A route to 1,4-prop[2]enoisoquinolines *via* the cyclisation of triene-conjugated nitrile ylides[1]

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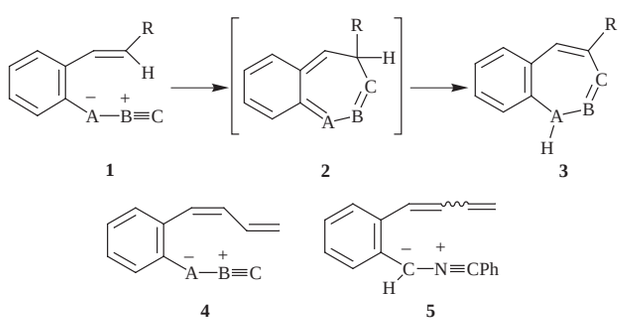
Triene-conjugated nitrile ylides of the types **18** and **20** with α,β aromatic and γ,δ; ε,ζ olefinic unsaturation undergo intramolecular cyclisation on to the γ,δ bond *via* a formal 1,1-cycloaddition reaction to give respectively *endo*- and *exo*-1-alkenylcyclopropa[*c*]isoquinolines **23** and **25** as primary products. The *endo*-isomers **23** rearrange spontaneously at 0 °C to give 1,4-dihydro-1,4-prop[2]enoisoquinolines **24** *via* an aza-Cope reaction. The *exo*-isomers **25** give the same product on heating at 70 °C *via* equilibration with the *endo* form **26** as the primary step, provided that the concentration of the latter at equilibrium is not strongly disfavoured by the steric effect of substituents R^1 and R^2. If it is then an alternative rearrangement also occurs to give the azabenzo[3,4]barbaralane derivative **29**.

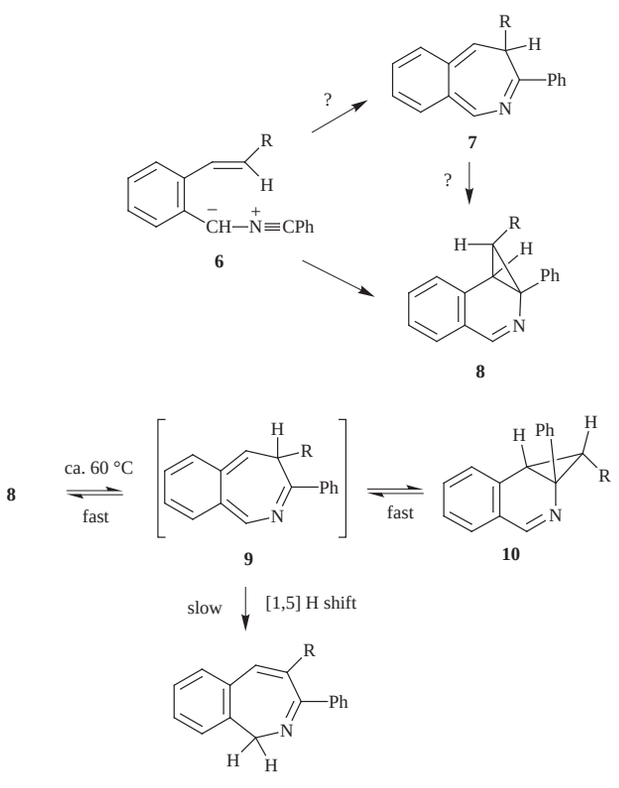
Introduction

The cyclisation of diene-conjugated 1,3-dipolar intermediates of the type **1** provides a general route[2] to the benzo-fused seven-membered heterocycles **3** *via* 1,7-electrocyclisation followed by a sigmatropic hydrogen shift. This paper reports the first studies on the analogous triene-conjugated systems **4** and is concerned with the generation and reactions of the nitrile ylides **5**.



Earlier work has shown that the diene-conjugated nitrile ylides, **6**, when generated at room temperature or below give cyclopropa[*c*]isoquinolines *e.g.* **8** as the primary isolated products (Scheme 1).[3,2b] It is not clear whether these products are formed by a single-step 1,1-cycloaddition reaction or *via* 1,7-electrocyclisation to give **7** followed by spontaneous ring contraction. However, it has been shown that the reaction is wholly stereospecific in that the *trans*-substituent at the terminal position in **6** goes into the *exo*-position of the product **8**.[2b] On heating, the cyclopropa[*c*]isoquinolines undergo an equilibration of the *exo*–*endo* isomers **8** and **10**, Scheme 1, *via* electrocyclic ring opening to give **9** followed by ring inversion and reclosure. In cases where there is a hydrogen atom at the C-1 position of the cyclopropa[*c*]isoquinoline this equilibration is accompanied by a slower [1,5]-hydrogen migration in **9** to give the 2-benzazepine **11** as the final product. In other cases the system reacts *via* various skeletal rearrangements.

In the analogous triene-conjugated system **5** there are obviously many possible intramolecular reaction paths *via* either electrocyclisation or cycloaddition reactions and the work was undertaken in order to find out whether any of them would be sufficiently dominant to be useful in a synthetic sense.



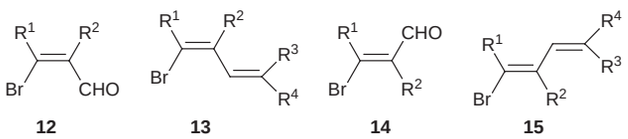
Scheme 1

Results and discussion

We report here on the reactions of both the *cis* and *trans* nitrile ylides **18a–f** and **20g–i** (substituents identified in Table 1). The nitrile ylide moieties were generated by the same method as used in earlier work *i.e.* the base induced 1,3-dehydrochlorination of imidoyl chlorides in THF at 0 °C. The amides **17** and **19**, used as precursors to the latter, were mostly prepared by the Suzuki coupling of the appropriate bromodiene, **13** or **15**, with 2-(benzoylaminomethyl)phenylboronic acid[2e] **16**, Scheme 2. The bromodienes were prepared *via* Arnold's bromoformylation reaction[4a,b] to give the bromoacrylaldehydes **12** and **14** and subsequent Wittig or Wadsworth–Emmons

Table 1 Identification of substituents for structures **13**, **15**, **17**–**20**, **23**–**26**

	Bromodienes	Amides	Nitrile Ylides	Products	R^1	R^2	R^3	R^4
	13a	**17a**	**18a**	**24a**	Me	Ph	H	Ph
	13b	**17b**	**18b**	**24b**	Me	Ph	H	Me
	13c	**17c**	**18c**	**24c**	Me	Ph	H	CO_2Me
	13d	**17d**	**18d**	**24d**	$(CH_2)_3$		H	Ph
	13e	**17e**	**18e**	**24e**	$(CH_2)_3$		H	CO_2Me
	13f	**17f**	**18f**		Me	Ph	Me	Me
		19g	**20g**	**25g**	H	H	H	Ph
	15h	**19h**	**20h**	**25h**	Me	Ph	H	Ph
	15i	**19i**	**20i**	**25i**	Me	Ph	Ph	H



olefination. The only exception to this general route was the amide **19g** which was prepared as shown in Scheme 2.

Reactions of the *cis* nitrile ylides 18a–f

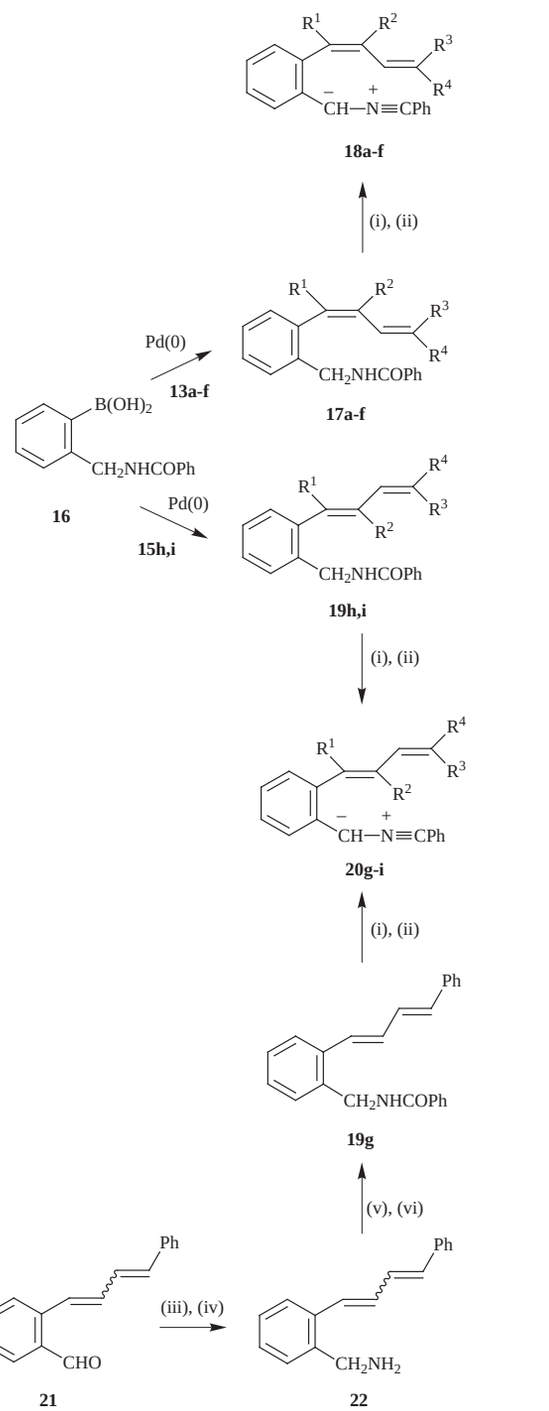
Most of the work in this paper is concerned with the reactions of the set of intermediates **18a**–**f** which have a *cis* double bond at the centre of the conjugated triene system. The objective, obviously, was to have a system in which the terminal alkene moiety was stereochemically capable of reaction with the nitrile ylide either *via* electrocyclisation or cycloaddition. It was clear from examination of molecular models that the transition state for an intramolecular cycloaddition of the nitrile ylide to the terminal alkene was stereochemically feasible and it was thought likely that this reaction path would be followed in preference to a 1,9-electrocyclisation process. In the event the nitrile ylides **18a**–**e** did neither of these things but gave instead the bridged isoquinolines **24a**–**e**, Scheme 3, in yields of 20–65% (not optimised). It seems most likely that these products are formed *via* a formal 1,1-cycloaddition of the nitrile ylide to the central alkene to give, as an intermediate, the cyclopropa-[*c*]isoquinoline system **23**, *cf.* the cyclisation of **6** to give **8**. The stereospecific nature of this reaction would be expected to give a product in which the remaining alkene moiety is in the *endo* position, as shown, and thus set-up for an aza-Cope rearrangement leading to the final products **24**. The intermediate **23** was not detected in any of these reactions, therefore the final step must be fast even at the low reaction temperature used (0 °C).

The only nitrile ylide in this group which failed to give a product of the type **24** was **18f** (R^3, R^4 = Me), the only example in which the terminal carbon of the diene system was di-substituted. In this case a very unstable intermediate with the spectroscopic characteristics required for **23f** was isolated but on standing it decomposed to give unidentified products. This is not inconsistent with the mechanism proposed since di-substitution would be expected to hinder the final Cope type rearrangement.

The products **24** were identified by X-ray crystallography [1] on **24a** and, for the other examples by their characteristic ^1H and ^{13}C NMR spectra. The ^1H absorptions for the protons on the bridged isoquinoline unit are shown for compound **24g**, the least substituted example.

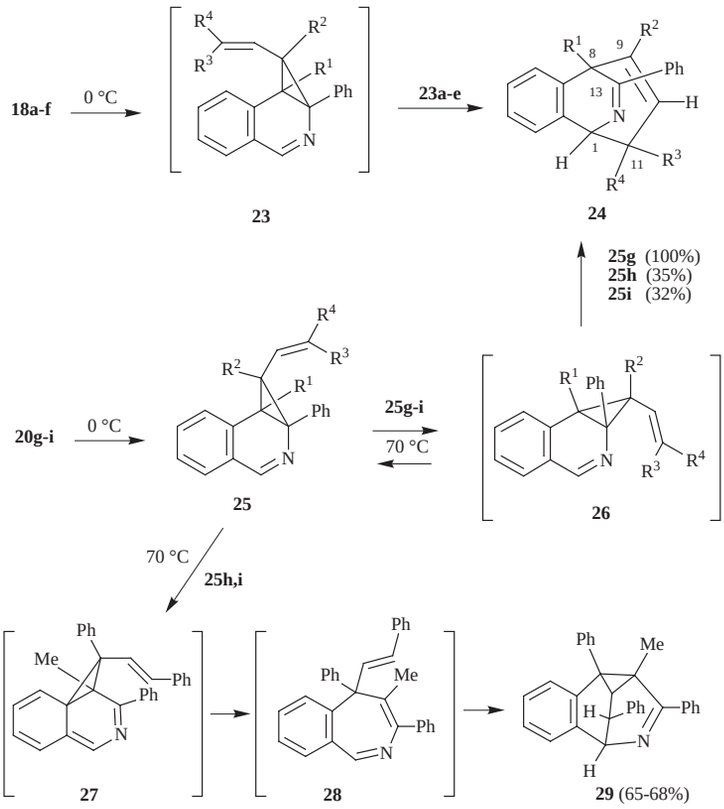
Reactions of the *trans* nitrile ylides 20g–i

The three species **20g**–**i**, which have *trans*-stereochemistry at the central double bond of the triene system, were studied principally for the purpose of obtaining further evidence on the mechanism of the reaction discussed above. If the mechanism proposed were correct then it would be expected that the *trans*-isomers would also react *via* a formal stereospecific 1,1-cyclo-

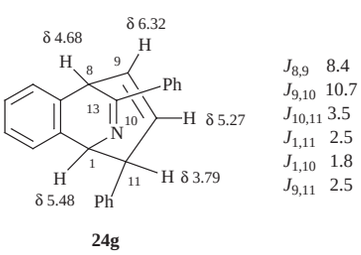


Scheme 2 *Reagents and conditions*: (i) $SOCl_2$–diethyl ether; (ii) LiN-$(SiMe_3)_2$, THF, 0 °C; (iii) NH_2OH; (iv) Zn, NH_4OH, NH_4OAc; (v) PhCOCl, Na_2CO_3; (vi) I_2, $CHCl_3$.

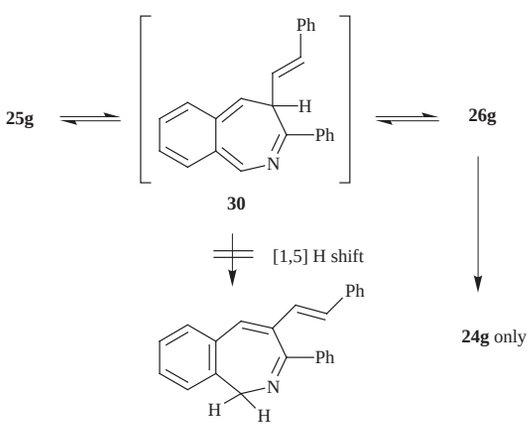
addition reaction to give the cyclopropa[*c*]isoquinolines **25**. These, having the remaining alkene unit in the *exo*-position, could not react further by the aza-Cope reaction and it was



Scheme 3



24g



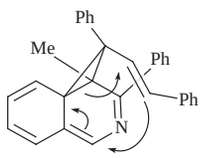
Scheme 4

expected that, for reactions carried out under the usual conditions at 0 °C, they would be stable enough to be isolated. It was further predicted that, on heating, these products **25** would undergo isomerisation to give the *endo*-isomers **26** (*cf.* the interconversion of **8** and **10**) and that the latter would rearrange spontaneously to give the bridged isoquinolines **24g**–**i**. In the event all three reactants gave the expected primary products **25g**–**i** (65–75%) which were identified by comparison of their NMR spectra with those of similar compounds **8** and **10** prepared in earlier work.[2b] On heating at *ca.* 70 °C these products **25g**–**i**, as predicted, were converted into the bridged isoquinolines **24g**–**i**, presumably *via* rearrangement to the *endo*-isomer **26** as shown in Scheme 3, in yields (35–100%) which were found to depend strongly on the substitution pattern of the reactant.

This was the only reaction path observed for the lightly-substituted compound **25g** (R^1, R^2, R^3 = H; R^4 = Ph) which was converted quantitatively into **24g**. That the 2-benzazepine **31**, Scheme 4, was not formed is also notable since such compounds are the normal products of analogous reactants *e.g.* **8**, **10** which lack the alkenyl group in the 1-position. Its absence indicates that the Cope rearrangement of **26g** is very fast compared to the rate of the sigmatropic hydrogen shift in the intermediate **30**.

The two more heavily substituted analogues **25h** (R^1 = Me, R^2, R^4 = Ph; R^3 = H) and its isomer **25i** (R^1 = Me, R^2, R^3 = Ph; R^4 = H) gave **24a** in yields of only 32 and 35% respectively in what turned out to be a minor reaction path. In both cases the major product was the azabenzo[3,4]barbaralane **29**, a new heterocyclic system, formed in 65 and 68% yield respectively. The product was identified by X-ray crystallography.[1] The reactants **25h** and **25i** differ only in the stereochemistry of the 1-alkenyl group and, remarkably, monitoring of the decomposition of the (*Z*)-isomer **25i** by ^{1}H NMR showed that the first step was its isomerisation into **25h**. It is thought that the most likely mechanism for the conversion of **25h** into **29** is the one shown in Scheme 3 which involves a [1,5]-sigmatropic carbon shift as the first step giving the intermediate **27**, followed by an electrocyclic ring expansion to give the 5*H*-2-benzazepine **28**. This is a known reaction[2b] for other cyclopropa[*c*]isoquinolines which lack the pendant alkenyl group and which gives 5*H*-2-benzazepines as isolable products. In this case however the compound **28** was not isolated but apparently reacted further *via* an intramolecular Diels–Alder reaction to give the isolated product **29**. This last step looks unlikely at first sight but its feasibility is supported by the work of Jones[5] on the all-carbon analogue which was found to follow the same path on heating at

90–100 °C. In that work it was argued that the driving force for the reaction was provided by the strong destabilisation of 5,5-substituted benzocycloheptatrienes of this type by *peri* interactions of the substituents with the *ortho* hydrogen atom of the benzene ring. By analogy, therefore, this looks to be the most likely route for the formation of **29**. However, it should be noted that other mechanisms which result in direct conversion of **27** into **29** are also possible *e.g.* (i) by a concerted ($\pi 2s + \pi 2s + \sigma 2s$) reaction **32**, or (ii) by the step-wise radical equivalent *via* **33**. It is also possible that the bridged isoquinoline **24a** could be formed from **20h**,**i** by an aza-Cope rearrangement of **27** rather than *via* **26h**.



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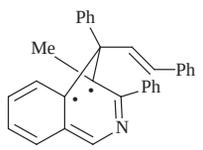

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A key question is why the lightly substituted cyclopropa[*c*]isoquinoline **25g** reacts to give **24g** in quantitative yield while this is the minor path in the decomposition of the more heavily substituted analogue **25h**. A certain answer is not yet possible but on present evidence it seems likely that it is related to the steric effect of the substituents R^1 and R^2 on the position of the equilibrium between **25** and its *endo*-isomer **26**. In **25g** both R^1 and $R^2 = H$ so that **26g** will be favoured but for **25h** both are bulkier groups ($R^1 = Me$ and $R^2 = Ph$) so that **26h** will be destabilised. If its equilibrium concentration is very low the rate of the irreversible conversion into **24a** will be low and the alternative reaction path to give **27** will become competitive, or may itself be promoted by the bulkier substituents. It is hoped to carry out further work into substituent effects on these reactions.

This work has shown that the cyclisation of the *cis* triene-conjugated nitrile ylides **18** provides an easy route to 1,4-prop[2]enoisoquinolines **24** which are of interest in that they have the basic skeleton of the isopavine family of alkaloids and also that the same products are accessible from the *trans* nitrile ylides **20** but in yields which are dependent on the nature of the substituents R^1–R^3.

Experimental

NMR spectra were run as solutions in deuteriochloroform unless otherwise stated. Chemical shifts are recorded as δ values. *J* Values are given in Hz. In the ^{13}C spectra carbon multiplicity was established by single frequency off-resonance decoupling or by DEPT. Mass spectra were obtained using electron ionisation at 70 eV unless otherwise stated. Preparative chromatography[6] was carried out on silica gel by the flash column method (Merck Kieselgel 60, 230–400 mesh), the 'dry column flash' method (15 mm, Fluka Kieselgel GF_{254}) or the 'medium pressure' (MPLC) technique using 100 × 2.5 cm columns (Merck Kieselgel 60, 230–400 mesh), and eluting solvents based on hexane admixed with ether or ethyl acetate. Ether refers to diethyl ether. 'Evaporation' of solvents indicates evaporation under reduced pressure using a rotary evaporator. All drying of solutions was done with anhydrous magnesium sulfate. Tetrahydrofuran (THF) was distilled from sodium and benzophenone as required. Cyclohexane, hexane and *N,N*-dimethylformamide (DMF) were distilled from calcium hydride as required. 1,2-Dimethoxyethane (DME) was passed through a column of activated alumina and stored over 4 Å molecular sieves.

Preparation of the bromodienes 13a–f, 15h,i

(*E*)- and (*Z*)-3-Bromo-2-phenylbut-2-enal, 1-bromo-2-formylcyclopentene, (*E*,*E*)-4-bromo-1,3-diphenylpenta-1,3-diene 13a and (*E*)-1-bromo-2-(2-phenylethenyl)cyclopentene 13d. These compounds were prepared by known routes.[4b]

(*E*,*E*)-2-Bromo-3-phenylhexa-2,4-diene 13b and (*E*,*Z*)-2-bromo-3-phenylhexa-2,4-diene as a mixture (4:1). *n*-Butyllithium (4.44 cm^3, 2.5 M solution in hexane) was added dropwise to a stirred solution of ethyltriphenylphosphonium bromide (4.12 g, 11.1 mmol) in THF (100 cm^3) at 0 °C and stirred for 1 h at room temperature. (*Z*)-3-Bromo-2-phenylbut-2-enal (2.50 g, 11.1 mmol) in THF (10 cm^3) was added dropwise and the mixture was stirred at room temperature for 1 h. After washing with aqueous ammonium chloride (10% w/v, 50 cm^3) and separation, the aqueous layer was further extracted with ether (2 × 50 cm^3). The combined organic phase was washed with water (50 cm^3), dried and evaporated to give a pale green oil. Flash column chromatography on silica, eluting with hexane gave a mixture of (*E*,*E*)- and (*E*,*Z*)-2-bromo-3-phenylhexa-2,4-diene in a ratio (4:1) which was used without further purification (1.37 g, 52%) [Found: 237.0297. $C_{12}H_{13}{}^{79}Br$ requires $(M + 1)^+$, 237.0279]; δ_H(200 MHz, $CDCl_3$) (* = major isomer) 1.29* (m, CH_3), 1.73 (d, *J* 6, CH_3), 2.12* (s, CH_3), 2.27 (s, CH_3), 5.16 (dd, *J* 16 and 7, CH), 5.58 (dd, *J* 11 and 6, CH), 6.74 (br d, *J* 16.1, CH), 6.83 (d, *J* 11, CH), 6.88–7.98 (5 H, m, Ar-H); δ_C(50 MHz, $CDCl_3$) 18.4 (CH_3), 25.6 (CH_3), 127.1 (CH), 127.5 (CH), 128.0 (CH), 128.1 (CH), 128.2 (2 × CH), 128.5 (CH), 128.8 (CH), 129.3 (CH), 131.0 (q), 138.6 (q), 141.6 (q); *m*/*z* (FAB) 237 (M + 1, 24%), 235 (20), 205 (12), 189 (59), 173 (90), 155 (55), 141 (47), 128 (54), 115 (100), 77 (52); ν_{max}(film)/cm^{-1} 1597, 1625, 1682 (diene).

Methyl (*E*,*E*)-5-bromo-4-phenylhexa-2,4-dienoate 13c. Methyl (triphenylphosphoranylidene)acetate (3.73 g, 11.1 mmol) and (*Z*)-3-bromo-2-phenylbut-2-enal (2.5 g, 11.1 mmol) in dry toluene (100 cm^3) were heated at reflux for 3 h under nitrogen. The reaction was cooled to room temperature and the solvent removed *in vacuo*. Flash column chromatography on silica, eluting with hexane gave methyl (*E,E*)-5-bromo-4-phenylhexa-2,4-dienoate as a yellow solid (2.87 g, 92%), mp 56–57 °C from hexane [Found: C, 55.8, H, 5.0%; $(M + 1)^+$, 281.0186. $C_{13}H_{13}BrO_2$ requires C, 55.7, H, 4.7%; $(M + 1)^+$, 281.0177]; δ_H(250 MHz, $CDCl_3$) 2.25 (3 H, s, CH_3), 3.70 (3 H, s, CH_3), 5.31 (1 H, d, *J* 15.6, CH), 7.04–7.41 (5 H, m, Ar-H), 8.02 (1 H, d, *J* 15.6, CH); δ_C(63 MHz, $CDCl_3$) 27.8 (CH_3), 51.5 (CH_3), 123.0 (CH, olefinic), 127.8 (CH), 128.7 (CH), 129.0 (CH), 130.9 (q), 136.6 (q), 137.6 (q), 145.2 (CH, olefinic), 167.2 (q); *m*/*z* (FAB) 285 (M + 1, 9%), 284 (M + 1, 29), 283 (99), 282 (38), 281 (100), 249 (42), 221 (19), 201 (61), 169 (35), 149 (29), 128 (48), 115 (75), 91 (83), 77 (49), 59 (62), 43 (89), 31 (56); ν_{max}(Nujol)/cm^{-1} 1724 (C=O).

Methyl 3-(2-bromocyclopent-1-enyl)propenoate 13e. Methyl (triphenylphosphoranylidene)acetate (7.68 g, 22.9 mol) and 1-bromo-2-formylcyclopentene (4.0 g, 22.9 mmol) in dry toluene (100 cm^3) were heated at reflux for 3 h under nitrogen. The reaction was cooled to room temperature and the solvent removed *in vacuo*. Flash column chromatography on silica, eluting with hexane–ether (4:1) gave methyl 3-(2-bromocyclopent-1-enyl)propenoate as a yellow crystalline solid (3.49 g, 66%), mp 63–64 °C from ethanol [Found: C, 47.1; H, 5.0%; $(M + 1)^+$, 231.0008. $C_9H_{11}BrO_2$ requires C, 47.0; H, 4.8%; $(M + 1)^+$, 231.0021]; δ_H(250 MHz, $CDCl_3$) 2.01–2.07 (2 H, m, CH_2), 2.41–2.50 (2 H, m, CH_2), 2.75–2.82 (2 H, m, CH_2), 3.75 (3 H, s, CH_3), 5.78 (1 H, d, *J* 15.8, CH), 7.51 (1 H, d, *J* 15.8, CH); δ_C(50 MHz, $CDCl_3$) 21.3 (CH_2), 30.8 (CH_2), 41.3 (CH_2), 51.5 (CH_3), 120.2 (CH), 130.1 (q), 136.7 (q), 137.8 (CH), 167.2 (q); *m*/*z* (FAB) 234 (M + 1, 7%), 233 (44), 232 (15), 231 (45), 217 (17), 183 (12), 151 (41), 119 (51), 109 (49), 69 (54), 57 (86), 43 (91), 29 (100); ν_{max}(Nujol)/cm^{-1} 1627 (C=C), 1725 (C=O).

(*E*)-2-Bromo-5-methyl-3-phenylhexa-2,4-diene 13f. Potassium *tert*-butoxide (1.25 g, 11.1 mmol) in THF (10 cm^3) was added

dropwise to a stirred solution of isopropyltriphenylphosphonium bromide (4.80 g, 11.1 mmol) in THF (100 cm^3) at 0 °C and stirred for 1 h at room temperature. (*Z*)-3-Bromo-2-phenylbut-2-enal (2.50 g, 11.1 mmol) in THF (10 cm^3) was added dropwise and stirred at room temperature for 1 h. The usual work-up gave a green oil. Flash column chromatography on silica, eluting with hexane gave (*E*)-2-bromo-5-methyl-3-phenylhexa-2,4-diene which was used without further purification (1.51 g, 54%) [Found: 251.0433. $C_{13}H_{15}{}^{79}Br$ requires $(M + 1)^+$, 251.0435]; δ_H(200 MHz, $CDCl_3$) 1.27 (3 H, s, CH_3), 1.78 (3 H, s, CH_3), 2.30 (3 H, s, CH_3), 6.07 (1 H, br, CH), 7.13–7.35 (5 H, m, Ar-H); δ_C(50 MHz, $CDCl_3$) 19.6 (CH_3), 26.4 (CH_3), 26.5 (CH_3), 121.7 (CH), 126.8 (CH), 128.1 (2 × CH), 129.0 (2 × CH), 137.2 (q), 138.1 (q), 140.2 (q), 145.8 (q); *m*/*z* (FAB) 252 (M + 1, 12%), 251 (23), 227 (10), 203 (30), 195 (72), 187 (100), 170 (61), 155 (28), 141 (45), 128 (51), 115 (92), 77 (23); ν_{max}(film)/cm^{-1} 1596, 1625, 1683 (diene).

(*E*,*Z*)-4-Bromo-1,3-diphenylpenta-1,3-diene 15h and (*Z*,*Z*)-4-bromo-1,3-diphenylpenta-1,3-diene 15i. *n*-Butyllithium (4.52 cm^3, 2.5 M solution in hexane) was added dropwise to a stirred solution of benzyltriphenylphosphonium bromide (5.66 g, 11.3 mmol) in THF (100 cm^3) at 0 °C and stirred for 1 h at room temperature. (*E*)-3-Bromo-2-phenylbut-2-enal (2.54 g, 11.3 mmol) in THF (10 cm^3) was added dropwise and stirred at room temperature for 1 h. The usual work-up gave a yellow oil. Dry column flash chromatography followed by MPLC on silica, eluting with hexane gave (a) (*E*,*Z*)-4-bromo-1,3-diphenylpenta-1,3-diene as a colourless oil (0.75 g, 22%) [Found: 298.0364. $C_{17}H_{15}{}^{79}Br$ requires M^+, 298.0357]; δ_H(200 MHz, $CDCl_3$) 2.72 (3 H, s, CH_3), 5.98 (1 H, d, *J* 15.7, CH), 7.14–7.49 (11 H, m, CH); δ_C(50 MHz, $CDCl_3$) 25.2 (CH_3), 123.9 (q), 125.6 (CH), 126.4 (2 × CH), 127.2 (CH), 127.6 (CH), 128.1 (2 × CH), 128.5 (2 × CH), 129.4 (2 × CH), 133.1 (CH), 137.1 (q), 140.1 (q), 140.8 (q); *m*/*z* (FAB) 299 (M + 1, 15%), 298 (18), 204 (53), 202 (69), 176 (14), 115 (100); ν_{max}(film)/cm^{-1} 1598 (diene); and (b) (*Z*,*Z*)-4-bromo-1,3-diphenylpenta-1,3-diene as a colourless oil (1.50 g, 44%) [Found: 300.0334. $C_{17}H_{15}{}^{81}Br$ requires $(M + 1)^+$, 300.0338]; δ_H(200 MHz, $CDCl_3$) 2.24 (3 H, s, CH_3), 6.09 (1 H, d, *J* 12.0, CH), 6.60 (1 H, d, *J* 12.0, CH), 7.20–7.50 (10 H, m, CH); δ_C(50 MHz, $CDCl_3$) 27.0 (CH_3), 121.1 (q), 127.4 (CH), 127.5 (CH), 127.9 (2 × CH), 128.0 (2 × CH), 128.3 (CH), 128.4 (2 × CH), 128.9 (2 × CH), 131.3 (CH), 136.6 (q), 136.7 (q), 140.6 (q); *m*/*z* (FAB) 301 (M + 1, 14%), 298 (16), 239 (11), 205 (28), 204 (55), 189 (22), 178 (21), 152 (23), 141 (57), 128 (25), 102 (16), 65 (11), 51 (37); ν_{max}(film)/cm^{-1} 1598 (diene).

Preparation of *N*-(2-alkadienylbenzyl)benzamides 17a–f and 19h–i

These compounds were synthesised by the Suzuki coupling reactions of 2-(benzoylaminomethyl)phenylboronic acid[2e] **16** with the appropriate bromodiene, Scheme 2. The method is described in detail for the first example.

(*E*,*E*)-*N*-[2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]-benzamide 17a. (*E*,*E*)-4-Bromo-1,3-diphenylpenta-1,3-diene **13a** (1.0 g, 3.36 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.19 g, 0.22 mmol, 5.6 mol% catalyst) were stirred in 1,2-dimethoxyethane (20 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)phenylboronic acid (0.95 g, 3.70 mmol) and sodium carbonate (0.97 g, 3.36 mmol) in water (5.5 cm^3) were added and the mixture was heated at reflux for 20 h. The reaction mixture was allowed to cool to room temperature and passed through a pad of alumina. The DME was removed *in vacuo* and dichloromethane (50 cm^3) was added. The organic layer was separated, dried and the solvent removed *in vacuo* to give a brown oil. Dry column flash chromatography on silica, eluting with hexane–ethyl acetate (9:1) gave (*E*,*E*)-*N*-[2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]-benzamide as a yellow solid (1.11 g, 77%), mp 81–83 °C from ethanol [Found: C, 86.7; H, 6.5; N, 3.3%; $(M + 1)^+$, 430.2174. $C_{31}H_{27}NO$ requires C, 86.7; H, 6.3; N, 3.3%; $(M + 1)^+$, 430.2171]; δ_H(200 MHz, $CDCl_3$) 1.92 (3 H, s, CH_3), 4.44 (1 H, dd, *J* 4.2 and 14.2, CH_2), 4.91 (1 H, dd, *J* 6.9 and 14.3, CH_2), 5.94 (1 H, d, *J* 16.1, CH), 6.42 (1 H, br, NH), 6.77 (1 H, d, *J* 16.0, CH), 6.93–7.68 (19 H, m); δ_C(50 MHz, $CDCl_3$) 23.4 (CH_3), 41.9 (CH_2), 126.2 (CH), 126.7 (CH), 126.9 (CH), 127.3 (CH), 127.7 (CH), 128.0 (CH), 128.2 (2 × CH), 128.4 (4 × CH), 128.8 (CH), 129.6 (CH), 129.7 (2 × CH), 131.1 (CH), 131.6 (CH), 133.8 (q), 135.4 (q), 137.0 (q), 137.4 (q), 138.7 (q), 138.9 (q), 142.5 (q), 166.8 (q); *m*/*z* (FAB) 431 (M + 1, 16%), 430 (32), 429 (17), 428 (11), 391 (10), 338 (18), 315 (19), 308 (49), 291 (40), 279 (60), 265 (39), 239 (45), 229 (56), 215 (100), 202 (90), 178 (52), 171 (31), 152 (42), 134 (26); ν_{max}(Nujol)/cm^{-1} 1635 (C=O), 3336 (NH).

(*E*,*E*)-*N*-[2-(1-Methyl-2-phenylpenta-1,3-dienyl)benzyl]benzamide 17b. 2-Bromo-3-phenylhexa-2,4-diene **13b** [as a 4:1 mixture of (*E*,*E*) and (*E*,*Z*) isomers, see above] (0.80 g, 3.37 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.19 g, 0.17 mmol, 5.0 mol% catalyst) were stirred in 1,2-dimethoxyethane (15 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)phenylboronic acid (1.00 g, 3.71 mmol) and sodium carbonate (0.96 g, 3.37 mmol) in water (4.5 cm^3) were added and the mixture heated at reflux for 20 h. The usual work-up gave a brown oil. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (9:1) gave (*E*,*E*)-*N*-[2-(1-methyl-2-phenylpenta-1,3-dienyl)benzyl]benzamide as a white solid (0.42 g, 35%), mp 138–140 °C from hexane–ethyl acetate [Found: C, 84.9; H, 6.9; N, 3.4%; $(M + 1)^+$, 368.2026. $C_{26}H_{25}NO$ requires C, 85.0; H, 6.9; N, 3.8%; $(M + 1)^+$, 368.2014]; δ_H(200 MHz, $CDCl_3$) 1.47 (3 H, m, CH_3), 1.81 (3 H, s, CH_3), 4.45 (1 H, dd, *J* 4.4 and 14.4, CH_2), 4.84 (1 H, dd, *J* 6.8 and 14.4, CH_2), 5.05 (1 H, m, CH), 5.96 (1 H, d, *J* 15.7, CH), 6.42 (1 H, br, NH), 7.10–7.75 (14 H, m); δ_C(63 MHz, $CDCl_3$) 18.2 (CH_3), 23.0 (CH_3), 42.1 (CH_2), 126.6 (CH), 126.8 (2 × CH), 127.4 (CH), 128.0 (CH), 128.2 (2 × CH), 128.3 (2 × CH), 128.9 (CH), 129.4 (2 × CH), 129.6 (2 × CH), 131.1 (CH), 131.4 (CH), 133.5 (q), 134.3 (q), 135.2 (q), 138.6 (q), 139.6 (q), 143.0 (q), 166.9 (q); *m*/*z* (FAB) 369 (M + 1, 67%), 368 (80), 367 (22), 366 (38), 247 (87), 231 (76), 216 (54), 205 (79), 191 (28), 178 (26), 165 (24), 155 (43), 141 (53), 134 (100); ν_{max}(Nujol)/cm^{-1} 1633 (C=O), 3365 (NH).

(*E*,*E*)-*N*-[2-(4-Methoxycarbonyl-1-methyl-2-phenylbuta-1,3-dienyl)benzyl]benzamide 17c. Methyl (*E*,*E*)-5-bromo-4-phenylhexa-2,4-dienoate **13c** (1.8 g, 6.4 mmol) and tetrakis-(triphenylphosphine)palladium(0) (0.32 g, 0.28 mmol, 4.4 mol% catalyst) were stirred in 1,2-dimethoxyethane (30 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)-phenylboronic acid (1.80 g, 7.04 mmol) and sodium carbonate (1.83 g, 6.4 mmol) in water (10 cm^3) were added and the mixture heated at reflux for 20 h. The usual work-up gave a brown solid. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (4:1) gave (*E*,*E*)-*N*-[2-(4-methoxycarbonyl-1-methyl-2-phenylbuta-1,3-dienyl)benzyl]benzamide as a yellow solid (2.32 g, 88%), mp 140–142 °C from pentane–DCM [Found: C, 78.8; H, 6.4; N, 3.0%; $(M + 1)^+$, 412.1920. $C_{27}H_{25}NO_3$ requires C, 78.9; H, 6.1; N, 3.4%; $(M + 1)^+$, 412.1913]; δ_H(250 MHz, $CDCl_3$) 1.93 (3 H, s, CH_3), 3.49 (3 H, s, CH_3), 4.49 (1 H, dd, *J* 5.0 and 14.4, CH_2), 4.72 (1 H, dd, *J* 5.8 and 14.4, CH_2), 5.22 (1 H, d, *J* 16.0, CH), 6.52 (1 H, br, NH), 7.15–7.48 (13 H, m), 7.71–7.76 (2 H, m); δ_C(63 MHz, $CDCl_3$) 24.0 (CH_3), 41.6 (CH_2), 51.1 (CH_3), 119.9 (CH), 126.8 (2 × CH), 127.3 (CH), 128.0 (CH), 128.1 (CH), 128.2 (2 × CH), 128.45 (CH), 128.5 (2 × CH), 129.3 (CH), 131.2 (CH), 133.9 (q), 134.7 (q), 137.4 (q), 137.5 (q), 141.3 (q), 144.2 (CH), 145.4 (q), 166.9 (q), 167.5 (q); *m*/*z* (FAB) 412 (M + 1, 38%), 380 (50), 259 (67), 230 (16), 215 (40), 189 (10), 165 (19), 105 (100), 91

(25), 77 (27), 45 (22), 31 (24); ν_{max}(Nujol)/cm^{-1} 1545 (amide), 1721 (ester), 3312 (amide).

(*E*)-*N*-{2-[2-(2-Phenylethenyl)cyclopentenyl]benzyl}benzamide 17d. (*E*)-1-Bromo-2-(2-phenylethenyl)cyclopentene **13d** (1.40 g, 5.64 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.28 g, 0.25 mmol, 4.4 mol% catalyst) were stirred in 1,2-dimethoxyethane (30 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)phenylboronic acid (1.54 g, 6.20 mmol) and sodium carbonate (1.61 g, 5.64 mmol) in water (9.0 cm^3) were added and the mixture heated at reflux for 20 h. The usual work-up gave a brown oil. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (4:1) gave (*E*)-*N*-{2-[2-(2-phenylethenyl)cyclopentenyl]benzyl}benzamide as a brown solid (1.65 g, 93%), mp 132–134 °C from pentane–DCM [Found: $(M + 1)^+$, 380.2020. $C_{27}H_{25}NO$ requires $(M + 1)^+$, 380.2014]; δ_H(250 MHz, $CDCl_3$) 2.01–2.13 (2 H, m, CH_2), 2.75–2.82 (4 H, m, CH_2), 4.61 (2 H, br, CH_2), 6.44 (1 H, br, NH), 6.49 (1 H, d, *J* 16.1, CH), 6.66 (1 H, d, *J* 16.1, CH), 7.11–7.68 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 22.3 (CH_2), 32.7 (CH_2), 39.7 (CH_2), 42.1 (CH_2), 123.1 (CH), 126.2 (2 × CH), 126.6 (2 × CH), 127.2 (CH), 127.5 (CH), 127.6 (CH), 128.2 (2 × CH), 128.4 (2 × CH), 129.2 (CH), 129.3 (CH), 130.3 (CH), 131.1 (CH), 133.9 (q), 136.0 (q), 137.1 (q), 137.8 (q), 138.2 (q), 142.0 (q), 166.8 (q); *m*/*z* (FAB) 381 (M + 1, 14%), 380 (58), 379 (21), 378 (12), 288 (13), 279 (100), 274 (14), 258 (61), 229 (45), 203 (30), 181 (28), 165 (83), 154 (34), 141 (43); ν_{max}(Nujol)/cm^{-1} 1634 (C=O), 3337 (NH).

(*E*)-*N*-(2-{2-[2-(Methoxycarbonyl)ethenyl]cyclopentenyl}benzyl)benzamide 17e. Methyl 3-(2-bromocyclopent-1-enyl)propenoate **13e** (2.42 g, 10.47 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.48 g, 0.42 mmol, 4.0 mol% catalyst) were stirred in 1,2-dimethoxyethane (50 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)phenylboronic acid (2.93 g, 11.52 mmol) and sodium carbonate (3.00 g, 10.47 mmol) in water (15 cm^3) were added and the mixture heated at reflux for 20 h. The usual work-up gave a brown oil. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (4:1) gave (*E*)-*N*-(2-{2-[2-(methoxycarbonyl)ethenyl]-cyclopentenyl}benzyl)benzamide as a yellow solid (3.25 g, 86%), mp 117–118 °C from ethanol [Found: C, 76.1; H, 6.2; N, 3.6%; $(M + 1)^+$, 362.1754. $C_{23}H_{23}NO_3$ requires C, 76.4; H, 6.4; N, 3.9%; $(M + 1)^+$, 362.1756]; δ_H(250 MHz, $CDCl_3$) 2.02 (2 H, m, CH_2), 2.62 (2 H, m, CH_2), 2.79 (2 H, br, CH_2), 3.60 (3 H, s, CH_3), 4.46 (2 H, br, CH_2), 5.71 (1 H, d, *J* 15.7, CH), 6.49 (1 H, br m, NH), 7.13 (1 H, d, *J* 15.7, CH), 7.04–7.73 (9 H, m); δ_C(63 MHz, $CDCl_3$) 22.1 (CH_2), 32.2 (CH_2), 40.2 (CH_2), 41.8 (CH_2), 51.3 (CH_3), 118.6 (CH), 126.8 (2 × CH), 127.6 (CH), 128.1 (CH), 128.2 (2 × CH), 128.9 (CH), 129.0 (CH), 131.2 (CH), 133.9 (q), 135.5 (q), 136.5 (q), 136.7 (q), 138.6 (q), 150.7 (q), 166.9 (q), 167.5 (q); *m*/*z* (FAB) 363 (M + 1, 9%), 362 (11), 302 (17), 279 (50), 181 (27), 153 (13), 129 (11), 105 (86), 91 (23), 77 (46), 60 (38), 46 (98), 30 (100); ν_{max}(Nujol)/cm^{-1} 1641 (C=C), 1700 (C=O), 3342 (NH).

(*E*)-*N*-[2-(1,4-Dimethyl-2-phenylpenta-1,3-dienyl)benzyl]benzamide 17f. (*E*)-2-Bromo-5-methyl-3-phenylhexa-2,4-diene **13f** (0.65 g, 2.6 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.14 g, 0.12 mmol, 4.8 mol% catalyst) were stirred in 1,2-dimethoxyethane (10 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)phenylboronic acid (0.76 g, 2.84 mmol) and sodium carbonate (0.74 g, 2.58 mmol) in water (3.5 cm^3) were added and the mixture heated at reflux for 20 h. The reaction mixture was allowed to cool to room temperature and passed through a pad of alumina. The DME was removed *in vacuo* and dichloromethane (50 cm^3) was added. The organic layer was separated, dried and the solvent removed *in vacuo* to give a yellow solid. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (9:1) gave (*E*)-*N*-[2-(1,4-dimethyl-2-phenylpenta-1,3-dienyl)benzyl]benzamide as a white solid (0.40 g, 41%), mp 131–132 °C from ethyl acetate (Found: C, 85.2; H, 7.4; N, 3.6%; $(M + 1)^+$, 382.2179. $C_{27}H_{27}NO$ requires C, 85.0; H, 7.1; N, 3.7; $(M + 1)^+$, 382.2171); δ_H(200 MHz, $CDCl_3$) 0.90 (3 H, s, CH_3), 1.42 (3 H, s, CH_3), 1.85 (3 H, s, CH_3), 4.33 (1 H, dd, *J* 4.1 and 14.0, CH_2), 4.71 (1 H, dd, *J* 6.5 and 14.0, CH_2), 5.59 (1 H, s, CH), 6.33 (1 H, br, NH), 6.91–7.67 (14 H, m, ArH); δ_C(63 MHz, $CDCl_3$) 19.5 (CH_3), 22.9 (CH_3), 27.4 (CH_3), 42.0 (CH_2), 125.2 (CH), 126.4 (CH), 126.8 CH), 127.2 (CH), 127.9 (CH), 128.1 (2 × CH), 128.4 (2 × CH), 129.4 (CH), 129.5 (2 × CH), 131.2 (CH), 134.5 (q), 134.7 (q), 135.1 (q), 135.6 (q), 137.4 (q), 141.6 (q), 143.8 (q), 167.1 (q); *m*/*z* (FAB) 383 (M + 1, 36%), 382 (100), 381 (44), 366 (12), 338 (11), 276 (24), 261 (63), 260 (61), 252 (20), 245 (62), 243 (45), 231 (69), 220 (63), 216 (85), 202 (90), 190 (49), 178 (16), 166 (46), 155 (67), 141 (80), 131 (40); ν_{max}(Nujol)/cm^{-1} 1635 (C=O), 3316 (NH).

(*Z*,*E*)-*N*-[2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]benzamide 19h. (*E*,*Z*)-4-Bromo-1,3-diphenylpenta-1,3-diene **15h** (0.65 g, 2.17 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.12 g, 0.11 mmol, 4.8 mol% catalyst) were stirred in 1,2-dimethoxyethane (10 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)phenylboronic acid (0.64 g, 2.39 mmol) and sodium carbonate (0.62 g, 2.17 mmol) in water (3.0 cm^3) were added and the mixture heated at reflux for 20 h. The usual work-up gave a yellow solid. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (9:1) gave (*Z*,*E*)-*N*-[2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)-benzyl]benzamide **19h** as a white solid (0.72 g, 77%), mp 116–118 °C from hexane–ethyl acetate (Found: C, 86.6; H, 6.5; N, 3.0. $C_{31}H_{27}NO$ requires C, 86.7; H, 6.3; N, 3.3%); δ_H(200 MHz, $CDCl_3$) 2.36 (3 H, s, CH_3), 4.18 (1 H, dd, *J* 4.4 and 14.9, CH_2), 4.68 (1 H, dd, *J* 6.8 and 14.3, CH_2), 5.84 (1 H, br, NH), 6.14 (1 H, d, *J* 16.0, CH), 6.99–7.82 (20 H, m, CH); δ_C(63 MHz, $CDCl_3$) 21.7 (CH_3), 41.1 (CH_3), 126.3 (2 × CH), 126.9 (CH), 127.4 (CH), 127.5 (CH), 128.2 (CH), 128.4 (2 × CH), 128.5 (2 × CH), 129.6 (CH), 130.6 (2 × CH), 131.3 (CH), 132.6 (CH), 134.1 (q), 134.3 (q), 135.7 (q), 137.6 (q), 139.4 (q), 143.4 (q), 167.1 (q); ν_{max}(Nujol)/cm^{-1} 1635 (C=O), 3345 (NH).

(*Z*,*Z*)-*N*-[2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]benzamide 19i. (*Z*,*Z*)-4-Bromo-1,3-diphenylpenta-1,3-diene **15i** (1.20 g, 4.01 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.22 g, 0.19 mmol, 4.8 mol% catalyst) were stirred in 1,2-dimethoxyethane (10 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethyl)phenylboronic acid (1.18 g, 4.61 mmol) and sodium carbonate (1.14 g, 4.01 mmol) in water (5.6 cm^3) were added and the mixture heated at reflux for 20 h. The usual work-up gave a brown oil. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (4:1) gave (*Z*,*Z*)-*N*-[2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]benzamide as a white solid (0.83 g, 48%), mp 135.5–137.5 °C from hexane–ethyl acetate (Found: C, 86.6; H, 6.5; N, 3.0. $C_{31}H_{27}NO$ requires C, 86.7; H, 6.3; N, 3.3%); δ_H(200 MHz, $CDCl_3$) 2.00 (3 H, d, *J* 1.1, CH_3), 4.04 (1 H, dd, *J* 3.7, 14.5, CH_2), 4.64 (1 H, dd, *J* 7.5, 14.5, CH_2), 5.43 (1 H, br, NH), 6.48 (1 H, dd, *J* 1.1, 12.1, CH), 6.65 (1 H, d, *J* 12.1, CH), 6.94–7.82 (19 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 24.0 (CH_3), 41.0 (CH_2), 126.3 (CH), 126.9 (2 × CH), 127.1 (CH), 127.2 (CH), 127.3 (CH), 127.5 (2 × CH), 128.0 (2 × CH), 128.1 (2 × CH), 128.2 (2 × CH), 129.2 (CH), 129.2 (CH), 129.5 (2 × CH), 130.3 (CH), 131.1 (CH), 134.2 (q), 134.3 (q), 134.5 (q), 134.6 (q), 137.3 (q), 139.7 (q), 142.8 (q), 167.1 (q); ν_{max}(Nujol)/cm^{-1} 1634 (C=O), 3340 (NH).

(*E*,*E*)-*N*-[2-(4-Phenylbuta-1,3-dienyl)benzyl]benzamide 19g

This compound was prepared as shown in Scheme 2, and is described below.

(i) 2-(4-Phenylbuta-1,3-dienyl)benzaldehyde oxime as a mixture of (*E*,*E*) and (*E*,*Z*) isomers. A solution of sodium acetate (1.34 g, 16.3 mmol) in water (25 cm^3) was added to a solution of hydroxylamine hydrochloride (1.14 g, 16.3 mmol) in water (25 cm^3) and the mixture added to a warm (35 °C) solution of 2-(4-phenylbuta-1,3-dienyl)benzaldehyde[7] as a mixture of (*E*,*E*) and (*E*,*Z*) isomers (3.47 g, 14.8 mmol) in ethanol (100 cm^3). A precipitate was formed and then water (50 cm^3) was added and the mixture was kept at *ca.* 5 °C overnight. Filtration gave the oxime as a pale yellow powder (2.51 g, 68%), mp 150–152 °C (from ethanol) (Found: M^+, 249.1153. $C_{17}H_{15}NO$ requires M^+, 249.1154); δ_H(200 MHz, $CDCl_3$) 6.5–7.1 (4 H, m, olefinic H), 7.2–7.85 (9 H, m, Ar-H), 8.41 and 8.57 (1 H, s, CH=N).

(ii) (*E*,*E*)-*N*-[2-(4-Phenylbuta-1,3-dienyl)benzyl]benzamide. A mixture of the oxime (2.5 g, 10.0 mmol), ammonium acetate (0.93 g, 12.1 mmol), zinc dust (4.92 g, 75.3 mmol), conc. aqueous ammonia (55 cm^3) and ethanol (25 cm^3) was heated under reflux under nitrogen for 17 h. The solvents were removed *in vacuo* and the residue was stirred for 1 h with aqueous potassium hydroxide (35% w/v, 50 cm^3). The mixture was extracted with ether (40 cm^3) and the extract was dried and evaporated to give *N*-2-(4-phenylbuta-1,3-dienyl)benzylamine as a mixture of (*E*,*E*) and (*E*,*Z*) isomers (1.58 g, 67%) as a white powder which was used without purification. Benzoyl chloride (1.33 g, 9.48 mmol) was added slowly to a mixture of the crude amine (1.58 g, 6.72 mmol) and sodium carbonate (2.42 g, 22.9 mmol) in dichloromethane (25 cm^3). The mixture was heated under reflux for 3 h, cooled and then stirred successively with water (20 cm^3) and aqueous sodium hydroxide (5 M, 50 cm^3). The organic layer was separated, washed with water (2 × 50 cm^3), dried and evaporated. The residue was dissolved in ethanol (20 cm^3) and heated under reflux for 1 h. On cooling, after the addition of hexane (5 cm^3), the crude amide (2.04 g, 85%) crystallised as a mixture of (*E*,*E*) and (*E*,*Z*) isomers in a ratio of 1:2, δ_H(200 MHz, $CDCl_3$) 4.67 (d, *J* 5.1, (*Z*) CH_2), 4.74 (d, *J* 5.1, (*E*) CH_2), 6.35 (1 H, br, NH), 6.5–7.8 (18 H, m). The mixture was not separable by chromatography. A solution of the amide, as an isomeric mixture (0.70 g) and iodine (18 mg) in chloroform (100 cm^3) was heated under reflux under nitrogen for 3 h. The solution was washed with saturated aqueous sodium metabisulfite (50 cm^3) and water (50 cm^3), dried and evaporated. The residue was crystallised from ethyl acetate to give (*E*,*E*)-*N*-[2-(4-phenylbuta-1,3-dienyl)benzyl]benzamide (0.56 g), mp 174.5–175.5 °C [Found: M^+, 339.1619. $C_{24}H_{21}NO$ requires M^+, 339.1623]; δ_H(200 MHz, $CDCl_3$) 4.74 (2 H, d, *J* 5.1, CH_2), 6.25 (1 H, br s, NH), 6.65–7.8 (18 H, m).

Generation and reactions of the nitrile ylides 18a–f and 20g–i derived from the corresponding amides 17a–f and 19g–i

The amides were converted into imidoyl chlorides by one of two general methods, **A** or **B**, illustrated respectively for the amides **17a** and **17b**. The crude imidoyl chorides, after removal of solvent and chlorination agent by evaporation under high vacuum were dissolved in THF and treated with lithium bis(trimethylsilyl)amide at 0 °C to generate the nitrile ylides. This and the general work-up method are given in detail for the first example.

Reaction of (*E*,*E*)-benzonitrilio[2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)phenyl]methanide 18a generated from the amide 17a. (*E*,*E*)-*N*-[2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]-benzamide **17a** (0.5 g, 1.17 mmol), dry ether (40 cm^3) and thionyl chloride (5.90 cm^3) were heated at reflux under dry nitrogen for 96 h (Method **A**). The solvent was removed *in vacuo* and the residue dried under high vacuum for 2–3 h. Dry THF (25 cm^3) was added and the solution cooled to 0 °C. Lithium bis(trimethylsilyl)amide (1.75 cm^3, 1.75 mmol) was added dropwise with rapid stirring under dry nitrogen. The mixture was stirred at 0 °C for 1 h, then allowed to warm to room temperature. Ammonium chloride (25% w/v, 25 cm^3) was added and the mixture stirred for 10 min. The organic layer was separated and the aqueous layer extracted with DCM (2 × 20 cm^3). The combined organic layers were dried and the solvent removed *in vacuo*. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (9:1) gave 8-methyl-9,11,13-triphenyl-12-azatricyclo[6.3.2.$0^{2,7}$]trideca-2(7),3,5,9,12-pentaene **24a** as a yellow crystalline solid (0.31 g, 65%), mp 181–182 °C from hexane–ethyl acetate [Found: C, 90.6; H, 6.4; N, 3.1%; $(M + 1)^+$, 412.2044. $C_{31}H_{25}N$ requires C, 90.5; H, 6.1; N, 3.4%; $(M + 1)^+$, 412.2065]; δ_H(250 MHz, $CDCl_3$) 1.39 (3 H, s, CH_3), 3.95 (1 H, dd, *J* 4.0 and 2.5, H-11), 5.32 (1 H, dd, *J* 4.0 and 1.7, H-10), 5.58 (1 H, dd, *J* 2.5 and 1.7, H-1), 7.15–7.67 (19 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 21.6 (CH_3), 45.6 (q), 48.0 (CH), 67.2 (CH), 120.8 (CH), 125.3 (CH), 126.3 (CH), 126.8 (CH), 127.0 (CH), 127.1 (CH), 127.8 (CH), 127.9 (CH), 128.2 (CH), 128.4 (CH), 129.3 (CH), 138.9 (q), 139.7 (q), 140.6 (q), 141.9 (q), 144.1 (q), 144.3 (q), 181.1 (q); *m*/*z* (FAB) 414 (M + 1, 67%), 413 (75), 412 (100), 397 (11), 362 (18), 334 (16), 320 (18), 307 (34), 293 (31), 278 (28), 253 (19), 239 (20), 215 (73), 191 (57), 165 (26), 128 (23), 91 (92); ν_{max}(Nujol)/cm^{-1} 1600 (C=N).

Reaction of (*E*,*E*)-benzonitrilio[2-(1-methyl-2-phenylpenta-1,3-dienyl)phenyl]methanide 18b generated from the amide 17b. Thionyl chloride (0.053 cm^3, 0.72 mmol) was added to (*E*,*E*)-*N*-[2-(1-methyl-2-phenylpenta-1,3-dienyl)benzyl]benzamide **17b** (0.2 g, 0.6 mmol) in dry DMF (0.72 g, 9.2 mmol) and stirred under a nitrogen atmosphere for 30 min (Method **B**). The solvent was removed *in vacuo* and the residue dried under high vacuum at 30–40 °C for 2–3 h. Dry THF (10 cm^3) was added and the solution cooled to 0 °C. Lithium bis(trimethylsilyl)-amide (3.52 cm^3, 3.52 mmol) was added dropwise with rapid stirring under dry nitrogen. The mixture was stirred at 0 °C for 1 h, then allowed to warm to room temperature. The usual work-up followed by dry column flash chromatography on silica, eluting with hexane–ethyl acetate (9:1) gave 8,11-dimethyl-9,13-diphenyl-12-azatricyclo[6.3.2.$0^{2,7}$]trideca-2(7),3,5,9,12-pentaene **24b** as a white crystalline solid (0.11 g, 46%), mp 149–150 °C from pentane–DCM [Found: C, 89.0; H, 6.9; N, 3.9%; $(M + 1)^+$, 350.1909. $C_{26}H_{23}N$ requires C, 89.35; H, 6.6; N, 4.0%; $(M + 1)^+$, 350.1909]; δ_H(200 MHz, $CDCl_3$) 1.16 (3 H, s, CH_3), 1.31 (3 H, d, *J* 7.3, CH_3), 2.60 (1 H, m, H-11), 4.90 (1 H, m, H-10), 5.15 (1 H, m, H-1), 6.93–7.39 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 17.9 (CH_3), 21.5 (CH_3), 37.0 (CH), 45.1 (q), 66.2 (q), 120.5 (CH), 125.3 (CH), 126.1 (CH), 126.6 (CH), 126.7 (CH), 127.3 (2 × CH), 127.6 (2 × CH), 127.9 (2 × CH), 128.0 (CH), 128.5 (2 × CH), 132.0 (CH), 139.1 (q), 139.6 (q), 141.9 (q), 142.3 (q), 144.0 (q), 181.3 (q); *m*/*z* (FAB) 350 (M + 1, 100%), 246 (77), 231 (19), 215 (24); ν_{max}(Nujol)/cm^{-1} 1624 (C=N).

Reaction of (*E*,*E*)-benzonitrilio[2-(4-methoxycarbonyl-1-methyl-2-phenylbuta-1,3-dienyl)phenyl]methanide 18c generated from the amide 17c. (*E*,*E*)-*N*-[2-(4-Methoxycarbonyl-1-methyl-2-phenylbuta-1,3-dienyl)benzyl]benzamide **17c** (0.5 g, 1.22 mmol), Method **A**, 144 h; followed by lithium bis(trimethylsilyl)amide (1.83 cm^3, 1.83 mmol) and the usual work-up and dry column flash chromatography on silica, eluting with hexane–ethyl acetate (4:1), gave 11-methoxycarbonyl-8-methyl-9,13-diphenyl-12-azatricyclo[6.3.2.$0^{2,7}$]trideca-2(7),3,5,9,12-pentaene **24c** as a mixture of diastereoisomers which resisted crystallisation from all solvent systems (96 mg, 20%) [Found: $(M + 1)^+$, 394.1816. $C_{27}H_{23}NO_2$ requires $(M + 1)^+$, 394.1810]; δ_H(250 MHz, $CDCl_3$) 1.29 (3 H, s, CH_3), 3.67 (3 H, s, CH_3), 3.82 (1 H, m, H-11), 5.39 (1 H, m, CH), 5.69 (1 H, m, CH), 6.99–7.68 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 21.4 (CH_3), 24.0 (CH_3), 44.0 (CH), 45.7 (CH), 52.1 (CH_3), 52.4 (CH_3), 61.2 (CH), 62.5 (CH), 120.7 (CH), 120.9 (CH), 123.6–145.4 (CH and q), 170.5 (q), 171.1 (q); ν_{max}(Nujol)/cm^{-1} 1644 (C=N), 1735 (C=O).

Reaction of (*E*)-benzonitrilio{2-[2-(2-phenylethenyl)cyclopentenyl]phenyl}methanide 18d generated from the amide 17d. (*E*)-*N*-{2-[2-(2-Phenylethenyl)cyclopentenyl]benzyl}benzamide **17d** (0.5 g, 1.32 mmol), Method **A**, 24 h; followed by lithium bis(trimethylsilyl)amide (1.98 cm^3, 1.98 mmol) and the usual work-up and dry column flash chromatography on silica, eluting with hexane–ethyl acetate (9:1), gave 7,15-diphenyl-16-azatetracyclo[6.6.2.$0^{1,5}$.$0^{9,14}$]hexadeca-5,9(14),10,12,15-pentaene† **24d** as a brown crystalline solid (0.3 g, 63%), mp 144–146 °C from hexane–ethyl acetate [Found: C, 89.7; H, 6.8; N, 3.7%; $(M + 1)^+$, 362.1908. $C_{27}H_{23}N$ requires C, 89.7; H, 6.4; N, 3.9%; $(M + 1)^+$, 362.1909]; δ_H(250 MHz, $CDCl_3$) 1.85 (2 H, m, CH_2), 2.29 (1 H, m, CH_2), 2.41 (1 H, m, CH_2), 2.66 (1 H, m, CH_2), 3.76 (1 H, m, H-11), 5.21 (1 H, m, H-10), 5.52 (1 H, m, H-1), 7.18–7.55 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 24.8 (CH_2), 33.6 (CH_2), 34.5 (CH_2), 45.0 (CH), 53.5 (q), 68.6 (CH), 119.3 (CH), 120.2 (CH), 125.5 (CH), 126.0 (CH), 126.5 (CH), 126.7 (CH), 127.4 (CH), 127.8 (CH), 128.2 (CH), 128.3 (CH), 139.1 (q), 139.4 (q), 141.2 (q), 142.5 (q), 146.8 (q), 181.4 (q); *m/z* (FAB) 363 (M + 2, 38%), 362 (M + 1, 100), 258 (24), 257 (23), 229 (12), 215 (17), 203 (11), 167 (17), 152 (12), 128 (12), 104 (11), 91 (36); ν_{max}(Nujol)/cm^{-1} 1621 (C=N).

Reaction of (*E*)-benzonitrilio(2-{2-[2-(methoxycarbonyl)ethenyl]cyclopentenyl}phenyl)methanide 18e generated from the amide 17e. (*E*)-*N*-(2-{2-[2-(Methoxycarbonyl)ethenyl]cyclopentenyl}benzyl)benzamide **17e** (0.5 g, 1.38 mmol), Method **A**, 96 h; followed by lithium bis(trimethylsilyl)amide (2.08 cm^3, 2.08 mmol) and dry column flash chromatography on silica, eluting with hexane–ethyl acetate (4:1), gave 7-methoxycarbonyl-15-phenyl-16-azatetracyclo[6.6.2.$0^{1,5}$.$0^{9,14}$]hexadeca-5,9(14),10,12,15-pentaene‡ **24e** (0.2 g, 42%) as a mixture of diastereoisomers in a *ca.* 1:1 ratio which were partially separated by MPLC eluting with hexane–ethyl acetate (6:1): (a) [Found: $(M + 1)^+$, 344.1648. $C_{23}H_{21}NO_2$ requires $(M + 1)^+$, 344.1651]; δ_H(200 MHz, $CDCl_3$) 1.70 (2 H, m, CH_2), 2.10 (1 H, m, CH_2), 2.25 (2 H, m, CH_2), 2.55 (1 H, m, CH_2), 3.57 (1 H, m, H-11), 3.61 (3 H, s, CH_3), 5.21 (1 H, m, CH), 5.60 (1 H, m, CH), 7.15–7.50 (9 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 24.8 (CH_2), 33.3 (CH_2), 34.4 (CH_2), 42.9 (CH), 52.3 (CH_3), 53.8 (q), 63.7 (CH), 114.2 (CH), 120.4 (CH), 126.0 (CH), 126.2 (CH), 127.0 (CH), 127.6 (2 × CH), 127.9 (2 × CH), 128.6 (CH), 137.1 (q), 142.3 (q), 147.3 (q), 171.8 (q); *m/z* (FAB) 344 (M + 1, 76%), 255 (13), 240 (46), 223 (16), 181 (53), 165 (23), 105 (100); ν_{max}(Nujol)/cm^{-1} 1625 (C=N), 1734 (C=O); and (b) [Found: $(M + 1)^+$, 344.1647. $C_{23}H_{21}NO_2$ requires $(M + 1)^+$, 344.1651]; δ_H(200 MHz, $CDCl_3$) 1.70 (2 H, m, CH_2), 2.10 (1 H, m, CH_2), 2.25 (2 H, m, CH_2), 2.55 (1 H, m, CH_2), 3.30 (1 H, m, H-11), 3.75 (3 H, s, CH_3), 5.08 (1 H, m, CH), 5.70 (1 H, m, CH), 7.15–7.53 (9 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 24.8 (CH_2), 33.3 (CH_2), 34.4 (CH_2), 42.9 (CH), 52.3 (CH_3), 53.8 (q), 63.7 (CH), 114.2 (CH), 120.4 (CH), 126.0 (CH), 126.2 (CH), 127.0 (CH), 127.6 (2 × CH), 127.9 (2 × CH), 128.6 (CH), 137.1 (q), 142.3 (q), 147.3 (q), 171.8 (q); *m/z* (FAB) 344 (M + 1, 82%), 343 (38), 255 (13), 240 (67), 223 (15), 181 (73), 165 (30), 105 (100); ν_{max}(Nujol)/cm^{-1} 1625 (C=N), 1731 (C=O).

Reaction of (*E*)-benzonitrilio[2-(1,4-dimethyl-2-phenylpenta-1,3-dienyl)phenyl]methanide 18f generated from the amide 17f. Thionyl chloride (0.048 cm^3, 0.65 mmol), (*E*)-*N*-[2-(1,4-dimethyl-2-phenylpenta-1,3-dienyl)benzyl]benzamide **17f** (0.2 g, 0.52 mmol) and DMF (0.6 g, 7.7 mmol), Method **B**, 30 min followed by the usual work-up and dry column flash chromatography on silica, eluting with hexane–ethyl acetate (9:1), gave (a) 7b-methyl-1-*exo*,1a-diphenyl-1-(2-methylprop-1-enyl)-1a,7b-dihydro-1*H*-cyclopropa[*c*]isoquinoline **23f** as a yellow solid (0.05 g, 20%), which decomposed at room temperature, [Found: $(M + 1)^+$, 364.2059. $C_{27}H_{25}N$ requires $(M + 1)^+$, 364.2065]; δ_H(250 MHz, $CDCl_3$) 1.25 (3 H, s, CH_3), 1.34 (3 H, s, CH_3), 1.57 (3 H, s, CH_3), 4.64 (1 H, s, CH), 7.06–7.67 (14 H, m, Ar-H), 8.25 (1 H, s, HC=N); δ_C(63 MHz, $CDCl_3$) 19.0 (CH_3), 21.2 (CH_3), 25.0 (CH_3), 35.5 (quat.), 36.4 (quat.), 62.5 (quat.), 122.7 (CH), 125.6 (CH), 126.2 (CH), 126.8 (CH), 127.6 (2 × CH), 127.8 (2 × CH), 128.4 (CH), 130.5 (2 × CH), 131.0 (2 × CH), 131.7 (quat.), 137.5 (quat.), 137.8 (quat.), 139.7 (quat.), 155.3 (HC=N); *m/z* (FAB) 362 (M + 1, 100%), 348 (15), 289 (12), 260 (32), 245 (17), 215 (21), 178 (22), 143 (65), 117 (29); ν_{max}(Nujol)/cm^{-1} 1624 (C=N); and (b) starting material (0.05 g, 20%).

Reaction of (*E*,*E*)-benzonitrilio[2-(4-phenylbuta-1,3-dienyl)phenyl]methanide 20g generated from the amide 19g. (*E*,*E*)-*N*-[2-(4-Phenylbuta-1,3-dienyl)benzyl]benzamide **19g** (0.10 g, 0.295 mmol), Method **A**, 20 h followed by lithium bis(trimethylsilyl)amide (1.2 cm^3, 1.2 mmol) and the usual work-up and dry column flash chromatography on silica, eluting with hexane–ether (6:1), gave (*E*)-1a-phenyl-1-*exo*-(2-phenylethenyl)-1a,7b-dihydro-1*H*-cyclopropa[*c*]isoquinoline **25g** (0.07 g, 75%) as a colourless oil (Found: M^+, 321.1501. $C_{24}H_{19}N$ requires M^+, 321.1517); δ_H(200 MHz, $CDCl_3$) 1.35 (1 H, dd, *J* 9.5 and 5.2, H-1), 3.08 (1 H, d, *J* 5.1, H-7b), 5.57 (1 H, dd, *J* 15.7 and 9.2, =CH), 6.43 (1 H, d, *J* 15.7, =CH), 7.1–7.65 (14 H, m, Ar-H), 8.19 (1 H, s, N=CH).

Reaction of (*Z*,*E*)-benzonitrilio[2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)phenyl]methanide 20h generated from the amide 19h. (*Z*,*E*)-*N*-[2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]benzamide **19h** (0.5 g, 1.17 mmol), Method **A**, 96 h followed by lithium bis(trimethylsilyl)amide (1.75 cm^3, 1.75 mmol) and the usual work-up and dry column flash chromatography on silica, eluting with hexane–ethyl acetate (9:1), gave (*E*)-7b-methyl-1-*endo*,1a-diphenyl-1-*exo*-(2-phenylethenyl)-1a,7b-dihydro-1*H*-cyclopropa[*c*]isoquinoline **25h** as a yellow crystalline solid (0.32 g, 65%), mp 167–169 °C from pentane–DCM [Found: C, 90.9; H, 6.5; N, 3.2%; $(M + 1)^+$, 412.2050. $C_{31}H_{25}N$ requires C, 90.5; H, 6.1; N, 3.4%; $(M + 1)^+$, 412.2065]; δ_H(200 MHz, $CDCl_3$) 1.80 (3 H, s, CH_3), 5.59 (1 H, d, *J* 15.7, =CH), 6.16 (1 H, d, *J* 15.7, =CH), 6.76–7.62 (19 H, m, Ar-H), 7.78 (1 H, s, N=CH); δ_C(63 MHz, $CDCl_3$) 19.8 (CH_3), 37.7 (q), 39.9 (q), 65.0 (q), 125.6 (CH), 125.7 (CH), 125.8 (2 × CH), 126.0 (CH), 126.1 (CH), 126.8 (CH), 127.2 (CH), 127.3 (CH), 127.6 (CH), 128.3 (3 × CH), 128.6 (2 × CH), 131.3 (2 × CH), 131.9 (CH), 132.5 (2 × CH), 134.3 (q), 134.7 (CH), 137.6 (q), 139.2 (q), 139.4 (q), 155.7 (HC=N); *m/z* (FAB); ν_{max}(Nujol)/cm^{-1} 1624 (C=N).

Reaction of (*Z*,*Z*)-benzonitrilio[2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)phenyl]methanide 20i generated from the amide 19i. (*Z*,*Z*)-*N*-[2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)benzyl]-benzamide **19i** (0.5 g, 1.17 mmol), Method **A**, 96 h followed by lithium bis(trimethylsilyl)amide (1.75 cm^3, 1.75 mmol) and the usual work-up and dry column flash chromatography on silica, eluting with hexane–ethyl acetate (9:1), gave (*Z*)-7b-methyl-**1**-*endo*,1a-diphenyl-1-*exo*-(2-phenylethenyl)-1a,7b-dihydro-1*H*-cyclopropa[*c*]isoquinoline **25i** as a colourless crystalline solid (0.34 g, 70%), mp 134–136 °C from pentane–DCM [Found: C, 90.2; H, 6.3; N, 3.3%; $(M + 1)^+$, 412.2085. $C_{31}H_{25}N$ requires C, 90.5; H, 6.1; N, 3.4%; $(M + 1)^+$, 412.2065]; δ_H(250 MHz, $CDCl_3$) 1.80 (3 H, s, CH_3), 6.15 (1 H, d, *J* 12.1, =CH), 6.53–7.81 (20 H, m, Ar-H, =CH), 7.77 (1 H, s, HC=N); δ_C(63 MHz, $CDCl_3$) 21.1 (CH_3), 35.3 (q), 36.0 (q), 63.6 (q), 125.2 (CH), 125.7 (CH), 126.1 (CH), 126.2 (CH), 126.3 (CH), 126.4 (CH), 126.9 (CH), 127.3 (2 × CH), 127.4 (CH), 128.2 (2 × CH), 128.4

† The correct IUPAC name for this compound is 9,15-diphenyl-16-azatetracyclo[6.6.2.$0^{1,11}$.$0^{2,7}$]hexadeca-2,4,6,10,15-pentaene.

‡ The correct IUPAC name for this compound is 9-methoxycarbonyl-15-phenyl-16-azatetracyclo[6.6.2.$0^{1,11}$.$0^{2,7}$]hexadeca-2,4,6,10,15-pentaene.

(CH), 128.7 (2 × CH), 130.7 (CH), 131.3 (2 × CH), 131.9 (CH), 132.8 (CH), 133.4 (CH), 135.2 (q), 137.2 (q), 138.7 (q), 155.0 (HC=N); ν_{max}(Nujol)/cm^{-1} 1624 (C=N).

Thermal isomerisation of 1-*exo*-(2-phenylethenyl)cyclopropa[*c*]-isoquinolines 25g–i

Thermal isomerisation of (*E*)-1a-phenyl-1-*exo*-(2-phenylethenyl)-1a,7b-dihydro-1*H*-cyclopropa[*c*]isoquinoline 25g. The reactant (35 mg, 0.109 mmol) in deuteriochloroform was heated at reflux for 7 h in an NMR tube. Evaporation of the solvent gave 11,13-diphenyl-12-azatricyclo[6.3.2.0^{2,7}]trideca-2(7),3,5,9,12-pentaene **24g** as an oil in quantitative yield [Found: M$^+$, 321.1524. $C_{24}H_{19}N$ requires M$^+$, 321.1517]; δ_H(200 MHz) 3.79 (1 H, ddd, *J* 3.5, 2.5, 2.5, H-11), 4.68 (1 H, d, *J* 8.4, H-8), 5.27 (1 H, dddd, *J* 10.6, 3.5, 1.7, 0.7, H-10), 5.48 (1 H, dd, *J* 2.5, 1.7, H-1), 6.32 (1 H, ddd, *J* 10.6, 8.4, 2.5, H-9), 7.2–7.6 (12 H, m, Ar-H), 7.88 (2 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 42.7 (C-11), 47.0 (C-8), 67.9 (C-1), 123.8 (C-10), 125.1 (C-9), 126.3 (CH), 126.6 (CH), 126.7 (CH), 127.5 (CH), 128.2 (CH), 128.3 (CH), 130.2 (CH), 130.4 (CH), 136.7 (CH), 136.9 (q), 138.7 (q), 140.5 (q), 140.6 (q), 175.9 (C-9).

Thermal isomerisation of (*E*)-7b-methyl-1-*endo*,1a-diphenyl-1-*exo*-(2-phenylethenyl)-1a,7b-dihydro-1*H*-cyclopropa[*c*]isoquinoline 25h. The reactant (0.05 g, 0.133 mmol) in dry perdeuteriobenzene (0.7 cm^3) was heated under reflux for 35 h. Evaporation of the solvent gave a brown oil. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate (9 : 1) gave 8-methyl-9,11,13-triphenyl-12-azatricyclo[6.3.2.0^{2,7}]trideca-2(7),3,5,9,12-pentaene **24a** as a crystalline solid (0.17 g, 35%), identical with the product from the nitrile ylide **18a**; and 10-methyl-8,11,13-triphenyl-12-azatetracyclo[7.3.1.0^{2,7}.0^{8,10}]trideca-2(7),3,5,11-tetraene§ **29** as a colourless crystalline solid (0.33 g, 65%), mp 116–118 °C from pentane–DCM (Found: (M + 1)$^+$, 412.2057. $C_{31}H_{25}N$ requires (M + 1)$^+$, 412.2065); δ_H(200 MHz, $CDCl_3$) 1.14 (3 H, s, CH_3), 2.53 (1 H, t, *J* 2.2, CH), 3.30 (1 H, s, CH), 5.10 (1 H, t, *J* 1.8, CH), 6.89–7.51 (19 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 23.5 (CH_3), 31.7 (q), 34.2 (CH), 37.0 (CH), 64.0 (CH), 125.9 (CH), 126.2 (CH), 126.6 (CH), 127.3 (2 × CH), 127.8 (3 × CH), 127.9 (2 × CH), 128.1 (CH), 128.3 (CH), 128.4 (2 × CH), 129.5 (CH), 130.1 (CH), 132.6 (CH), 135.5 (q), 137.0 (q), 138.1 (q), 141.2 (q); ν_{max}(Nujol)/cm^{-1} 1620 (C=N).

§ The correct IUPAC name for this compound is 12-methyl-2,11,13-triphenyl-10-azatetracyclo[7.3.1.0^{2,12}.0^{3,8}]trideca-3,5,7,10-tetraene.

Thermal isomerisation of (*Z*)-7b-methyl-1-*endo*,1a-diphenyl-1-*exo*-(2-phenylethenyl)-1a,7b-dihydro-1*H*-cyclopropa[*c*]isoquinoline 25i. The reactant (0.06 g, 0.146 mmol) in dry perdeuteriobenzene (0.7 cm^3) was heated under reflux. The reaction was monitored by ^{1}H NMR and was found to be complete after 35 h. Evaporation of the solvent gave a brown oil. Dry flash column chromatography on silica, eluting with hexane–ethyl acetate gave 8-methyl-9,11,13-triphenyl-12-azatricyclo[6.3.2.0^{2,7}]trideca-2(7),3,5,9,12-pentaene **24a** (18 mg, 32%), and 10-methyl-8,11,13-triphenyl-12-azatetracyclo[7.3.1.0^{2,7}.0^{8,10}]trideca-2(7),3,5,11-tetraene **29** (32 mg, 68%) identical with the products of the previous experiment.

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