Electrophilic Reactions of α-Amino Dienenitriles: Regiochemistry and Stereoselectivity of Trisubstituted Pentadienyl Anions

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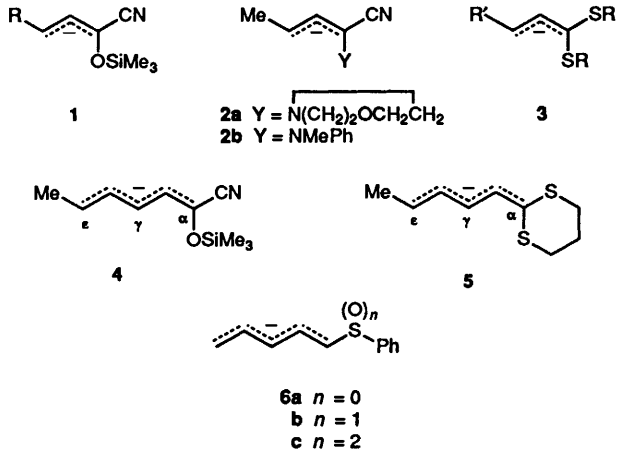
A pentadienyl anion **7a** generated from 2-*N*-methylanilinohepta-3,5-dienenitrile reacted at the γ-site with halogenoalkanes to give predominantly the products **9γ–22γ** having the 2*Z*,5*E*-configuration, while it reacted at the ε-site with conjugated aldehydes to give mainly the products **27ε–29ε** having the 2*Z*,4*E*-configuration. An intermediate of the pentadienyl ion **7a** having a lithium atom σ-bonded to the γ-carbon and chelated with the anilino group was proposed to account for the regio- and stereo-selectivities observed in the above reactions. The alkylation reactions in the presence of a dipolar co-solvent HMPA tended to enhance the 2*Z*-selectivity. The pentadienyl anions derived from the α-anilino dienenitriles **30–33** having different ε-substituents such as phenyl, phenylthio, benzyloxy and ethoxycarbonyl groups also reacted with halides and aldehydes both regio- and stereo-selectively.

Dithioacetal, cyanohydrin derivatives and α-amino nitrile are three widely used synthetic umpolungs of acyl groups.[1] The regiochemistry of corresponding allylic anions toward electrophiles has been extensively studied. These anions can function as equivalents of α,β-unsaturated acyl anions if reactions occur at the α-sites, or they can function as equivalents of β-anions of carboxylic acids if reactions take place at the γ-sites. The allylic

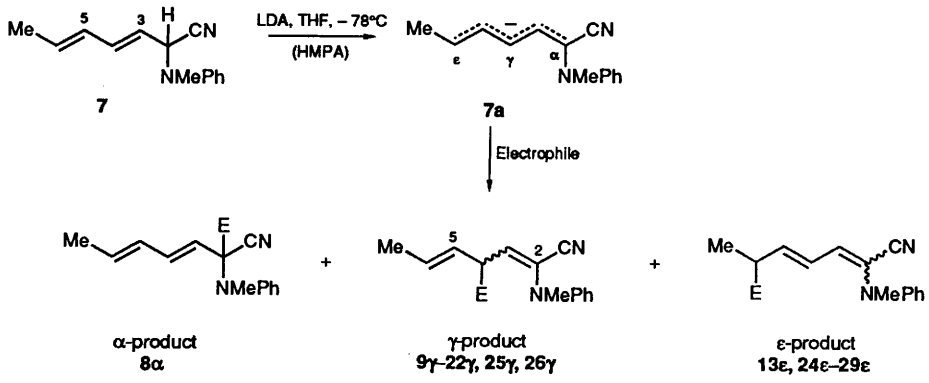


anions of cyanohydrin derivatives **1** appear to react invariably at the α-sites,[2] but the regioselectivity of the allylic anions of dithioacetal and aminonitrile is controlled by many factors, including the size of the SR or NRR′ group.[3] For example, the anion of 2-morpholinopent-3-enenitrile **2a** reacts exclusively at the α-site with halogenoalkanes,[3c] while alkylation of the anion of 2-*N*-methylanilinopent-3-enenitrile **2b** occurs at the γ-site.[3d–g] The α-alkylation is disfavoured in the latter case due to the steric hindrance of the bulky *N*-methylanilino group. Similar phenomena are observed in the reactions of 1,1-dithio-substituted allylic anions **3**, *i.e.* an increase in the size of the substituent on sulfur tends to increase the proportion of the γ-reaction.[3a,b] If the substituent is a pentadienyl system, the anion may react with electrophiles at the α-, γ- or ε-site. Many studies have concerned the reactivity of the parent pentadienyl anion and those having alkyl substitutents.[4] The regioselectivity of pentadienyl anions is apparently dependent on the substituents in addition to other controlling factors. Utilisation of pentadienyl anions in synthesis of natural products has also been realised.[5] However, the pentadienyl anion having heteroatom substituents is rarely investigated. Hunig and his co-workers have reported that the pentadienyl anion of cyanohydrin trimethylsilyl ether **4** undergoes alkylation exclusively at the α-site.[6] A study of dithiane pentadienyl anions such as **5** also indicates the α-selectivity in electrophilic reactions.[7] It has been shown that the phenylsulfinyl- and phenylsulfonyl-substituted pentadienyl anions **6b, c** react at the α-sites with iodomethane and carbonyl compounds whereas the regiochemistry of the corresponding phenylsulfenyl-substituted anion **6a** is dependent on the electrophile.[8] We describe herein the pentadienyl anions of the α-amino nitrile **7** and the related compounds **30–33**, which, depending on the electrophile, are preferentially attacked at the α-, γ- or ε-sites.

Results and Discussion

2-*N*-Methylanilinohepta-3,5-dienenitrile **7** was prepared by condensation of hexa-2,4-dienal, potassium cyanide and *N*-methylaniline according to Strecker's method.[9] The 3*E*,5*E*-configuration was characterised by the large coupling constants, $J_{3,4}$ 16 Hz and $J_{5,6}$ 15 Hz, in the NMR spectrum. Deprotonation of **7** with lithium diisopropylamide (LDA) in THF at −78 °C gave a pentadienyl anion **7a**, which subsequently reacted with a variety of electrophiles as shown in Table 1. The reactions with D_2O and aldehydes (entries 1 and 19–23) were quenched at −78 °C, while the other reaction mixtures were allowed to warm to room temperature. When D_2O was used as the electrophile, only the α-deuteriated compound **8α** was obtained. The anion **7a** reacted with oxygen at both terminal sites but not at the central γ-site (entry 18). The α-product was isolated as the corresponding amide, *N*-methyl-*N*-phenylhexa-2,4-dienamide **24α**.[11] On the other hand, the alkylations with halides occurred at the γ-site to give two geometric isomers predominating in the 2*Z*-configuration (entries 2–16). The 2*Z*-isomer was consistently more polar than the corresponding *E*-isomer. The 3-H resonance of the 2*Z*-isomer usually occurred at a lower field (~δ 6.2) due to the deshielding effect of the cyano group.[10] The anion **7a** reacted with aliphatic aldehydes at −78 °C to give the γ- and ε-addition products predominating in the 2*Z*-isomers. However, **7a** reacted with conjugated aldehydes exclusively at the ε-site to give the 2*Z*,4*E*-products, of which 3-H and C-3 appearing at low fields (approximately δ_H 6.6 and δ_C 145, respectively) indicated the 2*Z*-configuration and the large coupling constant ($J_{4,5}$ 16 Hz) supported the 4*E*-configuration.[10]

The alkylations in the presence of a dipolar co-solvent



Scheme 1

Table 1 Electrophilic reactions of the pentadienyl anion **7a** in THF (Scheme 1)[a]

Entry	Electrophile	Product (isolated yield) (%)	E
1	D_2O	**8α** (95)	D
2	MeI	**9γ*E*** (37) + **9γ*Z*** (53)	Me
3	EtI	**10γ*E*** (33) + **10γ*Z*** (41)[b]	Et
4	Me_2CHI	**11γ*E*** (30) + **11γ*Z*** (41)	Me_2CH
5	$PhCH_2Cl$	**12γ*E*** (29) + **12γ*Z*** (38)	$PhCH_2$
6	$CH_2{=}CHCH_2Br$	**13γ*E*** (19) + **13γ*Z*** (36) + **13ε*Z*** (9)	$CH_2{=}CHCH_2$
7	$PhCH{=}CHCH_2Cl$	**14γ*E*** (30) + **14γ*Z*** (44)	$PhCH{=}CHCH_2$
8	EtO_2CCH_2Br	**15γ*E*** (4) + **15γ*Z*** (80)	EtO_2CCH_2
9	$BrCH_2CH_2Br$	**16γ*E*** (10) + **16γ*Z*** (13)[c]	$BrCH_2CH_2$
11	$Br(CH_2)_3Br$	**17γ*E*** (36) + **17γ*Z*** (53)	$Br(CH_2)_3$
12	$BrCH{=}CHCH_2Br$	**18γ*E*** (35) + **18γ*Z*** (41)	$BrCH{=}CHCH_2$
13	$Br(CH_2)_2CHBrMe$	**19γ*E*** (31) + **19γ*Z*** (43)	$(CH_2)_2CHBrMe$
14	$Br(CH_2)_4Br$	**20γ*E*** (28) + **20γ*Z*** (45)	$Br(CH_2)_4$
15	$CH_2(CH_2)_2C(Br){=}CCH_2Cl$	**21γ*E*** (16) + **21γ*Z*** (66)[d]	$CH_2(CH_2)_2C(Br){=}CCH_2$
16	*o*-$BrC_6H_4CH_2Br$	**22γ*E*** (25) + **22γ*Z*** (70)[d]	*o*-$BrC_6H_4CH_2$
17	PhSSPh	**23ε*E*** (52)[e]	PhS
18	O_2	**24α** (15)[f] + **24ε*E*** (5) + **24ε*Z*** (64)	OH
19	$MeCH_2CHO$	**25γ*E*** (28) + **25γ*Z*** (38) + **25ε*Z*** (26)[g]	$MeCH_2CH(OH)$
20	$Me(CH_2)_2CHO$	**26γ*E*** (28) + **26γ*Z*** (53)[g,h]	$Me(CH_2)_2CH(OH)$
21	PhCHO	**27ε*Z*** (85)[g]	PhCH(OH)
22	$MeCH{=}CHCHO$	**28ε*Z*** (69)[g]	$MeCH{=}CHCH(OH)$
23	$PhCH{=}CHCHO$	**29ε*Z*** (79)[g]	$PhCH{=}CHCH(OH)$

[a] The reactions with D_2O and aldehydes (entries 1 and 19–23) were quenched at −78 °C, while the reactions of other entries were allowed to warm to room temperature. [b] Reaction in the presence of 3 equiv. HMPA gave **10γ*E*** (22%) + **10γ*Z*** (65%). [c] Starting material **7** (43%) was recovered. [d] Reaction performed in the presence of 3 equiv. HMPA. [e] Reaction in the presence of 3 equiv. HMPA gave **23γ*E*** (25%) + **23ε*E*** (25% + **23ε*Z*** (43%). [f] α-Product isolated as *N*-methyl-*N*-phenylhexa-2,4-dienamide. [g] Products consisted of the *erythro*- and *threo*-isomers. [h] Reaction gave **26γ*E*** (44%) + **26γ*Z*** (28%) when the reaction was warmed to −40 °C for 2 h, while it gave **26γ*E*** (21%) + **26γ*Z*** (27%) + **26ε*Z*** (13%) after being stirred for 1 h at room temp.

Table 2 Effects of co-solvent HMPA and temperature on the reactions of the pentadienyl anion **7a** with electrophiles in THF

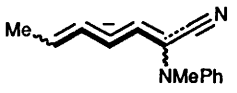
Electrophile	HMPA (equiv.)	*T*/°C (time/h)	Products ratio
EtI	0	−78 to 25	**10**, γ*E*:γ*Z* = 45:55
	3	−78 to 25	**10**, γ*E*:γ*Z* = 25:75
PhSSPh	0	−78 (1)	**23**, γ*Z*:ε*E*:ε*Z* = 17:17:17[a]
	0	−78 to 0	**23**, γ*Z*:ε*E*:ε*Z* = 7:40:53
	3	−78 to 25 (0.5)	**23**, γ*Z*:ε*E*:ε*Z* = 26:26:48
	0	−78 to 25 (2)	**23**, ε*E*:ε*Z* = 55:45
	0	−78 to 25 (16)	**23**, ε*E* (100%)
$Me(CH_2)_2CHO$	0	−78	**26**, γ*E*:γ*Z* = 35:65
	0	−78 to −40 (2)	**26**, γ*E*:γ*Z* = 60:40
	0	−78 to 25 (1)	**26**, γ*E*:γ*Z*:ε*Z* = 34:44:21

[a] Starting material **7** was recovered (49%).

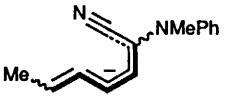
hexamethylphosphoramide (HMPA) (3 equiv.), *e.g.* entries 15 and 16, appeared to give a higher ratio of the 2*Z*-isomers of the γ-products. Effects of HMPA and temperature on the reactions of **7a** with representative electrophiles such as iodoethane, diphenyl disulfide and butyraldehyde were investigated, and the results are shown in Table 2. The reaction with EtI in the presence of HMPA tended to increase the proportion of the 2*Z*-isomer of **10γ**. The anion **7a** reacted sluggishly with diphenyl disulfide at −78 °C to give equal amounts of the γ*Z*-, ε*E*- and ε*Z*-isomers of **23** in addition to recovered starting material. However, a 16 h reaction with stirring at room temperature occurred predominantly at the ε-site and led to a single product

23ε*E* having the 2*E*,4*E*-configuration. When the reaction of **7a** with butyraldehyde was warmed to room temperature, **26ε*Z*** was also obtained as a minor product in addition to the γ-products.

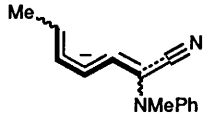
A parent pentadienyl anion is commonly considered to have three geometries for the η^5-coordination structure: the zigzag-like W-shape, the horseshoe U-shape and the sickle-like S-shape.[5] For example, pentadienyllithium exists as the W-shaped



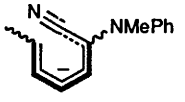
W-shaped η^5-structure



S-shaped η^5-structure

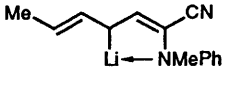


S-shaped η^5-structure



U-shaped η^5-structure

structure while pentadienylpotassium exists as the U-shaped structure in THF solution.[12] In principle, the amino nitrile pentadienyl anion **7a** may have 16 η^5-coordination forms which consist of four W-, four U- and eight S-shaped structures. However, the possible delocalisation by the cyano group,[1e] and even the existence of η^1- and η^3-coordination structures should not be overlooked. In such cases, the η^1-, η^3- and η^5-forms may also undergo equilibrium. It is thus difficult to predict the reactivity of a pentadienyl anion due to its possible existence of various coordination states. However, the observed regio- and stereo-selective reaction modes in the pentadienyl system of **7a** point to a probable W-shaped intermediate **A**,

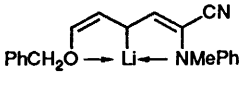


A

which is stabilised by having lithium atom σ-bonded to the γ-carbon and coordinated with the α-amino group.[13] This model explains the preference for formation of the 2*Z*-isomers in electrophilic reactions with halogenoalkanes and aldehydes regardless of the reactions occurring at either the γ- or ε-site. Except for the small electrophiles, *e.g.* D_2O and O_2, reactions at the α-site were impeded by the bulky *N*-methylanilino group. A similar model has been proposed to account for the γ- and 2*Z*-selectivity found in the reactions of an asymmetric allyllithium generated from 2-(*N*-methylanilino)-4-phenylbut-3-enenitrile.[14] The stereochemical outcome in asymmetric alkylations of a chiral ephedrino alkenenitrile further supports the η^1-chelated form as a favourable intermediate.[14] The preceding rationale is based on considering the reaction proceeding with a monomeric **A**, rather than the solvated free anion or the aggregate form. Although the effect of solvents was not thoroughly studied, a dipolar solvent HMPA might help to eliminate the degree of aggregate of **A** species to attain higher reactivity and better 2*Z*-selectivity.[14,15]

In the reaction of **7a** with diphenyl disulfide, the proportion of the ε-products increased at the expense of the γ-product as the temperature and time increased. The ε-product **23ε** incorporating the conjugated dienenitrile moiety is conceivably more stable than the γ-product **23γ**. Thus the reaction of **7a** and diphenyl disulfide is considered to involve a reversible process, and finally yielded the thermodynamically favoured **23ε*E*** product after a prolonged reaction time. For a similar reason, the γ-addition mode in the reaction of **7a** with butyraldehyde at −78 °C was partially changed to the ε-addition mode at room temperature. The exclusive formation of the ε-addition products in the reactions of **7a** and conjugated aldehydes (entries 21–23, Table 1) might be attributable to their highly reversible reaction.

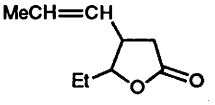
The pentadienyl anions of the aminonitriles **30–33** having different ε-substituents (Y) were also investigated (Table 3). The anion derived from **30** (Y = Ph) was treated with *o*-bromobenzyl bromide in the presence of HMPA to give exclusively the γ-product **34γ** predominating in the 2*Z*,5*E*-isomer. However, a similar alkylation of **31** (Y = PhS) having the 2*E*,4*E*-configuration retained the 2*E*-configuration in the γ-product **35γ**. Interestingly, the alkylated products **36γ** and **37γ** of **32** (Y = $PhCH_2O$) not only had the 2*Z*-configuration but also showed preference in the 5*Z*-configuration. A chelated intermediate **B** may be deduced to account for the stereochemical outcome.[16] The anion of **33** (Y = CO_2Et)



B

reacted with both a halide and an aldehyde at the carbon adjacent to the ethoxycarbonyl group. This regioselectivity is presumably affected by the potent stabilising ability of the ethoxycarbonyl group as usually observed in the reactions of crotonate anions.[17] Nonetheless, the ε-products **38ε–40ε** also prevailed in the 2*Z*-isomers.

In summary, we have shown the reactions of pentadienyl anions generated from the amino nitriles **7** and **30–33** are regio- and stereo-selective. The regiochemistry in reactions of **7a** is dependent on the attacking electrophiles. The selective γ-alkylations in **7a** are different from the α-reactions of the pentadienyl anions derived from the silyloxy nitrile **5** and the dithiane **6**. To demonstrate **7** as an equivalent of γ,δ-unsaturated carboxylic acid, the γ-products **25γ** and **26γ** obtained from the reactions with the aldehydes were subsequently hydrolysed to afford the β-propenyl-γ-lactones **41** and **42**,



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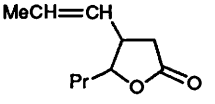


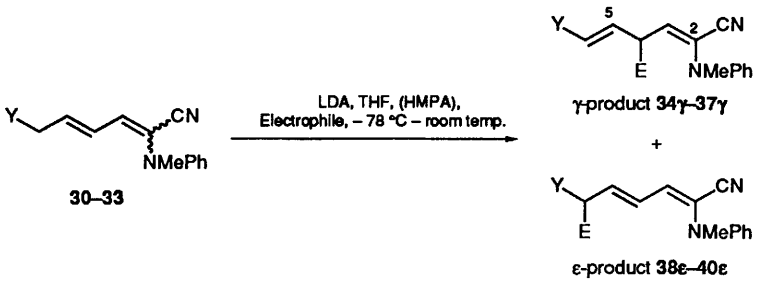
42

respectively. On the other hand, the ε-selective reactions furnished α-amino nitrile dienes such as **23ε** and **27ε–29ε**, which can be utilised in [4 + 2]cycloadditions[9] and as precursors of the corresponding trienes. We are investigating the intramolecular radical cyclisations of the γ-products **17γ–22γ** having bromoalkyl substituents in order to evaluate the stabilising power of captodative substitution.[18]

Experimental

M.p.s are not corrected. ^1H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR at 50 or 75 MHz using chlorotrimethylsilane as internal standard (*J* values in Hz). Mass spectra (using a Finnigan TSQ 46c spectrometer) were recorded at an ionising voltage of 70 eV. Merck silica gel 60F sheets were used for analytical thin-layer chromatography (TLC). Column chromatography was performed on SiO_2 (70–230 mesh) with elution of gradients of EtOAc and hexane. High-pressure liquid chromatography (HPLC) was carried out on a liquid chromatograph, equipped with a refractive index detector. The samples were analysed and/or separated on a Hibar Lichrosorb Si 60 (7 μm) column (25 cm × 1 cm) by the

Table 3



Reactant	Y	Electrophile[a]	Product (yield) (%), isomeric ratio	E
30[b]	Ph	*o*-$BrC_6H_4CH_2Br$	**34γ** (41), 2*E*,5*E*:2*Z*,5*E* = 33:67	*o*-$BrC_6H_4CH_2$
31[c]	PhS	*o*-$BrC_6H_4CH_2Br$	**35γ** (68), 2*E*,5*E* only	*o*-$BrC_6H_4CH_2$
32[d]	$PhCH_2O$	*o*-$BrC_6H_4CH_2Br$	**36γ** (61), 2*Z*,5*E*:2*Z*,5*Z* = 33:67	*o*-$BrC_6H_4CH_2$
32[d]	$PhCH_2O$	$Br(CH_2)_3I$	**37γ** (41), 2*Z*,5*Z* only	$Br(CH_2)_3$ or $I(CH_2)_3$
33[e]	CO_2Et	EtI	**38ε** (29), 2*E*,4*E*:2*Z*,4*E* = 59:41 + **39ε** (64),[f] 2*E*,4*E*:2*Z*,4*E* = 36:64	Et
33[e]	CO_2Et	EtCHO	**40ε** (98), 2*Z*,4*E* only	EtCHOH

[a] Alkylation reactions were performed in the presence of HMPA (3 equiv.) and the reaction mixture was stirred at room temp. for 4 h before work-up. The addition reaction with propionaldehyde was carried out at −78 °C for 0.5 h in the absence of HMPA. [b] The reactant was composed of (2*E*,4*E*)- and (2*Z*,4*E*)-2-(*N*-methylanilino)-6-phenylhexa-2,4-dienenitriles as well as the non-conjugated isomers (2*E*,5*E*)- and (2*Z*,5*E*)-2-(*N*-methylanilino)-6-phenylhexa-2,5-dienenitriles in a ratio of 22:33:20:25. [c] The reactant had the (2*E*,4*E*)-configuration. [d] The reactant was composed of the (2*E*,4*Z*)- and (2*Z*,4*Z*)-isomers in a ratio of 43:57. [e] The reactant was composed of the (2*E*,4*E*)-and (2*Z*,4*E*)-isomers in a ratio of 30:70. [f] Compound **39ε** is the double alkylated product.

indicated eluent with 5 cm^3 min^{-1} flow rate. THF was distilled from sodium benzophenone ketyl under N_2. 2-Bromo-1-chloromethylcyclopentene, for entry 15 was prepared from 2-bromocyclopentenecarbaldehyde[19] by reduction with $NaBH_4$ and subsequent treatment with TsCl–Et_3N.

Preparation of α-Amino Dienenitriles **7** *and* **30–33**.—2-*N*-Methylanilinohepta-3,5-dienenitrile **7** was prepared by condensation of hexa-2,4-dienal, potassium cyanide and *N*-methylaniline according to the Strecker's method.[9] Condensation of 2-(*N*-methylanilino)prop-2-enenitrile with phenylacetaldehyde (LDA, THF) afforded an alcohol, which was activated as the methanesulfonate (Et_3N, MsCl) and treated with Bu^{t}OK to give 2-(*N*-methylanilino)-6-phenylhexa-2,4-dienenitrile **30** and the non-conjugated isomer, 2-(*N*-methylanilino)-6-phenylhexa-2,5-dienenitrile. Preparation of 2-(*N*-methylanilino)-6-phenylthiohexa-2,4-dienenitrile **31** was achieved by the reaction of 2-(*N*-methylanilino)-2-phenylthioacetonitrile with 1,4-dibromobut-2-ene (Bu^{t}OK, THF).[20] The product **31** was accessed by a tandem alkylation–dehydrosulfenylation, followed by a reinsertion of the benzenethiolate ion. Condensation of (*N*-methylanilino)acetonitrile with (*Z*)-4-benzyloxybut-2-enal, which was obtained from oxidation of (*Z*)-4-benzyloxybut-2-enol (MnO_2, CH_2Cl_2),[21] directly yielded 6-benzyloxy-2-(*N*-methylanilino)hexa-2,4-dienenitrile **32** according to the Peterson procedure.[9] Condensation of ethyl 6-oxohexa-2,4-dienoate,[22] *N*-methylaniline and potassium cyanide, by a concurrent isomerisation, produced ethyl 6-cyano-6-(*N*-methylanilino)hexa-3,5-dienoate **33**.

Reaction of Pentadienyl Anion with Electrophiles.—Under an atmosphere of N_2, a solution of diisopropylamine (0.18 cm^3, 1.1 mmol) in THF (10 cm^3) was cooled to −15 °C and a solution of BuLi (1.6 mol dm^{-3} in hexane; 0.7 cm^3, 1.1 mmol) was added dropwise. After 15 min, the LDA solution was cooled to −78 °C, and a solution of compound **7** (212 mg, 1.0 mmol) in THF (5 cm^3) was added dropwise. The resulting orange-coloured solution of **7a** was stirred for 45 min, and treated at −78 °C with an appropriate electrophile (1.2 mmol) [accompanied by HMPA (3 mmol) in certain cases (Table 1)]. The reaction with the electrophile of D_2O or aldehyde was quenched at −78 °C after 30 min by addition of a THF solution of HOAc (3 mmol). Otherwise, the reaction with the electrophile of alkyl halide or PhSSPh or O_2 was warmed to room temperature and kept for a further 2 h before quenching with saturated aqueous NH_4Cl. The mixture was concentrated under reduced pressure, and the residue was taken up with EtOAc. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to give the crude products. Separation of products was accomplished by column chromatography (SiO_2) and/or HPLC with elution of the gradients of EtOAc in hexane indicated in each case. The reactions of the pentadienyl anions of **30–33** were carried out by similar procedures.

Hydrolysis of Compounds **25γ** *and* **26γ**.—A solution of compound **25γ** (170 mg, mixture of diastereoisomers) in THF (2 cm^3) and HCl (2 mol dm^{-3}, 10 cm^3) was heated to 70 °C under mild reflux for 16 h. The mixture was cooled, and extracted with EtOAc. The combined extracts were washed with aqueous NaOH (5%) and brine, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was separated on a SiO_2 column by elution with EtOAc (10% in hexane) to give the lactone **41** (90 mg, 92%, *trans*/*cis* = 1.4). Hydrolysis of compound **26γ** (270 mg, 0.77 mmol) by a similar procedure afforded the lactone **42** (122 mg, 94%, *trans*/*cis* = 1.5).

2-(N-*methylanilino*)[2-^{2}H]*hepta*-3,5-*dienenitrile* **8α**. Yellow oil; HPLC (1% EtOAc in hexane) t_R 430 s; ν_{max}(neat)/cm^{-1} 2232 (CN); δ_H($CDCl_3$) 1.82 (3 H, d, *J* 6.0, 7-H), 2.84 (3 H, s, N-Me), 5.54 (1 H, d, *J* 15, 3-H), 5.90 (1 H, dq, *J* 15, 6, 6-H), 6.13 (1 H, br dd, *J* 15, 10, 5-H), 6.60 (1 H, dd, *J* 15, 10, 4-H), 6.92–7.00 (3 H, m) and 7.24–7.34 (2 H, m); δ_C($CDCl_3$) 18.1 (q, C-7), 34.3 (q, N–C), 55.3 (t, C-2), 115.8 (s, C-1), 116.5 (d, 2 C, C-2′), 116.6 (d), 120.8 (d), 121.6 (d), 129.3 (d, 2 C, C-3′), 133.1 (d), 135.2 (d) and 148.6 (s, C-1′); *m*/*z* 213 (M^+, 27%), 198 (23), 106 (72) and 77 (100) (M^+, 213.1370. *M*, 213.1376).

4-*Methyl*-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **9γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.15; ν_{max}(neat)/cm^{-1} 2240 (CN); δ_H($CDCl_3$) 1.18 (3 H, d, *J* 7), 1.68 (3 H, dd, *J* 6, 1, 7-H), 3.11 (3 H, s, N–Me), 3.31–3.51 (1 H, m, 4-H), 5.48 (1 H, ddq, *J* 18, 6, 1, 5-H), 5.33–5.74 (1 H, m, 6-H), 5.69 (1 H,

d, *J* 10, 3-H), 6.92–7.03 (3 H, m) and 7.25–7.34 (2 H, m); $\delta_C(CDCl_3)$ 17.9 (q), 20.9 (q), 37.4 (d), 39.9 (q), 114.7 (s), 119.3 (d, 2 C), 120.1 (s), 122.2 (d), 125.1 (d), 129.2 (d, 2 C), 133.3 (d), 137.2 (d) and 146.6 (s); *m/z* 226 (M^+, 59%) and 211 (100) (Found: C, 79.7; H, 8.0; N, 12.3. $C_{15}H_{18}N_2$ requires C, 79.61; H, 8.02; N, 12.38%). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.12; ν_{max}(neat)/cm^{-1} 2215 (CN); $\delta_H(CDCl_3)$ 1.07 (3 H, d, *J* 7), 1.64 (3 H, d, *J* 6), 3.06 (3 H, s), 3.24–3.40 (1 H, m), 5.18–5.49 (2 H, m), 6.15 (1 H, d, *J* 10), 6.78 (2 H, dd, *J* 7, 1), 6.88 (1 H, dd, *J* 7, 7) and 7.28 (2 H, ddd, *J* 7, 7, 1); $\delta_C(CDCl_3)$ 17.9 (q), 19.8 (q), 35.1 (d), 38.4 (q), 114.2 (d, 2 C), 116.2 (s), 118.0 (s), 119.7 (d), 126.0 (d), 129.2 (d, 2 C), 131.7 (d), 146.2 (s) and 149.4 (d); *m/z* 226 (M^+, 24%) and 211 (Found: C, 79.9; H, 7.95; N, 12.3).

4-*Ethyl*-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **10γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.14; ν_{max}(neat)/cm^{-1} 2223 (CN); $\delta_H(CDCl_3)$ 0.96 (3 H, t, *J* 7), 1.37–1.64 (2 H, m), 1.70 (3 H, dd, *J* 7, 2), 3.13 (s), 3.35–3.63 (1 H), 5.34 (1 H, dd, *J* 15, 6), 5.53–5.63 (1 H, m), 5.70 (1 H, d, *J* 10), 6.94–7.02 (3 H, m) and 7.21–7.34 (2 H, m); $\delta_C(CDCl_3)$ 11.6 (q), 18.0 (q), 28.5 (t), 40.0 (q), 44.9 (d), 114.8 (s), 119.1 (d, 2 C), 120.9 (s), 122.1 (d), 126.1 (d), 129.2 (d, 2 C), 132.0 (d), 136.6 (d) and 146.6 (d); *m/z* 240 (M^+, 14%) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.11; ν_{max}(neat)/cm^{-1} 2212 (CN); $\delta_H(CDCl_3)$ 0.84 (3 H, t, *J* 7.5), 1.35–1.48 (2 H, m), 1.65 (3 H, d, *J* 6), 3.06 (3 H, s), 3.03–3.13 (1 H, m), 5.23 (1 H, ddd, *J* 15, 7, 1), 5.30–5.44 (1 H, m), 6.17 (1 H, d, *J* 10), 6.78 (2 H, d, *J* 7.5), 6.89 (1 H, t, *J* 7.5) and 7.28 (2 H, t, *J* 7.5); $\delta_C(CDCl_3)$ 11.6 (q), 17.9 (q), 27.6 (t), 38.3 (d), 42.8 (q), 114.4 (d, 2 C), 116.2 (s), 118.8 (s), 119.8 (d), 127.1 (d), 129.1 (d, 2 C), 130.2 (d), 146.2 (s) and 148.4 (d); *m/z* 240 (M^+, 15%) and 211 (100) (M^+, 240.1626. *M*, 240.1626).

4-*Isopropyl*-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **11γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.14; ν_{max}(neat)/cm^{-1} 2223 (CN); $\delta_H(CDCl_3)$ 0.95 (3 H, d, *J* 7), 0.96 (3 H, d, *J* 7), 1.63–1.77 (1 H, m), 1.70 (3 H, dd, *J* 6, 1), 2.96–3.04 (1 H, m), 3.13 (3 H, s), 5.31 (1 H, ddd, *J* 15, 7, 1), 5.58 (1 H, dq, *J* 15, 6), 5.79 (1 H, d, *J* 11, 3-H), 6.87–7.11 (2 H, m) and 7.26–7.33 (2 H, m); $\delta_C(CDCl_3)$ 18.0 (q), 19.9 (q), 20.3 (q), 32.9 (d), 40.0 (q), 50.4 (d), 114.9 (s), 118.9 (d, 2 C), 121.0 (s), 122.0 (d), 127.0 (d), 129.9 (d, 2 C), 130.8 (d), 136.2 (d) and 146.7 (s); *m/z* 254 (M^+, 18%) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.10; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 0.86 (3 H, d, *J* 7), 0.89 (3 H, d, *J* 6), 1.56–1.70 (1 H, m), 1.66 (3 H, dd, *J* 6, 1), 2.86–2.99 (1 H, m), 3.04 (3 H, s), 5.23 (1 H, ddd, *J* 15, 8, 1), 5.27–5.40 (1 H, m), 6.24 (1 H, *J* 11), 6.77 (2 H, d, *J* 8), 6.88 (1 H, t, *J* 7) and 7.24–7.81 (2 H, m); $\delta_C(CDCl_3)$ 18.0 (q), 20.1 (q), 20.3 (q), 32.2 (d), 38.2 (q), 48.3 (d), 114.4 (d, 2 C), 115.2 (s), 118.9 (d), 119.0 (s), 119.8 (d), 128.0 (d), 129.1 (d, 2 C), 146.2 (s) and 147.7 (d); *m/z* 254 (M^+, 21%) and 211 (M^+, 254.1781. *M*, 254.1783).

4-*Benzyl*-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **12γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.12; ν_{max}(neat)/cm^{-1} 2222 (CN); $\delta_H(CDCl_3)$ 1.71 (3 H, *J* 6), 2.66 (1 H, dd, *J* 13, 9), 2.99 (1 H, dd, *J* 13, 6), 3.01 (3 H, s), 3.58–3.69 (1 H, m), 5.46 (1 H, dd, *J* 16, 6.5), 5.60 (1 H, dq, *J* 16, 6), 5.68 (1 H, d, *J* 10.5), 6.66 (2 H, d, *J* 7), 6.95 (1 H, t, *J* 8) and 7.23–7.32 (7 H, m); $\delta_C(CDCl_3)$ 18.0 (q), 39.8 (q), 42.0 (t), 44.9 (d), 114.6 (s), 119.0 (d), 121.4 (s), 122.0 (d), 126.3 (d, 2 C), 126.4 (d), 128.4 (d, 2 C), 129.3 (d), 129.4 (d, 2 C), 131.5 (d), 135.9 (d), 138.7 (s) and 146.5 (s); *m/z* 302 (M^+, 7%) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.09; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 1.68 (3 H, d, *J* 6), 2.63 (1 H, dd, *J* 13, 9), 2.69 (3 H, s), 2.84 (1 H, dd, *J* 13, 5), 3.44–3.54 (1 H, m), 5.41 (2 H, m), 6.20 (1 H, d, *J* 10), 6.52 (2 H, d, *J* 8), 6.86 (1 H, t, *J* 8), 7.08 (2 H, d, *J* 8) and 7.20–7.32 (5 H, m); $\delta_C(CDCl_3)$ 18.0 (q), 37.7 (q), 41.4 (t), 43.3 (d), 114.5 (d, 2 C), 116.0 (s), 118.0 (s), 119.8 (d), 126.4 (d, 2 C), 127.2 (d), 128.0 (d, 2 C), 129.0 (d, 3 C), 129.9 (d), 138.6 (s), 146.2 (d) and 147.1 (d, C-3); *m/z* 302 (M^+, 5%) and 211 (100) (M^+, 302.1783. *M*, 302.1783).

4-*Allyl*-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **13γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.13; ν_{max}(neat)/cm^{-1} 2223 (CN); $\delta_H(CDCl_3)$ 1.69 (3 H, d, *J* 6), 2.13–2.21 (1 H, m), 2.29–2.38 (1 H, m), 3.10 (3 H, s), 3.32–3.39 (1 H, m), 4.98–5.09 (2 H, m), 5.37 (1 H, dd, *J* 15, 7), 5.54 (1 H, m), 5.64 (1 H, d, *J* 10), 5.79 (1 H, dq, *J* 15, 6), 6.88–7.05 (3 H, m) and 7.21–7.30 (2 H, m); $\delta_C(CDCl_3)$ 18.0 (q), 40.0 (t), 40.0 (1), 42.9 (d), 114.8 (s), 117.1 (t), 119.2 (s), 119.4 (d, 2 C), 122.3 (d), 126.3 (d), 129.2 (d, 2 C), 131.5 (d), 135.2 (d), 135.4 (d) and 146.5 (s); *m/z* 252 (M^+, 4%) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.08; ν_{max}(neat)/cm^{-1} 2212 (CN); $\delta_H(CDCl_3)$ 1.66 (3 H, d, *J* 6), 2.12–2.23 (2 H, m), 3.06 (3 H, s), 3.20–3.34 (1 H, m), 4.94–5.12 (2 H, m), 5.29 (1 H, dd, *J* 15, 7), 5.42 (1 H, dq, *J* 15, 6), 5.58–5.70 (1 H, m), 6.16 (1 H, d, *J* 10), 6.79 (2 H, d, *J* 8), 6.90 (1 H, t, *J* 7) and 7.27 (2 H, dd, *J* 8, 7); $\delta_C(CDCl_3)$ 17.9 (q), 38.3 (q), 39.0 (t), 40.8 (d), 114.4 (d, 2 C), 116.1 (s), 117.2 (t), 119.0 (s), 119.8 (d), 127.2 (d), 129.1 (d, 2 C), 129.8 (d), 134.9 (d), 146.1 (s, C-1′) and 147.5 (d, C-3); *m/z* 252 (M^+, 7%) and 211 (100).

6-*Methyl*-2-(N-*methylanilino*)*nona*-2,4,8-*trienenitrile* **13ε**. *Z*-Isomer: yellow oil: TLC (2% EtOAc in hexane) R_f 0.05; ν_{max}(neat) 2207 (CN); $\delta_H(CDCl_3)$ 0.97 (3 H, d, *J* 7), 1.98–2.12 (2 H, m), 2.23–2.35 (1 H, m), 3.12 (3 H, s), 4.90–5.06 (2 H, m), 5.60–5.75 (1 H, m), 6.03 (1 H, dd, *J* 15, 7, 5-H), 6.25 (1 H, dd, *J* 15, 11, 4-H), 6.58 (1 H, d, *J* 11, 3-H), 6.80 (2 H, d, *J* 8), 6.88 (1 H, t, *J* 8) and 7.27 (2 H, t, *J* 8); $\delta_C(CDCl_3)$ 19.3 (q), 37.0 (d), 38.6 (q), 40.6 (t), 114.8 (d, 2 C), 116.2 (s), 116.6 (t), 117.1 (s), 120.0 (d), 122.4 (d), 129.3 (d, 2 C), 136.0 (d), 143.0 (d), 146.3 (s) and 149.3 (d); *m/z* 252 (M^+, 8%) and 211 (100) (M^+, 252.1623. *M*, 252.1626).

4-*Cinnamyl*-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **14γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.09; ν_{max}(neat)/cm^{-1} 2222 (CN); $\delta_H(CDCl_3)$ 1.71 (3 H, dd, *J* 6, 1), 2.31 (1 H, ddd, *J* 14, 8, 8), 2.46–2.58 (1 H, m), 3.06 (3 H, s), 3.39–3.53 (1 H, m), 5.40 (1 H, ddq, *J* 15, 6, 1), 5.60 (1, H, dq, *J* 15, 6), 5.70 (1 H, d, *J* 10), 6.20 (1 H, dtd, *J* 16, 8, 2), 6.41 (1 H, d, *J* 16), 6.68–6.95 (3 H, m) and 7.09–7.40 (7 H, m); $\delta_C(CDCl_3)$ 18.0 (q), 39.3 (t), 40.0 (1), 43.3 (d), 114.2 (s), 119.2 (d, 2 C), 121.4 (s), 122.1 (d), 126.1 (d, 2 C), 126.4 (d), 127.1 (d), 127.2 (d), 128.5 (d, 2 C), 129.1 (d, 2 C), 131.5 (d), 132.4 (d), 135.5. (d), 137.2 (s), and 146.4 (s); *m/z* 328 (M^+, 12%), 327 (45) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOA3 in hexane) R_f 0.05; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 1.65 (3 H, dd, *J* 6, 1), 2.15–2.42 (2 H, m), 3.00 (3 H, s), 3.27–3.43 (1 H, m), 5.22–5.53 (2 H, m), 5.98 (1 H, dt, *J* 16, 6), 6.18 (1 H, d, *J* 10), 6.35 (1 H, dd, *J* 16, 1), 6.72 (2 H, dd, *J* 8, 1), 6.84 (1 H, td, *J* 8, 1) and 7.13–7.29 (7 H, m); $\delta_C(CDCl_3)$ 19.0 (q), 38.3 (t), 38.4 (1), 41.3 (d), 114.4 (d, 2 C), 116.1 (s), 119.3 (s), 119.8 (d), 126.0 (d, 2 C), 126.6 (d), 127.2 (d, 2 C), 128.4 (d, 2 C), 129.2 (d, 2 C), 129.8 (d, 2 C), 132.3 (d), 136.9 (s), 146.1 (s) and 147.5 (d, C-3); *m/z* 328 (M^+, 0.2%), 327 (2) and 211 (100) (M^+, 328.1941. *M*, 328.1939).

Ethyl 3-(2-*cyano*-2-N-*methylanilinovinyl*)*hex*-4-*enoate* **15γ**. *E*-Isomer: yellow oil; TLC (5% EtOAc in hexane) R_f 0.06; ν_{max}(neat of mixture)/cm^{-1} 2213 (CN) and 1734 (CO); $\delta_H(CDCl_3)$ 1.27 (3 H, t, *J* 7), 1.68 (3 H, d, *J* 6), 2.50 (2 H, dd, *J* 6, 1), 3.11 (3 H, s), 3.63–3.80 (1 H, m), 4.13 (2 H, q), 5.30–5.60 (2 H, m), 5.58 (1 H, d, *J* 10), 6.90–7.10 (3 H, m) and 7.30–7.45 (2 H); $\delta_C(CDCl_3)$ 14.0 (q), 17.8 (q), 38.2 (d), 39.8 (q), 40.3 (t), 60.2 (t), 114.6 (s), 118.2 (s), 122.8 (d, 2 C), 126.8 (d), 127.0 (d), 127.3 (d, 2 C), 130.4 (d), 130.7 (d), 147.0 (s) and 171.0 (s). *Z*-Isomer: yellow oil; TLC (5% EtOAc in hexane) R_f 0.06; $\delta_H(CDCl_3)$ 1.20 (3 H, t, *J* 7), 1.62 (3 H, dd, *J* 6, 1), 2.41 (2 H, dd, *J* 6, 1), 3.07 (3 H, s), 3.58–3.71 (1 H, m), 4.10 (2 H, q, *J* 7), 5.20–5.50 (1 H, m), 5.35 (1 H, dd, *J* 15, 6), 6.21 (1 H, d, *J* 10), 6.78 (2 H, dd, *J* 7, 1), 6.89 (1 H, ddd, *J* 7, 7, 1) and 7.26 (2 H, ddd, *J* 7, 7, 1); $\delta_C(CDCl_3)$ 14.1 (q), 17.8 (q), 37.5 (d), 38.3 (q), 39.1 (t), 60.5 (t), 114.7 (d, 2 C), 115.9 (s), 119.7 (s), 120.0 (d), 128.0 (d), 128.4 (d), 129.1 (d, 2 C), 145.4 (d), 146.1 (s) and 170.7 (s); *m/z* 298 (M^+, 43%), 297 (28) and 211 (100) (M^+, 298.1670. *M*, 298.1681).

4-(2-*Bromoethyl*)-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **16γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.10; ν_{max}(neat)/cm^{-1} 2226 (CN); δ_H($CDCl_3$) 1.70 (3 H, dd, *J* 6, 1), 1.94–2.08 (2 H, m), 3.12 (3 H, s), 3.80 (2 H, t, *J* 7), 5.86–3.45 (1 H, m), 5.28 (1 H, ddq, *J* 15, 8, 1), 5.50 (1 H, d, *J* 10), 5.64 (1 H, dqd, *J* 15, 6, 1), 6.97–7.08 (3 H, m) and 7.27–7.36 (2 H, m); δ_C($CDCl_3$) 18.0 (q), 30.3 (t), 38.2 (t), 40.2 (q), 42.3 (d), 114.4 (s), 120.6 (d, 2 C), 122.0 (s), 123.2 (d), 127.4 (d), 129.3 (d, 2 C), 130.5 (d), 130.6 (d) and 146.4 (s); *m*/*z* 320 ([M + 2]$^+$, 6%), 318 (M$^+$ for ^{79}Br, 5) and 211 (100). *Z*-Isomer: oil; TLC (2% EtOAc in hexane) R_f 0.06; ν_{max}(neat)/cm^{-1} 2213 (CN); δ_H($CDCl_3$) 1.64 (3 H, dd, *J* 6, 1), 1.86–1.97 (2 H, m), 3.22 (3 H, s), 3.28 (2 H, td, *J* 7, 1), 3.34–3.49 (1 H, m), 5.16 (1 H, ddq, *J* 15, 8, 1), 5.43 (1 H, dq, *J* 15, 6), 6.10 (1 H, d, *J* 10), 6.78 (2 H, dd, *J* 8, 1), 6.90 (1 H, t, *J* 8) and 7.28 (2 H, t, *J* 8); δ_C($CDCl_3$) 18.0 (q), 30.2 (t), 37.0 (t), 38.6 (q), 39.9 (d), 114.8 (d, 2 C), 116.0 (s), 119.8 (s), 120.2 (d), 128.3 (d), 128.8 (d), 129.2 (d, 2 C), 145.5 (d) and 146.1 (s); *m*/*z* 320 ([M + 2]$^+$, 6%), 318 (M$^+$ for ^{79}Br, 6), 212 (14) and 211 (100) (M$^+$, 318.0720. *M*, 318.0732).

4-(3-*Bromopropyl*)-2-(N-*methylanilino*)*hepta*-2,5-*diene* **17γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.12; ν_{max}(neat)/cm^{-1} 2223 (CN); δ_H($CDCl_3$) 1.47–1.62 (2 H, m), 1.70 (3 H, d, *J* 6), 1.81–1.94 (2 H, m), 3.12 (3 H, s), 3.18–3.30 (1 H, m), 3.43 (2 H, t, *J* 6), 5.33 (1 H, ddd, *J* 15, 7, 2), 5.57 (1 H, dq, *J* 15, 6), 5.59 (1 H, d, *J* 10), 7.00–7.11 (3 H, m) and 7.26–7.40 (2 H, m); δ_C($CDCl_3$) 17.4 (q), 30.3 (t), 33.4 (t), 33.9 (t), 40.0 (q), 42.7 (d), 114.6 (s), 119.7 (d), 119.9 (d, 2 C), 121.2 (s), 122.6 (d), 126.5 (d), 129.1 (d, 2 C), 133.4 (d) and 146.4 (s); *m*/*z* 334 ([M + 2]$^+$, 7%), 332 (M$^+$ for ^{79}Br, 7) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.08; ν_{max}(neat)/cm^{-1} 2211 (CN); δ_H($CDCl_3$) 1.42–1.60 (2 H, m), 1.60 (3 H, d, *J* 7), 1.68–1.92 (2 H, m), 3.06 (3 H, s), 3.09–3.25 (1 H, m), 3.31 (2 H, t, *J* 7), 5.21 (1 H, ddd, *J* 15, 6, 1), 5.31–5.49 (1 H, m), 6.13 (1 H, d, *J* 10), 6.77 (2 H, dd, *J* 8, 1), 6.70 (1 H, td, *J* 7, 1) and 7.28 (2 H, dd, *J* 7, 8); δ_C($CDCl_3$) 17.9 (q), 30.0 (t), 32.8 (t), 33.0 (t), 38.4 (q), 40.4 (d), 114.5 (d, 2 C), 116.0 (s), 119.1 (s), 120.0 (d), 127.8 (d), 129.2 (d, 2 C), 129.6 (d), 146.1 (s) and 147.2 (d); *m*/*z* 334 ([M + 2]$^+$, 8%), 332 (M$^+$ for ^{79}Br, 8) and 211 (100) (M$^+$, 332.0887. *M*, 332.0888).

7-*Bromo*-2(N-*methylanilino*)-4-*prop*-1-*enylhepta*-2,6-*diene-nitrile* **18γ**. (2*E*,6*Z*)-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.13; ν_{max}(neat)/cm^{-1} 2228 (CN); δ_H($CDCl_3$) 1.70 (3 H, dd, *J* 6, 2), 2.42 (2 H, ddd, *J* 7, 7, 1), 3.12 (3 H, s), 3.38–3.48 (1 H, m), 5.40 (1 H, ddq, *J* 15, 6.5, 1), 5.59 (1 H, dq, *J* 15, 6), 5.60 (1 H, d, *J* 10), 6.13 (1 H, dt, *J* 7, 7), 6.29 (1 H, dt, *J* 7, 1), 6.95–7.07 (3 H, m) and 7.27–7.35 (2 H, m); δ_C($CDCl_3$) 18.0 (q), 35.7 (t), 40.1 (d), 42.4 (1), 109.8 (d), 114.7 (s), 120.3 (d, 2 C), 121.6 (s), 122.9 (d), 126.7 (d), 129.2 (d, 2 C), 131.25 (d), 131.7 (d), 132.1 (d) and 146.4 (s); *m*/*z* 332 ([M + 2]$^+$, 11%), 330 (M$^+$ for ^{79}Br, 12) and 211 (100). (2*E*,6*E*)-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.11; ν_{max}(neat)/cm^{-1} 2228 (CN); δ_H($CDCl_3$) 1.70 (3 H, dd, *J* 6, 1), 2.10–2.39 (2 H, m), 3.12 (3 H, s), 3.27–3.44 (1 H, m), 5.34 (1 H, ddq, *J* 15, 6, 1), 5.54 (1 H, d, *J* 10), 5.58 (1 H, dq, *J* 15, 6), 6.15 (1 H, d, *J* 14), 6.10–6.27 (1 H, m), 6.96–7.07 (3 H, m) and 7.28–7.36 (2 H, m); δ_C($CDCl_3$) 18.0 (q), 39.0 (t), 40.1 (d), 42.6 (q), 106.5 (d), 114.6 (s), 120.2 (d, 2 C), 121.9 (s), 122.9 (d), 127.0 (d), 129.3 (d, 2 C), 130.9 (d), 132.3 (d), 134.8 (d) and 146.5 (s); *m*/*z* 332 ([M + 2]$^+$, 21%), 331 (33), 330 (M$^+$ for ^{79}Br, 29), 329 (31) and 211 (100).

(6*Z*,2*Z*)-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.08; ν_{max}(neat)/cm^{-1} 2216 (CN); δ_H($CDCl_3$) 1.66 (3 H, dd, *J* 6, 1), 2.33 (2 H, ddd, *J* 7, 7, 1), 3.07 (3 H, s), 3.27–3.42 (1 H, m), 5.20–5.52 (2 H, m), 5.98 (1 H, dt, *J* 7, 7), 6.19 (1 H, d, *J* 11), 6.24 (1 H, dt, *J* 7, 1), 6.77 (2 H, d, *J* 8), 6.90 (1 H, t, *J* 8) and 7.28 (2 H, t, *J* 8); δ_C($CDCl_3$) 18.0 (q), 34.6 (t), 38.5 (d), 40.2 (q), 110.05 (d), 114.6 (d, 2 C), 116.0 (s), 119.5 (s), 120.1 (d), 127.9 (s), 129.3 (d, 2 C), 129.4 (d), 131.1 (d), 146.2 (s) and 146.6 (d); *m*/*z* 332 ([M + 2]$^+$, 28%), 331 (34), 330 (M$^+$ for ^{79}Br, 32), 329 (30) and 211 (100). (6*E*,2*Z*)-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.06; ν_{max}(neat)/cm^{-1} 2216 (CN); δ_H($CDCl_3$) 1.66 (3 H, dd, *J* 6, 1), 2.01–2.24 (2 H, m), 3.06 (3 H, s), 3.19–3.34 (1 H, m), 5.24 (1 H, ddq, *J* 15, 7, 1), 5.43 (1 H, dq, *J* 15, 6), 5.99–6.17 (1 H, m), 6.05 (1 H, d, *J* 11), 6.09 (1 H, d, *J* 16), 6.77 (2 H, dd, *J* 8, 1), 6.91 (1 H, ddd, *J* 8, 8, 1) and 6.30 (2 H, ddd, *J* 8, 8, 1); δ_C($CDCl_3$) 18.0 (q), 37.9 (t), 38.4 (d), 40.6 (q), 106.7 (d), 114.6 (d, 2 C), 116.0 (s), 119.0 (s), 120.2 (d), 128.0 (d), 129.1 (d), 129.3 (d, 2 C), 134.4 (d), 146.1 (s) and 146.2 (d); *m*/*z* 332 ([M + 2]$^+$, 29%), 331 (38), 330 (M$^+$ for ^{79}Br, 35), 329 (27), 304 (20) and 211 (100) (M$^+$, 330.0733. *M*, 330.0732).

4-(3-*Bromobutyl*)-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **19γ**.—*E*-Isomer a: yellow oil; TLC (3% EtOAc in hexane) R_f 0.15; ν_{max}(neat)/cm^{-1} 2222 (CN); δ_H($CDCl_3$) 1.50–1.91 (10 H, m), 3.13 (3 H, s), 3.17–3.28 (1 H, m), 4.08–4.19 (1 H, m), 5.29 (1 H, ddq, *J* 15, 6, 1), 5.59 (1 H, d, *J* 10), 5.60 (1 H, dq, *J* 15, 6), 6.97 (2 H, d, *J* 8), 7.02 (1 H, t, *J* 7.5) and 7.29 (2 H, dd, *J* 8, 7.5); δ_C($CDCl_3$) 18.0 (q), 26.5 (q), 33.6 (t), 38.6 (t), 40.1 (q), 42.8 (d), 51.3 (d), 114.7 (s), 119.9 (d, 2 C), 121.1 (s), 122.7 (d), 126.5 (d), 129.2 (d, 2 C), 131.8 (d), 133.7 (d) and 146.5 (s); *m*/*z* 348 ([M + 2]$^+$, 22%), 347 (17), 346 (M$^+$ for ^{79}Br, 26), 345 (12) and 211 (100). *E*-Isomer b: oil; TLC (3% EtOAc in hexane) R_f 0.15; δ_H($CDCl_3$) 1.50–1.91 (10 H, m), 3.13 (3 H, s), 3.17–3.38 (1 H, m), 4.08–4.19 (1 H, m), 5.25 (1 H, ddq, *J* 15, 6, 1), 5.57 (1 H, d, *J* 10), 5.61 (1 H, dq, *J* 15, 6), 6.97 (2 H, d, *J* 8), 7.02 (1 H, t, *J* 7.5) and 7.29 (2 H, dd, *J* 8, 7.5); δ_C($CDCl_3$) 18.0 (q), 26.4 (q), 33.5 (t), 38.5 (t), 40.1 (q), 43.0 (d), 51.2 (d), 114.4 (s), 119.7 (d, 2 C), 120.9 (s), 122.5 (d), 126.7 (d), 129.3 (d, 2 C), 131.6 (d), 133.9 (d) and 146.5 (s). *Z*-Isomer c: yellow oil; TLC (3% EtOAc in hexane) R_f 0.08; ν_{max}(neat)/cm^{-1} 2211 (CN); δ_H($CDCl_3$) 1.39–1.80 (10 H, m), 3.06 (3 H, s), 3.10–3.18 (1 H, m), 3.97–4.03 (1 H, m), 5.16–5.24 (1 H, m), 5.33–5.42 (1 H, m), 6.14 (1 H, d, *J* 10), 6.76 (2 H, d, *J* 8), 6.89 (1 H, t, *J* 8) and 7.27 (2 H, t, *J* 8); δ_C($CDCl_3$) 18.0 (q), 26.4 (q), 32.5 (t), 38.5 (t), 38.5 (q), 40.6 (d), 50.8 (d), 114.5 (d, 2 C), 116.1 (s), 119.0 (s), 120.0 (d), 127.9 (d), 129.3 (d, 2 C), 129.6 (d), 146.2 (s) and 147.5 (d); *m*/*z* 348 ([M + 2]$^+$, 28%), 347 (23), 346 (M$^+$ for ^{79}Br, 30), 345 (18) and 211 (100) (M$^+$, 348.1017. *M* 348.1024) *Z*-Isomer d: oil; TLC (3% EtOAc in hexane) R_f 0.08; δ_H($CDCl_3$) 1.39–1.80 (10 H, m), 3.06 (3 H, s), 3.10–3.18 (1 H, m), 3.97–4.03 (1 H, m), 5.09–5.17 (1 H, m), 5.50–5.62 (1 H, m), 6.13 (1 H, d, *J* 10), 6.76 (2 H, d, *J* 8), 6.89 (1 H, t, *J* 8) and 7.27 (2 H, t, *J* 8); δ_C($CDCl_3$) 18.0 (q), 26.4 (q), 32.7 (t), 38.4 (t), 38.5 (q), 40.6 (d), 50.9 (d), 114.5 (d, 2 C), 116.1 (s), 117.1 (s), 120.0 (d), 127.7 (d), 129.3 (d, 2 C), 129.9 (d), 146.2 (s) and 147.4 (d).

8-*Bromo*-2-(N-*methylanilino*)-4-(*prop*-1-*enyl*)*oct*-2-*enenitrile* **20γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.13; ν_{max}(neat)/cm^{-1} 2223 (CN); δ_H($CDCL_3$) 1.45–1.52 (4 H, m), 1.70 (3 H, d, *J* 6), 1.77–1.91 (2 H, m), 3.12 (3 H, s), 3.18–3.26 (1 H, m), 3.42 (2 H, t, *J* 6.6), 5.32 (1 H, ddq, *J* 15, 7, 1.6), 5.60 (1 H, dq, *J* 15, 6), 5.64 (1 H, d, *J* 10), 6.91–7.03 (3 H, m) and 7.30 (2 H, t, *J* 8); δ_C($CDCl_3$) 17.9 (q), 25.6 (t), 32.4 (t), 33.6 (t), 34.5 (t), 40.0 (q), 43.1 (d), 114.7 (s), 116.6 (d), 119.5 (d, 2 C), 121.1 (s), 126.3 (d), 129.2 (d, 2 C), 131.8 (d), 135.1 (d) and 146.5 (s); *m*/*z* 348 ([M + 2]$^+$, 12%), 347 (10), 346 (M$^+$ for ^{79}Br, 13), 345 (8) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.10; ν_{max}(neat)/cm^{-1}2210 (CN); δ_H($CDCl_3$) 1.30–1.45 (4 H, m), 1.64 (3 H, dd, *J* 6, 1), 1.70–1.80 (2 H, m), 3.06 (3 H, s), 3.11–3.18 (1 H, m), 3.32 (2 H, t, *J* 6.6), 5.21 (1 H, ddq, *J* 15, 7.5, 1), 5.39 (1 H, dq, *J* 15, 6), 6.13 (1 H, d, *J* 10), 6.77 (2 H, d, *J* 8), 6.89 (1 H, t, *J* 7.5) and 7.27 (2 H, dd, *J* 8, 7.5); δ_C($CDCl_3$) 17.7 (q), 25.6 (t), 32.3 (t), 33.3 (5), 33.6 (t), 38.4 (q), 41.0 (d), 114.5 (d, 2 C), 116.2 (s), 119.0 (s), 120.0 (d), 127.5 (d), 129.2 (d, 2 C), 130.0 (d), 146.2 (s) and 147.8 (d); *m*/*z* 348 ([M + 2]$^+$, 26%), 347 (25), 346 (M$^+$ for ^{79}Br, 29), 345 (23) and 211 (100) (M$^+$, 346.1020. *M*, 346.1045).

4-(2-*Bromocyclopent*-1-*enylmethyl*)-2-(N-*methylanilino*)-*hepta*-2,5-*dienenitrile* **21γ**. *E*-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.21; ν_{max}(neat)/cm^{-1} 2220 (CN);

$\delta_H(CDCl_3)$ 1.71 (3 H, dd, *J* 6, 1), 1.80–2.05 (2 H, m), 2.27–2.71 (6 H, m), 3.11 (3 H, s), 3.39–3.56 (1 H, m), 5.41 (1 H, ddq, *J* 16, 6, 1), 5.58 (1 H, dq, *J* 16, 6), 5.66 (1 H, d, *J* 11), 6.94 (2 H, dd, *J* 8, 1), 7.01 (1 H, ddd, *J* 8, 8, 1) and 7.30 (2 H, dd, *J* 8, 8); $\delta_C(CDCl_3)$ 18.0 (q), 22.6 (t), 31.6 (t), 34.2 (t), 35.9 (t), 40.0 (d), 41.6 (q), 114.6 (s), 119.0 (s), 119.7 (d, 2 C), 122.5 (d), 126.2 (d), 129.2 (d, 2 C), 131.6 (d), 134.2 (d), 135.2 (s), 138.4 (s) and 146.5 (s); *m/z* 371 ([M + 1]$^+$, 31%), 369 ([M − 1]$^+$ for ^{79}Br, 30) and 211 (100). *Z*-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.18; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 1.65 (3 H, d, *J* 6), 1.70–1.93 (2 H, m), 2.09–2.41 (4 H, m), 2.58–2.65 (2 H, m), 3.04 (3 H, s), 3.33–3.46 (1 H, m), 5.30 (1 H, dd, *J* 15, 7), 5.43 (1 H, dq, *J* 15, 6), 6.20 (1 H, d, *J* 11), 6.73 (2 H, dd, *J* 8, 1), 6.89 (1 H, ddd, *J* 8, 8, 1) and 7.30 (2 H, ddd, *J* 8, 8, 1); $\delta_C(CDCl_3)$ 18.0 (q), 21.5 (t), 34.3 (t), 35.1 (t), 38.6 (t), 39.5 (d), 39.9 (q), 114.4 (d, 2 C), 116.1 (s), 118.3 (s), 119.2 (d), 119.9 (d), 127.2 (d, 2 C), 129.2 (d), 129.9 (s), 137.7 (s), 146.2 (s) and 147.2 (d); *m/z* 371 (M + 1$^+$, 8%), 369 ([M − 1$^+$] for ^{79}Br, 7) and 211 (100) (M$^+$, 370.1048. *M*, 370.1045).

4-(2-*Bromobenzyl*)-2-(N-*methylanilino*)*hepta*-2,5-*dienenitrile* **22γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.13; ν_{max}(neat)/cm^{-1} 2223 (CN); $\delta_H(CDCl_3)$ 1.73 (3 H, dd, *J* 6, 1), 2.89–2.94 (2 H, m), 3.04 (3 H, s), 3.70–3.80 (1 H, m), 5.50 (1 H, ddd, *J* 16, 6, 1), 5.57–5.68 (1 H, m), 5.75 (1 H, d, *J* 10), 6.72 (2 H, dd, *J* 7, 1), 6.98 (1 H, t, *J* 7), 7.13 (1 H, td, *J* 7, 2), 7.22–7.32 (4 H, m) and 7.59 (1 H, dd, *J* 8, 1); $\delta_C(CDCl_3)$ 17.9 (q), 39.9 (q), 41.4 (t), 44.0 (d), 114.3 (s), 119.5 (d, 2 C), 121.5 (s), 125.0 (s), 126.0 (d), 127.3 (d), 128.0 (d), 129.0 (d, 2 C), 131.3 (d), 131.5 (d), 132.8 (d), 133.5 (d), 138.3 (s) and 146.4 (s); *m/z* 382 ([M + 2$^+$], 6%), 380 (M$^+$ for ^{79}Br, 6) and 211 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.09; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 1.69 (3 H, d, *J* 5), 2.69 (3 H, s), 2.78 (1 H, dd, *J* 14, 4.4), 2.97 (1 H, dd, *J* 14, 5.5), 3.63–3.73 (1 H, m), 5.35–5.51 (2 H, m), 6.28 (1 H, d, *J* 10), 6.55 (2 H, d, *J* 8), 6.88 (1 H, t, *J* 8), 7.11 (2 H, d, *J* 8), 7.18–7.26 (3 H, m) and 7.52 (1 H, d, *J* 8); $\delta_C(CDCl_3)$ 17.8 (q), 37.7 (q), 41.1 (t), 41.5 (d), 114.4 (d, 2 C), 115.9 (s), 119.4 (s), 119.7 (d), 124.6 (s), 127.2 (d), 127.4 (d), 128.1 (d), 128.9 (d, 2 C), 129.4 (d), 131.3 (d), 132.8 (d), 138.0 (s), 146.0 (s) and 146.3 (d); *m/z* 382 ([M + 2$^+$], 19%), 380 (M$^+$, 19) and 211 (100) (M$^+$, 380.0885. *M*, 380.0888).

2-(N-*Methylanilino*)-4-*phenylthiohepta*-2,5-*dienenitrile* **23γ**. *Z*-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.16; ν_{max}(neat)/cm^{-1} 2212 (CN); $\delta_H(CDCl_3)$ 1.69 (3 H, d, *J* 6), 2.72 (3 H, s), 4.56 (1 H, dd, *J* 11, 7), 5.48 (1 H, ddd, *J* 14, 7, 1), 5.38–5.57 (1 H, m), 6.21 (1 H, d, *J* 11), 6.56 (2 H, d, *J* 8), 6.88 (1 H, t, *J* 8) and 7.18–7.46 (7 H, m); $\delta_C(CDCl_3)$ 17.9 (q), 38.2 (q), 48.6 (d), 115.1 (d), 115.7 (s), 119.0 (s), 120.4 (d), 125.7 (d), 128.6 (d), 129.0 (d, 2 C), 129.1 (d, 2 C), 130.1 (d), 132.3 (s), 134.7 (d, 2 C), 141.3 (d) and 145.9 (s); *m/z* 320 (M$^+$, 1%) and 211 (100).

2-(N-*Methylanilino*)-6-*phenylthiohepta*-2,4-*dienenitrile* **23ε**. *E*-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.11; ν_{max}(neat)/cm^{-1} 2222 (CN); $\delta_H(CDCl_3)$ 1.43 (3 H, d, *J* 7), 3.16 (3 H, s), 3.88 (1 H, dq, *J* 8.5, 7), 5.74 (1 H, dd, *J* 15, 8.5), 6.05 (1 H, d, *J* 11), 6.29 (1 H, dd, *J* 15, 11), 7.03 (2 H, dd, *J* 7.5, 1), 7.09 (1 H, t, *J* 8) and 7.28–7.42 (7 H, m); $\delta_C(CDCl_3)$ 20.3 (q), 40.1 (q), 46.2 (d), 114.3 (s), 117.4 (s), 122.2 (d, 2 C), 123.2 (d), 124.2 (d), 125.7 (d), 127.4 (d), 128.8 (d, 2 C), 129.3 (d, 2 C), 133.0 (d, 2 C), 134.2 (s), 136.9 (d) and 145.8 (s); *m/z* 320 (M$^+$, 1%) and 211 (100). *Z*-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.07; ν_{max}(neat)/cm^{-1} 2207 (CN); $\delta_H(CDCl_3)$ 1.38 (3 H, d, *J* 7), 2.89 (3 H, s), 3.71 (1 H, dq, *J* 7.5, 7), 5.88–6.07 (2 H, m), 6.50 (1 H, d, *J* 10), 6.70 (2 H, d, *J* 8), 6.87–6.96 (2 H, m) and 7.23–7.41 (6 H, m); $\delta_C(CDCl_3)$ 19.6 (q), 3.87 (q), 46.4 (d), 114.9 (d, 2 C), 116.7 (s), 117.5 (s), 120.2 (d), 122.8 (d), 127.7 (d), 128.8 (d, 2 C), 129.2 (d, 2 C), 133.6 (s), 133.7 (d, 2 C), 138.5 (d), 143.3 (d) and 146.0 (s); *m/z* 320 (M$^+$, 2%) and 211 (100) (M$^+$, 320.1345. *M*, 320.1347).

N-*Methyl*-N-*phenylhexa*-2,4-*dienamide* **24α**.—Solid, m.p. 73–75 °C; ν_{max}(KBr)/cm^{-1} 1652 (CO); $\delta_H(CDCl_3)$ 1.74 (3 H, d, *J* 6), 3.32 (3 H, s), 5.68 (1 H, d, *J* 15), 5.92–6.01 (2 H, m), 7.15 (2 H, d, *J* 7.5), 7.18 (1 H, dd, *J* 15, 10), 7.32 (1 H, t, *J* 7.5) and 7.38 (2 H, dd, *J* 7.5); $\delta_C(CDCl_3)$ 18.5 (q), 37.4 (q), 119.5 (d, 2 C), 127.3 (d), 129.5 (d, 3 C), 130.1 (d), 137.5 (d), 142.1 (d), 143.8 (s) and 166.6 (s); *m/z* 201 (M$^+$, 50%), 186 (19), 160 (17), 107 (76) and 95 (100) (M$^+$, 201.1168. *M*, 201.1154).

6-*Hydroxy*-2(N-*methylanilino*)*hepta*-2,4-*dienenitrile* **24ε**.—*E*-Isomer: yellow oil; TLC (30% EtOAc in hexane) R_f 0.20; ν_{max}(neat)/cm^{-1} 3397 (OH), 2221 (CN); $\delta_H(CDCl_3)$ 1.31 (3 H, d, *J* 6), 1.59 (1 H, br s, OH), 3.20 (3 H, s), 4.42 (1 H, dq, *J* 7, 7), 5.83 (1 H, dd, *J* 15, 7), 6.10 (1 H, d, *J* 11), 6.59 (1 H, dd, *J* 15, 11), 7.05–7.13 (3 H, m) and 7.33 (2 H, t, *J* 8); *m/z* 228 (M$^+$, 60%), 183 (62) and 171 (100) (M$^+$, 228.1266. *M*, 228.1266). *Z*-Isomer: yellow solid; m.p. 94–96 °C; TLC (30% EtOAc in hexane) R_f 0.15; ν_{max}(KBr)/cm^{-1} 3304 (OH), 2205 (CN); $\delta_H(CDCl_3)$ 1.23 (3 H, d, *J* 6), 1.90 (1 H, br s, OH), 3.12 (3 H, s), 4.32 (1 H, dq, *J* 6, 6), 6.10 (1 H, dd, *J* 15, 6), 6.41 (1 H, ddd, *J* 15, 11, 1), 6.59 (1 H, d, *J* 11), 6.80 (2 H, d, *J* 8), 6.90 (1 H, t, *J* 7.4) and 7.27 (2 H, dd, *J* 8, 7.4); $\delta_C(CDCl_3)$ 22.9 (q), 38.8 (q), 67.7 (d), 114.9 (d, 2 C), 116.0 (s), 117.8 (s), 120.2 (d), 121.8 (d), 129.2 (d, 2 C), 138.6 (d), 145.9 (d) and 146.1 (s); *m/z* 228 (M$^+$, 63%), 183 (60) and 171 (100).

5-*Hydroxy*-2-(N-*methylanilino*)-4-(*prop*-1-*enyl*)*hept*-2-*enenitrile* **25γ**. An inseparable mixture of isomers (a:b:c:d = 32:11:9:48), yellow oil; TLC (15% EtOAc in hexane) R_f 0.15; ν_{max}(neat)/cm^{-1} 3469 (OH) and 2213 (CN); $\delta_H(CDCl_3)$ *inter alia*, isomer a, 1.00 (3 H, t, *J* 7, 7-H), 3.42–3.52 (1 H, m, 5-H), 5.35 (1 H, dd, *J* 15, 7, 8-H), 5.67 (1 H, dq, *J* 15, 6, 9-H) and 5.75 (1 H, d, *J* 10, 3-H); isomer b, 1.01 (3 H, t, *J* 7) and 5.76 (1 H, d, *J* 10, 3-H); isomer c, 6.32 (1 H, d, *J* 10, 3-H); isomer d, 0.88 (3 H, t, *J* 7), 3.04 (3 H, s, NMe), 3.42–3.52 (1 H, m, 5-H) and 5.27–5.47 (2 H, m, 8-, 9-H; $\delta_C(CDCl_3)$ *inter alia*, isomer a, 40.4 (q, NMe), 49.8 (d, C-4), 75.1 (d, C-5), 114.6 (s, C-1) and 121.7 (s, C-2); isomer d, 38.2 (q), 47.2 (d), 75.3 (d), 116.1 (s), 120.3 (s) and 144.7 (d); *m/z* 270 (M$^+$, 1%) and 211 (100) (M$^+$, 270.1737. *M*, 270.1732).

7-*Hydroxy*-6-*methyl*-2-(N-*methylanilino*)*nona*-2,4-*dienenitrile* **25ε**. An inseparable mixture of two 2*Z*-isomers (45:55): yellow oil; TLC (15% EtOAc in hexane) R_f 0.10; ν_{max}(neat)/cm^{-1} 3459 (OH) and 2206 (CN); $\delta_H(CDCl_3)$ *inter alia* 6.08 (1 H, dd, *J* 15, 8, 5-H), 6.25 (1 H, dd, *J* 15, 10, 4-H) and 6.57/6.58 (1 H, d, *J* 10, 3-H); $\delta_C(CDCl_3)$ 9.9/10.2 (q, C-9), 14.3/16.5 (q, C-10), 27.2/27.6 (t, C-8), 38.6 (q, NMe), 42.9 (d, C-6), 76.4/76.2 (d, C-7), 114.9 (d, 2 C, C-2′), 116.5 (s, C-1), 117.0 (s, C-2), 120.1 (d), 123.9/124.6 (d), 129.2 (d, 2 C, C-3′), 139.1 (d), 146.3/145.4 (d, C-3) and 146.4 (s, C-1′); *m/z* 270 (M$^+$, 8%) and 211 (100) (M$^+$, 270.1737. *M*, 270.1732).

5-*Hydroxy*-2-(N-*methylanilino*)-4-(*propen*-1-*yl*)*oct*-2-*enenitrile* **26γ**. An inseparable mixture of four isomers (a:b:c:d = 31:3:9:57), yellow oil; TLC (15% EtOAc in hexane) R_f 0.16; ν_{max}(neat)/cm^{-1} 3455 (OH) and 2212 (CN); $\delta_H(CDCl_3)$ *inter alia* 2*E*-isomers (a/b), 0.94 (3 H, t, *J* 6), 3.12/3.13 (3 H, s), 5.68 (1 H, dq, *J* 15, 6) and 5.76/5.85 (1 H, d, *J* 10); 2*Z*-isomers (c/d), 0.87 (3 H, t, *J* 7), 3.05/3.04 (3 H, s), 5.27–5.46 (2 H) and 6.33/6.41 (1 H, d, *J* 10, 3-H); $\delta_C(CDCl_3)$ isomers a, 13.9 (q), 18.1 (q), 18.8 (t), 36.7 (t), 40.0 (q), 50.2 (d), 73.7 (d), 114.5 (s), 116.1 (s), 120.1 (d, 2 C), 122.7 (d), 127.9 (d), 128.2 (d, 2 C), 129.4 (d), 130.4 (d) and 146.4 (s); isomer d, 13.8 (q), 18.1 (q), 18.8 (t), 37.2 (t), 38.2 (1), 47.5 (d), 73.4 (d), 114.5 (d, 2 C), 116.0 (s), 119.9 (d), 120.2 (s), 122.7 (d), 129.1 (d, 2 C), 144.8 (d, C-3) and 146.2 (s); *m/z* 284 (M$^+$, 10) and 211 (100); (M$^+$, 284.1890. *M*, 284.1885).

7-*Hydroxy*-6-*methyl*-2-(N-*methylanilino*)*deca*-2,4-*dienenitrile* **26ε**, Two isomers, yellow oil; TLC (15% in EtOAc in hexane) R_f 0.13; ν_{max}(neat)/cm^{-1} 3443 (OH) and 2207 (CN); $\delta_H(CDCl_3)$

inter alia 0.94/0.92 (3 H, t, *J* 7, 10-H), 0.99/1.09 (3 H, d, *J* 7, Me), 6.09/6.10 (1 H, dd, *J* 15, 8.5, 5-H), 6.24/6.26 (1 H, dd, *J* 15, 10.5) and 6.59/6.60 (1 H, d, *J* 10.5, 3-H); $\delta_C(CDCl_3)$ 14.4/14.0 (q, C-10), 16.8/16.4 (q, C-11), 19.4/18.8 (t, C-9), 36.5/36.9 (t, C-8), 38.6 (q, NMe), 43.3/43.4 (d, C-6), 74.5/75.1 (d, C-7), 114.9 (d, 2 C, C-2′), 116.4/117.0 (s, CN), 120.1 (d), 121.7 (s), 124.6 (d), 129.2 (d, 2 C, C-3′), 139.1 (d), 140.1 (s, C-1′) and 145.4/146.3 (d, C-3); *m/z* 284 (M^+, 9%), 212 (23) and 211 (100).

7-*Hydroxy*-6-*methyl*-7-*phenyl*-2-(N-*methylanilino*)*hepta*-2,4-*dienenitrile* **27ε**. *Z*-isomer a: yellow oil; TLC (20% EtOAc in hexane) R_f 0.15; $\delta_H(CDCl_3)$ *inter alia*, 0.88 (3 H, d, *J* 7), 3.08 (3 H, s), 4.44 (1 H, d, *J* 7, 7-H), 6.14 (1 H, dd, *J* 15, 7.5, 5-H), 6.26 (1 H, dd, *J* 15, 10, 4-H) and 6.59 (1 H, d, *J* 10, 3-H); $\delta_C(CDCl_3)$ 16.5 (q), 38.6 (q), 45.1 (d), 76.0 (d), 116.6 (s), 116.9 (s, C-2) and 145.4 (d, C-3). *Z*-Isomer b: yellow oil; TLC (20% EtOAc in hexane) R_f 0.17; ν_{max}(neat)/cm^{-1} 3427 (OH) and 2207 (CN); $\delta_H(CDCl_3)$ *inter alia*, 1.01 (3 H, d, *J* 7), 3.02 (3 H, s), 4.55 (1 H, *J* 6), 5.85 (1 H, dd, *J* 15, 8.5), 6.14 (1 H, dd, *J* 15, 10) and 6.50 (1 H, d, *J* 10); $\delta_C(CDCl_3)$ *inter alia*, 14.8 (q), 38.7 (q), 44.5 (d), 77.5 (d), 116.6 (s), 116.9 (s) and 145.2 (d); *m/z* 318 (M^+, 4%) and 211 (100) (M^+, 318.1737. *M*, 318.1732).

7-*Hydroxy*-6-*methyl*-2-(N-*methylanilino*)*deca*-2,4,8-*triene-nitrile* **28ε**. An inseparable mixture of two 2*Z*-isomers (55:45), yellow oil; TLC (15% EtOAc in hexane) R_f 0.13; $\delta_H(CDCl_3)$ *inter alia*, 0.96/0.95 (3 H, d, *J* 7), 1.68 (3 H, d, *J* 7), 3.12 (3 H, s), 3.92/3.83 (1 H, dd, *J* 6, 6), 5.38/5.40 (1 H, dd, *J* 15, 6), 5.62–5.74 (1 H, m), 6.09 (1 H, dd, *J* 15.5, 8), 6.25/6.27 (1 H, dd, *J* 15.5, 10, 4-H) and 6.58/6.60 (1 H, d, *J* 10, 3-H); $\delta_C(CDCl_3)$ *inter alia* 14.9/16.0 (q), 17.6/17.7 (q), 38.6 (q), 43.0/43.5 (d, C-6), 77.0/76.3 (d, C-7), 116.4 (s), 117.0 (s) and 145.1/145.8 (d, C-3); *m/z* 282 (M^+, 3%) and 211 (100) (M^+, 282.1725. *M*, 282.1732).

7-*Hydroxy*-6-*methyl*-2-(N-*methylanilino*)-9-*phenylnona*-2,4,8-*trienenitrile* **29ε**. An inseparable mixture of two 2*Z*-isomers (45:55), yellow oil; TLC (15% EtOAc in hexane) R_f 0.13; ν_{max}(neat)/cm^{-1} 3435 (OH) and 2206 (CN); $\delta_H(CDCl_3)$ *inter alia*, 1.04/1.05 (3 H, d, *J* 7), 3.10/3.11 (3 H, s), 4.10/4.18 (1 H, t, *J* 7), 6.32/6.26 (1 H, dd, *J* 15, 7) and 6.60/6.55 (1 H, d, *J* 11); $\delta_C(CDCl_3)$ *inter alia*, 14.9/16.1 (q), 38.6 (q), 43.7/43.3 (d), 76.3/75.9 (d), 116.6 (s), 117.0 (s) and 145.1 (d); *m/z* 344 (M^+, 0.1%) and 211 (100) (M^+, 344.1879. *M*, 344.1888).

2-(N-*Methylanilino*)-6-*phenylhexa*-2,4-*dienenitrile* **30**. *E*-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.18; ν_{max}(neat)/cm^{-1} 2224 (CN); $\delta_H(CDCl_3)$ 3.18 (3 H, s), 3.51 (2 H, d, *J* 7), 5.96 (1 H, dt, *J* 15, 7), 6.20 (1 H, d, *J* 11), 6.50 (1 H, dt, *J* 15, 11) and 7.03–7.35 (10 H, m); $\delta_C(CDCl_3)$ 39.4 (t), 40.0 (q), 114.7 (s), 120.1 (s), 121.6 (d, 2 C), 122.4 (d), 124.3 (d), 125.6 (d), 126.3 (d), 126.7 (d), 128.4 (d, 2 C), 128.5 (d, 2 C), 129.2 (d, 2 C), 136.0 (d), 139.5 (s) and 146.0 (s); *m/z* 274 (M^+, 81%) and 273 (100).

Z-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.14; ν_{max}(neat)/cm^{-1} 2209 (CN); $\delta_H(CDCl_3)$ 3.12 (3 H, s), 3.44 (2 H, d, *J* 6), 6.17 (1 H, dt, *J* 16, 6), 6.22 (1 H, dd, *J* 16, 11), 6.60 (1 H, d, *J* 11), 6.78 (2 H, dd, *J* 7, 1), 6.91 (1 H, t, *J* 7), 7.07 (2 H, t, *J* 7) and 7.20–7.35 (5 H, m); *m/z* 274 (M^+, 78%) and 273 (100).

2-(N-*Methylanilino*)-6-*phenylthiohexa*-2,4-*dienenitrile* **31**. *E*-Isomer: yellow oil; TLC (3% EtOAc in hexane) R_f 0.17; ν_{max}(neat)/cm^{-1} 2225 (CN); $\delta_H(CDCl_3)$ 3.15 (3 H, s), 3.63 (2 H, d, *J* 7.5), 5.79 (1 H, dt, *J* 15, 7.5), 6.04 (1 H, d, *J* 11), 6.48 (1 H, dd, *J* 15, 11) and 7.01–7.35 (10 H, m); $\delta_C(CDCl_3)$ 36.9 (t), 40.1 (q), 114.2 (s), 121.1 (s), 122.2 (d), 122.5 (d, 2 C), 124.3 (d), 126.4 (d), 128.4 (d), 128.8 (d, 2 C), 129.2 (d, 2 C), 130.1 (d, 2 C), 130.4 (d), 135.4 (s) and 145.7 (s); *m/z* 306 (M^+, 44%), 262 (8), 248 (10) and 197 (100) (M^+, 306.1190. *M*, 306.1191).

6-*Benzyloxy*-2-(N-*methylanilino*)*hexa*-2,4-*dienenitrile* **32**. (2*E*,4*Z*)-Isomer: yellow oil; TLC (5% EtOAc in hexane) R_f 0.13; ν_{max}(neat)/cm^{-1} 2212 (CN); $\delta_H(CDCl_3)$ 3.15 (3 H, s), 4.15 (2 H, d, *J* 6.6), 4.51 (2 H, s), 5.71 (1 H, dt, *J* 11, 6.6), 6.30 (1 H, d, *J* 12), 6.59 (1 H, dd, *J* 12, 11), 7.07–7.17 (3 H, m) and 7.22–7.37 (7 H, m); $\delta_C(CDCl_3)$ 40.3 (q), 65.9 (t), 72.2 (t), 114.0 (s), 116.0 (d), 122.6 (s), 123.1 (d, 2 C), 124.8 (d), 127.0 (d), 127.6 (d), 127.8 (d, 3 C), 128.3 (d, 2 C), 129.3 (d, 2 C), 137.9 (s) and 145.6 (s); *m/z* 304 (M^+, 9%), 213 (79), 197 (60), 183 (31) and 169 (100). (2*Z*,4*Z*)-Isomer: yellow oil; TLC (5% EtOAc in hexane) R_f 0.11; ν_{max}(neat)/cm^{-1} 2208 (CN); $\delta_H(CDCl_3)$ 3.13 (3 H, s), 4.21 (2 H, dd, *J* 6, 1.6), 4.54 (2 H, s), 5.88 (1 H, dtd, *J* 11, 6, 1), 6.31 (1 H, ddd, *J* 10, 11, 1.6), 6.80 (2 H, d, *J* 8), 6.90–6.94 (2 H, m) and 7.21–7.38 (7 H, m); $\delta_C(CDCl_3)$ 38.9 (q), 66.1 (t), 72.7 (t), 115.2 (d, 2 C), 119.0 (s), 120.4 (d), 122.6 (s), 123.6 (d), 127.6 (d), 127.9 (d, 2 C), 128.5 (d, 2 C), 129.2 (d, 2 C), 132.7 (d), 135.4 (d), 137.5 (s) and 145.9 (s); *m/z* 304 (M^+, 18%), 213 (83, 197 (57), 183 (29) and 169 (100 (M^+, 304.1580. *M*, 304.1576).

Ethyl 6-*cyano*-6-(N-*methylanilino*)*hexa*-3,5-*dienoate* **33**. *E*-Isomer: yellow oil; TLC (10% EtOAc in hexane) R_f 0.14; ν_{max}(neat)/cm^{-1} 2228 (CN); $\delta_H(CDCl_3)$ 1.27 (3 H, t, *J* 7), 3.16–3.23 (2 H, m), 3.20 (3 H, s), 4.16 (2 H, q, *J* 7), 5.89 (1 H, dt, *J* 15, 7), 6.15 (1 H, d, *J* 11), 6.53 (1 H, ddt, *J* 15, 11, 1), 7.04–7.14 (3 H, m) and 7.28–7.38 (2 H, m); $\delta_C(CDCl_3)$ 14.1 (q), 38.2 (t), 40.1 (q), 60.8 (t), 114.3 (s), 121.1 (s), 122.4 (d, 2 C), 122.9 (d), 124.2 (d), 127.1 (d), 129.1 (d), 129.2 (d, 2 C), 145.8 (s) and 171.1 (s); *m/z* 270 (M^+, 57%), 269 (49) and 197 (100).

Z-Isomer: oil; TLC (10% EtOAc in hexane) R_f 0.12; ν_{max}(neat)/cm^{-1} 2212 (CN); $\delta_H(CDCl_3)$ 1.24 (3 H, t, *J* 7), 3.13 (3 H, s), 3.15 (2 H, d, *J* 7), 4.14 (2 H, q, *J* 7), 6.20 (1 H, dt, *J* 15, 7), 6.32 (1 H, dd, *J* 15, 10), 6.63 (1 H, d, *J* 10), 6.80 (2 H, dd, *J* 8, 1), 6.91 (1 H, ddd, *J* 8, 8, 1) and 7.28 (2 H, ddd, *J* 8, 8, 1); δ_C-($CDCl_3$) 14.0 (q), 38.2 (t), 38.7 (1), 60.9 (t), 114.8 (d, 2 C), 116.6 (s), 117.5 (s), 120.2 (d), 126.6 (d), 129.2 (d 2 C), 134.2 (d), 138.5 (d), 146.1 (s) and 170.2 (s); *m/z* 270 (M^+, 57%), 269 (46) and 197 (100) (M^+, 270.1371. *M*, 270.1368).

4-(2-*Bromobenzyl*)-2-(N-*methylanilino*)-6-*phenylhexa*-2,4-*dienenitrile* **34γ**. *E*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.17; ν_{max}(neat)/cm^{-1} 2212 (CN); $\delta_H(CDCl_3)$ 3.01 (1 H, dd, *J* 13, 9), 3.07 (3 H, s), 3.18 (1 H, dd, *J* 13, 7), 3.85–4.01 (1 H, m), 5.74 (1 H, d, *J* 11), 6.22 (1 H, dd, *J* 16, 7), 6.51 (1 H, d, *J* 16), 6.76 (2 H, dd, *J* 8, 1), 7.00 (1 H, td, *J* 7, 1), 7.12–7.40 (11 H, m) and 7.59 (1 H, dd, *J* 8, 1); $\delta_C(CDCl_3)$ 40.1 (q), 41.5 (t), 44.6 (d), 114.3 (s), 120.3 (d, 2 C), 122.2 (s), 122.9 (d), 125.1 (s), 126.3 (d, 2 C), 127.5 (d), 127.6 (d), 128.2 (d), 128.6 (d, 2 C), 129.2 (d, 2 C), 130.0 (d), 130.8 (d), 130.9 (d), 131.6 (d), 133.0 (d), 136.9 (s), 138.1 (s) and 146.4 (s); *m/z* 444 ([M + 2]$^+$, 12%), 443 (56), 442 (M^+ for ^{79}Br, 11), 441 (55), 354 (55), 352 (17) and 273 (100). *Z*-Isomer: yellow oil; TLC (2% EtOAc in hexane) R_f 0.14; ν_{max}(neat)/cm^{-1} 2223 (CN); $\delta_H(CDCl_3)$ 3.08 (1 H, dd, *J* 13, 7), 3.17 (3 H, s), 3.24 (1 H, dd, *J* 13, 8), 3.70–3.85 (1 H, m), 6.06 (1 H, dd, *J* 15, 7), 6.15 (1 H, d, *J* 11), 6.36 (1 H, d, *J* 15), 7.00–7.38 (14 H, m) and 7.53 (1 H, dd, *J* 8, 1); $\delta_C(CDCl_3)$ 42.6 (q), 45.3 (t), 49.2 (d), 119.7 (d), 120.3 (s), 120.3 (s), 121.7 (d, 2 C), 123.8 (d), 124.8 (s), 125.4 (d), 125.9 (d), 126.6 (d), 127.0 (d), 127.6 (d, 2 C), 128.6 (d, 2 C), 129.2 (d), 129.3 (d, 2 C), 131.5 (d), 132.8 (d), 138.2 (s), 139.1 (s), 143.0 (d) and 146.0 (s); *m/z* 444 ([M + 2]$^+$, 14%), 443 (53), 442 (M^+ for ^{79}Br, 17), 441 (54) and 273 (100) (M^+, 442.1048. *M*, 442.1045).

4-(2-*Bromobenzyl*)-2-(N-*methylanilino*)-6-*phenylthiohexa*-2,5-*dienenitrile* **35γ**. *E*-Isomer: yellow oil; TLC (4% EtOAc in hexane) R_f 0.08; ν_{max}(neat)/cm^{-1} 2226 (CN); $\delta_H(CDCl_3)$ 3.07 (3 H, s), 2.95 (1 H, dd, *J* 13, 8), 3.08 (1 H, dd, *J* 13, 7), 3.78–3.96 (1 H, m), 5.58 (1 H, d, *J* 10), 5.87 (1 H, dd, *J* 15, 7.6), 6.25 (1 H, dd, *J* 15, 1), 6.79 (2 H, dd, *J* 8, 1), 7.02 (1 H, td, *J* 7.5, 1), 7.11–7.30 (10 H, m) and 7.58 (1 H, dd, *J* 8, 1); $\delta_C(CDCl_3)$ 40.1 (q), 41.4 (t), 44.7 (d), 114.1 (s), 120.8 (d, 2 C), 122.5 (s), 123.2 (d), 124.2 (d), 125.1 (s), 126.6 (d), 127.5 (d), 128.3 (d), 128.6 (d), 129.0 (d, 2 C), 129.2 (d, 2 C), 129.3 (d, 2 C), 131.6 (d), 133.0 (d), 133.8 (d), 135.1 (s), 137.8 (s) and 146.2 (s); *m/z* 4.75 ([M + 1]$^+$ for ^{79}Br, 0.1%) and 305 (100) (M^+, 474.0776. *M*, 474.0766).

6-*Benzyloxy*-4-(2-*bromobenzyl*)-2-(N-*methylanilino*)*hexa*-2,5-*dienenitrile* **36γ**. (2*Z*,5*E*)-Isomer: yellow oil; TLC (10% EtOAc in hexane) R_f 0.21; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 2.63

(3 H, s), 2.62–3.00 (2 H, m), 3.52–3.62 (1 H, m), 4.69 (2 H, s), 4.78 (1 H, dd, *J* 13, 9), 6.16 (1 H, d, *J* 13), 6.23 (1 H, d, *J* 10), 6.53 (2 H, dd, *J* 8, 1), 6.84 (1 H, td, *J* 8, 1), 7.04–7.36 (10 H, m) and 7.50 (1 H, d, *J* 8); $\delta_C(CDCl_3)$ 37.7 (q), 37.8 (d), 42.2 (t), 71.4 (t), 103.8 (d), 114.5 (d, 2 C), 116.1 (s), 119.0 (s), 119.9 (d), 124.7 (s), 127.4 (d), 127.5 (d, 2 C), 128.0 (d), 128.3 (d), 128.5 (d, 2 C), 129.1 (d, 2 C), 131.5 (d), 133.0 (d), 136.6 (s), 138.0 (s), 146.0 (s), 146.6 (d) and 148.0 (d); *m/z* 473 ([M + 1]$^+$ of ^{79}Br, 3%), 471 (4), 303 (68) and 91 (100). (2*Z*,5*Z*)-Isomer: yellow oil; TLC (10% EtOAc in hexane) R_f 0.19; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 2.74 (3 H, s), 2.88 (2 H, dd, *J* 8, 4), 4.10–4.27 (1 H, m), 4.33 (1 H, dd, *J* 9, 6), 6.07 (1 H, d, *J* 6), 6.33 (1 H, d, *J* 10), 6.52 (2 H, dd, *J* 8, 1), 6.82 (1 H, td, *J* 7, 1), 7.07–7.32 (10 H, m) and 7.47 (1 H, dd, *J* 8, 1); $\delta_C(CDCl_3)$ 34.6 (d), 38.0 (q), 40.9 (t), 73.9 (t), 105.1 (d), 114.4 (d, 2 C), 116.3 (s), 119.0 (s), 119.5 (d), 124.8 (s), 127.2 (d), 127.3 (d, 2 C), 127.9 (d), 128.0 (d), 128.4 (d, 2 C), 129.0 (d, 2 C), 131.4 (d), 132.8 (d), 137.0 (s), 138.2 (s), 146.3 (s), 146.4 (d) and 147.3 (d); *m/z* 473 ([M + 1]$^+$ of ^{79}Br, 5%), 471 (6), 303 (65) and 91 (100) (M$^+$, 472.1156. *N*, 472.1151).

4-(2-*Benzyloxyvinyl*)-7-*iodo*-2-(N-*methylanilino*)*hept*-2-*ene*-*nitrile* **37γ**. (2*Z*,5*Z*)-Isomer: yellow oil; TLC (5% EtOAc in hexane) R_f 0.15; ν_{max}(neat)/cm^{-1} 2211 (CN); $\delta_H(CDCl_3)$ 1.42–1.55 (2 H, m), 1.67–1.81 (2 H, m), 3.00 (3 H, s), 3.08 (2 H, t, *J* 7), 3.65–3.82 (1 H, m), 4.19 (1 H, dd, *J* 9, 6), 4.70 (2 H, s), 6.11 (1 H, d, *J* 6), 6.15 (1 H, dd, *J* 10, 1), 6.76 (2 H, dd, *J* 8, 1), 6.88 (1 H, td, *J* 8, 1) and 7.18–7.34 (7 H, m); $\delta_C(CDCl_3)$ 6.1 (t), 30.8 (t), 32.6 (d), 35.3 (t), 38.4 (q), 74.1 (t), 105.5 (d), 114.5 (d, 2 C), 116.3 (s), 118.8 (s), 119.8 (d), 127.5 (d, 2 C), 128.1 (d), 128.5 (d, 2 C), 129.2 (d, 2 C), 136.9 (s), 146.4 (s), 146.5 (d) and 147.8 (d); *m/z* 472 (M$^+$, 25%), 443 (22), 381 (16), 303 (68), 211 (12), 145 (17) and 91 (100); (M$^+$, 472.0998. *M*, 472.1013).

Ethyl 7-*cyano*-7-(N-*methylanilino*)*hepta*-4,6-*diene*-3-*carboxylate* **38ε**. *E*-Isomer: yellow oil, TLC (15% EtOAc in hexane) R_f 0.18; ν_{max}(neat)/cm^{-1} 2222 (CN); $\delta_H(CDCl_3)$ 0.94 (3 H, t, *J* 7), 1.29 (3 H, t, *J* 7), 1.70–1.95 (2 H, m), 2.81–3.12 (1 H), 3.22 (3 H, s), 4.16 (2 H, q, *J* 7), 5.81 (1 H, dd, *J* 15, 7), 6.13 (1 H, d, *J* 11), 6.53 (1 H, dd, *J* 15, 11), 7.05–7.18 (3 H, m) and 7.23–7.35 (2 H, m).

Z-Isomer: yellow oil, TLC (15% EtOAc in hexane) R_f 0.18; $\delta_H(CDCl_3)$ 0.86 (3 H, t, *J* 7), 1.23 (3 H, t, *J* 7), 1.50–1.70 (2 H, m), 2.81–3.12 (1 H, m), 3.15 (3 H, s), 4.11 (2 H, q, *J* 7), 6.10 (1 H, dd, *J* 15, 7), 6.32 (1 H, dd, *J* 15, 11), 6.61 (1 H, d, *J* 11), 6.72 (2 H, d, *J* 7.5), 6.91 (1 H, t, *J* 7.5) and 7.27 (2 H, t, *J* 7.5); *m/z* 298 (M$^+$, 34%), 269 (16) and 225 (100) (M$^+$, 298.1676. *M*, 298.1681).

Ethyl 7-*cyano*-3-*ethyl*-7-(N-*methylanilino*)*hepta*-4,6-*diene*-3-*carboxylate* **39ε**. *E*-Isomer: yellow oil; TLC (15% EtOAc in hexane) R_f 0.24; ν_{max}(neat)/cm^{-1} 2228 (CN); $\delta_H(CDCl_3)$ 0.83 (6 H, t, *J* 7), 1.26 (3 H, t, *J* 7), 1.60–1.80 (4 H, m), 3.22 (3 H, s), 4.19 (2 H, q, *J* 7), 6.05 (1 H, d *J* 15), 6.26 (1 H, d, *J* 10), 6.48 (1 H, dd, *J* 15, 10), 7.03–7.13 (3 H, m) and 7.27–7.40 (2 H, m).

Z-Isomer: yellow oil; TLC (15% EtOAc in hexane) R_f 0.24; $\delta_H(CDCl_3)$: 0.73 (6 H, t, *J* 7), 1.24 (3 H, t, *J* 7), 1.50–1.73 (4 H, m), 3.17 (3 H, s), 4.15 (2 H, q, *J* 7), 6.25 (1 H, d, *J* 15, 3-H), 6.28 (1 H, dd, *J* 15, 10), 6.62 (1 H, d, *J* 10), 6.82 (2 H, dd, *J* 8, 1), 6.90 (1 H, td, *J* 8, 1) and 7.27 (2 H, td, *J* 8, 1), *m/z* 326 (M$^+$, 27%), 297 (38) and 253 (100) (M$^+$, 326.1986. *M*, 326.1994).

Ethyl 8-*cyano*-3-*hydroxy*-8-(N-*methylanilino*)*octa*-5,7-*diene*-4-*carboxylate* **40ε**. Two isomers, *threo*/*erythro* = 64:36. *Z*-*threo*-Isomer: yellow oil; TLC (20% EtOAc in hexane) R_f 0.12; ν_{max}(neat)/cm^{-1} 3479 (OH), 2210 (CN) and 1727 (CO); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 7), 1.23 (3 H, t, *J* 7 H), 1.25–1.50 (2 H, m), 2.69 (1 H, br, *J* 4, OH), 3.07 (1 H, dd, *J* 9, 4), 3.16 (3 H, s), 3.80–3.92 (1 H, m), 4.14 (2 H, q, *J* 7), 6.19 (1 H, dd, *J* 15, 9), 6.35 (1 H, dd, *J* 15, 10), 6.59 (1 H, d, *J* 10), 6.83 (2 H, dd, *J* 8, 1), 6.91 (1 H, td, *J* 7.5, 1) and 7.28 (2 H, dd, *J* 8, 7.5); $\delta_C(CDCl_3)$ 9.9 (q), 14.0 (q), 27.2 (t), 38.8 (q), 54.3 (d), 61.3 (t), 73.1 (d), 115.2 (d, 2 C), 117.9 (s), 120.4 (d), 127.0 (s), 128.1 (d), 129.3 (d, 2 C), 135.1 (d), 137.3 (d), 146.2 (s) and 172.5 (s); *m/z* 328 (M$^+$, 3%), 270 (53), 241 (28) and 224 (100).

Z-*erythro*-Isomer: yellow oil, TLC (20% EtOAc in hexane) R_f 0.10; ν_{max}(neat)/cm^{-1} 3494 (OH), 2224 (CN) and 1726 (CO); $\delta_H(CDCl_3)$ 0.97 (3 H, t, *J* 7), 1.29 (3 H, t, *J* 7), 1.36–1.55 (2 H, m), 2.54 (1 H, dd, *J* 11, 7), 3.21 (3 H, s), 3.70–3.76 (1 H, m), 4.19 (2 H, q, *J* 7), 5.81 (1 H, dd, *J* 15, 11), 5.98 (1 H, dd, *J* 15, 11), 6.55 (1 H, d, *J* 11), 6.83 (2 H, dd, *J* 8, 1), 6.92 (1 H, td, *J* 7.5, 1) and 7.29 (2 H, dd, *J* 8, 7.5); $\delta_C(CDCl_3)$ 9.7 (q), 14.1 (q), 27.7 (t), 40.2 (q), 55.5 (d), 61.2 (t), 73.8 (d), 115.3 (d, 2 C), 116.8 (s), 121.7 (d), 122.2 (s), 127.2 (d), 129.3 (d, 2 C), 136.1 (d), 137.0 (d), 145.7 (s) and 173.0 (s); *m/z* 328 (M$^+$, 3%), 270 (37), 241 (26) and 224 (100) (M$^+$, 328.1783. *M* 328.1787).

5-*Ethyl*-4-*prop*-1-*enyl*-4,5-*dihydrofuran*-2(3H)-*one* **41**. *trans*-Isomer: yellow oil; TLC (10% EtOAc in hexane) R_f 0.28; ν_{max}(neat)/cm^{-1} 1779 (CO); $\delta_H(CDCl_3)$ 0.99 (3 H, t, *J* 7), 1.50–1.81 (2 H, m), 1.65 (3 H, dd, *J* 6, 1), 2.36 (1 H, dd, *J* 17, 10), 2.61 (1 H, dd, *J* 17, 8), 2.59–2.76 (1 H, m), 4.00 (1 H, td, *J* 8, 4), 5.29 (1 H, ddq, *J* 15, 8, 1) and 5.56 (1 H, dq, *J* 15, 6); $\delta_C(CDCl_3)$ 10.0 (q), 17.8 (q), 26.4 (t), 36.0 (t), 45.0 (d), 86.4 (d), 128.6 (d), 128.9 (d) and 176.1 (s); *m/z* 155 ([M + 1]$^+$, 2%), 97 (12) and 69 (100). *cis*-Isomer: yellow oil, TLC (10% EtOAc in hexane) R_f 0.23; ν_{max}(neat)/cm^{-1} 1768 (CO); $\delta_H(CDCl_3)$ 0.95 (3 H, t, *J* 7), 1.44–1.63 (2 H, m), 1.66 (3 H, dd, *J* 6, 1), 2.34 (1 H, dd, *J* 17, 6), 2.63 (1 H, dd, *J* 17, 8), 3.03–3.12 (1 H, m), 4.31–4.44 (1 H, m), 5.32 (1 H, ddq, *J* 15, 6, 1) and 5.54 (1 H, dq, *J* 15, 6); $\delta_C(CDCl_3)$ 10.0 (q), 17.8 (q), 23.9 (t), 35.2 (t), 42.0 (d), 85.0 (d), 126.6 (d), 128.8 (d) and 176.6 (s); *m/z* 154 (M$^+$, 3%), 97 (11) and 69 (100) (M$^+$, 154.1009. *M*, 154.0993).

4-*Prop*-1-*enyl*-5-*propyl*-4,5-*dihydrofuran*-2(3H)-*one* **42**. *trans*-Isomer: yellow oil; TLC (10% EtOAc in hexane) R_f 0.29; ν_{max}(neat)/cm^{-1} 1772 (CO); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 6), 1.31–1.66 (4 H, m), 1.64 (3 H, dd, *J* 6, 1.6), 2.34 (1 H, dd, *J* 16.6, 10), 2.58 (1 H, dd, *J* 16.6, 8), 2.62–2.73 (1 H, m), 4.04 (1 H, td, *J* 8, 3.5), 5.27 (1 H, ddq, *J* 15, 8, 1.6) and 5.55 (1 H, dq, *J* 15, 6); $\delta_C(CDCl_3)$ 13.7 (q), 17.8 (q), 19.0 (t), 35.5 (t), 35.8 (t), 45.5 (d), 85.0 (d), 128.5 (d), 128.9 (d) and 176.2 (s); *m/z* 169 ([M + 1]$^+$, 3%), 97 (13) and 69 (100). *cis*-Isomer: yellow oil, TLC (10% EtOAc in hexane) R_f 0.24; ν_{max}(neat)/cm^{-1} 1772 (CO); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 7), 1.27–1.55 (4 H, m), 1.66 (3 H, dd, *J* 6, 1.4), 2.33 (1 H, dd, *J* 17, 6), 2.62 (1 H, dd, *J* 17, 8), 3.01–3.31 (1 H, m), 4.39–4.50 (1 H, m), 5.32 (1 H, ddq, *J* 15, 9, 1.4) and 5.52 (1 H, dq, *J* 15, 6); $\delta_C(CDCl_3$, 75 MHz) 13.7 (q), 17.8 (q), 18.9 (t), 32.8 (t), 35.1 (t), 42.1 (d), 83.4 (d), 126.7 (d), 128.8 (d) and 176.6 (s); *m/z* 169 ([M + 1]$^+$, 3%), 97 (12) and 69 (100) (M$^+$, 168.1146. *M*, 168.1150).

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