Intramolecular [3 + 2]Cycloadditions: Synthesis of 1-Methylene-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indenes and an unsuccessful approach to Ergot Alkaloids

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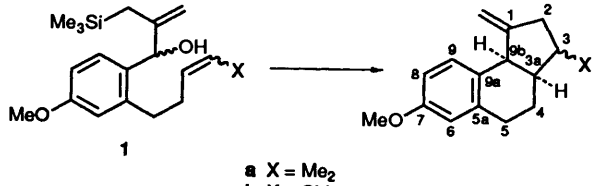
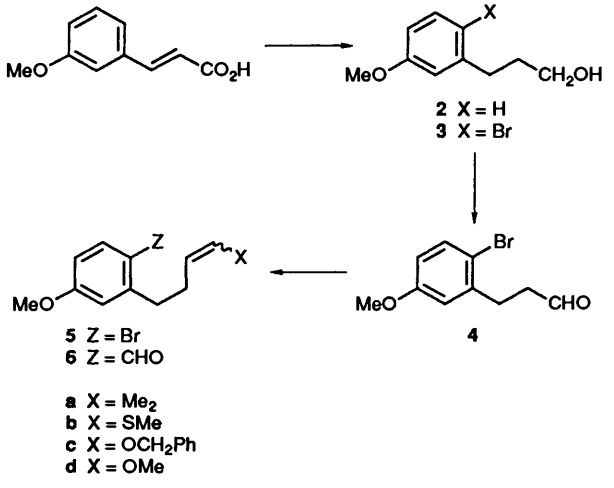
1-(1-Hydroxy-2-trimethylsilylmethylprop-2-enyl)-2-(4-substituted-but-3-enyl)-4-methoxybenzenes, prepared by a short synthesis, underwent intramolecular [3 + 2]cycloadditions to produce the title indenes. An analogous intramolecular cycloaddition was attempted with *N*-benzyl-4-(2-methoxyvinyl)-3-(2-hydroxy-3-trimethylsilylmethylbut-3-enyl)indoline, in an attempt to produce a key intermediate for ergot alkaloid synthesis, but this was unsuccessful.

Intermolecular cycloadditions involving allyl cations [1] and oxyallyl cations [2] have been widely employed in synthesis, but there are few examples known of their intramolecular versions.[3] We have previously reported our initial studies of intramolecular [3 + 2]cycloadditions of the type shown in Scheme 1,[4] and in this paper we provide full experimental details of these experiments, together with new results.



Scheme 1

The various substrates **1**, were prepared *via* the route shown in Scheme 2. Thus 3-methoxycinnamic acid was reduced to 3-(3-methoxyphenyl)propanol **2**, which was brominated and the



Scheme 2

bromide **3** was then oxidised to yield 3-(2-bromo-5-methoxyphenyl)propanal **4** in an overall yield of around 34%. Wittig reactions were carried out with a variety of ylides to provide the alkenes **5** (see Schemes 1 and 2) as a mixture of *E*- and *Z*-isomers (except for compound **5a**) in yields of 30–75%. These were used without further purification for the formation of the aldehydes **6**. These formylations proceeded in good yield (62–75%), as did

Table 1

Substrate	*Z*/*E* Ratio	Cycloadduct ratio	Total yield (%)
1a	—	**14**	62
1b	2:3	**15**	40–50
1c	3:7	**16**:**17** (5:1)	30
1d	1:3	**18**:**19** (3:1)	86
1d	*E* only	**18**:**19** (3:1)	81
1d	1:1	**18**:**19** (3:1)	44

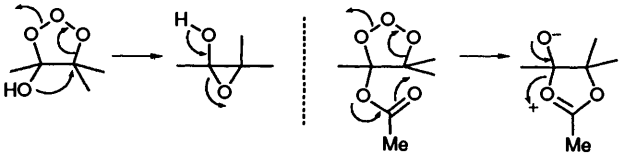
the Grignard reactions with 2-bromomagnesioallyl(trimethyl)-silane (all in the 70–85% region except for the thioenol ether **6b**, for which the yield was 24%) to produce the desired cycloaddition substrates **1**.

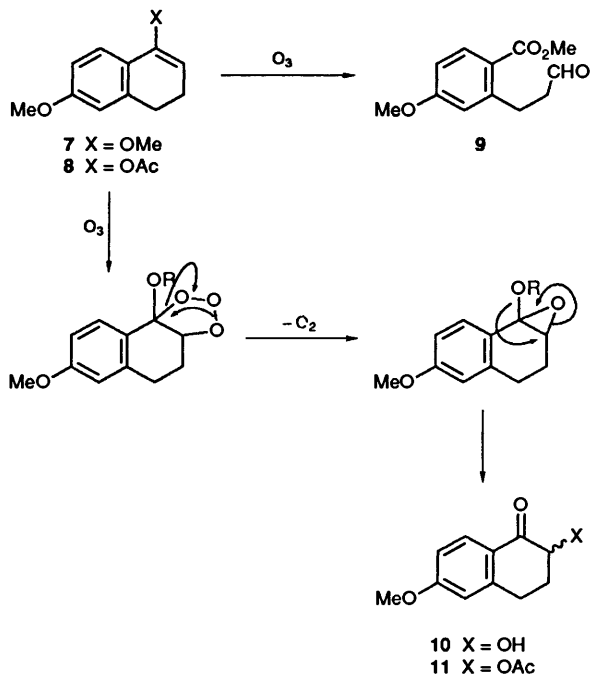
This successful six-stage synthesis was not achieved without a considerable amount of frustration, and an alternative strategy involving ozonolysis of the enol ether **7** and enol acetate **8** of 6-methoxy-1-tetralone provided interesting though non-usable products. Thus ozonolysis of **7** yielded both the expected ester aldehyde **9** and the hydroxy ketone **10** (in yields of 15 and 18% respectively). Whilst ozonolysis of **8** yielded exclusively the acetoxy ketone **11** (*ca.* 40%). Compounds **10** and **11** are presumably produced *via* rearrangement of the type shown in Scheme 3.*

The cycloadditions were carried out using a mixture of titanium tetrachloride (1 mol dm^{-3} in CH_2Cl_2) and *N*-methylaniline at −78 °C, and the results of the various reactions are shown in Table 1. Although these cycloadditions cannot be concerted, each of the substrates **1** can be converted into a relatively stable carbocationic intermediate. In particular, the probable intermediates from **1a** and **1d**, *viz.* **12** and **13**, are likely to be particularly stable, and perhaps, not surprisingly, the yields of cycloadducts in these two cases were particularly good (62 and 85%, respectively).

Of greater interest was the stereochemistry of the products. For the simplest cycloadduct **14**, the stereochemistry at the junction between the B and C rings was clearly *cis* as evidenced by the NOE enhancement of 3.7% between the two bridgehead

* A referee has commented: 'The favourable five-membered intermediate for the acetate may explain why the rearrangement is favoured in this case.'





Scheme 3

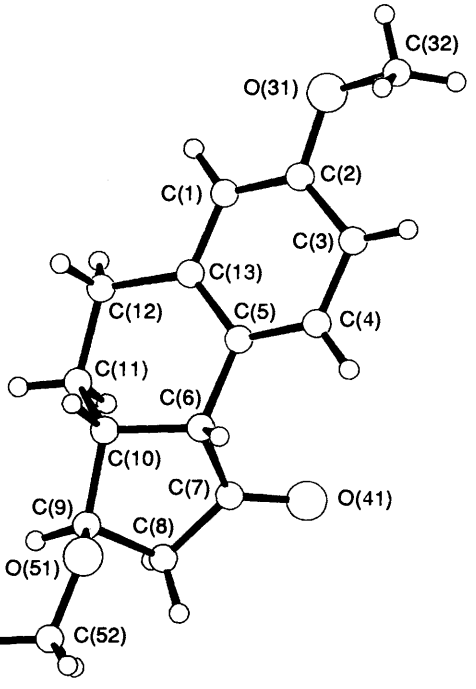
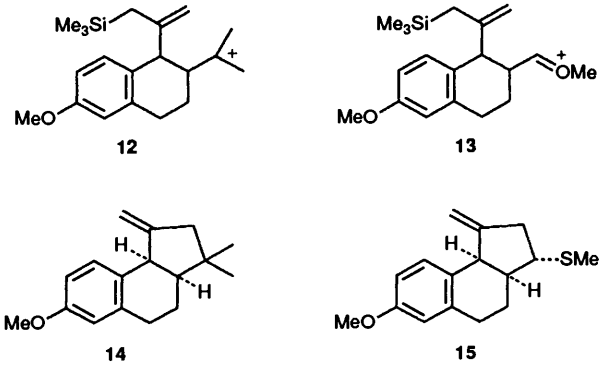
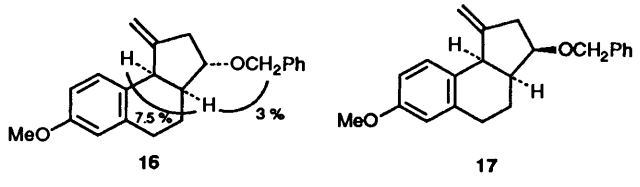


Fig. 1 ORTEP representation of compound **20**



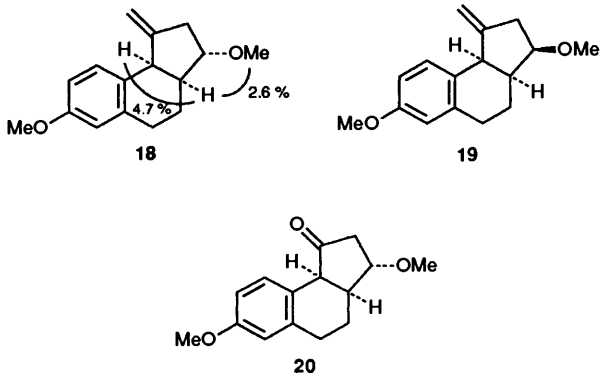
hydrogens. The cycloadduct **15** was the sole product obtained from the precursor **1b**, which was a mixture of *E* and *Z*-thioenol ethers in the ratio of 3:2. Once again NMR spectral studies suggested that the stereochemistry was as shown (all *syn*), since there was a 7.7% NOE enhancement between the bridgehead hydrogens and zero enhancement between the benzylic hydrogen (9b-H) and the hydrogen α to the thiomethyl group (3-H). In addition the *J* value of 7.4 Hz for the coupling between the bridgehead hydrogens was also consistent with the estimated dihedral angle of 0°.

The two cycloadducts formed from precursor **1c** have been assigned the structures **16** and **17** (ratio 5:1). The major, all *syn*



isomer, exhibited NOE enhancements as shown. The minor, *syn, anti* isomer (putative structure only) exhibited a resonance for the hydrogen α to the benzyloxymethyl group (3-H) that was 0.4 ppm more deshielded than the corresponding hydrogen in cycloadduct **16**, as expected for an equatorial hydrogen.

Finally, the cycloaddition studies with precursor **1d** were the most extensive, and used not only mixtures of enol ether isomers (*E*:*Z* of 3:1 and 1:1), but also the pure *E*-isomer, isolated following preparative HPLC. In each instance the major cycloadduct was always the all-*syn* product **18** rather than the *syn, anti* product **19** (ratios 3–5:1). As before, the structural assignments were made on the basis of NOE measurements (shown



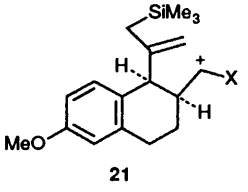
for structure **18**), with evidence for the *cis*-relationship of the bridgehead hydrogens provided by a *J* value of 6 Hz (dihedral angle of 0°). Final proof for the structure of **18** was provided by an X-ray crystallographic investigation carried out on the ketone **20**, obtained by ozonolysis of **18**. The ORTEP representation is shown in the Fig. 1, and non-hydrogen atom coordinates are provided in Table 2.

The stereoselectivity observed in these cycloadditions probably reflects the different stabilities of the possible cycloadducts arising from common intermediates of general structure **21**. Encouraged by the relative efficiency and stereoselectivity of this intramolecular cycloaddition, we turned our attention to a more demanding target: the ring system of the ergot alkaloids. Our retrosynthetic analysis is shown in Scheme 4.

The key 3,4-disubstituted indole **22** was prepared according to the methods of Kozikowski[5] and Oppolzer[6] with certain minor modifications, and the overall route is shown in Scheme

Table 2 Atomic coordinates ($\times 10^4$) (esds)

Atom	*x*	*y*	*z*
C(1)	4466(18)	−221(12)	3892(5)
C(2)	2885(20)	492(13)	3933(5)
C(3)	1845(17)	1174(13)	3358(5)
C(4)	2668(19)	1071(14)	2741(5)
C(5)	4294(17)	368(10)	2709(5)
C(6)	5204(17)	465(12)	2053(5)
C(7)	4504(22)	−394(12)	1467(6)
C(8)	5962(18)	−823(15)	1045(6)
C(9)	7715(23)	−99(14)	1411(6)
C(10)	7289(20)	48(13)	2150(5)
C(11)	7699(18)	−1327(13)	2562(5)
C(12)	7157(19)	−1080(14)	3281(6)
C(13)	5266(17)	−289(11)	3291(5)
O(31)	2256(12)	574(10)	4575(4)
C(32)	827(20)	1603(15)	4659(7)
O(41)	2776(18)	−737(10)	1327(4)
O(51)	7975(14)	1347(11)	1172(4)
C(52)	8773(23)	1447(22)	555(7)



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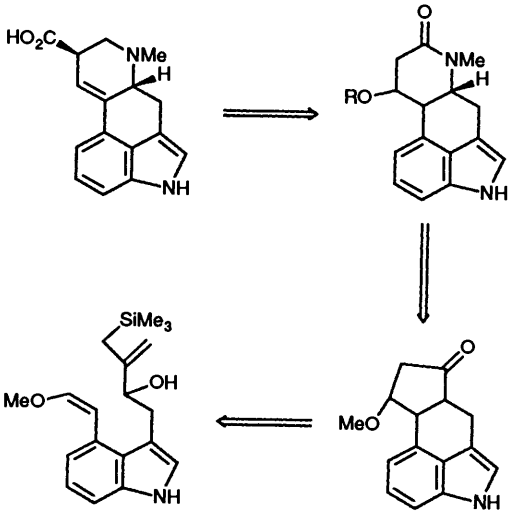
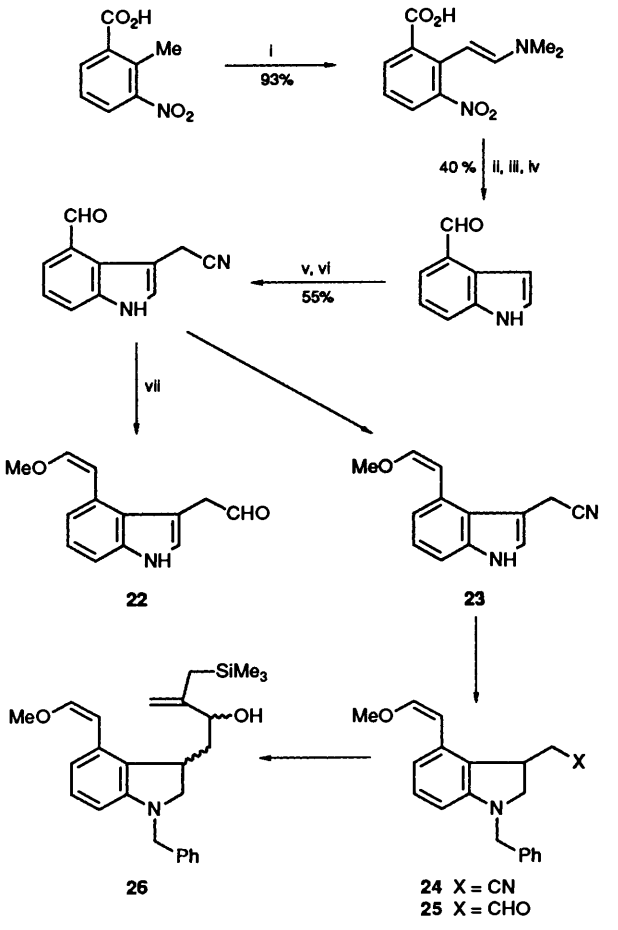


Scheme 4

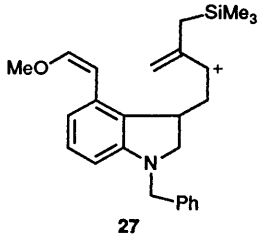
5. Reaction of compound **22** with 2-bromomagnesioallyl(trimethyl)silane at temperatures ranging from −78 °C to room temperature led to complete consumption of the aldehyde and an intractable mixture of products. Reasoning that the Grignard product was unstable by virtue of its hydroxy β to the indole ring, we synthesised the indoline **24** *via* reduction (with sodium cyanoborohydride) of the nitrile **23** and *N*-benzylation. Reaction of this compound with diisobutylaluminium hydride (DIBAL) yielded the aldehyde **25**, which reacted with the usual Grignard reagent to provide the desired substrate for cycloaddition **26** as a mixture of isomers (13% overall from nitrile **23**).

Attempted cycloadditions initiated by titanium tetrachloride, trimethylsilyl triflate, ethylaluminium dichloride, and tetrakis(triphenylphosphine)palladium(0), all led to a slow consumption of the substrate **26**, but provided no identifiable products. The failure of these reactions may possibly be ascribed to the relative



Scheme 5 *Reagents and conditions:* i, $Me_2NCH(OMe_2)$, DMF, 130 °C; ii, H_2/Pd; iii, DIBAL, DCM; iv, MnO_2, DCM; v, Me_2NH–HCHO; vi, KCN–MeI, Me_2CHOH; vii, DIBAL, DCM

non-rigidity of the system, thus denying access to a transition state favourable for intramolecular cycloaddition, or more probably due to the instability of the intermediate allyl cation **27**. In order to address this problem we are in the process of preparing the alternative substrate **28**, which should give rise to a more stable intermediate, and these results will be described in due course.



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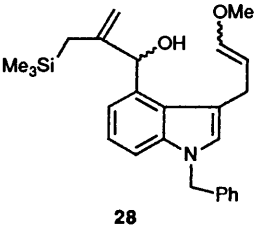

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Experimental

General experimental details are given in ref. 7.

3-(3-*Methoxyphenyl*)*propan*-1-*ol* **2**.—A suspension of 3-methoxycinnamic acid (13.35 g, 0.075 mol) in diethyl ether (200 cm^3) was added dropwise with vigorous stirring to a suspension of lithium aluminium hydride (5.5 g, 0.15 mol) in diethyl ether (100 cm^3) at 0 °C under nitrogen. The mixture was allowed to warm to room temp. and stirred overnight. After addition of water (5.5 cm^3), aqueous sodium hydroxide (15%; 5.5 cm^3) and further water (16 cm^3), the resulting solid was filtered off and washed

successively with ether, methanol, and water. The combined washings were concentrated to remove organic solvents and then extracted with ether. This ethereal extract was dried, concentrated and the title alcohol isolated following flash chromatography (ether–light petroleum, 3:2) as a colourless oil (7.78 g, 63%); $\nu_{max}(CDCl_3)/cm^{-1}$ 3350 (OH), 3000, 2940, 1600, 1260 and 1150; δ_H(60 MHz, $CDCl_3$) 1.8 (m, 2 H, 2-H), 2.8 (t, 2 H, 3-H), 3.65 (t, 2 H, 1-H), 3.9 (s, 3 H, OMe) and 6.6–7.4 (m, 4 H, ArH) (Found: M^+, 166.0994. $C_{10}H_{14}O_2$ requires *M*, 166.0994).

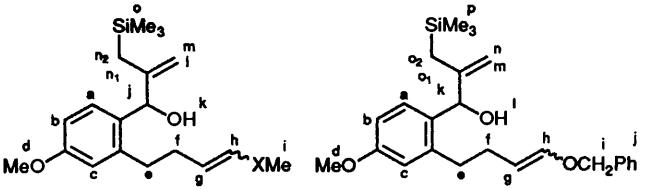
3-(2′-*Bromo*-5′-*methoxyphenyl*)*propan*-1-*ol* **3**.—Bromine (7.4 g, 2.4 cm^3, 0.046 mol) in chloroform (25 cm^3) was added dropwise to a vigorously stirred solution of the alcohol **2** (7.24 g, 0.042 mol) in chloroform (75 cm^3) at 0 °C. The reaction was followed by thin layer chromatography (TLC) (the reaction was usually complete after 4–5 h) and worked-up by the addition of aqueous sodium metabisulfite, with extraction of the products into dichloromethane (DCM). Chromatography (ether–light petroleum, 3:2) provided the title bromide **3** as a golden oil (7.0 g, 66%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3350 (OH), 2950, 2880, 1600, 1480, 1280 and 1250 ; δ_H(220 MHz, $CDCl_3$) 1.45 (br s, 1 H, OH), 1.9 (m, 2 H, 2-H), 2.8 (m, 2 H, 3-H), 3.75 (t, 2 H, *J* 6.5, 1-H), 3.8 (s, 3 H, OMe), 6.65 (dd, 1 H, *J* 2.2, 8.8, 4-H), 6.8 (d, 1 H, *J* 2.2, 6′-H) and 7.4 (d, 1 H, *J* 8.8, 3′-H) (Found: M^+, 244.0094. $C_{10}H_{13}BrO_2$ requires *M*, 244.0098).

3-(2′-*Bromo*-5′-*methoxyphenyl*)*propanal* **4**.—The bromo alcohol **3** (2.25 g, 9.2 mmol) in DCM (15 cm^3) was added dropwise to pyridinium chlorochromate (3.1 g, 0.014 mol) in DCM (40 cm^3) containing 4A sieves. After 3 h, the mixture was diluted with ether (40 cm^3), and filtered through a silica column. The solvent was evaporated and the product **4** (1.85 g, *ca.* 80%) used without further purification. For spectroscopic purposes, a sample was purified by silica chromatography (ether–light petroleum, 3:2 as eluent); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 2950, 2850, 2730, 1730 (C=O), 1600, 1470 and 1250; $\delta_H(CDCl_3)$ 2.8 (t, 2 H, *J* 8.6, 2-H), 3.05 (t, 2 H, *J* 8.6, 3-H), 3.8 (s, 3 H, OMe), 6.65 (dd, 1 H, *J* 4, 8.8, 4′-H), 6.8 (d, 1 H, *J* 4, 6′-H), 7.4 (d, 1 H, *J* 8.8, 3′-H) and 9.8 (br s, CHO) (Found: M^+, 241.9942. $C_{10}H_{11}BrO_2$ requires *M*, 241.9942).

5-(2′-*Bromo*-5′-*methoxyphenyl*)-2-*methylpent*-2-*ene* **5a**.—Butyllithium (1.6 mol dm^{-3} in THF; 20.3 cm^3, 32 mmol) was added dropwise to a solution of isopropyltriphenylphosphonium iodide (19.4 g, 0.048 mol, previously dried *in vacuo* at 40 °C) in THF (150 cm^3) at −78 °C under an atmosphere of nitrogen. After 1.5 h the mixture was warmed to room temp. and stirred at that temperature for a further 1.5 h. The solution was cooled to −78 °C prior to the addition of the bromo aldehyde **4** (7.8 g, 32 mmol) in tetrahydrofuran (THF) (30 cm^3). After 0.5 h, the reaction mixture was warmed to room temp. and stirred for a further 3 h at that temperature. After addition of water, the products were extracted into ether, and purification effected by silica chromatography (light petroleum as eluent) to yield compound **5a** (2.94 g, 34%) as a colourless oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 2929, 2858, 1595, 1571, 1471, 1278 and 1240; δ_H(220 MHz, $CDCl_3$) 1.6 and 1.7 (2 s, 6 H, 2 × Me), 2.3 (m, 2 H, 4-H), 2.7 (t, 2 H, *J* 8.6, 5-H), 3.8 (s, 3 H, OMe), 5.2 (m, 1 H, 3-H), 6.6 (dd, 1 H, *J* 4, 8.8, 4′-H), 6.75 (d, 1 H, *J* 4, 6′-H), 7.4 (d, 1 H, *J* 8.8, 3′-H); *m*/*z* 270 (M^+).

5-(2′-*Formyl*-5′-*methoxyphenyl*)-2-*methylpent*-2-*ene* **6a**.—Butyllithium (1.6 mol dm^{-3} in hexane; 3.4 cm^3, 5.4 mmol) was added dropwise to the bromide **5a** (1.33 g, 5 mmol) in THF (20 cm^3) at −78 °C under an atmosphere of nitrogen. After 2 h *N*,*N*-dimethylformamide (DMF) (0.75 g, 0.76 cm^3, 0.01 mol) was added, and the reaction mixture stirred for a further 2 h. Ether was added followed by HCl (2 mol dm^{-3}; 5 cm^3), and the mixture allowed to warm to room temp. After partition of the mixture between ether and brine, the organic phase was isolated, and the products purified by silica chromatography (ether–light petroleum, 1:9 as eluent) to yield the desired aldehyde **6a** (0.75 g, 70%) as a colourless oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2927, 2855, 2724, 1689 (C=O), 1600, 1566, 1496, 1287 and 1250; δ_H(220 MHz, $CDCl_3$) 1.5 and 1.7 (2 s, 6 H, 2 × Me), 2.34 (m, 2 H, 4-H), 3.05 (t, 2 H, *J* 8.5, 5-H), 3.9 (s, 3 H, OMe), 5.2 (m, 1 H, 3-H), 6.78 (d, 1 H, *J* 4, 6′-H), 6.85 (dd, 1 H, *J* 8.8, 4, 4′-H), 7.8 (d, 1 H, *J* 8.8, 3′-H), 10.1 (s, 1 H, CHO) (Found: M^+, 218.1298. $C_{14}H_{18}O_2$ requires *M*, 218.1306).

1-(1-*Hydroxy*-2-*trimethylsilylmethylprop*-2-*enyl*)-4-*methoxy*-2-(4-*methylpent*-3-*enyl*)*benzene* **1a**.—2-Bromoallyltrimethylsilane (0.52 g, 0.46 cm^3, 2.6 mmol) in THF (0.5 cm^3) was added to magnesium turnings (0.068 g, 3 mmol) in THF (1 cm^3) under an atmosphere of nitrogen. Further THF (2 cm^3) was added once the reaction started, and after 2 h, a solution of the aldehyde **6a** (0.44 g, 1.8 mmol) in THF (2 cm^3) was added. The mixture was stirred for 3 h at room temp., prior to the addition of saturated aqueous ammonium chloride, and the products were extracted into ether. Silica chromatography (ether–light petroleum, 1:9 as eluent) provided the expected product **1a** (0.47 g, 87%) as a colourless oil (mixture of epimers); $\nu_{max}(CHCl_3)/cm^{-1}$ 3590 (OH), 2957, 1636, 1607, 1577, 1496, 1464, 1248 and 854 (Si–C); δ_H(200 MHz, $CDCl_3$) 0.04, s, 9 H, $SiMe_3$), 1.1–1.35 and 1.55 (2 m, 2 H, $SiCH_2$), 1.55 and 1.7 (2 s, 6 H, 2 × Me), 2.3 (m, 2 H, 2-CH_2), 2.75 (t, *J* 8.5, 1-CH_2), 3.8 (s, 3 H, OMe), 4.9 and 5.2 (2 s, 2 H, =CH_2), 5.25 (m, 2 H, CHO and =CH), 6.75 (m, 2 H, 3-, 5-H), 7.3 (d, 1 H, *J* 8.5, 6-H) (Found: M^+, 332.2169. $C_{20}H_{32}O_2Si$ requires *M*, 332.2163).



1b and 1d **1c**

1-(1-*Hydroxy*-2-*trimethylsilylmethylprop*-2-*enyl*)-4-*methoxy*-2-(4-*methylthiobut*-3-*enyl*)*benzene* **1b**.—2-Bromoallyltrimethylsilane (0.28 g, 0.25 cm^3, 1.4 mmol, 1.5 equiv.) in THF (0.5 cm^3, dry) was added to magnesium turnings (0.037 g, 1 mmol, 1.2 equiv., oven dried) and a crystal of iodine, stirring in THF (0.5 cm^3, dry) under N_2. When the Grignard reagent began to form, THF (1 cm^3, dry) was added and the reaction mixture stirred for a further 2 h. The aldehyde **6b** (0.2 g, 8.4×10^{-4} mol) (prepared from **4** in an overall yield of 45% using methylthiomethyltriphenylphosphonium chloride) in THF (1 cm^3, dry) was added and the mixture stirred for a further 3 h. Saturated aqueous ammonium chloride was added, and the mixture was then partitioned between diethyl ether and brine. The aqueous phase was re-extracted with DCM, the combined organic phases dried ($MgSO_4$), and the solvent removed under reduced pressure. Purification by flash chromatography (silica Merck 9385, ether–light petroleum, 2:3) gave the title compound, a colourless oil (0.07 g, 24%), as an isomeric mixture (*Z*/*E*, 2:3); TLC (silica, ether–light petroleum, 2:3) R_f 0.71; $\nu_{max}(CHCl_3)/cm^{-1}$ 3597 (O–H), 2956, 2923, 2837, 1679, 1607, 1577, 1498, 1249 and 852 (Si–CH_3); δ_H(60 MHz, $CDCl_3$) 0.04 (s, 9 H, H_o), 1.2 (d, J_{ml} 14, 1 H, H_{n_2}), 1.6 (d, 1 H, J_{lm} 14, H_{n_1}), 2.2 (s, 3 H, H_i); 2.2–2.9 (m, 4 H, H_e, H_f), 3.8 (s, 3 H, H_d), 4.85 (s, 1 H, H_m), 5.15 (m, 2 H, H_l,H_j), 5.15–5.8 (m, 1 H, $H_{gcis,trans}$), 5.85–6.0 (d, J_{gh} 9, H_{hcis}), 5.9–6.12 (*d*, J_{gh} 15, H_{htrans}), 6.7 (m, 2 H, H_b, H_c) and 7.3 (d, 1 H, H_a); *m*/*z* (EI) 350 (M^+), 335 and 303.

2-(4-*Benzyloxybut*-3-*enyl*)-1-(1-*hydroxy*-2-*trimethylsilylmethylprop*-2-*enyl*)-4-*methoxybenzene* **1c**.—The allylic alcohol **1c** was prepared in 69% yield (*Z*:*E* ratio 3:7) from aldehyde **6c**, itself prepared from **4** in an overall yield of 50% using benzyloxymethyl(triphenyl)phosphonium chloride; $\nu_{max}(CHCl_3)/cm^{-1}$ 3587 (O–H), 1650 (C=C), 1606, 1247, 851 and 738; δ_H(250 MHz, $CDCl_3$) 0.05 (s, 9 H, H_p), 1.15, (dd, 1 H, 1 H, $J_{o_1o_2}$ 15, H_{o_2}), 1.55 [dd (obscured), 1 H, H_{o_1}], 1.7 (d, H_{ltrans}), 1.8 (d, H_{lcis}), 2.25 (m, H_{ftrans}), 2.45 (m, H_{fcis}), 2.75 (t, 2 H, H_e), 3.8 (s, 3 H, H_d), 4.45 (m, H_{gcis}), 4.65 (s, H_{itrans}), 4.7 (s, H_{icis}), 4.85 (s, 1 H, H_n), 4.9 (dt, J_{hg} 13, J_{fg} 8, H_{gtrans}), 5.1 (s, 1 H, H_m), 5.15 (m, 1 H, H_k), 6.0 (d, J_{gh} 6, H_{hcis}), 6.3 (d, J_{gh} 13, H_{htrans}), 6.7 (m, 2 H, H_b, H_c) and 7.3 (m, 6 H, H_j, H_a); *m*/*z* (EI) 410 (M^+).

1-(1-*Hydroxy*-2-*trimethylsilylmethylprop*-2-*enyl*)-4-*methoxy*-2-(4-*methoxybut*-3-*enyl*)*benzene* **1d**.—The allylic alcohol **1d** was prepared in 81% yield from aldehyde **6d**, itself prepared from **4** in an overall yield of 37% using methoxymethyl(triphenyl)-phosphonium chloride; $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 (O–H), 2955, 2832, 1653, 1606, 1575, 1499, 1464, 1247 and 852 (Si–CH_3); δ_H(250 MHz, $CDCl_3$) 0.03 (s, 9 H, H_o), 1.15 (d, $J_{n_2n_1}$ 15, 1 H, H_{n_1}), 1.55 (d, $J_{n_1n_2}$ 15, 1 H, H_{n_2}), 1.7 (d, J_{jk}, 4, 1 H, H_k), 2.2 (m, 2 H, H_f), 2.7 (m, 2 H, H_e), 3.5 (s, H_{itrans}), 3.55 (s, H_{icis}), 3.8 (s, 3 H, H_d), 4.4 (m, H_{gcis}), 4.75 [dt (obscured), J_{hg} 13, J_{fg} 7, H_{gtrans}], 4.875 (s, 1 H, H_m), 5.15 (s, 1 H, H_l), 5.2 (m, 1 H, H_j), 5.9 (dt, J_{gh} 7, J_{fh} 1, H_{hcis}), 6.35 (d, J_{gh} 13, H_{htrans}), 6.725 (s, 1 H, H_c), 6.75 [dd (obscured), 1 H, J_{ab} 7, J_{cb} 2, H_b], 7.32 (d, J_{ba} 7, 1 H, H_a) (Found: C, 68.3; H, 9.1. $C_{19}H_{30}O_3Si$ requires C, 68.23; H, 9.04%).

3,3-*Dimethyl*-1-*methylene*-2,3,3a,4,5,9b-*hexahydro*-1H-*benz*[e]*indene* **14**.—*N*-Methylaniline (0.26 g, 0.26 cm^3, 2.4 mmol) was added to a solution of $TiCl_4$ (1 mol dm^{-3} in DCM; 0.46 g, 2.4 cm^3, 2.4 mmol) in DCM (2 cm^3) at 0 °C under an atmosphere of nitrogen. After 0.5 h, the allylic alcohol **1a** (0.4 g, 1.2 mmol) in DCM (1 cm^3) was added at −20 °C, and the mixture was stirred at this temperature for 1 h. After addition of ether, the mixture was warmed to room temp. and washed sequentially with HCl (1 mol dm^{-3}) and brine. The organic phase was isolated and purified by silica chromatography (ether–light petroleum, 1:9 as eluent) to yield the indene **14** (0.16 g, 62%) as a colourless oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 2955, 2868, 2836, 1646, 1607, 1577, 1499, 1260 and 1245; δ_H(400 MHz, $CDCl_3$) 1.07 (s, 3 H, Me-β), 1.17 (s, 3 H, Me-α), 1.3 (m, 1 H, 4-H_β), 1.8 (m, 2 H, 4-H_α and 3a-H), 2.3 (s, 2 H, 2-CH_2), 2.7–2.8 (m, 2 H, 5-H), 3.78 (s, 3 H, OMe), 3.79 (m, 1 H, 9b-H), 4.7 and 4.87 (2 d, 2 H, *J* 2, =CH_2), 6.65 (d, 1 H, *J* 3, 6-H), 6.75 (dd, 1 H, *J* 3, 8.4, 8-H) and 7.1 (d, 1 H, *J* 8.4, 9-H); NOE enhancements, 3a-H to 9b-H (3.4%), 9b-H to 3a-H (3.7%), Me-α to 9b-H, and 3a-H to 4-H_α (7.4%) (Found: C, 84.6; H, 9.6. $C_{17}H_{22}O$ requires C, 84.25; H, 9.15%).

7-*Methoxy*-1-*methylene*-3-*methylthio*-2,3,3a,4,5,9b-*hexahydro*-1H-*benz*[e]*indene* **15**.—*N*-Methylaniline (0.1 g, 0.1 cm^3, 1 mmol) was added to a solution of titanium tetrachloride (1 mol dm^{-3} in DCM; 1 cm^3, 1 mmol) in DCM (2 cm^3) at 0 °C under an atmosphere of nitrogen. After 0.5 h, the allylic alcohol **1b** (0.17 g, 0.5 mmol) in DCM (0.5 cm^3) was added at −20 °C, and the reaction mixture stirred for 1 h at that temperature. After addition of ether, and sequential washing with HCl (1 mol dm^{-3}) and brine, the organic phase was separated, and the products purified by silica chromatography (ether:light petroleum 1:4 as eluent). One cycloadduct **15** (0.06 g, 47%) was obtained as a colourless oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3079, 2920, 2873, 1653, 1607, 1498, 1464, 1249 and 1231; δ_H(400 MHz, $CDCl_3$) 1.53–1.63 (m, 1 H, 4-H_β), 1.65–1.75 (m, 1 H, 4-H_α), 2.15 (s, 3 H, SMe), 2.3–2.4 (ddd, 1 H, *J* 14.3, 7.4, 3.9, 3a-H), 2.43–2.5 (br d, 1 H, 2-H_α), 2.7 (m, 2 H, 5-CH_2), 2.83–2.9 (ddd, 1 H, *J* 17, 8, 2, 2-H_β), 2.95–3.0 (m, 1 H, 3-H), 3.78 (s, 3 H, OMe), 3.8 (m, 1 H, 9a-H), 4.7 and 4.75 (2 d, 2 H, *J* 1.5, =CH_2), 6.65 (d, 1 H, *J* 2.7, 6-H), 6.73–6.76 (dd, 1 H, *J* 2.7, 8.4, 8-H) and 7.1–7.2 (d, 1 H, *J* 8.4, 9-H) (Found: C, 73.6; H, 7.6. $C_{16}H_{20}OS$ requires C, 73.80; H, 7.74%).

3-*Benzyloxy*-7-*methoxy*-1-*methylene*-2,3,3a,4,5,9b-*hexahydro*-1H-*benz*[e]*indenes* **16** *and* **17**.—*N*-Methylaniline (0.19 cm^3, 1.8 mmol) was added to a solution of titanium tetrachloride (1 mol dm^{-3} in DCM; 1.8 cm^3, 1.8 mmol) in DCM (10 cm^3) at 0 °C under an atmosphere of nitrogen. After 0.5 h, the allylic alcohol **1c** (0.37 g, 0.9 mmol) in DCM (2 cm^3) was added at −20 °C, and the solution stirred for 1 h. After dilution with ether, the mixture was warmed to room temp., and washed sequentially with HCl (1 mol dm^{-3}) and brine. Purification was achieved by silica chromatography (ether–light petroleum, 1:9 as eluent) and provided a mixture of the indenes **16** and **17** (0.085 g, 29%) in a ratio of 5:1. $\nu_{max}(CHCl_3)/cm^{-1}$ 2833, 1652, 1240, 1092, 1067 and 740; δ_H(400 MHz, $CDCl_3$) 1.3–1.43 (m, 1 H, 4-H_β), 1.63–1.7 (m, 1 H, 4-H_α), 2.5 (m, 1 H, 3a-H), 2.58–2.65 (br d, 1 H, 2-H_α), 2.68–2.75 (m, 2 H, 5-CH_2), 2.75–2.8 (m, 1 H, 2-H_β), 3.78 (s, 3 H, OMe), 3.8 (m, 2 H, 9b-H, 3-H), 4.55 (s, 2 H, OCH_2Ph), 4.7 and 4.92 (2 d, 2 H, *J* 1.5, =CH_2), 6.63–6.68 (d, 1 H, 3, 6-H), 6.75 (d, 1 H, *J* 3, 9, 8-H), 7.03 (d, 1 H, *J* 9, 9-H) and 7.25–7.4 (m, 5 H, Ph); NOE enhancements for **16** 3a-H to 9b-H (7.5%), 3a-H to OCH_2 (3%) and 4-H_β to 3-H (4%) (Found: M^+, 320.1770. $C_{22}H_{24}O_2$ requires *M*, 320.1776)

3,7-*Dimethoxy*-1-*methylene*-2,3,3a,4,5,9b-*hexahydro*-1H-*benz*[e]*indenes* **18** *and* **19**.—*N*-Methylaniline (0.4 cm^3, 3.3 mmol) was added to titanium tetrachloride (1 mol dm^{-3} in DCM; 3 cm^3, 3 mmol) in DCM (15 cm^3) at 0 °C. After 0.5 h, the allylic alcohol **1d** (0.55 g, 1.7 mmol) in DCM (5 cm^3) was added at −20 °C, and the mixture stirred at that temperature for 1 h. After addition of ether, the mixture was warmed to room temp., washed with HCl (1 mol dm^{-3}) and then brine, and the organic layer isolated. Purification of the products by silica chromatography (ether–light petroleum, 1:9) provided a mixture of the indenes **18** and **19** (0.38 g, 86%) in ratios varying from 3 to 5:1; $\nu_{max}(CHCl_3)/cm^{-1}$ 3050, 2930, 2836, 1653, 1607, 1500, 1464, 1248 and 1239; δ_H(400 MHz, $CDCl_3$) (discrete signals for **19** are shown in square brackets) 1.3–1.4 (m, 1 H, 4-H_β), 1.64–1.71 (m, 1 H, 4-H_α), 2.37–2.43 (m, 1 H, 3a-H), 2.48–2.54 (br d, 1 H, *J* 18, 2-H_α), 2.65–2.79 (m, 3 H, 2-H_β and 5-CH_2), 3.34 (s, 3 H, OMe), [3.40 (s, 3 H, OMe)], 3.56–3.58 (ddd, 1 H, *J* 2.1, 2.1, 9; 3-H), 3.7 (br d, 1 H, *J* 6, 9b-H), 3.78 (s, 3 H, ArOMe), [4.0 (ddd, 1 H, *J* 8.8, 8.8, 5.8, 3-H)], 4.68 and 4.92 (2 d, 2 H, *J* 2, =CH_2), 6.64 (d, 1 H, *J* 3, 6-H), [6.645 (d, 1 H, *J* 3, 6-H)], 6.73–6.76 (dd, 1 H, *J* 9, 3, 8-H) and 7.05 (d, 1 H, *J* 9, 9-H); NOE enhancements for **18**: 9b-H to 3a-H (4.7%), 3a-H to 9b-H (3.6%) and OMe to 3a-H (2.2%) (Found: M^+, 244.1463. $C_{16}H_{20}O_2$ requires *M*, 244.1463).

3,7-*Dimethoxy*-2,3,3a,4,5,9b-*hexahydro*-1H-*benz*[e]*inden*-1-*one* **20**.—Ozone was passed through a solution of the indene **18** (0.65 g, 27 mmol) in methanol (30 cm^3) held at −78 °C. After the reaction was judged to be complete, thiourea (0.15 g, 20 mmol) in methanol (2 cm^3) was added and the solution allowed to warm to room temp. The solvent was removed, and the residue was partitioned between water and ether. The ethereal extract was purified by silica chromatography (ether–light petroleum, 1:1) to yield the ketone **20** (0.34 g, 52%) as a colourless crystalline solid, m.p. 68–70 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 2930, 2832, 1740 (C=O), 1608, 1500, 1460, 1242, 1079 and 1039; δ_H(400 MHz, $CDCl_3$) 1.2–1.35 (m, 1 H, 4-H_α), 1.9–2.0 (m, 1 H, 4-H_β), 2.46 (m, 2 H, 2-CH_2), 2.7–2.82 (m, 3 H, 3a-H, 5-CH_2), 3.38 (s, 3 H, OMe), 3.5 (1 H, d, *J* 8, 9b-H), 3.78 (s, 3 H, ArOMe),

3.85 (m, 1 H, 3-H), 6.6 (d, 1 H, *J* 3, 6-H), 6.8 (dd, 1 H, *J* 9, 3, 8-H) and 7.35 (d, 1 H, *J* 9, 9-H) (Found: C, 73.05; H, 7.4. $C_{15}H_{18}O_3$ requires C, 73.15; H, 7.37%).

Methyl 2-(2-*Dimethylaminovinyl*)-3-*nitrobenzoate*.—A solution of methyl 2-methyl-3-nitrobenzoate (47.5 g, 0.24 mol) and dimethylformamide dimethyl acetal (87 g, 97 cm^3, 0.73 mol) in DMF (200 cm^3) was heated at 130 °C for 8 h. On cooling, the DMF was removed under reduced pressure and the resultant oil was partitioned between ether and water. The organic phase was separated and washed with brine, and evaporation provided the title compound as a dark red oil (57 g, 93%) which was used without purification; δ_H(60 MHz, $CDCl_3$) 2.8 (s, 6 H, NMe_2), 3.9 (s, 3 H, OMe), 5.6 (d, *J* 14, CH=N), 6.3 (d, 1 H, *J* 14, CH=), 7.2 (m, 1 H, 5-H) and 7.7 (m, 2 H, 4-H, 6-H); *m/z* 250 (M^+).

Methyl 1H-*Indole*-4-*carboxylate*.—The aforementioned enamine (19 g, 180 mmol) in benzene (250 cm^3) was hydrogenated (50 psi,* 6.5 h) using 10% palladium on charcoal (3.9 g). After filtration through a pad of Celite, the solvent was removed under reduced pressure, and the mixture purified by silica chromatography (DCM as eluent) to produce the title compound as a yellow, powdery solid (9 g, 68%), m.p. 63–65 °C; ν_{max}($CHCl_3$)/cm^{-1} 3476 (NH), 2995, 1704 (C=O), 1436, 1341, 1277 and 1193; δ_H(220 MHz, $CDCl_3$) 4.0 (s, 3 H, OMe), 7.1–7.6 (m, 4 H, 2-, 3-, 5-, 6-H), 7.9 (m, 1 H, 7-H) and 8.7 (br s, 1 H, NH) (Found C, 68.6; H, 5.2; N, 7.9. $C_{10}H_9NO_2$ requires C, 68.56; H, 5.18; N, 8.00%).

Indol-4-*ylmethanol*.—The aforementioned ester (4.5 g, 25 mmol) in diethyl ether (40 cm^3) at −78 °C was reduced with DIBAL (1 mol dm^{-3} in DCM; 64 cm^3, 0.064 mol, added dropwise). The reaction was complete after 4 h, and water was then added prior to warming to room temp. After addition of a saturated aqueous citric acid, the products were extracted into DCM. The organic extract was washed with brine and the products isolated by silica chromatography (ether–light petroleum, 3:2). The title methanol was isolated as a white crystalline solid (3.3 g, 87%), m.p. 55–56 °C (lit.,[5,6] 56–57 °C); ν_{max}($CHCl_3$)/cm^{-1} 3606 (OH), 3417 (NH), 2977, 2878, 1614, 1501, 1437, 1343 and 1182; δ_H(220 MHz, $CDCl_3$) 1.8 (br s, 1 H, OH), 4.95 (s, 2 H, CH_2), 6.65–7.3 (m, 5 H, ArH) and 8.4 (br s, 1 H, NH) (Found: C, 73.45; H, 6.17; N, 9.48. C_9H_9NO requires C, 73.45; H, 6.16; N, 9.52%).

Indole-4-*carbaldehyde*.—The aforementioned alcohol (2.1 g, 14 mmol) in DCM (50 cm^3) was stirred with activated manganese dioxide (7.3 g, 84 mmol) at room temp. overnight. When the reaction was complete, the mixture was filtered through Celite, and the product isolated following silica chromatography (ether–light petroleum, 4:1 as eluent) as a yellow crystalline powder (1.4 g, 68%), m.p. 143–144 °C (lit.,[5,6] 143–144 °C); ν_{max}($CHCl_3$)/cm^{-1} 3475 (NH), 1679 (C=O), 1572, 1440, 1348 and 1264; δ_H(220 MHz, $CDCl_3$) 7.2–7.5 and 7.65–7.75 (2 m, 5 H, ArH), 8.8 (br s, 1 H, NH) and 10.25 (s, 1 H, CHO) (Found: C, 74.1; H, 4.9; N, 9.5. C_9H_7NO requires C, 74.47; H, 4.86; N, 9.65%).

3-*Dimethylaminomethylindole*-4-*carbaldehyde*.—Dimethyl amine (33% aq.; 4.5 cm^3, 26 mmol) and formaldehyde (37–45% aq.; 2.0 cm^3, 26 mmol) were added to glacial acetic acid (30 cm^3) at 0 °C. Indole-4-carbaldehyde (2.53 g, 17 mmol) was then added and the mixture shaken until homogeneous (*ca.* 5 min). The solution was then stirred for 3.5 h prior to the addition of water, and washing with ether. The aqueous layer was made alkaline with NaOH (2 mol dm^{-3}) and extracted with DCM. The organic extract was then washed with brine, and the product isolated as an orange gum (3.16 g, 90% crude yield); ν_{max}($CHCl_3$)/cm^{-1} 3473 (NH), 2814, 1669 (C=O), 1610, 1564 and 1464; δ_H(220 MHz, $CDCl_3$) 2.25 (s, 6 H, NMe_2), 3.75 (s, 2 H, CH_2), 7.25 (s, 1 H, 2-H), 7.2–7.35 (m, 1 H, 6-H), 7.55 (m, 1 H, 7-H), 7.75 (m, 1 H, 5-H), 8.7 (br s, 1 H, NH) and 10.65 (s, 1 H, CHO).

3-*Cyanomethylindole*-4-*carbaldehyde*.—An aqueous solution of potassium cyanide (4.1 g, 60 mmol) was added to a stirred solution of the Mannich product (3.2 g, 160 mmol) in propan-2-ol (50 cm^3) at 0 °C. Iodomethane (9 g, 4 cm^3, 60 mmol) was then added, and the resultant reaction mixture was stirred overnight at room temp. After filtration, the products were extracted into ethyl acetate, and purified using silica chromatography (ethyl acetate as eluent) to provide the title compound as a yellow powdery solid (1.75 g, 55% from 1*H*-indole-4-carbaldehyde), m.p. 159–163 °C (lit.,[5,6] 166–168 °C); ν_{max}($CHCl_3$)/cm^{-1} 3458 (NH), 3051, 2984, 2304 (CN), 1689 (C=O), 1613, 1565, 1351; δ_H(250 MHz; $CDCl_3$) 4.3 (s, 2 H, CH_2), 7.2–7.8 (m, 4 H, ArH), 10.05 (s, 1 H, CHO) and 10.8 (br s, 1 H, NH) (Found: M^+, 184.0629. $C_{11}H_8N_2O$ requires *M*, 184.0636).

3-*Cyanomethyl*-4-(2-*methoxyvinyl*)*indole* **23**.—A solution of butyllithium (1.6 mol dm^{-3} in hexane; 13.7 cm^3, 22 mmol) was added dropwise to a suspension of methoxymethyl(triphenyl)-phosphonium chloride (8.2 g, 24 mmol) in THF (50 cm^3) under an atmosphere of nitrogen at −78 °C. After 1 h, the red solution was cooled to −78 °C prior to the addition of 3-cyanomethylindole-4-carbaldehyde (1.75 g, 9.5 mmol) in THF (2 cm^3). The mixture was stirred for 15 min at −78 °C and then for 1.5 h at room temp., prior to addition of saturated aqueous ammonium chloride. The products were extracted into DCM, and purified by silica chromatography (ether–light petroleum, 3:2 as eluent) to provide an isomeric mixture (*Z*/*E* 6:1) of the alkenes **23** as an amorphous brown solid (1.23 g, 61%), m.p. 91–93 °C (lit.,[5,6] 90–93 °C); ν_{max}($CHCl_3$)/cm^{-1} 3475 (NH), 3005, 2935, 2251 (CN), 1645 (C=C), 1609, 1452, 1411, 1279, 1265 and 1103; δ_H(250 MHz, $CDCl_3$) 3.75 (s, 3 H, OMe), 4.0 (s, 2 H, CH_2), 5.6 (d, $\frac{6}{7}$ H, *J* 8, CH=C), 6.25 (d, $\frac{6}{7}$ H, *J* 8, =CHO), 6.3 (d, $\frac{1}{7}$ H, *J* 13, CH=), 6.9 (d, $\frac{1}{7}$ H, *J* 13, =CHO) and 7.1–7.3 (m, 4 H, ArH), (br s, 1 H, NH) (Found: M^+, 212.0949. $C_{13}H_{12}N_2O$ requires *M*, 212.0949).

N-*Benzyl*-3-*cyanomethyl*-4-(2-*methoxyvinyl*)*indoline* **24**.—Sodium cyanoborohydride (0.19 g, 3 mmol) was added in small portions, over 5 h, to the indole **23** (0.63 g, 3 mmol) dissolved in glacial acetic acid (15 cm^3), until no starting material remained. The reaction mixture was then poured into water and the pH adjusted to *ca.* 8 with saturated aqueous sodium hydrogen carbonate. The crude product was extracted into ether and then purified by chromatography (ether–light petroleum, 4:1 as eluent) to yield a yellow oil (0.37 g, 55%). This was dissolved in acetone (15 cm^3) containing anhydrous potassium carbonate (0.28 g, 2 mmol), and treated with benzyl bromide (0.24 cm^3, 2 mmol). The mixture was stirred at room temp. overnight prior to addition of water, and removal of the acetone under reduced pressure. The products were extracted into ether and purified by silica chromatography (ether–light petroleum, 3:7 as eluent) to yield the *N*-benzylindoline **24** as a yellow oil (0.3 g, 58%); ν_{max}($CHCl_3$)/cm^{-1} 3051, 1648, 1457, 1440, 1276 and 1257; δ_H(220 MHz; $CDCl_3$) 2.5 (m, 2 H, CH_2CN), 3.4 (s, 2 H, CH_2N), 3.6 (m, 1 H, 3-H), 3.75 (s, 3 H, OMe), 4.1 and 4.4 (2 d, 2 H, *J* 15, CH_2Ph), 5.15 (d, 1 H, *J* 7, CH=), 6.25 (d, 1 H, *J* 7, =CHO), 6.4 (d, 1 H, 8, 7-H), 7.1 (m, 1 H, 6-H) and 7.2–7.4 (m, 6 H, 5-H, Ph) (Found: M^+, 304.1576. $C_{20}H_{20}N_2O$ requires *M*, 304.1569.

N-*Benzyl*-3-*formylmethyl*-4-(2-*methoxyvinyl*)*indoline* **25**.—A solution of DIBAL (1 mol dm^{-3} in DCM; 1 cm^3, 1 mmol) was

* 1 psi ≈ 6.9 × 10^3 Pa.

added dropwise to a solution of the *N*-benzylindoline **24** (0.16 g, 0.5 mmol) in DCM (5 cm^3) at −78 °C. After 1 h the reaction was quenched by the addition of water, and the mixture allowed to warm to room temp. Citric acid solution was added and the products extracted into DCM. Purification by silica chromatography (DCM eluent) yielded the desired aldehyde **24** as a colourless crystalline solid (0.13 g, 86%), m.p. 99–101 °C; $\nu_{max}(CHCl_3)$ 3057, 3050, 2829, 1722 (C=O), 1653, 1585, 1480, 1281 and 1103; δ_H(220 MHz, $CDCl_3$) 2.75 (m, 2 H, CH_2CHO), 3.15 (m, 2 H, CH_2N), 3.75 (m, 1 H, 3-H), 3.8 (s, 3 H, OMe), 4.1 and 4.45 (2 d, 2 H, *J* 15, CH_2Ph), 5.1 (d, 1 H, *J* 7, CH=), 6.2 (d, 1 H, *J* 7, =CHO), 6.35 (d, 1 H, *J* 8, 7-H), 7.1 (m, 1 H, 6-H), 7.2–7.4 (m, 6 H, 5-H, Ph) and 9.7 (t, 1 H, *J* 4.5, CHO) (Found: C, 77.95; H, 6.9; N, 4.7. $C_{20}H_{21}NO_2$ requires C, 78.15; H, 6.89; N, 4.56%).

N-*Benzyl*-4-(2-*methoxyvinyl*)-3-(3′-*trimethylsilylmethyl*-2′-*hydroxy*-*but*-3′-*enyl*)*indoline* **26**.—The indoline **25** (100 mg, 0.35 mmol) in THF (1 cm^3) was added to 1-(trimethylsilylmethyl)-vinylmagnesium bromide (*ca.* 0.7 mmol) in THF (1 cm^3). After 0.5 h, the reaction was quenched by the addition of saturated aqueous ammonium chloride, and the products extracted into DCM. Purification using silica chromatography (ether–light petroleum, 1:1 as eluent) provided the title compound as a stereoisomeric mixture (*ca.* 1:1 with respect to C-3) as a yellow oil (70 mg, *ca.* 50%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 (OH), 2952, 2826, 1647, 1581, 1475, 1453, 1440, 1401, 1250, 1102 and 849; δ_H(400 MHz; $CDCl_3$) (isomer A) −0.076 (s, $SiMe_3$), 1.25–1.28 and 1.52–1.55 (2 d, *J* 13.2, CH_2Si), 1.74–1.99 (m, 1′-CH_2), 3.18–3.40 (m, 2-CH_2, CHO), 3.67–3.68 (m, 3-H), 3.75 and 3.755 (2 s, 2 × OMe), 3.76 (m, OH), 3.98–4.02 and 4.41–4.45 (2 d, *J* 15, CH_2Ph), 4.59 and 4.89 (2 s, CH_2=), 5.3–5.32 (d, *J* 7.1, CH=), 6.33–6.35 (d, *J* 7.1, =CHO), 6.44–6.46 (d, *J* 7.8, 7-H), 7.02–7.07 (m, 6-H), 7.25–7.35 (m, Ph) and 7.38–7.40 (d, *J* 7.8, 5-H); (isomer B, discrete signals) −0.003 (s, $SiMe_3$), 1.31–1.34 and 1.53–1.56 (2 d, *J* 13.9, CH_2Si), 3.52–3.57 (m, CHO), 3.9–3.95 and 4.48–4.52 (2 d, *J* 14.3, CH_2Ph), 4.63 (s, CH_2=), 5.20–5.22 (d, *J* 7, CH=), 6.14–6.16 (d, *J* 7, =CHO) and 6.33–6.35 (d, *J* 7.7, 7-H) (Found: M^+, 421.2437. $C_{26}H_{35}NO_2Si$ requires *M*, 421.2427).

Crystal Data.—$C_{15}H_{18}O_3$, *M* = 246.1, *F*(000) = 528, *a* = 7.168(5), *b* = 9.1366(9), *c* = 19.662(17) Å, *β* = 97.5(1)°, *U* = 1276.8 $Å^3$, d_c = 1.28 cm^{-3}, *Z* = 4, *λ* = 0.7107 A, *μ* = 0.95 cm^{-1}, spacegroup $P2_1/a$.

Crystallography.—A crystal of approximate size 0.4 × 0.2 × 0.2 mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected *via* variable width *w* scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of (1.5 + sin*μ*/tan*θ*). 2302 Independent reflections were measured of which 1281 with $I > 2\sigma(I)$ were used in subsequent refinement. The structure was determined by direct methods. The C and O atoms were refined anisotropically with the hydrogen atoms included in calculated positions. Methyl hydrogen atoms were refined as rigid groups. The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final *R* values were 0.086 (R_w = 0.092). In the final cycle of refinement the maximum shift/error ratio was 0.08. In the final different Fourier map, the maximum and minimum peaks were 0.37 e $Å^{-3}$ and −0.22 e $Å^{-3}$. Calculations were carried out using SHELX76[8] and some of our own programs on the Amdahl 5870 at the University of Reading. In the final cycle of refinement, no shift was greater than 0.1 *σ*. Positional parameters are given in Table 2. Molecular dimensions, thermal parameters and hydrogen atom positions are available on request from the CCDC.*

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* For details, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, issue 1.

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