) 443 (M^+ + 2, 60), 441 (M^+, 57), 428 (20), 426 (20), 316 (20), 314 (23), 259 (100), 257 (91), 235 (61), 178 (28), 151 (41); HRMS calcd for $C_{17}H_{17}BrIN$ 440.95891, found 440.95916.

*N-[(2'-Bromobiphenyl-2-yl)methylene]-4-chlorobenzenamine (**2a**)*, yield = 72%, mp = 74-76 °C (from light petroleum); 60 MHz ^{1}H-NMR δ 6.78-7.68 (11 H, m, Ar-*H*), 8.10 (1 H, s, -N=C*H*-), 8.15-8.43 (1 H, m, Ar-*H*); MS *m/e* (rel inten) 372 (M^+ + 4, <1), 370 (M^+ + 2, <1), 368 (M^+, <1), 292 (40), 290 (100), 254 (7), 178 (22), 165 (7), 152 (10), 151 (9). Anal. calcd for $C_{19}H_{13}BrClN$: C, 61.57; H, 3.53; Br, 21.56; Cl, 9.56; N, 3.78. Found: C, 61.40; H, 3.55; Br, 21.65; Cl, 9.60; N, 3.80.

*N-[(2'-Bromobiphenyl-2-yl)methylene]-tert-butylamine (**2b**)*, yield = 97%, bp (15 mbar) = 126-127 °C; 60 MHz ^{1}H-NMR δ 1.10 (9 H, s, *tert*-Bu), 6.83-7.62 (7 H, m, Ar-*H*), 7.92 (1 H, s, -N=C*H*-), 7.97-8.22 (1 H, m, Ar-*H*); MS *m/e* (rel inten) 302 (M^+ + 2 - 15, 5), 300 (M^+ - 15, 4), 245 (7), 243 (7), 236 (M^+ - 79, 7), 180 (100), 179 (13), 165 (10), 152 (7), 151 (5), 57 (15). Anal. calcd for $C_{17}H_{18}BrN$: C, 64.57; H, 5.74; Br, 25.26; N, 4.43. Found: C, 64.39; H, 5.77; Br, 25.39; N, 4.45.

*N-[(5'-Bromo-2'-iodobiphenyl-2-yl)methylene]-4-chlorobenzenamine (**31**)*, yield = 40%, mp = 145-147 °C (from light petroleum/benzene); 200 MHz ^{1}H-NMR δ 7.02 (2 H, A part of AA'BB', *J* = 8.6 Hz, Ar-*H*), 7.17-7.27 (2 H, m, Ar-*H*), 7.30 (2 H, B part of AA'BB', *J* = 8.6 Hz, Ar-*H*), 7.48 (1 H, d, *J* = 2.4 Hz, Ar-*H*),

7.53-7.58 (2 H, m, Ar-*H*), 7.80 (1 H, d, J = 8.3 Hz, Ar-*H*), 8.08 (1 H, s, -N=C*H*-), 8.30-8.36 (1 H, m, Ar-*H*); MS *m/e* (rel inten) 372 (M^+ + 4 - 127, 32), 370 (M^+ + 2 - 127, 100), 368 (M^+ - 127, 82), 290 (13), 288 (15), 254 (9), 253 (9), 177 (30), 151 (15), 127 (20), 111 (13), 75 (22). Anal. calcd for $C_{19}H_{12}BrClIN$: C, 45.95; H, 2.44; Br, 16.09; Cl, 7.14; I, 25.56; N, 2.82. Found: C, 45.84; H, 2.44; Br, 16.15; Cl, 7.16; I, 25.59; N, 2.82.

*N-(3-Bromofluoren-9-ylidene)-4-chlorobenzenamine (**33**)*, yield = 41%, yellow solid, mp = 151-153 °C (from ethanol/benzene); this imine was obtained as a mixture of the (*E*)- and (*Z*)-isomer: the isomer ratio was ca. 56:44 but it was not possible to distinguish the signals of each isomer and to determine the prevalent one; 200 MHz ^{1}H-NMR δ 6.50 (1 H, d, J = 8.1 Hz), 6.68 (1 H, m), 6.89-7.06 (4.4 H, m), 7.11 (1 H, dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz), 7.33-7.62 (9 H, m), 7.72-7.77 (2.6 H, m), 7.90 (0.8 H, m); MS *m/e* (rel inten) 371 (M^+ + 4, 22), 369 (M^+ + 2, 100), 367 (M^+, 64), 334 (4), 332 (4), 288 (6), 287 (9), 253 (29), 252 (11), 126 (13); HRMS calcd for $C_{19}H_{11}BrClN$ 366.97633, found 366.97619. Anal. calcd for $C_{19}H_{11}BrClN$: C, 61.90; H, 3.01; Br, 21.67; Cl, 9.62; N, 3.80. Found: C, 61.76; H, 3.02; Br, 21.76; Cl, 9.65; N, 3.81.

*2-Bromo-6-(4-chlorophenyl)phenanthridine (**20**).* Following the reported procedure for the synthesis of phenanthridine derivatives,[14] a benzene (30 mL) solution of 5-bromo-N-[(4-chlorophenyl)methylene]-2-aminobiphenyl (1.85 g, 5 mmol) and DPDC (10 mmol) was kept at 60 °C for 4 h. The solvent was evaporated and the residue crystallised to give 1.38 g (75%) of the title phenanthridine, mp = 206-208 °C (from ethanol/benzene); 200 MHz ^{1}H-NMR δ 7.56 (2 H, A part of AA'BB', J = 8.7 Hz), 7.63-7.74 (3 H, m + B part of AA'BB', J = 8.7 Hz), 7.81-7.96 (2 H, m), 8.09 (2 H, m), 8.63 (1 H, bd, J = 8.2 Hz), 8.75 (1 H, d, J = 2.1 Hz); MS *m/e* (rel inten) 371 (M^+ + 4, 22), 370 (M^+ + 3, 37), 369 (M^+ + 2, 86), 368 (M^+ + 1, 100), 367 (M^+, 67), 366 (67), 334 (31), 332 (32), 289 (13), 288 (10), 287 (32), 253 (16), 252 (18), 251 (17), 144 (19), 126 (38); HRMS calcd for $C_{19}H_{11}BrClN$ 366.97633, found 366.97659. Anal. calcd for $C_{19}H_{11}BrClN$: C, 61.89; H, 3.01; Br, 21.68; Cl, 9.62; N, 3.80. Found: C, 61.70; H, 3.02; Br, 21.80; Cl, 9.67; N, 3.81.

*Reactions of haloimines **1a,b**, **14a,b**, **18a,b**, **2a,b**, and **31** with tri-n-butyltin hydride.*

General procedure. A benzene (40 mL) solution of imine (1 mmol), tri-*n*-butyltin hydride (1.2 equiv) and AIBN (0.3 equiv, unless otherwise stated) was refluxed to complete disappearance of the starting material. The solvent was evaporated and the residue diluted with diethyl ether and stirred with an aqueous solution of potassium fluoride (10^{-4} g/l) for 30 min.[39] Tri-*n*-butyltin fluoride was filtered off and the organic phase separated, dried over sodium sulfate, and the solvent removed. The residue was chromatographed on a silica gel column to give the reported products; in some cases, HPLC or GC quantitative analyses of the reaction mixtures were carried out as well. The following reactions were performed according to this general procedure.

*From **1a**.* **1a** (2.09 g, 5 mmol), tri-*n*-butyltin hydride (1.75 g, 6 mmol), and AIBN (0.25 g, 1.5 mmol) gave, after 5 h of reflux, 9-[(4-chlorophenyl)methyl]-9H-carbazole (**3a**) (71%), mp = 164-167 °C (from light petroleum/benzene) [60 MHz ^{1}H-NMR δ 5.37 (2 H, s, -CH_2-), 6.77-8.20 (12 H, m, Ar-*H*); MS *m/e* (rel inten) 293 (M^+ + 2, 17), 291 (M^+, 47), 180 (4), 166 (11), 127 (32), 125 (100), 89 (12); HRMS calcd for $C_{19}H_{14}ClN$ 291.08148, found 291.08180. Anal. calcd for $C_{19}H_{14}ClN$: C, 78.21; H, 4.84; Cl, 12.15; N, 4.80. Found: C, 78.10; H, 4.86; Cl, 12.22; N, 4.82], and 5-(4-chlorophenyl)phenanthridine (**4**) (9%), mp = 160-161 °C (from light petroleum/benzene) (lit.[14] mp = 160-161 °C). The yields of **3a** and **4** were determined by HPLC. The reaction also afforded trace amounts of two dimeric compounds [MS *m/e* (rel inten) 582 (M^+ + 2, 2), 580 (M^+, 4), 292 (33), 290 (100), 254 (6) and 582 (M^+ + 2, 2), 580 (M^+, 4), 292 (35), 290 (100), 254 (5), respectively]. A GC-MS analysis of the reaction mixture showed the presence of little amounts of compounds probably arising from coupling between **7a** (or **9a**) and the α-cyano-*iso*-propyl radical.

*From **1b**.* **1b** (1.82 g, 5 mmol), tri-*n*-butyltin hydride (1.75 g, 6 mmol), and AIBN (0.25 g, 1.5 mmol) yielded, after 24 h of reflux, 9-(2,2-dimethylpropyl)-9H-carbazole (**3b**) (45%), mp = 76-79 °C (from light

petroleum/benzene) [60 MHz ^{1}H-NMR δ 1.00 (9 H, s, *tert*-Bu), 3.88 (2 H, s, -C*H*$_2$-), 6.90-7.47 (6 H, m, Ar-*H*), 7.77-8.07 (2 H, m, Ar-*H*); MS *m/e* (rel inten) 237 (M^+, 64), 222 (3), 181 (49), 180 (100), 167 (5), 166 (5), 152 (22); HRMS calcd for $C_{17}H_{19}N$ 237.15175, found 237.15139. Anal. calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.96; H, 8.11; N, 5.93], and phenanthridine (**5**) (19%), mp = 108-109 °C (from light petroleum/benzene) (mp of a commercial sample = 107-109 °C). The yields of **3b** and **5** were determined by HPLC.

*From **14a***. **14a** (1.12 g, 2.25 mmol), tri-*n*-butyltin hydride (0.66 g, 2.25 mmol), and AIBN (0.41 g, 2.48 mmol) afforded, after 17 h of reflux, 3-bromo-9-[(4-chlorophenyl)methyl]-9H-carbazole (**17a**) (44%), mp = 148-150 °C (from light petroleum/benzene) [60 MHz ^{1}H-NMR δ 5.31 (2 H, s, -C*H*$_2$-), 7.67-8.23 (11 H, m, Ar-*H*); MS *m/e* (rel inten) 373 (M^+ + 4, 7), 371 (M^+ + 2, 26), 369 (M^+, 21), 293 (7), 291 (24), 246 (2), 244 (2), 127 (34), 125 (100); HRMS calcd for $C_{19}H_{13}BrClN$ 368.99198, found 368.99229. Anal. calcd for $C_{19}H_{13}BrClN$: C, 61.57; H, 3.53; Br, 21.56; Cl, 9.56; N, 3.78. Found: C, 61.45; H, 3.54; Br, 21.63; Cl, 9.59; N, 3.79], and 9-bromo-5-(4-chlorophenyl)phenanthridine (**10**) (2%), mp = 213-215 °C (from light petroleum /benzene) [mp and spectroscopic data are identical to those obtained in the previously described synthesis of **10**]. A very careful GC analysis of the reaction mixture showed the complete absence of phenanthridine **20**. The reaction also gave trace amounts of a possible dimeric compound [MS *m/e* (rel inten) 372 (M^+/2 + 4, 25), 370 (M^+/2 + 2, 100), 368 (M^+/2, 80), 332 (10), 290 (18), 288 (50), 253 (15), 177 (20), 127 (90), 126 (25)], and a coupling product with α-cyano-*iso*-propyl radical [MS *m/e* (rel inten) 440 (M^+ + 4, 4), 438 (M^+ + 2, 14), 436 (M^+, 10), 372 (26), 370 (100), 368 (78), 290 (6), 289 (8), 288 (13), 127 (19)].

*From **14b***. **14b** (0.90 g, 2.04 mmol), tri-*n*-butyltin hydride (0.60 g, 2.04 mmol), and AIBN (0.37 g, 2.24 mmol) gave, after 24 h of reflux, 3-bromo-9-(2,2-dimethylpropyl)-9H-carbazole (**17b**) (44%), mp = 97-99 °C (from light petroleum) [60 MHz ^{1}H-NMR δ 0.93 (9 H, s, *tert*-Bu), 3.83 (2 H, s, -C*H*$_2$-), 6.87-8.16 (7 H, m, Ar-*H*); MS *m/e* (rel inten) 317 (M^+ + 2, 34), 315 (M^+, 35), 302 (2), 300 (2), 260 (100), 258 (96), 179 (31), 178 (11); HRMS calcd for $C_{17}H_{18}BrN$ 315.06226, found 315.06260. Anal. calcd for $C_{17}H_{18}BrN$: C, 64.56; H, 5.74; Br, 25.27; N, 4.43. Found: C, 64.48; H, 5.76; Br, 25.33; N, 4.43], and 9-bromophenanthridine (**13**) (21%), mp = 118-120 °C (from light petroleum/benzene) (lit.[23] mp = 118-119 °C). A very careful GC analysis of the reaction mixture showed the complete absence of phenanthridine **23**.

*From **18a***. **18a** (2.48 g, 5 mmol), tri-*n*-butyltin hydride (1.46 g, 5 mmol), and AIBN (0.90 g, 5.5 mmol) yielded, after 48 h of reflux, **17a** (28%), mp = 148-150 °C (from light petroleum/benzene) [spectroscopic data are identical to those described for **17a** obtained in the above reaction of **14a**], and 2-bromo-6-(4-chlorophenyl)phenanthridine (**20**) [mp and spectroscopic data are identical to those obtained in the previously described synthesis of **20**]. A very careful GC analysis of the reaction mixture showed the complete absence of phenanthridine **10**. The reaction also gave trace amounts of a possible dimeric compound [MS *m/e* (rel inten) 372 (M^+/2 + 4, 25), 370 (M^+/2 + 2, 100), 368 (M^+/2, 80), 332 (10), 290 (20), 288 (55), 253 (20), 177 (25), 127 (100), 125 (30)].

*From **18b***. **18b** (2.21 g, 5 mmol), tri-*n*-butyltin hydride (1.46 g, 5 mmol), and AIBN (0.90 g, 5.5 mmol) gave, after 24 h of reflux, **17b** (35%), mp = 97-99 °C (from light petroleum) [spectroscopic data are identical to those described for **17b** obtained in the above reaction of **14b**], and 2-bromophenanthridine (**23**) (21%), mp = 159-162 °C (from light petroleum/benzene) (lit.[22] mp = 162-163 °C). A very careful GC analysis of the reaction mixture showed the complete absence of phenanthridine **13**.

*From **2a***. **2a** (1.11 g, 3 mmol), tri-*n*-butyltin hydride (1.05 g, 3.6 mmol), and AIBN (0.12 g, 0.75 mmol) gave, after 7 h of reflux, N-(9H-fluoren-9-ylidene)-4-chlorobenzenamine (**25**) (4%), mp = 149-151 °C (from ethanol) (lit.[35] mp = 147-148 °C), and N-(9H-fluoren-9-yl)-4-chlorobenzenamine (**24a**) (54%), mp = 115-116 °C (from light petroleum/benzene) (lit.[35] mp = 115-116 °C). The yields of **25** and **24a** were determined by GC

analysis. Besides **25** and **24a**, the reaction afforded small amounts of a possible dimeric compound, mp = 169-172 °C; 200 MHz ^{1}H-NMR δ 4.75 (1 H, bs), 5.98 (2 H, A part of AA'BB', J = 8.8 Hz), 6.77 (2 H, B part of AA'BB', J = 8.8 Hz), 7.26 (2 H, ddd, $J_1 = J_2$ = 7.3 Hz, J_3 = 1.0 Hz), 7.43 (2 H, ddd, $J_1 = J_2$ = 7.3 Hz, J_3 = 1.0 Hz), 7.55 (2 H, bd, J = 7.3 Hz), 7.74 (2 H, bd, J = 7.3 Hz); MS *m/e* (rel inten) 292 ($M^+/2$ + 2, 30), 290 ($M^+/2$, 100), 254 (6), 165 (19).

From 2b. **2b** (1.26 g, 4 mmol), tri-*n*-butyltin hydride (1.40 g, 4.8 mmol), and AIBN (0.16 g, 1 mmol) gave, after 8 h of reflux, N-*tert*-butyl-N-(9H-fluoren-9-yl)amine (**24b**) (10%), mp = 108-110 °C (from light petroleum/benzene) (lit.[36] mp not reported), and biphenyl-2-ylcarbonitrile[37] (**26**) (70%).

From 31. **31** (2.48 g, 5 mmol), tri-*n*-butyltin hydride (1.75 g, 6 mmol), and AIBN (0.20 g, 1.25 mmol) were refluxed for 7 h. A GC-MS analysis of the reaction mixture showed the presence of N-(3-bromo-9H-fluoren-9-yl)-4-chlorobenzenamine (**32**), a possible dimeric compound analogous to that observed in the above reaction of **2a** [MS *m/e* (rel inten) 372 ($M^+/2$ + 4, 26), 370 ($M^+/2$ + 2, 100), 368 ($M^+/2$, 72), 288 (11), 245 (23), 243(23) 165 (29)], N-(3-bromo-9H-fluoren-9-ylidene)-4-chlorobenzenamine (**33**), identified by comparison with the authentic specimen previously synthesised (see above), and very small trace amounts of its possible isomer N-(1-bromo-9H-fluoren-9-ylidene)-4-chlorobenzenamine (**34**), detected only in a very concentrated sample of the reaction mixture [MS *m/e* (rel inten) 371 (M^+ + 4, 22), 369 (M^+ + 2, 100), 367 (M^+, 64), 289 (10), 288 (30), 253 (29), 252 (11), 126 (13)]. After column chromatography, we obtained **32** (50%), oil [200 MHz ^{1}H-NMR δ 4.05 (1 H, bs, -CH-N*H*-), 5.50 (1 H, bs, -C*H*-NH-), 6.64 (2 H, A part of AA'BB', J = 8.9 Hz, Ar-*H*), 7.14 (2 H, B part of AA'BB', J = 8.9 Hz, Ar-*H*), 7.32 (1 H, dd, J_1 = 7.3 Hz, J_2 = 1.3 Hz, Ar-*H*), 7.36-7.47 (3 H, m, Ar-*H*), 7.54 (1 H, bd, J = 7.3 Hz, Ar-*H*), 7.67 (1 H, bd, J = 6.9 Hz, Ar-*H*), 7.83 (1 H, bs, Ar-*H*); MS *m/e* (rel inten) 373 (M^+ + 4, 7), 371 (M^+ + 2, 25), 369 (M^+, 21), 290 (4), 245 (99), 243 (100), 164 (40), 163 (32); HRMS calcd for $C_{19}H_{13}BrClN$ 368.99198, found 368.99175. Anal. calcd for $C_{19}H_{13}BrClN$: C, 61.57; H, 3.53; Br, 21.56; Cl, 9.56; N, 3.78. Found: C, 61.41; H, 3.54; Br, 21.64; Cl, 9.62; N, 3.79], **33** (trace amounts), mp = 151-153 °C, 3-bromo-9H-fluoren-9-one (5%), mp = 164-166 °C (from ethanol) (lit.[28] mp = 165.5-166 °C), and 1-bromo-9H-fluoren-9-one[38] (very small trace amounts detected by GC analysis of a very concentrated sample of a column fraction).

Reaction of 3-bromo-2'-iodobiphenyl with 4-chlorophenylisonitrile. A solution of tri-*n*-butyltin hydride (0.46 g, 1.56 mmol) and AIBN (0.25 g, 1.56 mmol) in ethyl acetate (20 mL) was added dropwise in 2 h to a refluxing solution of 3-bromo-2'-iodobiphenyl (2.60 g, 7.25 mmol) and 4-chlorophenylisonitrile (0.20 g, 1.45 mmol) in ethyl acetate (50 mL). The mixture was refluxed for additional 7 h. The solvent was then removed and tri-*n*-butyltin iodide eliminated *via* the previously described reaction with potassium fluoride. A GC-MS analysis of the residue showed trace amounts of 3-bromobiphenyl, unreacted 3-bromo-2'-iodobiphenyl, a compound probably containing two molecules of isonitrile and the α-cyano-*iso*-propyl moiety, whose structure was not investigated [MS *m/e* (rel inten) 345 (M^+ + 4, 12), 343 (M^+ + 2, 49), 341 (M^+, 62), 277 (12), 275 (68), 273 (100), 113 (23), 111 (68), 75 (58)], an unidentifiable (dimeric?) compound [MS *m/e* (rel inten) 372 (27), 370 (100), 368 (71), 288 (13), 245 (31), 243 (91), 127 (44)], and ketimines **33** and **34** in a 2.8:1 ratio. After column chromatography we obtained a mixture of 3-bromo-[28] and 1-bromo-9H-fluoren-9-one[38] (15%) in a 2.8:1 ratio.

Reaction of 9-benzyl-9H-carbazole with DPDC. A solution of the title carbazole (1.03 g, 4 mmol) and DPDC (6 mmol) in benzene (20 mL) was kept at 60 °C for 9 h. The solvent was removed and the residue chromatographed to give bis(9H-carbazol-9-yl) (10%), mp = 224-226 °C (lit.[40] mp = 221 °C), 9-benzoyl-9H-carbazole (25%), mp = 97-98 °C (from light petroleum/benzene) (lit.[41] mp = 98 °C), and 9H-carbazole (15%), mp = 246-248 °C (from light petroleum/benzene) (mp of a commercial sample = 245-247 °C).

Reaction of N-(phenylmethylene)-2-iodobenzenamine (41) with phenylacetylene. A solution of tri-*n*-butyltin hydride (0.35 g, 1.20 mmol) and AIBN (0.19 g, 1.20 mmol) in ethyl acetate (25 mL) was added dropwise in 2 h, under a nitrogen atmosphere, to a refluxing solution of **41** (0.31 g, 1 mmol), phenylacetylene (1.02 g, 10 mmol), and AIBN (0.02 g) in ethyl acetate (25 mL). The final reaction mixture was quantitatively analysed by GC and the main products were N-(phenylmethylene)benzenamine (42%), 1-benzyl-2-phenylindole (**43**) (24%), and 2,3-diphenylquinoline (**44**) (3%), besides unreacted **41** (7%). A GC-MS analysis showed the presence of other compounds derived from attack of tri-*n*-butylstannyl- and α-cyano-*iso*-propyl radicals to phenylacetylene.

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