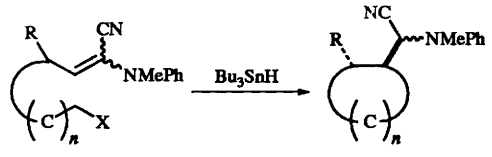
Free-radical cyclisations of 2-aminoalka-2,5-dienenitriles

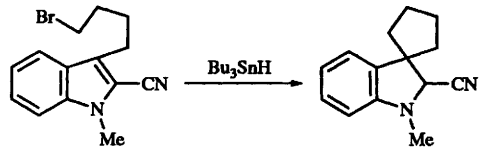
Chau-Chen Yang and Jim-Min Fang*
Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

The intramolecular free-radical cyclisations of a series of 2-(*N*-methylanilino)alka-2,5-dienenitriles **5–16** have been studied. These compounds have two alkenyl groups orientated in equal proximity to the radical centres. One alkenyl group contains both the cyano and the *N*-methylanilino substituents, while the other contains either an electron-withdrawing or an electron-donating group. Intramolecular free-radical cyclisations occur exclusively or predominantly on the amino-cyano substituted alkenyl group (C-3 attack). The radical cyclisation of 4-(2-bromobenzyl)methyl-3,5-dimethyl-2-(*N*-methylanilino)hepta-2,5-diene-1,7-dinitrile also occur exclusively at C-3.

We have demonstrated earlier that various cycloalkyl α-amino nitriles **2** can be obtained in a stereoselective manner by the intramolecular free-radical cyclisations of α-anilinoalkenenitriles **1**.[1a] These reactions were facilitated by the aminonitrile substituents. Further investigation shows that this effect may play an essential role in nucleophilic-type radical cyclisations of 2-cyano 3-substituted indoles **3** to give spiro-annelated indolines **4**.[1b]



1 **2**



3 **4**

We report herein the preparation of 2-(*N*-methylanilino)-alka-2,5-dienenitriles **5–16** and their intramolecular radical cyclisations. These compounds have two alkenyl groups orientated in equal proximity to the radical centres. One alkenyl group contains both the cyano and *N*-methylanilino substituents, while the other contains either an electron-withdrawing or electron-donating group. The radical cyclisation may occur in two competitive pathways, with attack at C-3 (path a in Scheme 1) or attack at C-5 (path b). The observed regioselectivity can thus reflect the influence of amino-cyano substitution in the free-radical cyclisations.

Results and discussion

The dienenitrile **5** was treated with Bu_3SnH (1.2 equiv.) and a radical initiator azoisobutyronitrile (AIBN) (0.2 equiv.) in refluxing deoxygenated anhydrous benzene to effect the intramolecular free-radical cyclisation, giving **17a** and **17b** (34:66) in 77% yield. Both **17a** and **17b** had the *trans* configuration since they were derived from an *exo*-transition state **B** (Scheme 1).[1a,2] Although the starting material **5** generally existed as a mixture of 2*E*- and 2*Z*-isomers, the subsequent radical cyclisation gave the same ratio of diastereoisomers **17a** and **17b** differing in their C-2 chirality. The structures of **17a** and **17b** were tentatively assigned as such by analogy to those of **21a** and **21b** (see below). The less polar isomer **17a** exhibited smaller chemical shifts for the 2-H and C-2 signals than those of **17b** (Table 2).

Table 1 Free-radical cyclisations of 2-aminoalka-2,5-dienenitriles (1.2 equiv. of Bu_3SnH, 0.2 equiv. of AIBN, PhH, 80 °C, 6 h)

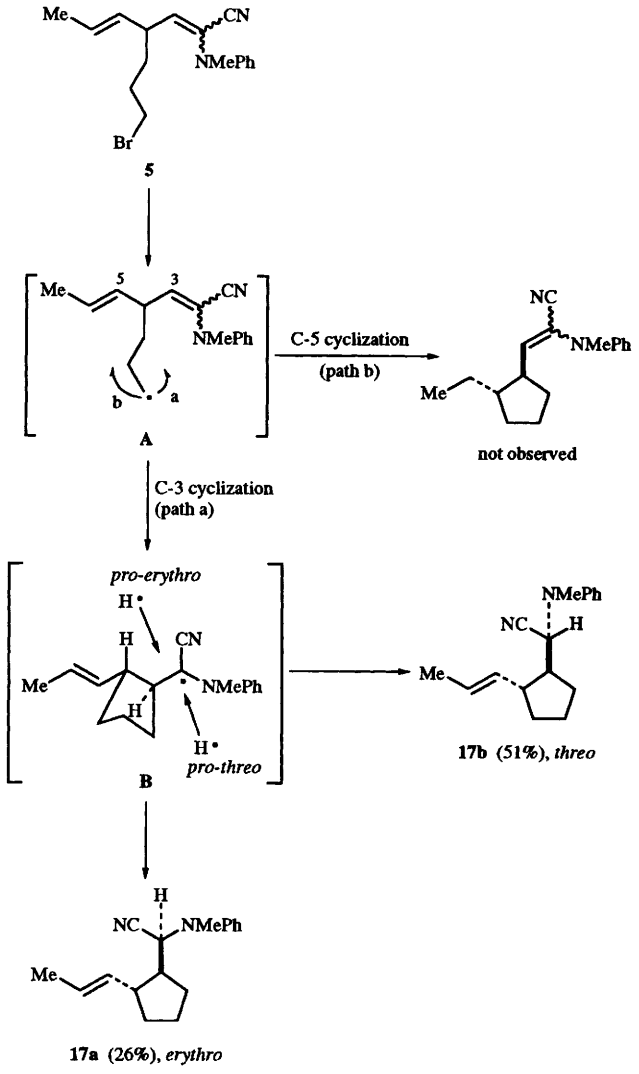
Substrate	Products (yield, %; ratio of isomers)
5	**17** (77; **a**:**b** = 34:66)
6	**18** (69; **a**:**b** = 37:63)
7	**19** (87; **a**:**b**:**c**:**d** = 39:29:25:7)
8	**20** (82; **a**:**b** = 40:60)
9[a]	**21** (38; **a**:**b** = 54:46) + **22** (60; **a**:**b** = 61:39)
10	**23** (82; **a**:**b** = 63:37)
11	**24** (81; **a**:**b**:**c** = 20:69:11)
12	**25** (89; **a**:**b** = 54:46)
13	**26** (75; **a**:**b**:**c**:**d** = 25:10:52:23) + **27** (19)
14	**28** (62; **a**:**b** = 55:45)
15	**29** (88; **a**:**b** = 12:88)
16	**30** (40; **a**:**b**:**c** = 55:25:20)

[a] The reaction was carried out in the presence of 1.2 equiv. of AIBN.

The intramolecular radical cyclisations of other dienenitriles, having methyl, phenyl, benzyloxy, phenylsulfanyl, methoxycarbonyl or cyano substituents at C-6, were similarly carried out (Table 1), whereas the reaction of **9** was conducted in the presence of an excess of AIBN (1.2 equiv.). The phenyl radical generated from **9** attacked exclusively at C-3 to give 38% of **21** (**a**/**b** = 54:46) and 60% of **22** (**a**/**b** = 61:39) by trapping the intermediate amino-cyano α-radical with a hydrogen atom or a dimethylacetonitrile radical. All the cyclisation products had a *trans* configuration. Compounds **21b** and **22b** had the (2*RS*,1′*RS*,2′*RS*)-structures as shown by the X-ray diffraction analyses (Table 3). The atomic coordinates together with the bond lengths and bond angles for these crystallographic studies have been deposited with the Cambridge Crystallographic Data Centre.†

A study of the reactions with alkyl, vinyl or phenyl radicals (Table 1), showed that most of the radical cyclisations occurred exclusively at C-3 (path a). Free-radical cyclisations of the dienenitrile **13** with a methoxycarbonyl group at C-6 occurred, however, at both C-3 and C-5 to give **26** and **27** (4:1). When two stereoisomers were obtained in individual cyclisation, the less polar isomer consistently had 2-H and C-3 resonances at higher

† For details, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.



Scheme 1 *Reagents and conditions:* Bu_3SnH, AIBN, PhH, 80 °C, 6 h

Table 2 Comparison of 2-H and C-2 signals in the isomers of cyclisation products (300 MHz, $CDCl_3$, TMS)

Less polar isomer	δ_{2-H}	δ_{C-2}	More polar isomer	δ_{2-H}	δ_{C-2}
17a	4.15	57.5	**17b**	4.49	58.2
18a	4.22	58.0	**18b**	4.26	58.3
20a	4.22	57.4	**20b**	4.33	57.8
21a	4.24	57.9	**21b**	4.42	58.9
23a	4.37	58.0	**23b**	4.49	58.8
24a (*Z*)	4.56	57.4	**24b** (*Z*)	4.77	58.1
25a	4.29	58.1	**25b**	4.47	59.0
26a (*E*)	4.37	57.9	**26b** (*E*)	4.42	59.1
26c (*Z*)	4.39	58.0	**26d** (*Z*)	4.68	58.9

fields (Table 2). These results of regioselective cyclisations indicated that the aminonitrile substituents enhanced the reaction rates, either by the polar effects or by stabilising the intermediate α-radicals.‡ The radical cyclisation of 4-(2-bromobenzyl-3,5-dimethyl-2-(*N*-methylanilino)hepta-2,5-diene-1,7-dinitrile **14** also occurred exclusively at C-3. Such great preference for C-3 attack may be a result of the 2,3-double bond having more substituents than the 5,6-double bond.[4] The electron-donating amino group may also exert a synergistic effect with the electron-withdrawing cyano group in stabilising the intermediate α-radicals.[3a,5]

The amino nitrile **15** underwent the free-radical cyclisation efficiently to form the cyclohexanes **29** in 88% yield. The free-radical reaction of **16** gave the cyclohexenes **30**, presumably *via* the mechanism shown in Scheme 2. The radical **C** generated from **16** cyclised to give an unstable vinylcyclobutane intermediate **D**, which ruptured to afford the amino-cyano-substituted hept-6-enyl radicals **E** and subsequently recyclised to the observed products **30**.

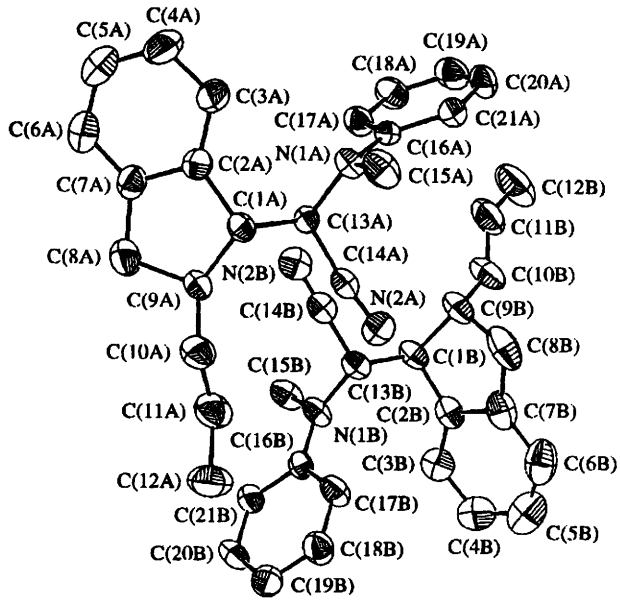


Fig. 1 ORTEP drawing of **21b**

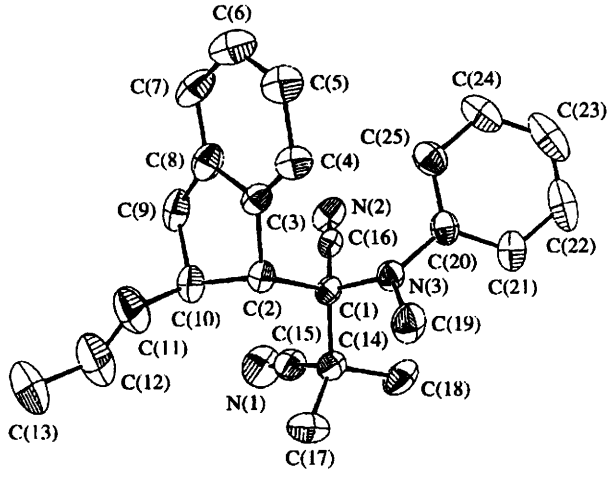
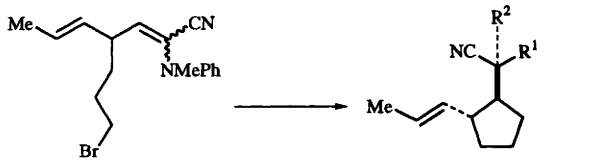


Fig. 2 ORTEP drawing of **22b**

Preparation of 2-(*N*-methylanilino)alka-2,5-dienenitriles

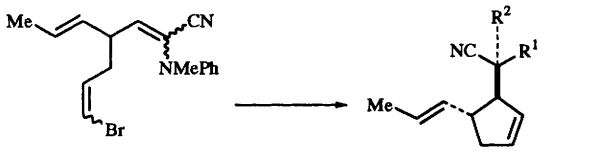
Condensation of hexa-2,4-dienal, potassium cyanide and *N*-methylaniline according to Strecker's method gave 2-(*N*-methylanilino)hepta-3,5-dienenitrile,[6] which underwent regioselective γ-alkylations with dihalides to give the hepta-2,5-dienenitriles **5**–**9**, **15** and **16** predominating in the 2*Z*-

‡ The rate of cyclisation of hex-5-enyl radical is greatly enhanced by introduction of a cyano substituent at C-6. 6-Cyano-6-methoxyhex-5-enyl radical cyclises slightly faster than 6-cyanohex-5-enyl radical.[3a,b] The nucleophilic alkyl radical is considered to add more rapidly to the electrophilic alkenenitrile due to the electron-withdrawing effect of the cyano group. Alternatively, the π-electron-accepting cyano group may increase exothermicity of the radical cyclisation by stabilising the intermediate α-radical and thus facilitates the radical reaction. For detailed discussion, see ref. 3*c*.



5

17a R^1 = NMePh, R^2 = H
17b R^1 = H, R^2 = NMePh



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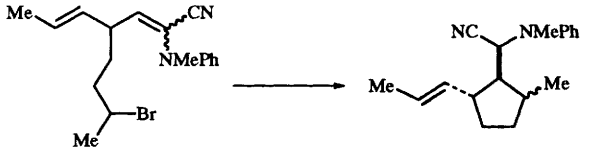
18a R^1 = NMePh, R^2 = H
18b R^1 = H, R^2 = NMePh



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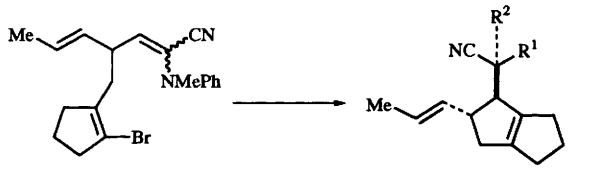
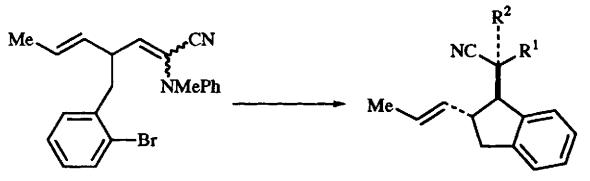


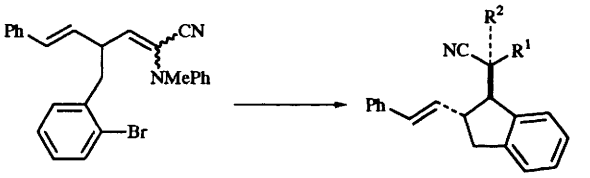
8

20a R^1 = NMePh, R^2 = H
20b R^1 = H, R^2 = NMePh



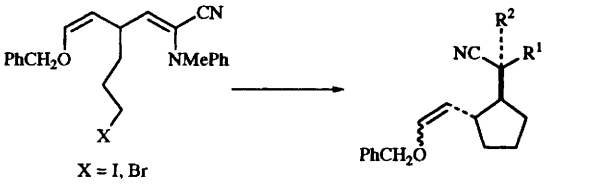
9

21a R^1 = NMePh, R^2 = H
21b R^1 = H, R^2 = NMePh
22a R^1 = $Me_2C(CN)$, R^2 = NMePh
22b R^1 = NMePh, R^2 = $Me_2C(CN)$



10

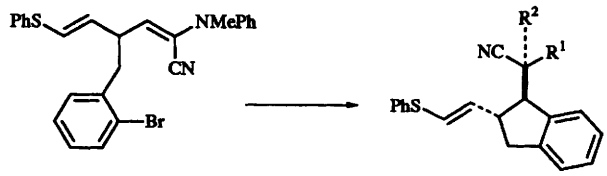
23a R^1 = NMePh, R^2 = H
23b R^1 = H, R^2 = NMePh



X = I, Br

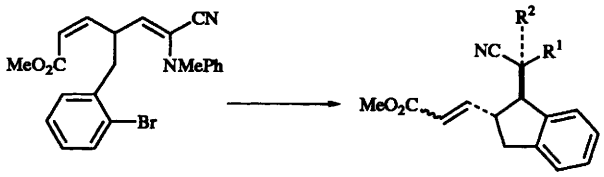
11

24a (*Z*) R^1 = NMePh, R^2 = H
24b (*Z*) R^1 = H, R^2 = NMePh
24c (*E*) R^1 = H, R^2 = NMePh



12

25a R^1 = NMePh, R^2 = H
25b R^1 = H, R^2 = NMePh



13

26a (*E*) R^1 = NMePh, R^2 = H
26b (*E*) R^1 = H, R^2 = NMePh
26c (*Z*) R^1 = NMePh, R^2 = H
26d (*Z*) R^1 = H, R^2 = NMePh

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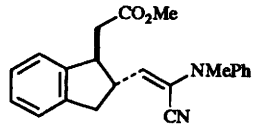

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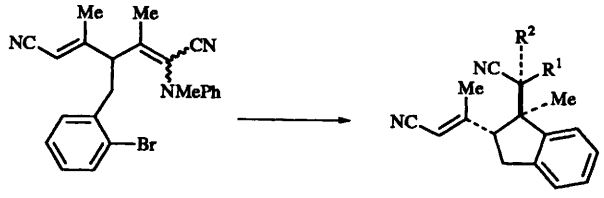
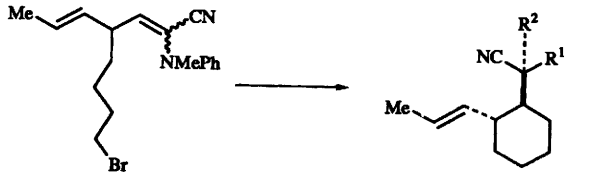


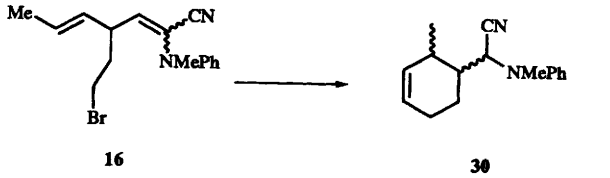
14

28a R^1 = NMePh, R^2 = H
28b R^1 = H, R^2 = NMePh



15

29a R^1 = NMePh, R^2 = H
29b R^1 = H, R^2 = NMePh

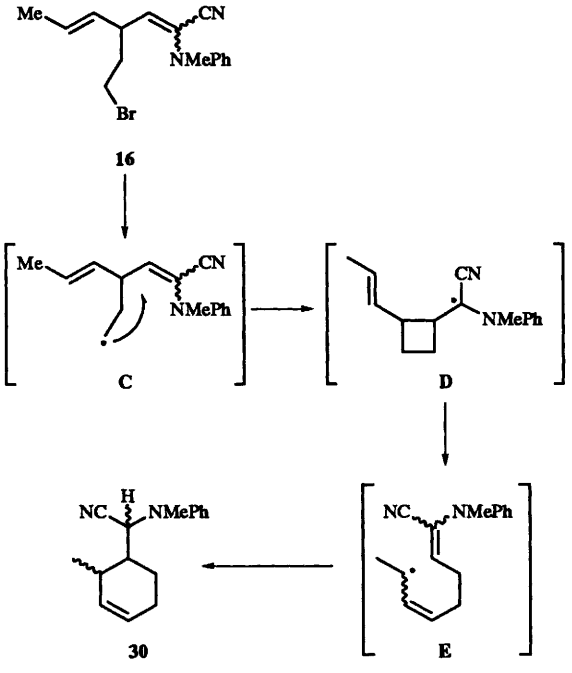


16

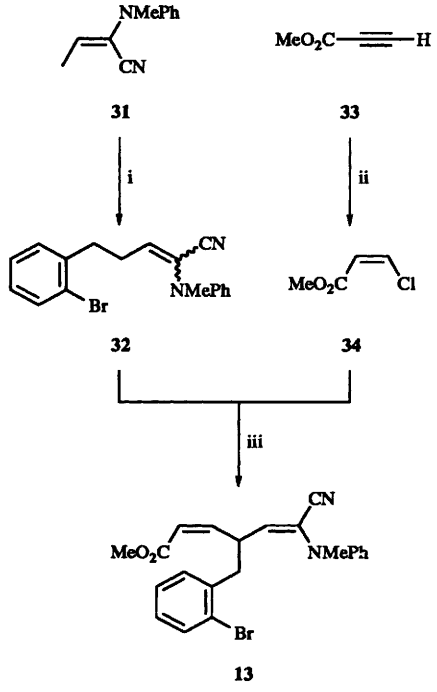
30

Table 3 Crystal data for (2*RS*,1′*RS*,2′*RS*)-2-(2,3-dihydro-2-prop-1-enyl-1*H*-indan-1-yl)-2-(*N*-methylanilino)acetonitrile **21b** and (2*RS*,1′*RS*,2′*RS*)-2-(2,3-dihydro-2-prop-1-enyl-1*H*-indan-1-yl)-3,3-dimethyl-2-(*N*-methylanilino)butane-1,4-dinitrile **22b**. The X-ray data were collected on a CAD-4 diffractometer. The analyses were carried out on a microVAX III computer using NRC SDP software.

	21b	**22b**
Formula	$C_{21}H_{22}N_2$	$C_{25}H_{27}N_3$
Space group	P_{-1}	$P_{21/c}$
a/Å	11.013(3)	10.388(2)
b/Å	11.847(3)	20.755(5)
c/Å	14.212(3)	10.633(2)
α/°	87.68(2)	90
β/°	93.23(2)	109.76(1)
γ/°	106.16(2)	90
V/Å^3	1854.2(3)	2292.5(3)
Crystal size (mm)	0.3 × 0.2 × 0.1	0.4 × 0.2 × 0.1
Z	4	4
T/K	298	298
Radiation	Mo-Kα (=0.7107 Å)	Mo-Kα (= 0.7107 Å)
$2\theta_{max}$/°	2–45	2–45
Scan speed (deg min^{-1})	1.618–8.24	1.648–8.24
Scan parameters	2 (0.70–0.35 tan θ)	2 (0.65 + 0.35 tan θ)
No. of measurements	4636	2805
No. of observed reflections	2150 (> 2σ)	1350 (> 2σ)
R	0.054	0.052
R_w	0.056	0.054
S	2.12	2.02



Scheme 2 *Reagents and conditions:* Bu_3SnH, AIBN, PhH, 80 °C, 6 h



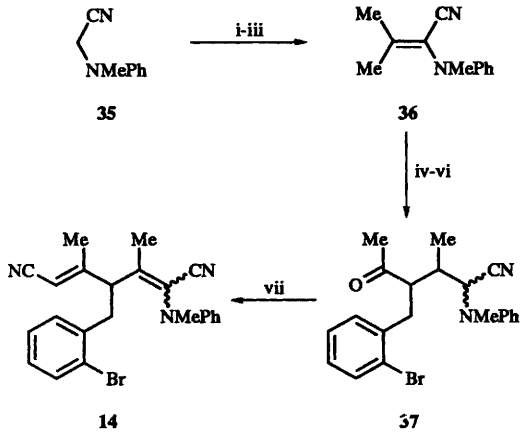
Scheme 3 *Reagents and conditions:* i, LDA, THF, HMPA; *o*-$BrC_6H_4CH_2Br$, −78 °C to 25 °C; ii, conc. HCl, CuCl cat.; MeOH, H_2SO_4; iii, LDA, THF, −78 °C; 77%

configuration.[7] By similar procedures, the hexadienenitriles **10**–**12** having phenyl, benzyloxy or a phenylsulfanyl substituent at C-6 were prepared by γ-alkylations of appropriate amino-cyanopentadienyl anions.[7] Compound **13** was prepared by condensation of 5-(2-bromophenyl)-2-(*N*-methylanilino)pent-2-enenitrile **32** with methyl 3-chloroacrylate (Scheme 3). Acetylation of 3-methyl-2-(*N*-methylanilino)but-2-enenitrile **36**, followed by alkylation with 2-bromobenzyl bromide, afforded a 5-oxo-2-amino nitrile **37** (Scheme 4). Subsequent Wittig–Horner reaction of **37** with diethyl cyanomethylphosphonate resulted in the desired heptadienedinitrile **14**.

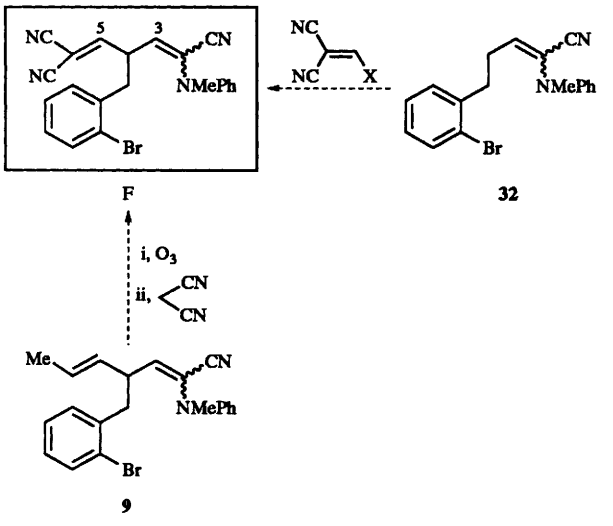
4-(2-Bromobenzyl)-6-cyano-2-(*N*-methylanilino)hepta-2,5-diene-1,7-dinitrile **F** is an ideal substrate for the study of the captodative effect in free-radical cyclisations.[5] Attempts to prepare this substrate, either from **9** or from **32**, however, failed (Scheme 5). Ozonolysis of **9** occurred selectively at the 2,3-double bond, giving *N*-methyl-*N*-phenylcyanoformamide, instead of the desired cleavage at the 5,6-double bond. Treatment of **32** with chloromethylenemalononitrile or phenylsulfanylmethylenemalononitrile in varied bases LDA–THF, LHMDS–THF or Bu^{t}OK–Bu^{t}OH gave, respectively, diisopropylaminomethylenemalononitrile, intractable polymer or starting material.

Conclusions

The current study shows that the amino-cyano substituents in compounds **5**–**16** facilitate radical cyclisations on specific double bonds. As α-amino nitriles are readily elaborated to



Scheme 4 *Reagents and conditions:* i, LDA, THF; Me_2CO, −78 °C; ii, Ac_2O, pyridine, CH_2Cl_2; iii, Bu^{t}OK, THF, −78 °C; 71%; iv, LDA, THF; Ac_2O; v, MeONa, MeOH, 25 °C, 10 min; vi, LDA, THF, HMPA; *o*-$BrC_6H_4CH_2Br$, −78 °C to 25 °C; 47%; vii, $NCCH_2P(O)(OEt)_2$, NaH, THF, −78 to 25 °C; 82%



Scheme 5

amines, amides, carbonyl compounds and α-amino acids,§ the present method can be useful in the preparation of functionalized cyclopentanes, cyclopentenes, cyclohexanes, indanes and bicyclo[3.3.0]octenes.

Experimental

Mps are uncorrected. ^1H NMR spectra were recorded at 200 or 200 MHz and ^{13}C NMR 50 or 75 MHz using chlorotrimethylsilane as an internal standard (*J* values in Hz). Mass spectra (using a Finnigan TSQ 46C spectrometer) were recorded at an ionizing voltage of 70 eV. Merck silica gel 60F sheets were used for analytical thin-layer chromatography. Column chromatography was performed on SiO_2 (70–230 mesh); gradient of EtOAc and hexane were used as eluents. High-pressure liquid chromatography was carried out on a liquid chromatograph equipped with a refractive index detector. The samples were analysed and/or separated on Hibar Lichrosorb Si60 (7 μm) column (25 × 1 cm) with the indicated eluent with a 5 cm^3 min^{-1} flow rate. Benzene and THF were distilled from sodium benzophenone ketyl under N_2. The X-ray diffraction data were collected on a CAD-4 diffractometer. The analyses were carried out on a microVAX III computer using NRC SDP software.

Compounds **5–12**, **15** and **16** were prepared by reported procedures.[6,7]

Methyl 4-(2-bromophenylmethyl)-6-cyano-6-(*N*-methylanilino)-hexa-2,5-dienoate 13

Under a nitrogen atmosphere, a THF solution (5 cm^3) of 5-(2-bromophenyl)-2-(*N*-methylanilino)pent-2-enenitrile **32** (300 mg, 0.88 cm^3) was added dropwise to a cold (−78 °C) LDA solution prepared from BuLi (1.6 mol dm^{-3} hexane solution; 0.6 cm^3) and a THF solution (10 cm^3) of diisopropylamine (0.15 cm^3, 0.95 mmol). The orange solution was stirred at −78 °C for 45 min, after which a THF solution (5 cm^3) of methyl 3-chloroacrylate[8] (130 mg, 1.1 mmol) was added to it; the colour faded immediately and the mixture was warmed to 25 °C. Saturated aqueous NH_4Cl was added to the mixture and the THF was removed under reduced pressure. The residue was extracted with EtOAc (6 cm^3 × 5) and the combined extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated. Chromatography of the residue on a silica-gel column with EtOAc–hexane (10:90) as eluent gave the title compound **13** (285 mg, 77%) of 2*Z*,5*Z*-configuration as a yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.14; ν_{max}(neat)/cm^{-1} 2227 (CN) and 1721 (CO); $\delta_H(CDCl_3)$ 3.02 (2 H, dd, *J* 8, 2), 3.03 (3 H, s, NMe), 3.75 (3 H, s, OMe), 4.96–5.13 (1 H, m, 4-H), 5.56 (1 H, d, *J* 10, 5-H), 5.83 (1 H, d, *J* 12, 2-H), 6.12 (1 H, dd, *J* 12, 10, 3-H), 6.76 (2 H, d, *J* 8), 7.00 (1 H, ddd, *J* 8, 8, 1), 7.08–7.30 (4 H, m), 7.37 (1 H, ddd, *J* 8, 8, 1) and 7.56 (1 H, d, *J* 8); $\delta_C(CDCl_3)$ 40.0 (q), 40.7 (t), 40.8 (q), 51.5 (d), 113.9 (s, CN), 120.4 (d), 120.7 (d, 2 C), 122.8 (s, C-6), 123.1 (d), 125.0 (s), 127.5 (d), 127.7 (d), 128.2 (d), 129.0 (d, 2 C), 131.8 (d), 132.6 (d), 137.4 (s), 146.1 (s), 146.8 (d, C-5) and 165.9 (s, C-1); *m/z* 426 (3%, $[M + 2]^+$), 424 (3, M^+) and 255 (100) (Found: M^+, 426.0755. Calc. for $C_{22}H_{21}{}^{81}BrN_2O_2$: *M*, 426.0767).

4-(2-Bromophenylmethyl)-3,5-dimethyl-2-(*N*-methylanilino)-hepta-2,5-diene-1,7-dinitrile 14

Under a nitrogen atmosphere, a THF solution (5 cm^3) of 3-methyl-2-(*N*-methylanilino)but-2-enenitrile (0.94 g, 5.1 mmol) was added dropwise to a cold (−78 °C) LDA solution prepared from BuLi (1.6 mol dm^{-1} hexane solution; 3.6 cm^3) and a THF solution (10 cm^3) of diisopropylamine (0.90 cm^3, 6.9 mmol). The orange solution was stirred for 45 min after which acetic anhydride (0.72 cm^3, 7.1 mmol) was added to it and the mixture was warmed to 25 °C. Saturated aqueous NH_4Cl was added to the mixture from which THF was removed under reduced pressure. The residue was extracted with EtOAc (5 cm^3 × 4) and the combined extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated. Chromatography of the residue on a silica gel column with EtOAc–hexane (5:95) as eluent gave 5-acetoxy-3-methyl-2-(*N*-methylanilino)hexa-2,4-dienenitrile (1.01 g, 74%). The product (900 mg, 3.3 mmol) was saponified by MeONa (180 mg, 3.3 mmol) in MeOH (10 cm^3) at 25 °C for 10 min to give 3-methyl-2-(*N*-methylanilino)-5-oxohex-2-enenitrile (650 mg, 86%).

A THF solution (5 cm^3) of 3-methyl-2-(*N*-methylanilino)-5-oxohex-2-enenitrile (385 mg, 1.7 mmol) was added dropwise to a cold (−78 °C) LDA solution prepared from BuLi (1.6 mol dm^{-1} hexane solution; 1.2 cm^3) and a THF solution (10 cm^3) of diisopropylamine (0.34 cm^3, 2.0 mmol). The brown solution was stirred for 45 min after which a THF solution (5 cm^3) of 2-bromobenzyl bromide (500 mg, 2.0 mmol) was added dropwise to it; the mixture was then warmed to 25 °C. Saturated aqueous NH_4Cl was added to the mixture from which THF was removed

§ For use of α-amino nitriles in organic synthesis, such as the acid- or base-catalysed hydrolyses of α-amino nitriles to carbonyl compounds and α-amino acids, see the review in ref. 8*a*. For reductive decyanation and alkylative decyanation of α-amino nitriles to amines, see ref. 8*b*. For oxidative conversion of α-amino nitriles to amides, see refs. 8*c* and 8*d*.

under reduced pressure. The residue was extracted with EtOAc (5 cm^3 × 4) and the combined extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated. Chromatography of the residue on a silica-gel column with EtOAc–hexane (10:90) as eluent to give the alkylation product **37** (590 mg, 73%) containing *E*- and *Z*-isomers (54:46).

To a cold (−78 °C) THF suspension (10 cm^3) of NaH (dispersed in 60% mineral oil; 30 mg, 1.1 mmol) was added diethyl cyanomethylphosphonate (0.13 cm^3, 0.8 mmol). The mixture was stirred for 45 min after which, a THF solution (5 cm^3) of **37** (230 mg, 0.58 mmol) was added dropwise to it. The mixture was warmed to 25 °C and stirred for 24 h. Saturated aqueous NH_4Cl was added to the mixture from which THF was removed under reduced pressure. The residue was extracted with EtOAc (6 cm^3 × 5) and the combined extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated. Chromatography of the residue on a silica-gel column with EtOAc–hexane (10:90) as eluent gave (2*E*,5*E*)-**14** (100 mg, 41%) and (2*Z*,5*E*)-**14** (100 mg, 41%) accompanied by recovery of **37** (56 mg).

(2*E*,5*E*)-**14**: white solid, mp 131–133 °C; TLC [EtOAc–hexane (10:90)] R_F 0.11; ν_{max}(KBr)/cm^{-1} 2218 (CN); δ_H($CDCl_3$) 1.72 (3 H, s), 2.18 (3 H, s), 2.86 (3 H, s), 3.10 (1 H, dd, *J* 13.5, 11), 3.25 (1 H, dd, *J* 13.5, 4.5), 4.24 (1 H, dd, *J* 11, 4.5, 4-H), 5.44 (1 H, s, 6-H), 6.28 (2 H, d, *J* 8), 6.83 (1 H, ddd, *J* 8, 8, 1), 7.12–7.25 (4 H, m), 7.34 (1 H, dd, *J* 8, 8) and 7.65 (1 H, dd, *J* 8, 1); δ_C($CDCl_3$) 13.4 (q), 21.2 (q), 35.5 (t), 37.5 (q), 50.6 (d, C-4), 97.7 (d), 113.8 (d, 2 C), 114.4 (s), 116.2 (s), 119.8 (d), 120.1 (s), 124.8 (s), 127.8 (d), 129.0 (d), 129.2 (d, 2 C), 130.9 (d), 133.5 (d), 136.2 (s), 145.6 (s), 150.8 (s) and 162.2 (s); *m*/*z* 421 (8%), 419 (8, M^+ for ^{79}Br) and 250 (100). (2*Z*,5*E*)-**14**: yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.10; ν_{max}(neat)/cm^{-1} 2249 and 2217; δ_H($CDCl_3$) 1.96 (3 H, s), 2.17 (3 H, s), 2.46 (3 H, s), 2.89 (1 H, dd, *J* 14, 10), 3.14 (1 H, dd, *J* 14, 5.6), 4.28 (1 H, dd, *J* 10, 5.6), 5.15 (1 H, s), 6.60 (2 H, d, *J* 8), 6.88 (1 H, ddd, *J* 8, 8, 1), 7.02 (1 H, dd, *J* 8, 1), 7.11 (1 H, ddd, *J* 8, 8, 1), 7.18–7.26 (3 H, m) and 7.52 (1 H, dd, *J* 8, 1); δ_C($CDCl_3$) 16.4 (q), 21.2 (q), 36.3 (t), 38.7 (q), 47.0 (d), 98.4 (d), 114.5 (s), 115.0 (d, 2 C), 116.2 (s), 120.0 (s), 120.5 (d), 124.8 (s), 127.8 (d), 129.0 (d), 129.3 (d, 2 C), 130.6 (d), 133.4 (d), 136.8 (s), 147.1 (s), 151.7 (s) and 162.4 (s); *m*/*z* 422 (13%), 421 (24), 420 (13), 419 (23, M^+) and 250 (100) (Found: M^+, 419.1001. Calc. for $C_{23}H_{22}{}^{79}BrN_3$: *M*, 419.0998).

trans-2-(*N*-Methylanilino)-2-(prop-1-enylcyclopentyl)acetonitrile 17

Compound **5** [a mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-isomers (40:60), 200 mg, 0.60 mmol] in deoxygenated anhydrous benzene (15 cm^3) was heated to reflux under an atmosphere of N_2. A mixture of Bu_3SnH (0.20 cm^3, 0.72 mmol) and AIBN (20 mg, 0.12 mmol) in benzene (15 cm^3) was added drop-by-drop at a rate of 0.1 cm^3 min^{-1} by means of a syringe pump. After completion of the addition, the reaction mixture was kept under reflux for 6 h and then cooled and concentrated under reduced pressure. The residue was chromatographed on a silica-gel column with hexane as eluent to remove most of the tin compounds; subsequently elution with EtOAc gave the crude cyclization products **17**. The EtOAc solution was concentrated to *ca.* 10 cm^3 and then treated with a small amount of Et_3N (0.5 cm^3) to precipitate out the residual tin compounds. The white precipitates were filtered off, and the filtrate was concentrated and chromatographed on a silica-gel column with EtOAc–hexane (2:98) as eluent to give **17** (116 mg, 77%) containing two isomers (**a**:**b** = 34:66) which was separated by HPLC. **17a**: White solid; mp 40–41 °C; TLC [EtOAc–hexane (2:98)] R_F 0.10; ν_{max}(KBr)/cm^{-1} 2214 (CN); δ_H($CDCl_3$) 1.46–1.72 (4 H, m), 1.68 (3 H, d, *J* 6), 1.72–1.92 (2 H, m), 2.19–2.28 (1 H, m), 2.34–2.43 (1 H, m), 2.87 (3 H, s), 4.15 (1 H, d, *J* 10, 2-H), 5.44 (1 H, dd, *J* 16, 8), 5.58 (1 H, dq, *J* 16, 6), 6.90–6.93 (3 H, m) and 7.28 (2 H, dd, *J* 8, 8); δ_C($CDCl_3$) 17.8 (q), 24.0 (t), 29.5 (t), 32.7 (t), 35.1 (q), 47.2 (d), 47.3 (d), 57.5 (d, C-2), 115.6 (d, 2 C, C-2′), 117.3 (s, CN), 120.0 (d), 125.8 (d), 129.3 (d, 2 C, C-3′), 133.8 (d) and 149.1 (s, C-1′); *m*/*z* 254 (14%, M^+) and 145 (100) (Found: M^+, 254.1783. Calc. for $C_{17}H_{22}N_2$: *M*, 254.1783). **17b**: White solid, mp 107–109 °C; TLC [EtOAc–hexane (2:98)] R_F 0.08; ν_{max}(KBr)/cm^{-1} 2225 (CN); δ_H($CDCl_3$) 1.52–1.72 (4 H, m), 1.55 (3 H, dd, *J* 7, 2), 1.82–1.89 (1 H, m), 1.92–2.01 (1 H, m), 2.09–2.14 (1 H, m), 2.26–2.32 (1 H, m), 2.65–2.74 (1 H, m), 2.88 (3 H, s), 4.49 (1 H, d, *J* 7, H-2), 5.31 (1 H, ddd, *J* 16, 8, 2), 5.44 (1 H, dq, *J* 16, 7), 6.83 (2 H, d, *J* 8.5), 6.87 (1 H, dd, *J* 8.5, 8.5) and 7.26 (2 H, ddd, *J* 8.5, 8.5, 1); δ_C($CDCl_3$) 17.8 (q), 23.8 (t), 29.2 (t), 33.6 (t), 34.3 (q), 46.9 (d, 2 C), 58.2 (d), 116.4 (d, 2 C), 117.3 (s), 120.5 (d), 125.4 (d), 129.3 (d, 2 C), 133.9 (d) and 149.6 (s); *m*/*z* 254 (12%, M^+) and 145 (100).

trans-2-(*N*-Methylanilino)-2-(5-prop-1-enylcyclopent-2-enyl)acetonitrile 18

The free-radical cyclisation of **6** [a mixture of 2*E*- and 2*Z*-isomers (46:54), 165 mg], by a procedure similar to that for **17**, gave **18a** (32 mg, 25%) and **18b** (55 mg, 44%). **18a**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.09; ν_{max}(neat)/cm^{-1} 2222 (CN); δ_H($CDCl_3$) 1.64 (3 H, d, *J* 5), 2.15–2.23 (1 H, m), 2.56–2.70 (1 H, m), 2.91 (3 H, s), 2.98–3.08 (2 H, m), 4.22 (1 H, d, *J* 9, 2-H), 5.38–5.44 (2 H, m), 5.75–5.83 (1 H, m), 5.91–5.97 (1 H, m), 6.86–7.01 (3 H, m) and 7.25–7.34 (2 H, m); δ_C($CDCl_3$) 17.8 (q), 34.8 (q), 38.9 (t), 44.4 (d), 54.0 (d), 58.0 (d, C-2), 116.1 (d, 2 C), 116.3 (s, CN), 120.4 (d), 125.1 (d), 128.8 (d), 129.4 (d, 2 C), 134.0 (d), 134.1 (d) and 149.4 (s); *m*/*z* 252 (8%, M^+) and 145 (100). **18b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.07; ν_{max}(neat)/cm^{-1} 2232 (CN); δ_H($CDCl_3$) 1.68 (3 H, dd, *J* 5, 1), 2.20–2.31 (1 H, m), 2.65–2.78 (1 H, m), 2.92 (3 H, s), 2.99–3.12 (2 H, m), 4.26 (1 H, d, *J* 9, 2-H), 5.43–5.63 (2 H, m), 5.65–5.77 (1 H, m), 5.81–5.88 (1 H, m), 6.89 (2 H, d, *J* 8), 6.91 (1 H, ddd, *J* 8, 8, 1) and 7.28 (2 H, ddd, *J* 8, 8, 1); δ_C($CDCl_3$) 17.8 (q), 34.7 (q), 39.5 (t), 44.0 (d), 54.0 (d), 58.3 (d), 116.5 (d, 2 C), 117.1 (s), 120.7 (d), 125.8 (d), 129.2 (d), 129.5 (d, 2 C), 132.7 (d), 133.6 (d) and 149.6 (s); *m*/*z* 252 (11%, M^+), 145 (100) (Found: M^+, 252.1630. Calc. for $C_{17}H_{20}N_2$: *M*, 252.1626).

2-(*N*-Methylanilino)-2-(5-methyl-2-prop-1-enylcyclopentyl)acetonitrile 19

The free-radical cyclisation of **7** [a mixture of 2*E*- and 2*Z*-isomers (42:58), 174 mg], by a procedure similar to that for **17**, gave a mixture of **19a** and **19b** (79 mg, 59%; 55:45), **19c** (29 mg, 22%) and **19d** (8 mg, 6%). **19a**/**19b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.10; ν_{max}(neat)/cm^{-1} 2225 (CN); δ_H($CDCl_3$) 1.05 (3 H, d, *J* 7, Me)/1.15 (d, *J* 4.5), 1.20–1.56 (2 H, m), 1.43 (d, *J* 5, Me)/1.33 (d, *J* 5.4), 1.41–2.10 (4 H, m), 2.30–2.52 (1 H, m)/2.18–2.31 (1 H, m), 2.82 (3 H, s, NMe)/2.86 (s), 4.39 (1 H, d, *J* 11, 2-H)/4.30 (d, *J* 9), 5.32–5.52 (2 H, m)/5.13–5.34 (2 H, m), 6.83–6.91 (3 H, m) and 7.24–7.30 (2 H, m); δ_C($CDCl_3$) 15.2 (q), 17.8/22.0 (q), 32.0/31.0 (t), 32.7/33.7 (t), 34.8/33.9 (q, NMe), 36.0/37.6 (d), 47.9/44.3 (d), 55.1/49.7 (d), 58.3/54.2 (d, C-2), 115.8/115.7 (d, 2 C, C-2′), 117.7/116.2 (s, CN), 120.1/119.9 (d), 124.7/123.7 (d), 129.3/129.2 (d, 2 C, C-3′), 134.6/134.8 (d) and 149.5/149.7 (s, C-1′); *m*/*z* 268 (6%, M^+), 145 (84) and 107 (100). **19c**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.09; ν_{max}(neat)/cm^{-1} 2225 (CN); δ_H($CDCl_3$) 1.06 (3 H, d, *J* 6.6), 1.31–1.39 (1 H, m), 1.44–1.93 (4 H, m), 1.64 (3 H, d, *J* 7), 1.93–2.03 (1 H, m), 2.40–2.47 (1 H, m), 2.88 (3 H, s), 4.27 (1 H, d, *J* 10, 2-H), 5.35–5.56 (2 H, m), 6.88–6.92 (3 H, m) and 7.28 (2 H, dd, *J* 8, 8, 1); δ_C($CDCl_3$) 17.9 (q), 21.1 (q), 32.3 (t), 33.4 (t), 34.9 (q), 38.5 (d), 47.0 (d), 53.6 (d), 58.8 (d), 116.3 (d, 2 C), 117.2 (s), 120.5 (d), 125.0 (d), 129.3 (d, 2 C), 134.6 (d) and 149.6 (s); *m*/*z* 268 (7%, M^+), 145 (100) and 107 (90) (Found: M^+, 268.1934. Calc. for $C_{18}H_{24}N_2$: *M*, 268.1939). **19d**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.07; ν_{max}(neat)/cm^{-1} 2225

(CN); $\delta_H(CDCl_3)$ 0.83 (3 H, d, *J* 7), 1.42–1.53 (1 H, m), 1.68 (3 H, dd, *J* 6, 1), 1.75–1.86 (1 H, m), 1.95–2.07 (1 H, m), 2.10–2.19 (1 H, m), 2.22–2.26 (1 H, m), 2.44–2.49 (1 H, m), 2.89 (3 H, s), 3.71–3.75 (1 H, m), 4.25 (1 H, *J* 11, 2-H), 5.47 (1 H, dd, *J* 17, 8), 5.48 (1 H, dq, *J* 17, 6), 6.90 (2 H, dd, *J* 8), 6.94 (1 H, dd, *J* 8, 8) and 7.28 (2 H, dd, *J* 8, 8); $\delta_C(CDCl_3)$ 15.2 (q), 17.8 (q), 31.4 (t), 31.7 (t), 34.9 (q), 35.6 (d), 44.5 (d), 49.4 (d), 54.4 (d), 116.4 (d, 2 C), 117.7 (s), 120.6 (d), 126.0 (d), 129.3 (d, 2 C), 134.3 (d) and 149.2 (s); *m/z* 268 (13%, M^+), 145 (100) and 107 (53).

trans-2-(*N*-Methylanilino)-2-(3-prop-1-enylbicyclo[3.3.0]oct-1(5)-en-2-yl)acetonitrile 20

The free-radical cyclisation of **8** [a mixture of (2*E*)- and (2*Z*)-isomers (20:80), 144 mg], by a procedure similar to that for **17**, gave **20a** (48 mg, 33%) and **20b** (72 mg, 49%). **20a**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.10; ν_{max}(neat)/cm^{-1} 2223 (CN); $\delta_H(CDCl_3)$ 1.52–1.72 (2 H, m), 1.63 (3 H, d, *J* 6), 1.90–2.03 (2 H, m), 2.12–2.32 (4 H, m), 2.86 (3 H, s), 2.85–2.93 (1 H, m), 3.02–3.12 (1 H, m), 4.22 (1 H, d, *J* 10, 2-H), 5.34 (1 H, dd, *J* 16, 6), 5.50 (1 H, dq, *J* 16, 6), 6.86–6.96 (3 H, m) and 7.25–7.32 (2 H, m); $\delta_C(CDCl_3)$ 17.7 (q), 26.8 (t), 27.8 (t), 29.2 (t), 34.5 (q), 35.4 (t), 50.7 (d), 51.0 (d), 57.4 (d, C-2), 116.1 (d, 2 C), 118.0 (s), 120.3 (d), 126.2 (d), 129.2 (d, 2 C), 134.8 (d), 142.4 (s), 146.2 (s) and 148.9 (s, C-1′); *m/z* 292 (8%, M^+) and 147 (100). **20b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.08; ν_{max}(neat)/cm^{-1} 2231 (CN); $\delta_H(CDCl_3)$ 1.52–1.62 (2 H, m), 1.67 (3 H, d, *J* 6), 1.92–2.31 (5 H, m), 2.48–2.63 (1 H, m), 2.81–2.93 (1 H, m), 2.91 (3 H, s), 3.10–3.18 (1 H, m), 4.33 (1 H, d, *J* 9, 2-H), 5.42–5.58 (2 H, m), 6.85–6.89 (3 H, m) and 7.24–7.32 (2 H, m); $\delta_C(CDCl_3)$ 17.9 (q), 26.8 (t), 27.9 (t), 29.2 (t), 34.6 (q), 35.9 (t), 50.0 (d), 51.0 (d), 57.8 (d, C-2), 116.3 (d, 2 C), 117.2 (s), 120.4 (d), 125.1 (d), 129.3 (d, 2 C), 134.4 (d), 144.0 (s), 148.2 (s) and 149.6 (s); *m/z* (rel. intensity) 292 (13%, M^+) and 147 (100) (Found: M^+, 292.1935. Calc. for $C_{20}H_{24}N_2$: *M*, 292.1939).

trans-2-(2,3-Dihydro-2-prop-1-enyl-1*H*-indan-1-yl)-2-(*N*-methylanilino)acetonitrile 21 and trans-2-(2,3-dihydro-2-prop-1-enyl-1*H*-indan-1-yl)-3,3-dimethyl-2-(*N*-methylanilino)-butane-1,4-dinitrile 22

The free-radical cyclisation of **9** [a mixture of (2*E*)- and (2*Z*)-isomers (26:74), 305 mg], by a procedure similar to that for **17** except that 1.2 equiv. of AIBN was used, gave **21a** (49 mg, 21%), **21b** (43 mg, 18%), **22a** (107 mg, 37%) and **22b** (69 mg, 23%). **21a**: Yellow oil; TLC [EtOAc–hexane (5:95)] R_F 0.24; ν_{max}(neat)/cm^{-1} 2225 (CN); $\delta_H(CDCl_3)$ 1.60 (3 H, d, *J* 4.5), 2.71 (1 H, dd, *J* 16, 1.5, 3-H), 2.99 (3 H, s), 3.08–3.15 (1 H, m, 2-H), 3.21 (1 H, dd, *J* 16, 7.5, 3-H), 3.45 (1 H, dd, *J* 11, 2, 1-H), 4.24 (1 H, d, *J* 11), 5.42–5.49 (2 H, m), 6.88–6.95 (3 H, m), 7.22–7.32 (5 H, m) and 7.59–7.63 (1 H, m); $\delta_C(CDCl_3)$ 17.8 (q), 34.5 (q), 37.2 (t), 43.8 (d), 53.0 (d), 57.9 (d), 116.3 (d, 2 C), 117.5 (s, CN), 120.7 (d), 125.0 (d), 125.2 (d), 126.1 (d), 126.8 (d), 128.3 (d), 129.4 (d, 2 C), 133.8 (d), 140.0 (s), 142.8 (s) and 149.4 (s); *m/z* 302 (7%, M^+), 157 (30), 145 (100). **21b**: White solid, mp 69–71 °C; TLC [EtOAc–hexane (5:95)] R_F 0.21; ν_{max}(KBr)/cm^{-1} 2225 (CN); $\delta_H(CDCl_3)$ 1.67 (3 H, d, *J* 5), 2.80 (1 H, dd, *J* 16, 4.5, 3-H), 2.98 (3 H, s), 3.00–3.07 (1 H, m, 2-H), 3.28 (1 H, dd, *J* 16, 8, 3-H), 3.46 (1 H, dd, *J* 10, 4.5, 1-H), 4.42 (1 H, d, *J* 10), 5.52–5.61 (2 H, m), 6.73 (2 H, d, *J* 8), 6.87 (1 H, ddd, *J* 8, 8, 1) and 7.11–7.39 (6 H, m); $\delta_C(CDCl_3)$ 17.8 (q), 35.0 (q), 38.2 (t), 45.5 (d), 51.8 (d), 58.9 (d), 116.8 (s), 116.9 (d, 2 C), 120.9 (d), 124.7 (d), 126.1 (d), 126.7 (d), 128.0 (d), 129.1 (d), 129.2 (d, 2 C), 133.2 (d), 141.1 (s), 142.4 (s) and 149.6 (s); *m/z* 302 (4%, M^+), 157 (24), 146 (64), 145 (100) and 129 (80) (Found: M^+, 302.1781. Calc. for $C_{21}H_{22}N_2$: *M*, 302.1783). The crystal data for **21b** are reported.

22a: White solid, mp 110–112 °C; TLC [EtOAc–hexane (5:95)] R_F 0.15; ν_{max}(KBr)/cm^{-1} 2230 (CN); $\delta_H(CDCl_3)$ 1.52 (3 H, s), 1.58 (3 H, dd, *J* 6, 1), 1.68 (3 H, s), 2.45 (1 H, d, *J* 17, 3′-H), 3.24 (3 H, s), 3.26 (1 H, dd, *J* 8, 8, 2′-H), 3.67 (1 H, dd, *J* 17, 8, 3′-H), 4.24 (1 H, s, 1′-H), 5.24 (1 H, ddd, *J* 15, 8, 1), 5.48 (1 H, dq, *J* 15, 6), 7.04 (1 H, dd, *J* 8, 8), 7.23–7.33 (7 H, m) and 7.85 (1 H, d, *J* 8); $\delta_C(CDCl_3)$ 17.7 (q), 27.6 (q), 27.8 (q), 37.7 (q), 38.6 (t), 40.4 (s), 44.7 (d), 59.3 (d), 71.6 (s), 116.0 (s, CN), 119.7 (s, CN), 123.0 (d), 123.1 (d, 2 C), 124.6 (d), 125.7 (d), 125.9 (d), 128.5 (d, 2 C), 128.7 (d), 134.1 (d), 138.4 (s), 145.9 (s) and 149.1 (s); *m/z* 369 (2%, M^+) and 212 (100) (Found: M^+, 369.2208. Calc. for $C_{25}H_{27}N_3$: *M*, 369.2205). **22b**: White solid, mp 146–148 °C; TLC [EtOAc–hexane (5:95)] R_F 0.10; ν_{max}(KBr)/cm^{-1} 2250 and 2230; $\delta_H(CDCl_3)$ 1.63 (3 H, s), 1.65 (3 H, d, *J* 7), 1.84 (3 H), 2.76 (1 H, d, *J* 16.6), 3.28 (3 H, s), 3.59 (1 H, t, *J* 8), 3.81 (1 H, dd, *J* 16.6, 8, 3-H), 4.01 (1 H, s), 5.56 (1 H, dq, *J* 14, 7), 5.57 (1 H, dd, *J* 14, 8), 6.61 (2 H, dd, *J* 8, 1), 6.93 (1 H, ddd, *J* 8, 1), 7.06–7.16 (3 H, m) and 7.25–7.36 (3 H, m); $\delta_C(CDCl_3)$ 17.8 (q), 25.1 (q), 28.1 (q), 38.7 (t), 38.8 (q), 43.5 (d), 43.6 (s), 56.9 (d), 72.1 (s), 116.9 (s), 123.4 (s), 123.6 (d), 124.4 (d, 2 C), 124.9 (d), 125.1 (d), 126.5 (d), 127.8 (d), 128.1 (d, 2 C), 128.5 (d), 134.3 (d), 139.8 (s), 144.1 (s) and 149.3 (s); *m/z* 369 (1%, M^+) and 212 (100). The crystal data for **22b** are reported.

trans-2-(2,3-Dihydro-2-(2-phenylvinyl-1*H*-indan-1-yl)-2-(*N*-methylanilino)acetonitrile 23

The free-radical cyclisation of **10** [a mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-isomers (33:67), 100 mg], by a procedure similar to that for **17**, gave **23a** (41 mg, 52%) and **23b** (24 mg, 30%). **23a**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.13; ν_{max}(neat)/cm^{-1} 2225; $\delta_H(CDCl_3)$ 2.82–2.96 (1 H, m), 3.05 (3 H, s), 3.28–3.44 (2 H, m), 3.63 (1 H, dd, *J* 11, 1.5), 4.37 (1 H, d, *J* 11), 6.25 (1 H, dd, *J* 16, 8), 6.45 (1 H, d, *J* 16), 6.46 (1 H, dd, *J* 8), 1), 6.96–7.06 (2 H, m), 7.20–7.41 (10 H, m) and 7.68–7.72 (1 H, m); $\delta_C(CDCl_3)$ 34.7 (q), 37.3 (t), 44.6 (d), 52.9 (d), 58.0 (d), 116.5 (d, 2 C), 117.4 (s), 119.6 (d), 120.9 (d), 125.3 (d), 126.1 (d, 2 C), 127.0 (d), 127.4 (d), 128.5 (d, 2 C), 129.5 (d, 2 C), 129.9 (d), 132.5 (d), 137.0 (s), 139.8 (s), 142.6 (s) and 149.4 (s); *m/z* 364 (22%, M^+), 145 (74) and 91 (100) (Found: M^+, 364.1917. Calc. for $C_{26}H_{24}N_2$: *M*, 364.1939). **23b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.10; ν_{max}(neat)/cm^{-1} 2234; $\delta_H(CDCl_3)$ 2.82–2.92 (1 H, m), 3.00 (3 H, s), 3.22–3.35 (1 H, m), 3.41 (1 H, dd, *J* 16, 8), 3.59 (1 H, dd, *J* 10, 4), 4.49 (1 H, d, *J* 10), 6.28 (1 H, dd, *J* 16, 8), 6.56 (1 H, d, *J* 16), 6.74 (2 H, d, *J* 8), 6.94 (1 H, dd, *J* 8, 8) and 7.12–7.41 (11 H, m); $\delta_C(CDCl_3)$ 35.2 (q), 38.1 (t), 45.7 (d), 52.2 (d), 58.8 (d), 114.7 (s), 116.9 (d, 2 C), 121.1 (d), 124.5 (d), 124.9 (d), 126.2, (d, 2 C), 126.9 (d), 127.4 (d), 128.2 (d), 128.5 (d, 2 C), 129.3 (d, 2 C), 130.7 (d), 132.0 (d), 137.0 (s), 140.8 (s), 140.9 (s) and 149.6 (s); *m/z* 364 (8%, M^+), 219 (43), 145 (86) and 91 (100).

trans-2-[2-(2-Benzyloxyvinyl)cyclopentyl]-2-(*N*-methylanilino)-acetonitrile 24

The free-radical cyclisation of **11** [(2*Z*,5*Z*)-configuration, 180 mg, X = Br or I (1:1)], by a procedure similar to that for **17**, gave **24a** (20 mg, 16%), **24b** (77 mg, 56%) and **24c** (12 mg, 9%). **24a** (*Z*-configuration): Yellow oil; TLC [EtOAc–hexane (5:95)] R_F 0.14; ν_{max}(neat)/cm^{-1} 2221; $\delta_H(CDCl_3)$ 1.22–1.40 (3 H, m), 1.69–2.13 (4 H, m), 2.88 (3 H, s), 2.87–2.95 (1 H, m), 4.32 (1 H, dd, *J* 9.5, 6), 4.56 (1 H, d, *J* 6), 4.68 (1 H, d, *J* 12), 4.77 (1 H, d, *J* 12), 6.09 (1 H, dd, *J* 6, 1), 6.79 (2 H, dd, *J* 8, 1), 6.86 (1 H, ddd, *J* 8, 8, 1) and 7.18–7.31 (7 H, m); $\delta_C(CDCl_3)$ 24.1 (t), 29.4 (t), 32.8 (t), 35.1 (q), 39.2 (d), 48.5 (d), 57.4 (d), 73.9 (t), 110.2 (d), 115.6 (d, 2 C), 117.4 (s, CN), 119.8 (d), 127.5 (d, 2 C), 128.0 (d), 128.5 (d, 2 C), 129.3 (d, 2 C), 137.3 (s), 145.3 (d) and 149.6 (s); *m/z* 346 (4%, M^+), 145 (49), 107 (70) and 91 (100) (Found: M^+, 346.2036. Calc. for $C_{23}H_{26}N_2O$: *M*, 346.2045). **24b** (*Z*-configuration): Yellow oil; TLC [EtOAc–hexane (5:95)] R_F 0.12; ν_{max}(neat)/cm^{-1} 2224; $\delta_H(CDCl_3)$ 1.39–1.69 (4 H, m), 1.82–2.01 (2 H, m), 2.16–2.29 (1 H, m), 2.85 (3 H, s), 2.80–2.92 (1 H, m), 2.19 (1 H, d, *J* 10), 4.45 (1 H, dd, *J* 9, 6), 4.77 (1 H, d, *J* 12), 4.87 (1 H, d, *J* 12), 6.11 (1 H, d, *J* 6), 6.88 (2 H, d, *J* 8), 6.90

(1 H, ddd, *J* 8, 8, 1) and 7.22–7.37 (7 H, m); $\delta_C(CDCl_3)$ 23.3 (t), 29.3 (t), 34.2 (t), 34.3 (q), 39.7 (d), 47.6 (d), 58.1 (d), 73.8 (t), 110.3 (d), 116.3 (d, 2 C), 117.7 (s, CN), 120.4 (d), 127.6 (d, 2 C), 127.9 (d), 128.5 (d, 2 C), 129.3 (d, 2 C), 138.8 (s), 144.4 (d) and 145.4 (s); *m/z* 346 (4%, M^+), 145 (56), 107 (72) and 91 (100). **24c** (*E*-configuration): Yellow oil; TLC [EtOAc–hexane (5:95)] R_F 0.08; ν_{max}(neat)/cm^{-1} 2205; $\delta_H(CDCl_3)$ 1.45–1.70 (4 H, m), 1.78–2.00 (2 H, m), 2.09–2.40 (2 H, m), 2.87 (3 H, s), 4.15 (1 H, d, *J* 10), 4.75 (2 H, s), 4.92 (1 H, dd, *J* 13, 9), 6.45 (1 H, d, *J* 13), 6.88–6.95 (3 H, m) and 7.19–7.36 (7 H, m); $\delta_C(CDCl_3)$ 23.7 (t), 29.3 (t), 34.5 (q), 34.7 (t), 42.9 (d), 47.7 (d), 58.1 (d), 71.4 (t), 108.2 (d), 113.5 (s, CN), 116.5 (d, 2 C), 120.6 (d), 127.6 (d, 2 C), 127.8 (d), 128.4 (d, 2 C), 129.3 (d, 2 C), 137.1 (s), 146.5 (d) and 149.6 (s); *m/z* 346 (8, M^+), 145 (50), 107 (52) and 91 (100).

trans-2-(2,3-Dihydro-2-(2-phenylsulfanylvinyl)-1*H*-indan-1-yl)-2-(*N*-methylanilino)acetonitrile 25

The free-radical cyclisation of **12** (2*E*,5*E*-configuration, 150 mg), by a procedure similar to that for **17**, gave **25a** (61 mg, 48%) and **25b** (52 mg, 41%). **25a**: White solid, mp 134–136 °C; TLC [EtOAc–hexane) 2:98)] R_F 0.13; ν_{max}(KBr)/cm^{-1} 2234; $\delta_H(CDCl_3)$ 2.82 (1 H, dd, *J* 19, 6), 3.00 (3 H, s), 3.21–3.30 (2 H, m), 3.55 (1 H, dd, *J* 11, 2), 4.29 (1 H, d, *J* 11), 5.93 (1 H, dd, *J* 15, 8), 6.19 (1 H, d, *J* 15), 6.92 (2 H, d, *J* 8), 6.93 (1 H, ddd, *J* 8, 8, 1), 7.14–7.33 (10 H, m) and 7.62–7.66 (1 H, m); $\delta_C(CDCl_3)$ 34.8 (q), 37.0 (t), 44.9 (d), 52.5 (d), 58.1 (d), 116.6 (d, 2 C), 117.2 (s), 121.1 (d), 122.6 (d), 125.5 (d), 126.0 (d), 126.4 (d), 127.1 (d), 128.5 (d), 128.8 (d, 2 C), 129.0 (d, 2 C), 129.1 (s), 129.5 (d, 2 C), 137.0 (d), 139.5 (s), 142.2 (s) and 149.3 (s); *m/z* 396 (0.1%, M^+), 251 (100), 145 (60) and 141 (64) (Found: M^+, 396.1634. Calc. for $C_{26}H_{24}N_2S$: *M*, 396.1660). **25b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.10; ν_{max}(neat)/cm^{-1} 2215; $\delta_H(CDCl_3)$ 2.89 (1 H, dd, *J* 14, 4), 3.00 (3 H, s), 3.16–3.29 (1 H, m), 3.35 (1 H, dd, *J* 15, 8), 3.55 (1 H, dd, *J* 10, 4), 4.47 (1 H, d, *J* 10), 6.00 (1 H, dd, *J* 15, 8), 6.36 (1 H, d, *J* 15), 6.76 (2 H, d, *J* 8), 6.90 (1 H, ddd, *J* 8, 8, 1), 7.10–7.36 (10 H, m) and 7.38 (1 H, dd, *J* 8, 8); $\delta_C(CDCl_3)$ 35.3 (q), 38.1 (t), 45.9 (d), 51.5 (d), 59.0 (d), 116.7 (s), 117.2 (d, 2 C), 121.3 (d), 123.9 (d), 124.8 (d), 126.1 (d), 128.5 (d), 127.0 (d), 128.2 (d), 129.0 (d, 2 C), 129.1 (d, 2 C), 129.3 (d, 2 C), 135.5 (s), 135.9 (d, 140.7 (s) and 148.8 (s); *m/z* 396 (2%, M^+), 251 (100), 145 (62) and 141 (60).

Methyl *trans*-2-{1-[cyano(*N*-methylanilino)methyl]-2,3-dihydroindan-2-yl}acrylate 26 and methyl *trans*-2-{2-[2-cyano-2-(*N*-methylanilino)vinyl]-2,3-dihydroindan-1-yl}-acetate 27

The free-radical cyclisation of **13** (2*E*,5*Z*-configuration, 280 mg), by a procedure similar to that for **17**, gave an inseparable mixture **26a**/**26b** (45 mg, 6:4; 20%), **26c** (90 mg, 40%), **26d** (40 mg, 17%) and **27** (40 mg, 17%). **26a**/**26b** (6:4, 2*E*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.21; ν_{max}(neat)/cm^{-1} 2234 (CN), 1719 (CO) and 1641; $\delta_H(CDCl_3)$ 2.72/2.78 (1 H, dd, *J* 16, 4), 2.93/2.90 (3 H, s, NMe), 3.38 (1 H, dd, *J* 16, 8), 3.52 (1 H, dd, *J* 11, 4)/3.72 (1 H, dd, *J* 10.8), 3.56 (3 H, s, OMe), 4.39 (1 H, d, *J* 11)/4.68 (1 H, d, *J* 10), 4.39–4.48 (1 H, m), 5.75/5.86 (1 H, d, *J* 11), 6.14/6.28 (1 H, dd, *J* 11, 10), 6.82–6.94 (3 H, m), 7.10–7.32 (5 H, m) and 7.63–7.68 (1 H, m); $\delta_C(CDCl_3)$ 34.9/35.0 (q), 37.2/38.1 (t), 40.9/41.7 (d), 51.1/51.3 (q), 52.6/52.2 (d), 58.0/58.9 (d), 116.6/116.2 (d, 2 C), 117.3/116.8 (s, CN), 118.8/120.0 (d), 120.8/121.0 (d), 125.2/124.8 (d), 125.8/126.0 (d), 127.0 (d), 128.4/128.2 (d), 129.3 (d, 2 C), 139.6/140.8 (s), 142.4/142.2 (s), 149.2/149.3 (s), 150.7/151.2 (d) and 166.1/166.4 (s, CO); *m/z* 346 (20%, M^+), 320 (50), 201 (78) and 169 (100) (Found: M^+, 346.1673. Calc. for $C_{22}H_{22}N_2O_2$: *M*, 346.1681). **26c** (2*Z*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.13; ν_{max}(neat)/cm^{-1} 2224, 1721 (CO) and 1653; $\delta_H(CDCl_3)$ 2.81 (1 H, d, *J* 16), 2.96 (3 H, s), 3.20–3.33 (1 H, m), 3.55 (1 H, dd, *J* 11, 1), 3.68 (3 H, s), 3.67–3.75 (1 H, m), 4.37 (1 H, d, *J* 11), 5.81 (1 H, d, 15, 5), 6.86–7.02 (4 H, m), 7.16–7.33 (5 H, m) and 7.58–7.62 (1 H, m); $\delta_C(CDCl_3)$ 34.7 (q), 36.0 (t, 43.3 (d), 51.5 (q, OMe), 52.0 (d), 57.9 (d), 116.6 (d, 2 C), 117.0 (s), 120.6 (d), 121.2 (d), 125.2 (d), 126.1 (d), 127.3 (d), 128.7 (d), 129.5 (d, 2 C), 138.9 (s), 141.7 (s), 149.2 (s), 150.1 (d) and 166.7 (s); *m/z* 347 (20%, $[M + 2]^+$), 346 (40, M^+), 320 (35), 272 (30), 201 (34), 169 (28), 145 (100), 141 (40), 115 (20) and 77 (24). **26d** (2*Z*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.11; ν_{max}(neat)/cm^{-1} 2234, 1721 and 1656; $\delta_H(CDCl_3)$ 2.90 (1 H, dd, *J* 16, 3), 2.98 (3 H, s), 3.22–3.30 (1 H, m), 3.39 (1 H, dd, *J* 16, 8), 3.57 (1 H, dd, *J* 10, 4), 3.71 (3 H, s), 4.42 (1 H, d, *J* 10), 5.97 (1 H, dd, *J* 16, 1), 6.70 (2 H, dd, *J* 8, 1), 6.90 (1 H, ddd, *J* 8, 8, 1), 7.00 (1 H, dd, *J* 16, 8.5) and 7.14–7.36 (6 H, m); $\delta_C(CDCl_3)$ 35.2 (q), 37.1 (t), 44.4 (d), 51.1 (q), 51.6 (d), 59.1 (d), 116.4 (s), 117.0 (d, 2 C), 121.2 (d), 121.3 (d), 124.9 (d), 126.3 (d), 127.1 (d), 128.4 (d), 129.3 (d, 2 C), 140.1 (s), 141.3 (s), 149.4 (s), 149.6 (d) and 166.8 (s); *m/z* 346 (28%, M^+), 320 (48), 201 (40), 169 (29) and 145 (100).

27 (2*E*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.14; ν_{max}(neat)/cm^{-1} 2227 (CN), 1734 (CO) and 1597; $\delta_H(CDCl_3)$ 2.64–2.88 (4 H, m), 3.16 (3 H, s), 3.19–3.33 (2 H, m), 3.44–3.55 (1 H, m), 3.59–3.90 (1 H, m), 3.77 (3 H, s), 5.81 (1 H, d, *J* 10) and 7.02–7.37 (9 H, m); $\delta_C(CDCl_3)$ 38.0 (t), 38.6 (t), 40.2 (q), 47.8 (d, 2 C), 51.8 (q), 114.8 (s), 120.7 (d, 2 C), 122.1 (s), 123.2 (d), 123.3 (d), 124.4 (d), 126.8 (d), 127.9 (d), 129.2 (d, 2 C), 131.5 (d), 141.4 (s), 144.0 (s), 146.3 (s) and 172.9 (s); *m/z* 346 (44%, M^+) and 272 (100) (Found: M^+, 346.1672. Calc. for $C_{22}H_{22}N_2O_2$: *M*, 346.1681).

trans-3-{1-[Cyano (*N*-methylanilino)methyl]-2,3-dihydro-1-methylindan-2-yl}but-2-enenitrile 28

The free-radical cyclisation of **14** [a mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-isomers (50:50), 190 mg], by a procedure similar to that for **17**, gave a mixture of **28a** and **28b** (95 mg, 55:45, 62%). Analytical samples of **28a** and **28b** were obtained by HPLC. **28a**: Yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.16; ν_{max}(neat)/cm^{-1} 2215; $\delta_H(CDCl_3)$ 1.37 (3 H, s), 1.79 (3 H, d, *J* 1), 2.46 (3 H, s), 2.75 (1 H, dd, *J* 18, 13), 2.82 (1 H, dd, *J* 18, 6), 3.26 (1 H, dd, *J* 13, 6), 4.54 (1 H, s), 5.08 (1 H, d, *J* 1), 6.54 (2 H, d, *J* 8), 6.82 (2 H, dd, *J* 8, 1), 7.10–7.24 (4 H, m) and 7.35 (1 H, dd, *J* 8, 1); $\delta_C(CDCl_3)$ 18.8 (q), 20.4 (q), 35.8 (t), 37.1 (q), 53.6 (d), 55.8 (s), 63.0 (d), 98.4 (d), 115.6 (d, 2 C), 115.9 (s), 120.3 (s), 120.8 (d), 124.5 (d), 124.9 (d), 127.7 (d), 129.4 (d, 2 C), 129.6 (d), 142.0 (s), 143.6 (s), 150.0 (s) and 164.8 (s); *m/z* 341 (27%, M^+), 315 (23), 196 (61), 146 (55) and 145 (100). **28b**: Yellow oil; TLC [EtOAc–hexane (10:90)] R_F 0.15; ν_{max}(neat)/cm^{-1} 2214 (CN); $\delta_H(CDCl_3)$ 1.53 (3 H, s), 1.86 (3 H, d, *J* 1, Me), 2.78 (1 H, dd, *J* 14, 9), 3.03 (3 H, s), 3.32 (1 H, dd, *J* 14, 5), 4.00 (1 H, dd, *J* 9, 5), 4.44 (1 H, s), 5.16 (1 H, d, *J* 1), 6.90 (2 H, dd, *J* 8, 1), 6.94–7.02 (2 H, m) and 7.25–7.40 (5 H, m); $\delta_C(CDCl_3)$ 18.8 (q), 19.4 (q), 35.4 (t), 38.4 (q), 52.7 (d), 56.8 (s), 62.6 (d), 98.3 (d), 115.9 (s), 116.5 (d, 2 C), 120.3 (s), 121.3 (d), 124.7 (d), 124.9 (d , 127.7 (d), 129.0 (d), 129.7 (d, 2 C), 141.2 (s), 144.7 (s), 150.5 (s) and 165.2 (s); *m/z* 341 (5%, M^+), 315 (28), 196 (63), 181 (22), 146 (46) and 145 (100) (Found: M^+, 341.1891. Calc. for $C_{23}H_{23}N_3$: *M*, 341.1892).

2-(*N*-Methylanilino)-2-prop-1-enylcyclohexylacetonitrile 29

The free-radical cyclisation of **15** [a mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-isomers (38:62), 174 mg], by a procedure similar to that for **17**, gave **29a** (14 mg, 11%) and **29b** (104 mg, 77%). **29a**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.09; ν_{max}(neat)/cm^{-1} 2224; $\delta_H(CDCl_3)$ 1.02–1.35 (2 H, m), 1.42–1.82 (5 H, m), 1.73 (3 H, d, *J* 5.5), 1.90–2.05 (1 H, m), 2.62–2.72 (1 H, m), 2.85 (3 H, s), 3.00–3.12 (1 H, m), 4.14 (1 H, d, *J* 8, 2-H), 5.61–5.72 (2 H, m), 6.85 (2 H, d, *J* 8), 6.88 (1 H, dd, *J* 8, 8) and 7.26 (2 H, dd, *J* 8, 8); $\delta_C(CDCl_3)$ 18.3 (q), 20.9 (t), 23.9 (t), 25.9

(t), 32.5 (t), 34.6 (q), 39.4 (d), 41.6 (d), 58.5 (d, C-2), 116.2 (d, 2 C), 117.1 (s), 120.5 (d), 121.7 (d), 129.1 (d), 129.3 (d, 2 C) and 149.6 (s); *m/z* 268 (3%, M^+), 146 (30) and 145 (100). **29b**: White solid, mp 46–47 °C; TLC [EtOAc–hexane (2:98)] R_F 0.07; ν_{max}(KBr)/cm^{-1} 2223; δ_H($CDCl_3$) 1.11–1.40 (4 H, m), 1.64 (3 H, d, *J* 5), 1.59–2.04 (6 H, m), 2.85 (3 H, s), 4.29 (1 H, d, *J* 7.5, 2-H), 5.35–5.53 (2 H, m), 6.86–6.91 (3 H, m) and 7.27 (2 H, dd, *J* 8, 8); δ_C($CDCl_3$) 17.7 (q), 24.9 (t), 25.1 (t), 27.4 (t), 33.1 (t), 35.1 (q), 44.0 (d), 45.8 (d), 57.6 (d, C-2), 116.2 (d, 2 C), 117.9 (s), 120.2 (d), 126.3 (d), 129.2 (d, 2 C), 134.7 (d) and 149.8 (s); *m/z* 268 (8%, M^+), 146 (32) and 145 (100) (Found: M^+, 268.1935. Calc. for $C_{18}H_{24}N_2$: *M*, 268.1939).

2-(2-Methylcyclohex-3-enyl)-2-(*N*-methylanilino)acetonitrile 30

The free-radical cyclisation of **16** [a mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-isomers (43:57), 70 mg], by a procedure similar to that for **17**, gave **30a** (12 mg, 22%), **30b** (5 mg, 10%) and **30c** (4 mg, 8%). The starting material **16** was recovered (30%, *E*/*Z* = 2:1). **30a**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.09; ν_{max}(neat)/cm^{-1} 2212; δ_H($CDCl_3$) 1.03 (3 H, d, *J* 7), 1.29–1.47 (2 H, m), 1.80–1.93 (1 H, m), 1.98–2.12 (2 H, m), 2.17–2.36 (1 H, m), 2.46–2.65 (1 H, m), 2.89 (3 H, s), 4.26 (1 H, d, *J* 11.5, 2-H), 5.68–5.74 (2 H, m), 6.80–6.97 (3 H, m) and 7.24–7.34 (2 H, m); δ_C($CDCl_3$) 18.0 (q), 19.3 (t), 25.5 (t), 35.5 (d), 34.3 (q), 38.7 (d), 57.3 (d, C-2), 116.6 (d, 2 C), 116.9 (s), 120.6 (d), 126.1 (d), 129.3 (d, 2 C), 132.2 (d) and 150.1 (s); *m/z* 240 (15%, M^+) and 145 (100) (Found: M^+, 240.1623. Calc. for $C_{16}H_{20}N_2$: *M*, 240.1626). **30b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.07; ν_{max}(neat)/cm^{-1} 2224; δ_H($CDCl_3$) 1.11 (3 H, d, *J* 7), 1.57–1.76 (1 H, m), 1.86–2.20 (4 H, m), 2.30–2.50 (1 H, m), 2.88 (3 H, s), 4.52 (1 H, d, *J* 11, 2-H), 5.52–5.79 (2 H, m), 6.85–6.94 (3 H, m) and 7.23–7.33 (2 H, m); δ_C($CDCl_3$) 20.0 (t), 21.1 (t), 21.3 (q), 29.2 (d), 34.2 (q), 39.2 (d), 56.5 (d, C-2), 116.2 (d, 2 C), 117.1 (s), 120.5 (d), 125.7 (d), 129.3 (d, 2 C), 130.7 (d) and 149.8 (s); *m/z* 240 (6%, M^+) and 145 (100). **30c**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.06; ν_{max}(neat)/cm^{-1} 2225; δ_H($CDCl_3$) 1.18 (3 H, d, *J* 7), 1.69–1.77 (2 H, m), 1.83–1.91 (2 H, m), 2.03–2.19 (1 H, m), 2.25–2.40 (1 H, m), 2.88 (3 H, s), 4.44 (1 H, d, *J* 11, 2-H), 5.56–5.75 (2 H, m), 6.88–6.94 (3 H, m) and 7.24–7.33 (2 H, m); δ_C($CDCl_3$) 18.1 (q), 20.8 (t), 21.6 (t), 31.3 (d), 34.1 (q), 39.9 (d), 55.4 (d, C-2), 116.2 (d, 2 C), 116.5 (s), 120.6 (d), 125.8 (d), 129.4 (d, 2 C), 130.3 (d) and 149.2 (s); *m/z* 240 (6%, M^+) and 145 (100).

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