

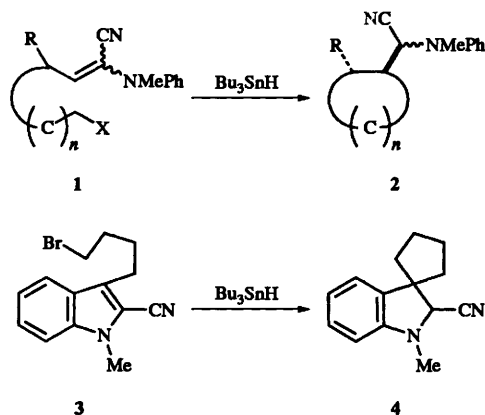
Free-radical cyclisations of 2-aminoalka-2,5-dienitriles

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The intramolecular free-radical cyclisations of a series of 2-(*N*-methylanilino)alka-2,5-dienitriles **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 -anilinoalkene nitriles **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-annulated indolines **4**.^{1b}



We report herein the preparation of 2-(*N*-methylanilino)-alka-2,5-dienitriles **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 dienitrile **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 dia-

Table 1 Free-radical cyclisations of 2-aminoalka-2,5-dienitriles (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)

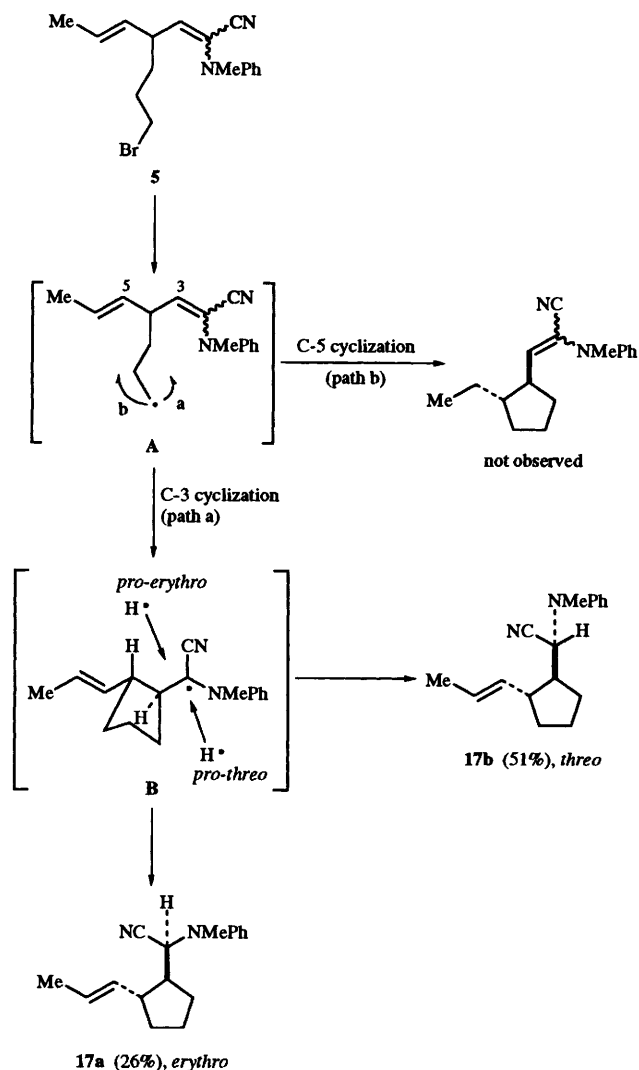
^a The reaction was carried out in the presence of 1.2 equiv. of AIBN.

stereoisomers **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).

The intramolecular radical cyclisations of other dienitriles, 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 dimethylacetone 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 dienitrile **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	$\delta_{2\text{-H}}$	$\delta_{\text{C-2}}$	More polar isomer	$\delta_{2\text{-H}}$	$\delta_{\text{C-2}}$
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 (<i>Z</i>)	4.56	57.4	24b (<i>Z</i>)	4.77	58.1
25a	4.29	58.1	25b	4.47	59.0
26a (<i>E</i>)	4.37	57.9	26b (<i>E</i>)	4.42	59.1
26c (<i>Z</i>)	4.39	58.0	26d (<i>Z</i>)	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 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. 3c.

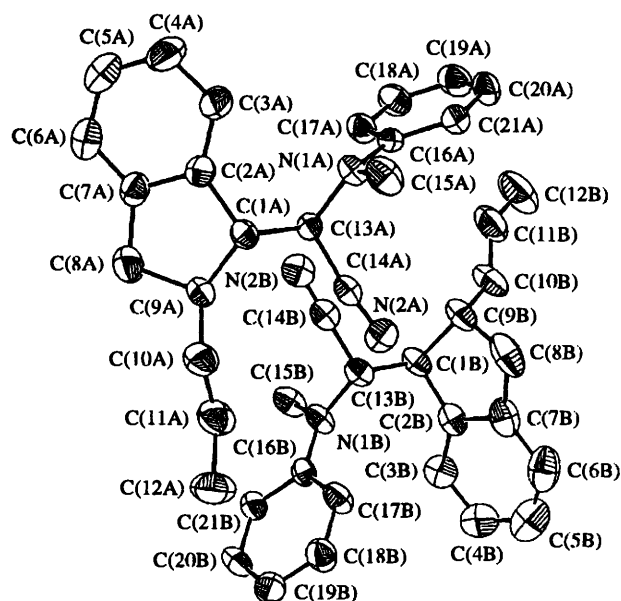


Fig. 1 ORTEP drawing of **21b**

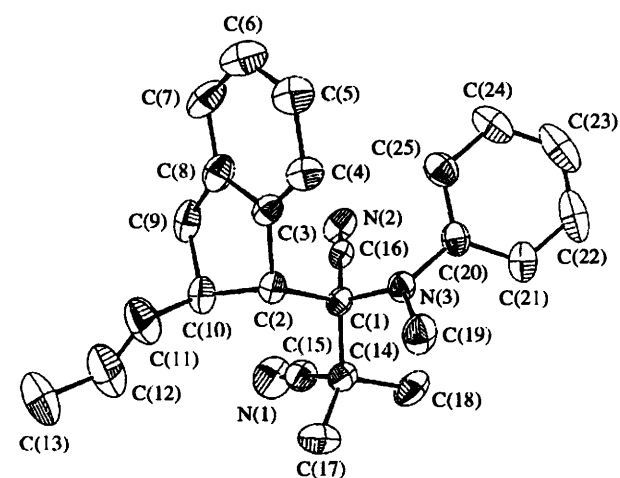


Fig. 2 ORTEP drawing of **22b**

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 recycled to the observed products **30**.

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

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

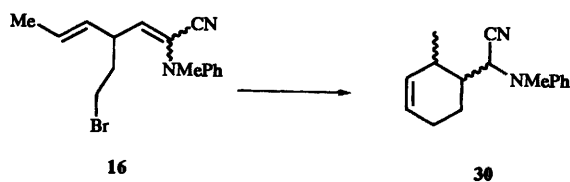
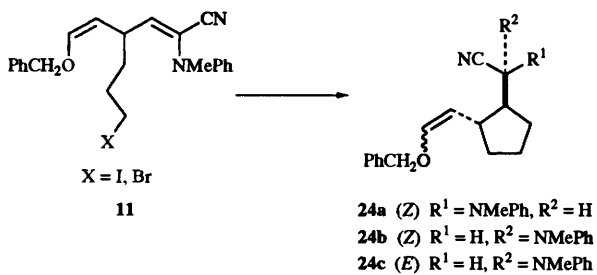
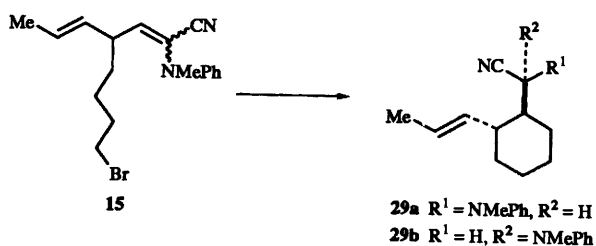
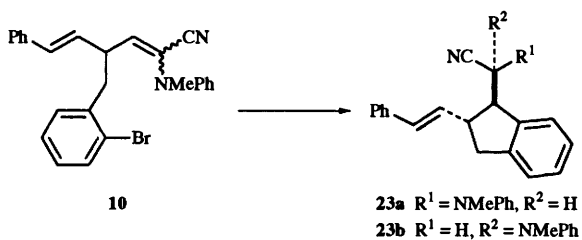
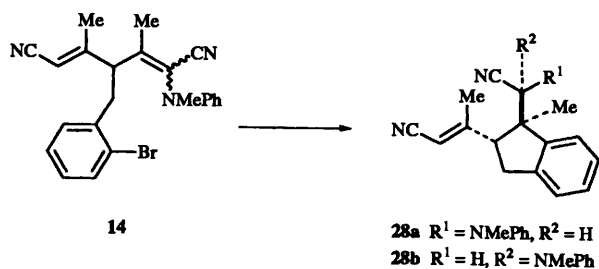
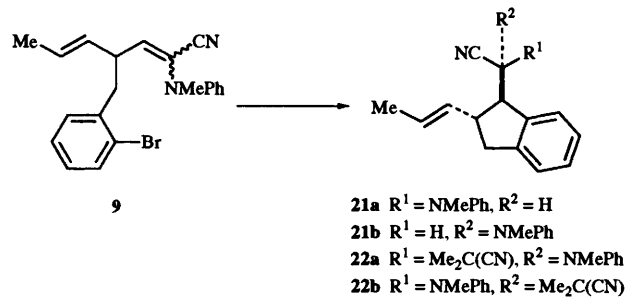
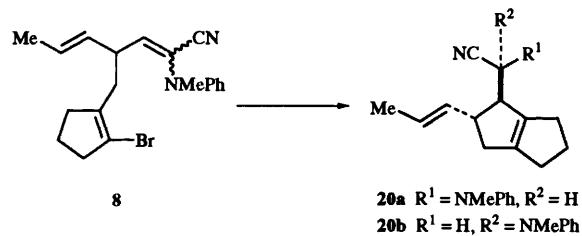
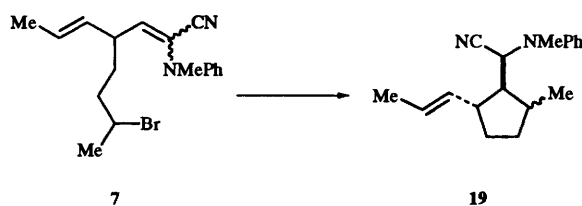
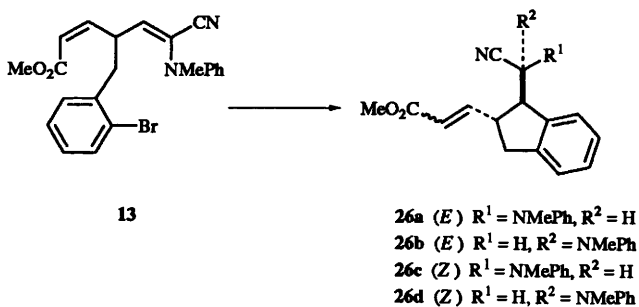
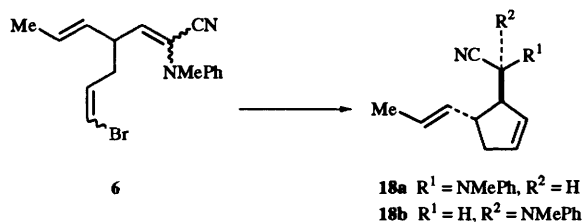
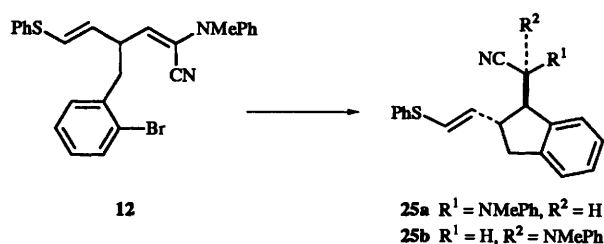
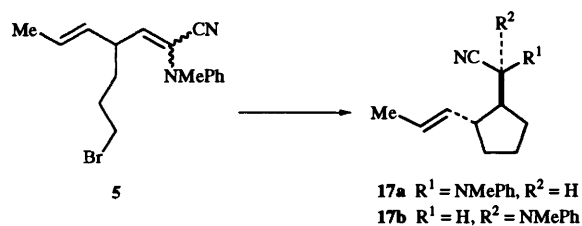
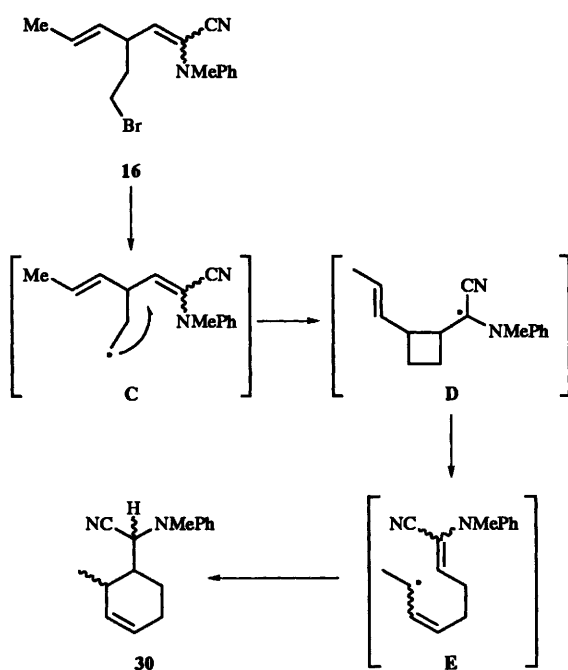


Table 3 Crystal data for (2*RS*,1'*RS*,2'*RS*)-2-(2,3-dihydro-2-prop-1-enyl-1*H*-indan-1-yl)-2-(*N*-methylanilino)acetonitrile **21b** and (2*RS*,1'*RS*,2'*RS*)-2-(2,3-dihydro-2-prop-1-enyl-1*H*-indan-1-yl)-3,3-dimethyl-2-(*N*-methylanilino)butane-1,4-dinitrile **22b**. The X-ray data were collected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

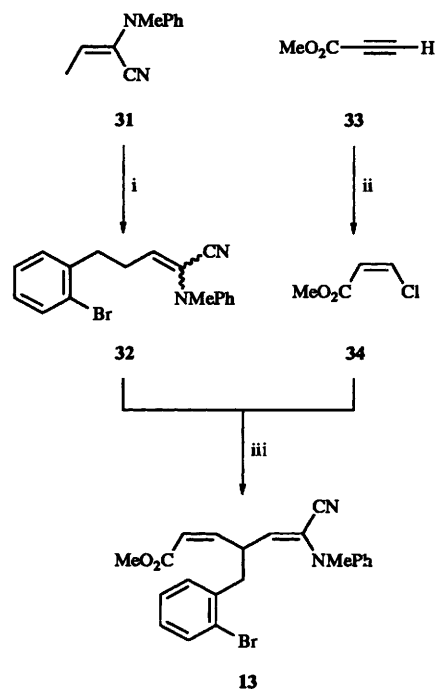
	21b	22b
Formula	C ₂₁ H ₂₂ N ₂	C ₂₅ H ₂₇ N ₃
Space group	<i>P</i> ₁	<i>P</i> _{21/c}
<i>a</i> /Å	11.013(3)	10.388(2)
<i>b</i> /Å	11.847(3)	20.755(5)
<i>c</i> /Å	14.212(3)	10.633(2)
α /°	87.68(2)	90
β /°	93.23(2)	109.76(1)
γ /°	106.16(2)	90
<i>V</i> /Å ³	1854.2(3)	2292.5(3)
Crystal size (mm)	0.3 × 0.2 × 0.1	0.4 × 0.2 × 0.1
<i>Z</i>	4	4
<i>T</i> /K	298	298
Radiation	Mo-K α (= 0.7107 Å)	Mo-K α (= 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 (> 2 σ)	1350 (> 2 σ)
<i>R</i>	0.054	0.052
<i>R</i> _w	0.056	0.054
<i>S</i>	2.12	2.02



Scheme 2 Reagents and conditions: Bu₃SnH, AIBN, PhH, 80 °C, 6 h

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 aminocyanopentadienyl anions.⁷ Compound **13** was prepared by condensation of 5-(2-bromophenyl)-2-(*N*-methylanilino)pent-2-enitrile **32** with methyl 3-chloroacrylate (Scheme 3). Acetylation of 3-methyl-2-(*N*-methylanilino)but-2-enitrile **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-

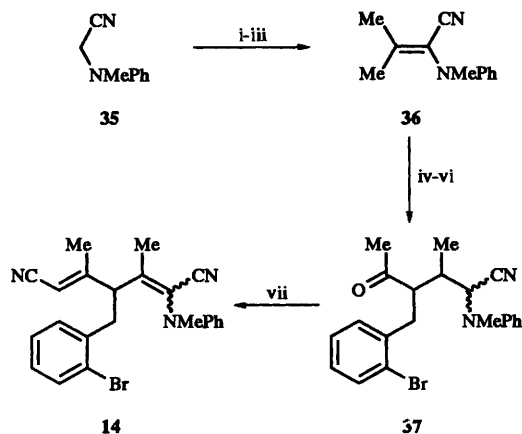


Scheme 3 Reagents and conditions: i, LDA, THF, HMPA; *o*-BrC₆H₄CH₂Br, -78 °C to 25 °C; ii, conc. HCl, CuCl cat.; MeOH, H₂SO₄; iii, LDA, THF, -78 °C; 77%

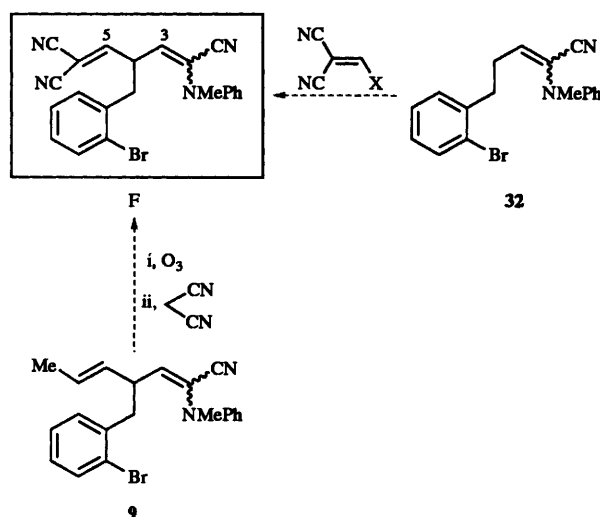
double bond, giving *N*-methyl-*N*-phenylcyanoformamide, instead of the desired cleavage at the 5,6-double bond. Treatment of **32** with chloromethylenemalononitrile or phenylsulfanylmethylenemalononitrile in varied bases LDA–THF, LHMDS–THF or Bu^tOK–Bu^tOH gave, respectively, diisopropylaminomethylenemalononitrile, 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; Me₂CO, -78 °C; ii, Ac₂O, pyridine, CH₂Cl₂; iii, Bu^tOK, THF, -78 °C; 71%; iv, LDA, THF; Ac₂O; v, MeONa, MeOH, 25 °C, 10 min; vi, LDA, THF, HMPA; *o*-BrC₆H₄CH₂Br, -78 °C to 25 °C; 47%; vii, NCCH₂P(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 ¹³C 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 SiO₂ (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 μ m) column (25 \times 1 cm) with the indicated

§ 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. 8a. For reductive decyanation and alkylative decyanation of α -amino nitriles to amines, see ref. 8b. For oxidative conversion of α -amino nitriles to amides, see refs. 8c and 8d.

eluent with a 5 cm³ min⁻¹ flow rate. Benzene and THF were distilled from sodium benzophenone ketyl under N₂. 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 cm³) of 5-(2-bromophenyl)-2-(*N*-methylanilino)pent-2-enenitrile **32** (300 mg, 0.88 cm³) was added dropwise to a cold (-78 °C) LDA solution prepared from BuLi (1.6 mol dm⁻³ hexane solution; 0.6 cm³) and a THF solution (10 cm³) of diisopropylamine (0.15 cm³, 0.95 mmol). The orange solution was stirred at -78 °C for 45 min, after which a THF solution (5 cm³) of methyl 3-chloroacrylate⁸ (130 mg, 1.1 mmol) was added to it; the colour faded immediately and the mixture was warmed to 25 °C. Saturated aqueous NH₄Cl was added to the mixture and the THF was removed under reduced pressure. The residue was extracted with EtOAc (6 cm³ \times 5) and the combined extracts were washed with brine, dried (Na₂SO₄), 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); δ_{H} (CDCl₃) 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); δ_{C} (CDCl₃) 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 C₂₂H₂₁⁸¹BrN₂O₂: *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 cm³) 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⁻³ hexane solution; 3.6 cm³) and a THF solution (10 cm³) of diisopropylamine (0.90 cm³, 6.9 mmol). The orange solution was stirred for 45 min after which acetic anhydride (0.72 cm³, 7.1 mmol) was added to it and the mixture was warmed to 25 °C. Saturated aqueous NH₄Cl was added to the mixture from which THF was removed under reduced pressure. The residue was extracted with EtOAc (5 cm³ \times 4) and the combined extracts were washed with brine, dried (Na₂SO₄), 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 cm³) at 25 °C for 10 min to give 3-methyl-2-(*N*-methylanilino)-5-oxohex-2-enenitrile (650 mg, 86%).

A THF solution (5 cm³) 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⁻³ hexane solution; 1.2 cm³) and a THF solution (10 cm³) of diisopropylamine (0.34 cm³, 2.0 mmol). The brown solution was stirred for 45 min after which a THF solution (5 cm³) of 2-bromobenzyl bromide (500 mg, 2.0 mmol) was added dropwise to it; the mixture was then warmed to 25 °C. Saturated aqueous NH₄Cl was added to the mixture from which THF was removed

under reduced pressure. The residue was extracted with EtOAc (5 cm³ × 4) and the combined extracts were washed with brine, dried (Na₂SO₄), 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 cm³) of NaH (dispersed in 60% mineral oil; 30 mg, 1.1 mmol) was added diethyl cyanomethylphosphonate (0.13 cm³, 0.8 mmol). The mixture was stirred for 45 min after which, a THF solution (5 cm³) 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 NH₄Cl was added to the mixture from which THF was removed under reduced pressure. The residue was extracted with EtOAc (6 cm³ × 5) and the combined extracts were washed with brine, dried (Na₂SO₄), filtered and concentrated. Chromatography of the residue on a silica-gel column with EtOAc–hexane (10:90) as eluent gave (*2E,5E*)-**14** (100 mg, 41%) and (*2Z,5E*)-**14** (100 mg, 41%) accompanied by recovery of **37** (56 mg).

(*2E,5E*)-**14**: white solid, mp 131–133 °C; TLC [EtOAc–hexane (10:90)] *R*_F 0.11; *v*_{max}(KBr)/cm^{–1} 2218 (CN); δ_{H} (CDCl₃) 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} (CDCl₃) 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 ⁷⁹Br) and 250 (100). (*2Z,5E*)-**14**: yellow oil; TLC [EtOAc–hexane (10:90)] *R*_F 0.10; *v*_{max}(neat)/cm^{–1} 2249 and 2217; δ_{H} (CDCl₃) 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} (CDCl₃) 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 C₂₃H₂₂⁷⁹BrN₃: *M*, 419.0998).

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

Compound **5** [a mixture of (*2E,5E*)- and (*2Z,5E*)-isomers (40:60), 200 mg, 0.60 mmol] in deoxygenated anhydrous benzene (15 cm³) was heated to reflux under an atmosphere of N₂. A mixture of Bu₃SnH (0.20 cm³, 0.72 mmol) and AIBN (20 mg, 0.12 mmol) in benzene (15 cm³) was added drop-by-drop at a rate of 0.1 cm³ 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 cm³ and then treated with a small amount of Et₃N (0.5 cm³) 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; *v*_{max}(KBr)/cm^{–1} 2214 (CN); δ_{H} (CDCl₃) 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} (CDCl₃) 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 C₁₇H₂₂N₂: *M*, 254.1783). **17b**: White solid, mp 107–109 °C; TLC [EtOAc–hexane (2:98)] *R*_F 0.08; *v*_{max}(KBr)/cm^{–1} 2225 (CN); δ_{H} (CDCl₃) 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} (CDCl₃) 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 *2E*- and *2Z*-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; *v*_{max}(neat)/cm^{–1} 2222 (CN); δ_{H} (CDCl₃) 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} (CDCl₃) 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; *v*_{max}(neat)/cm^{–1} 2232 (CN); δ_{H} (CDCl₃) 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} (CDCl₃) 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 C₁₇H₂₀N₂: *M*, 252.1626).

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

The free-radical cyclisation of **7** [a mixture of *2E*- and *2Z*-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; *v*_{max}(neat)/cm^{–1} 2225 (CN); δ_{H} (CDCl₃) 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} (CDCl₃) 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; *v*_{max}(neat)/cm^{–1} 2225 (CN); δ_{H} (CDCl₃) 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} (CDCl₃) 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 C₁₈H₂₄N₂: *M*, 268.1939). **19d**: Yellow oil; TLC [EtOAc–hexane (2:98)] *R*_F 0.07; *v*_{max}(neat)/cm^{–1} 2225

(CN); $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 (*2E*)- and (*2Z*)-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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2223 (CN); $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2231 (CN); $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{20}\text{H}_{24}\text{N}_2$: *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 (*2E*)- and (*2Z*)-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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2225 (CN); $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2225 (CN); $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{21}\text{H}_{22}\text{N}_2$: *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; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2230 (CN); $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{25}\text{H}_{27}\text{N}_3$: *M*, 369.2205). **22b**: White solid, mp 146–148 °C; TLC [EtOAc–hexane (5:95)] R_{F} 0.10; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2250 and 2230; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 (*2E*,*5E*)- and (*2Z*,*5E*)-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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2225; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{26}\text{H}_{24}\text{N}_2$: *M*, 364.1939). **23b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_{F} 0.10; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2234; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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** [(*2Z*,*5Z*)-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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2221; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}$: *M*, 346.2045). **24b** (*Z*-configuration): Yellow oil; TLC [EtOAc–hexane (5:95)] R_{F} 0.12; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2224; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2205; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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)-1H-indan-1-yl)-2-(*N*-methylanilino)acetonitrile 25

The free-radical cyclisation of **12** (*2E,5E*-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; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2234; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{26}\text{H}_{24}\text{N}_2\text{S}$: *M*, 396.1660). **25b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_{F} 0.10; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2215; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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** (*2E,5Z*-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, *2E*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_{F} 0.21; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2234 (CN), 1719 (CO) and 1641; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$: *M*, 346.1681). **26c** (*2Z*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_{F} 0.13; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2224, 1721 (CO) and 1653; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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%, $[\text{M} + 2]^+$), 346 (40, M^+), 320 (35), 272 (30), 201 (34), 169 (28), 145 (100), 141 (40), 115 (20) and 77 (24). **26d** (*2Z*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_{F} 0.11; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2234, 1721 and 1656; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 (*2E*-configuration): Yellow oil; TLC [EtOAc–hexane (10:90)] R_{F} 0.14; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2227 (CN), 1734 (CO) and 1597; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$: *M*, 346.1681).

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

The free-radical cyclisation of **14** [a mixture of (*2E,5E*)- and (*2Z,5E*)-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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2215; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2214 (CN); $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{23}\text{H}_{23}\text{N}_3$: *M*, 341.1892).

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

The free-radical cyclisation of **15** [a mixture of (*2E,5E*)- and (*2Z,5E*)-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; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2224; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2223; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{18}\text{H}_{24}\text{N}_2$: M , 268.1939).

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

The free-radical cyclisation of **16** [a mixture of (*2E,5E*)- and (*2Z,5E*)-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; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2212; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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 $\text{C}_{16}\text{H}_{20}\text{N}_2$: M , 240.1626). **30b**: Yellow oil; TLC [EtOAc–hexane (2:98)] R_F 0.07; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2224; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2225; $\delta_{\text{H}}(\text{CDCl}_3)$ 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); $\delta_{\text{C}}(\text{CDCl}_3)$ 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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