Intramolecular Addition of Vinyl and Aryl Radicals to Oxime Ethers in the Synthesis of Five-, Six- and Seven-membered Ring Systems

Susan E. Booth,[a] Paul R. Jenkins,*[,a] Christopher J. Swain[b] and Joseph B. Sweeney[a]
[a] *Department of Chemistry, The University, Leicester LE1 7RH, UK*
[b] *Merck, Sharp and Dohme, Terlings Park, Eastwick Road, Harlow, Essex CM20 2QR, UK*

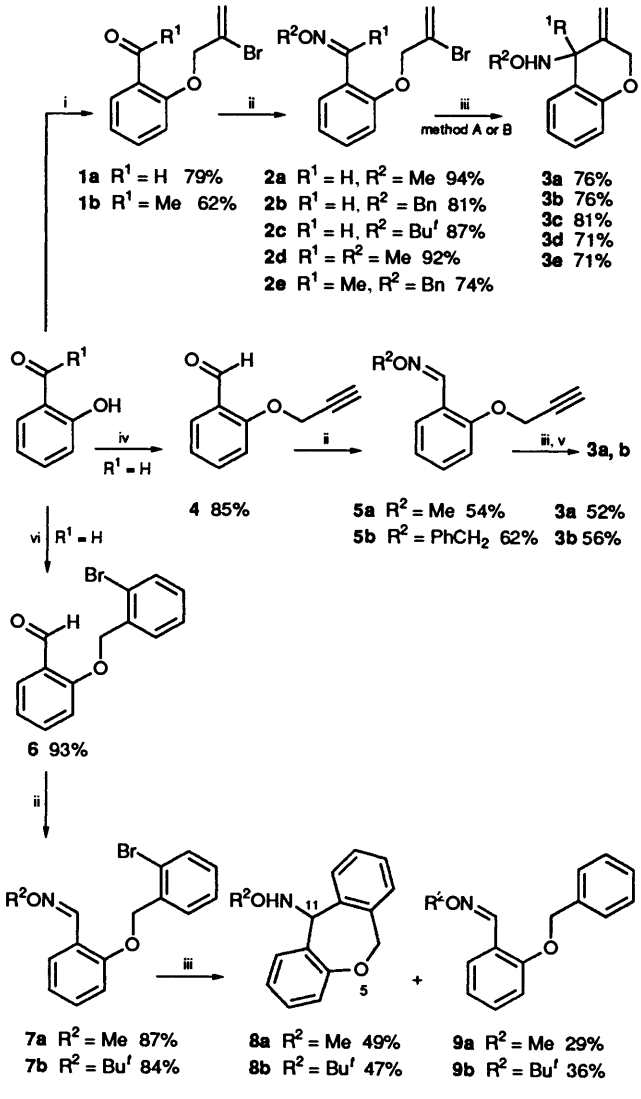
The oxime ethers **2a–e** have been cyclised with Bu_3SnH to the alkoxyamino-3-methylidenechromanes **3a–e**. Seven-membered ring formation was observed when the oxime ethers **7a, b** were converted into the dibenzo[*b,e*]oxepines **8a, b** under similar conditions. 1-Methoxyaminoindanes **12a, b** were produced from the cyclisation of the substrates **11a, b** and the *cis*-fused cyclic products **15a, b** and **18** were obtained from compounds **14a, b** and **17**, respectively.

The construction of carbocyclic rings using intramolecular radical cyclisation has become a common strategy in organic synthesis.[1] The first example of the intramolecular trapping of a radical by an oxime ether was reported by Corey and Pyne in 1983.[2] The particular advantage of using an oxime ether seems to lie in the extra stability of the alkoxy aminyl radical ($R^1\ddot{O}$–$\dot{N}$–R^2) produced in the cyclisation. One possible explanation of this phenomenon is the stabilising effect on the aminyl radical by a lone pair on the adjacent oxygen. From the synthetic point of view the use of the oxime ether introduces a nitrogen atom onto the carbocyclic framework thus making this strategy suitable for the synthesis of alkaloids and related target molecules. More recently reports have appeared on the synthesis of five- and six-membered carbocyclic rings using this process.[3] Our preliminary communication of part of these results[4] was prompted by the report of Enholm *et al.*[5] on the cyclisation of vinyl radicals onto oxime ethers. As part of a synthetic programme we undertook a study of the cyclisation of vinyl and aryl radicals onto oxime ethers and we now report the results in full.

Results and Discussion

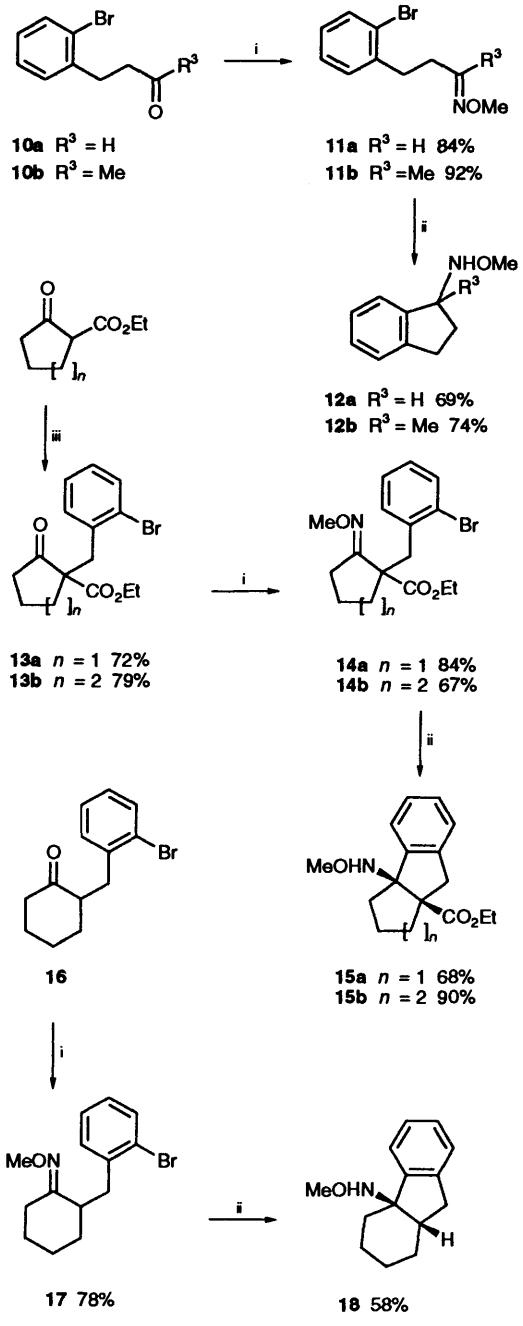
The starting point for the investigation were the ethers **1a** and **b**, which were prepared by standard procedures. The aldehyde **1a** was converted into three oxime ethers **2a–c**, while the ketone **1b** was used to produce the oxime ethers **2d** and **e**. When a benzene solution of azoisobutyronitrile (AIBN) was added *via* a syringe pump to a solution of the oxime ether **2a** and Bu_3SnH in benzene (Method A, Scheme 1) efficient cyclisation to the methoxyamine **3a** occurred. The oxime ethers **2b** and **c** were also effectively converted into the cyclised alkoxyamines **3b** and **c**, respectively, under the same conditions. However, only modest yields (< 35%) of cyclised products **3d** and **e** were obtained using this procedure on the oxime ethers **2d** and **e**. When 1 mol equiv. of AIBN was added to the benzene solution of the substrate and Bu_3SnH (Method B) cyclisation to **3d** and **e** occurred in good yield.

We next investigated the generation of a vinyl radical by the addition of Bu_3SnH to the prop-2-ynyl ether **4** using a procedure first developed by Stork and Mook and applied by many other authors;[6] although the ether **4** has been used many times before[7] our synthesis differs from the procedure reported in the literature.[8] The oxime ethers **5a** and **b** were prepared from the aldehyde **4**; treatment of **5a** with Bu_3SnH using Method A followed by destannylation with acetic acid resulted in the formation of the alkoxyamine **3a**, and this procedure was also followed to convert the oxime ether **5b** into the alkoxyamine **3b**.



Scheme 1 *Reagents and conditions:* i, $BrCH_2CBr{=}CH_2$, K_2CO_3, Me_2CO, reflux 5 h; ii, R^2ONH_2·HCl, pyridine, room temp.; iii, Bu_3SnH, AIBN, PhH, reflux; iv, $BrCH_2C{\equiv}CH$, K_2CO_3, Me_2CO, reflux; v, $MeCO_2H$; vi, 2-bromobenzyl bromide, K_2CO_3, Me_2CO, reflux

Presumably the Bu_3Sn· adds to the terminal carbon of the acetylene producing a vinyl radical which cyclises in the usual way onto the oxime ether group. Treatment of the crude vinyl



Scheme 2 *Reagents and conditions:* i, $MeONH_2$·HCl, pyridine, room temp.; ii, Bu_3SnH, AIBN, benzene, reflux; iii, NaH, 2-bromobenzyl bromide

stannane product with acetic acid causes destannylation giving the 3-methylidene substituted products **3a** and **b**.

The addition of an aryl radical to an oxime ether was investigated by the alkylation of 2-hydroxybenzaldehyde with 2-bromobenzyl bromide to give the aldehyde **6** which was converted into two oxime ethers **7a** and **b**. A solution of Bu_3SnH and AIBN in benzene was added, over 8 h using a syringe pump, to a refluxing solution of the oxime ether **7a** to produce the methoxyamine **8a** (49% yield) along with the reduction product **9a** (29%). The cyclisation product **8b** and the reduction product **9b** were obtained when the oxime ether **7b** was treated with Bu_3SnH under similar conditions in 47 and 36% yield, respectively. Two further examples of aromatic radical cyclisations are shown in Scheme 2. The aldehyde **10a** and ketone **10b** were prepared by standard procedures[9] and converted into the oxime ethers **11a** and **b**. Treatment of **11a** with Bu_3SnH using Method C gave the indane **12a** in 69% yield, and similar treatment of **11b** produced **12b** in 74% yield.

We next turned our attention to the synthesis of more complex cyclic products as shown in Scheme 2. Alkylation of ethyl 2-oxocyclopentanecarboxylate and ethyl 2-oxocyclohexanecarboxylate with 2-bromobenzyl bromide led to the keto esters **13a** and **b** which were readily converted into the oxime ethers **14a** and **b**. Single stereoisomers of these oxime ethers were obtained which we assume have the *E*-configuration with the OMe group *anti* to the adjacent quaternary carbon. The oxime ether **14a** was treated with Bu_3SnH using method A to give the alkoxyamine **15a** in 68% yield. We assign the *cis* configuration to **15a** on the basis of ample literature precedent[10] and a related radical cyclisation which has been shown to give the *cis* product.[11] The analogous sequence starting from the substituted cyclohexanone **13b** efficiently produced the cyclic product **15b** which we assume to have the *cis* configuration by analogy to the cyclisation of **14a**. Finally the ketone **16**, prepared by alkylation of cyclohexanone enamine with 2-bromobenzyl bromide, was converted into the oxime ether **17** and cyclised to the alkoxyamine **18**.

Experimental

All 90 MHz ^1H NMR spectra were recorded on a Varian EM-390 spectrometer, high-field ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded on a Bruker AM-300 spectrometer at the University of Leicester. Highfield ^1H NMR (360 and 250 MHz) and ^{13}C NMR (90.5 and 63.5 MHz) spectra were recorded on Bruker AM-360 and Bruker AM-250 spectrometers at Merck, Sharp and Dohme, Harlow. COSY and NOE experiments were recorded using the highfield (400 MHz) NMR service at the University of Warwick. Standard mass spectra and accurate mass measurements were made at either the SERC Mass Spectrometry Centre, University College of Swansea or at Merck, Sharp and Dohme, Harlow. Elemental analysis was carried out by Butterworth Laboratories, Teddington, Middlesex. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

Flash chromatography was carried out according to the method of Still *et al.*[12] using silica gel (Kiesel 60) manufactured by Merck and Co. TLC was conducted on pre-coated aluminium sheets (60–254) with a 0.2 mm thickness, manufactured by Merck and Co.

Light petroleum, referring to the fraction with b.p. 40–60 °C, and ethyl acetate were distilled prior to use. THF was distilled from sodium metal in the presence of benzophenone. Diethyl ether was distilled from lithium aluminium hydride. Methanol and ethanol were distilled from magnesium and iodine.

2-(2-*Bromoallyloxy*)*benzaldehyde* **1a**.—A solution of 2,3-dibromoprop-1-ene (9.82 g, 49.1 mmol) and 2-hydroxybenzaldehyde (5.00 g, 40.9 mmol) in acetone (20 cm^3) was heated at reflux with anhydrous potassium carbonate (11.32 g, 81.9 mmol) for 4 h, after which it was diluted with water and extracted with diethyl ether. The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography of the residue on silica gel with dichloromethane–light petroleum (1:1, v/v) as eluent gave the product **1a** as a clear colourless oil (10.09 g, 79%); R_f (dichloromethane–light petroleum, 3:7, v/v) 0.24; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3070–3015w, 2990–2910w, 2860w, 1690s, 1600s, 1580m, 1480s and 1450s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 4.76 (2 H, t, $J_{1',3'E} = J_{1',3'Z}$ 1.1, 1'-H), 5.74 (1 H, dt, $J_{3'Z,3'E}$ 2.2, 3'*Z*-H), 6.10 (1 H, dt, 3'*E*-H), 6.87 (1 H, d, $J_{3,4}$ 8.5, 3-H), 7.02 (1 H, t, $J_{5,4} = J_{5,6}$ 7.6, 5-H), 7.42 (1 H, dt, $J_{4,6}$ 1.8, 4-H), 7.73 (1 H, dd, 6-H) and 10.59 (1 H, s, HC=O).

2-(2-*Bromoallyloxy*)*phenyl Methyl Ketone* **1b**.—2-Hydroxyphenyl methyl ketone (2.00 g, 14.69 mmol), 2,3-dibromoprop-1-ene (3.52 g, 17.63 mmol) and anhydrous potassium carbonate (4.06 g, 29.38 mmol) were heated at reflux in anhydrous acetone (20 cm^3) for 5 h. Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) afforded the *ketone* **1b** (2.32 g, 62%) as needles, m.p. 45–46 °C [from light petroleum (b.p. 60–80 °C)] (Found: C, 51.7; H, 4.4. $C_{11}H_{11}BrO_2$ requires C, 51.79; H, 4.35%); R_f (diethyl ether–light petroleum, 1:9, v/v) 0.29; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3070w–3010w, 2990w–2910w, 2860w, 1670s (CO), 1595s, 1575m, 1480s, 1445s, 1050s and 895s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.66 (3 H, s, Me), 4.73 (2 H, t, $J_{1',3'E} = J_{1',3'Z}$ 1.1, 1'-H), 5.72 (1 H, dt, $J_{3'Z,3'E}$ 2.2, 3'*Z*-H), 6.02 (1 H, dt, 3'*E*-H), 6.89 (1 H, dd, $J_{3,5}$ 0.9 and $J_{3,4}$ 8.4, 3-H), 7.02 (1 H, td, $J_{5,4} = J_{5,6}$ 7.6, 5-H), 7.42 (1 H, ddd, $J_{4,6}$ 1.8, 4-H) and 7.73 (1 H dd, 6-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 32.0 (Me), 72.2 (C-1'), 112.7 (C-3), 119.2 (C-3'), 121.4 (C-5), 126.4 (C-1), 128.6 (C-2'), 130.5 (C-6), 133.5 (C-4), 156.7 (C-2) and 119.3 (C=O); *m/z* (CI^+) 254/256 (M^+, 79%), 238/240 (3), 175 (100), 160 (3), 147 (6), 131 (8), 121 (34), 92 (8), 77 (8) (Found: MH^+, 255.0021. $C_{11}H_{11}BrO_2$ requires *M*, 255.0021).

2-(2-*Bromoallyloxy*)*benzaldehyde* O-*Methyloxime* **2a**.—2-(2-Bromoallyloxy)benzaldehyde **1a** (2.00 g, 7.84 mmol) and *O*-methylhydroxylamine hydrochloride (0.98 g, 11.8 mmol) were stirred for 24 h at room temperature in pyridine (20 cm^3). Pyridine was removed under reduced pressure and the residue diluted with diethyl ether and washed with water. The organic phase was dried and evaporated to dryness. Chromatography of the residue on silica gel with dichloromethane–light petroleum (7:3, v/v) as the eluent afforded a mixture of *E* and *Z* isomers of the *oxime ether* **2a** as a clear colourless oil (2.11 g, 94%); R_f (dichloromethane–light petroleum, 3:7, v/v) 0.38 and 0.23; ν_{max}(film)/cm^{-1} 3080w, 3005w, 2960–2900m, 2810w, 1645m (C=N), 1600m, 1570w, 1480s, 1260–1230s, 1055s and 920s.

Major isomer (*E*): δ_H(360 MHz; $CDCl_3$; Me_4Si) 3.97 (3 H, s, Me), 4.66 (2 H, dd, $J_{1',3'Z}$ 1.2 and $J_{1',4'E}$ 1.6, 1'-H), 5.68 (1 H, dt, $J_{3'Z,3'E}$ 2.1, 3'*Z*-H), 5.98 (1 H, dt, 3'*E*-H), 6.84 (1 H, dd, $J_{3,5}$ 0.6 and $J_{3,4}$ 8.3, 3-H), 6.99 (1 H, ddd, $J_{5,4}$ 7.5 and $J_{5,6}$ 7.8, 5-H), 7.31 (1 H, ddd, $J_{4,6}$ 1.7, 4-H), 7.81 (1 H, dd, 6-H) and 8.50 (1 H, s, CH=N); δ_C(90.5 MHz; $CDCl_3$; Me_4Si) 61.9 (OMe), 72.0 (C-1'), 112.6 (C-3), 118.1 (C-3'), 121.3 (C-1), 121.7 (C-5), 128.6 (C-2'), 128.7 (C-4), 130.9 (C-6), 144.3 (CH=N) and 155.6 (C-2); *m/z* (EI^+) 269/271 (M^+, 29%), 240/242 (38), 221/223 (90), 190 (72), 159 (100), 144 (39), 119 (80), 91 (90) and 77 (31) (Found: M^+, 269.0025. $C_{11}H_{12}BrNO_2$ requires *M*, 269.0051).

2-(2-*Bromoallyloxy*)*benzaldehyde* O-*Benzyloxime* **2b**.—2-(2-Bromoallyloxy)benzaldehyde **1a** (1.00 g, 4.15 mmol) and *O*-benzylhydroxylamine hydrochloride (0.79 g, 4.98 mmol) in pyridine (20 cm^3) were stirred at room temperature for 24 h. Work-up as for compound **2a** followed by chromatography on silica gel with dichloromethane–light petroleum (b.p. 60–80 °C; 3:2, v/v) as eluent gave a mixture of *E* and *Z* isomers of the *oxime ether* **2b** (1.16 g, 81%) as a clear, colourless oil, R_f [dichloromethane–light petroleum (b.p. 60–80 °C), 3:7, v/v] 0.33 and 0.15; ν_{max}(film)/cm^{-1} 3060w, 3023m, 2920m, 2862m, 1634m, 1598s, 1570w, 1480s, 1360s, 1335m and 1250–1220s; *m/z* (EI^+) 346/348 (M^+, 25%), 91 (100) and 77 (10) (Found: M^+, 345.0364. $C_{17}H_{16}BrNO_2$ requires *M*, 345.0364).

Major isomer (*E*) (R_f 0.33): δ_H(360 MHz; $CDCl_3$; Me_4Si) 4.64 (2 H, t, $J_{1',3'E} = J_{1',3'Z}$ 1.2, 1'-H), 5.21 (2 H, s, OCH_2Ph), 5.67 (1 H, dt, $J_{3'Z,3'E}$ 3.4, 3'*Z*-H), 5.97 (1 H, dt, 3'*E*-H), 6.83 (1 H, d, $J_{3,4}$ 8.4, 3-H), 6.98 (1 H, dd, $J_{5,4}$ 7.5 and $J_{5,6}$ 7.8, 5-H), 7.25–7.38 (4 H, complex m, 4-H, and H_m and H_p in $PhCH_2$), 7.42 (2 H, dd, $J_{o,p}$ 1.6 and $J_{o,m}$ 7.7, H_o in $PhCH_2$), 7.82 (1 H, dd, $J_{6,4}$ 1.7, 6-H) and 8.58 (1 H, s, CH=N); δ_C(90.5 MHz; $CDCl_3$; Me_4Si) 72.0 (C-1'), 76.4 (PhCH_2), 112.6 (C-3), 118.1 (C-3'), 121.3 (C-1), 121.7 (C-5), 126.6 (C-2'), 126.8 (C-4), 127.6 (C_p in $PhCH_2$), 128.4 (C_m and C_o in $PhCH_2$), 131.0 (C-6), 137.6 (C-1 in $PhCH_2$), 144.8 (CH=N) and 155.6 (C-2).

Minor isomer (*Z*) (R_f 0.15): δ_H(300 MHz; $CDCl_3$; Me_4Si) 4.58 (2 H, dd, $J_{1',3'Z}$ 1.2 and $J_{1',3'E}$ 1.6, 1'-H), 5.20 (2 H, s, OCH_2Ph), 5.63 (1 H, dt, $J_{3'Z,3'E}$ 3.7, 3'*Z*-H), 5.93 (1 H, dt, 3'*E*-H), 6.77 (1 H, dd, $J_{3,5}$ 0.6 and $J_{3,4}$ 8.3, 3-H), 6.94 (1 H, td, $J_{5,4} = J_{5,6}$ 7.6, 5-H), 7.22–7.42 (6 H, complex m, 4-H, and H_o, H_m and H_p in $PhCH_2$), 7.81 (1 H, dd, $J_{6,4}$ 1.7, 6-H) and 8.57 (1 H, s, CH=N); δ_C($CDCl_3$; 75.5 MHz; Me_4Si) 71.8 (C-1'), 76.2 (PhCH_2), 112.5 (C-3), 118.1 (C-3'), 121.2 (C-1), 121.6 (C-5), 126.5 (C-2'), 126.6 (C-4), 127.8 (C_p in $PhCH_2$), 128.27 (C_m in $PhCH_2$), 128.31 (C_o in $PhCH_2$), 130.9 (C-6), 137.5 (C-1 in $PhCH_2$), 144.7 (CH=N) and 155.5 (C-2).

2-(2-*Bromoallyloxy*)*benzaldehyde* O-tert-*Butyloxime* **2c**.—2-(2-Bromoallyloxy)benzaldehyde **1a** (1.00 g, 4.15 mmol) was stirred with *O-tert*-butylhydroxylamine hydrochloride (0.62 g, 4.98 mmol) and pyridine (20 cm^3) for 24 h at room temperature. Work-up as for compound **2a** followed by chromatography on silica gel with diethyl ether–light petroleum (b.p. 60–80 °C; 3:7, v/v) as eluent afforded a single isomer of the *oxime ether* **2c** as a clear colourless oil (1.13 g, 3.16 mmol, 87%); R_f [diethyl ether–light petroleum (b.p. 60–80 °C), 1:4, v/v] 0.54; ν_{max}(film)/cm^{-1} 3070w, 3018w, 2970–2900m, 2860w, 1640m (C=N), 1600m, 1570w and 1480s, 1260–1230s, 1055s and 920s; δ_H(360 MHz; $CDCl_3$; Me_4Si) 1.29 [9 H, s, $C(CH_3)_3$], 4.58 (2 H, dd, $J_{1',3'Z}$ and $J_{1',3'E}$ < 1.0, 1'-H), 5.60 (1 H, dt, $J_{3'Z,3'E}$ 3.1, 3'*Z*-H), 5.91 (1 H, dt, 3'*E*-H), 6.76 (1 H, d, $J_{3,4}$ 8.3, 3-H), 6.91 (1 H, dd, $J_{5,4}$ 7.5 and $J_{5,6}$ 7.7, 5-H), 7.21 (1 H, ddd, $J_{4,6}$ 1.6, 4-H), 7.79 (1 H, dd, 6-H) and 8.40 (1 H, s, *CH*=NOMe); δ_C(90.5 MHz; $CDCl_3$; Me_4Si) 27.6 [$C(CH_3)_3$], 72.0 (C-1'), 79.0 [$C(CH_3)_3$], 112.6 (C-3), 118.0 (C-3'), 121.6 (C-5), 122.3 (C-1), 128.5 (C-4), 128.7 (C-2'), 130.4 (C-6), 142.7 (*CH*=NOBu^t) and 155.4 (C-2); *m/z* (EI^+) 311/313 (M^+, 3%), 255/257 (3), 238/240 (10), 176 (13), 159 (5), 131 (3), 119 (5), 91 (10), 77 (5), 57 (100) and 41 (20) (Found: MH^+, 312.0599. $C_{14}H_{18}BrNO_2$ requires *M*, 312.0599).

2-(2-*Bromoallyloxy*)*phenyl Methyl Ketone* O-*Methyloxime* **2d**.—2-(2-Bromoallyloxy)phenyl methyl ketone **1b** (2.00 g, 7.84 mmol) and *O*-methylhydroxylamine hydrochloride (0.79 g, 9.41 mmol) were stirred for 24 h at room temperature in pyridine (20 cm^3). Work-up as for compound **2a** followed by chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) as the eluent yielded a 6:1 ratio of *E* to *Z* isomers of the *oxime ether* **2d** as a clear colourless oil (2.05 g, 92%); R_f (diethyl ether–light petroleum, 3:10, v/v) 0.43; ν_{max}(film)/cm^{-1} 3065m, 3020w, 2960–2910m, 2860w, 1645w (C=N), 1600s, 1575w, 1485s, 1440s, 1230s, 1040s, 885s and 750s; *m/z* (CI^+) 284/286 (M^+, 100%), 204 (4) and 174 (10); *m/z* (EI^+) 239/241 (4%), 204 (4), 172 (10), 133 (4), 119 (4), 105 (8), 91 (100), 77 (8) and 39 (73) (Found: MH^+, 284.0286. $C_{12}H_{14}BrNO_2$ requires *M*, 286.0286).

Major isomer (*E*): δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.20 (3 H, s, Me), 3.93 (3 H, s, OMe), 4.55 (2 H, dd, $J_{1',3'Z}$ and $J_{1',3'E}$ < 1.0, 1'-H), 5.60 (1 H, dt, $J_{3'Z,3'E}$ 1.9, 3'*Z*-H), 5.91 (1 H, dt, 3'*E*-H), 6.76 (1 H, dd, $J_{3,5}$ 0.7 and $J_{3,4}$ 8.1, 3-H), 6.92 (1 H, ddd, $J_{5,6}$ 7.5 and $J_{5,4}$ 7.7, 5-H), 7.22 (1 H, ddd, $J_{4,6}$ 1.7, 4-H) and 7.31 (1 H, dd, 6-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 16.1 (Me), 61.5 (OMe), 71.8 (C-1'), 112.3 (C-3), 118.0 (C-3'), 121.4 (C-5), 126.7 (C-1), 127.3 (C-2'), 129.8 (C-4), 130.0 (C-6), 155.3 (C=N) and 155.6 (C-2).

Minor isomer (*Z*): δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.17 (3 H, s, Me), 3.78 (3 H, s, OMe), 4.55 (2 H, dd, 1'-H masked by *E* isomer), 5.60 (1 H, m, 3'*Z*-H masked by *E* isomer), 5.98 (1 H, dt, $J_{3'E,1'}$ < 1.0, $J_{3'Z,3'E}$ 1.9, 3'*E*-H) and 6.80–7.35 (4 H, complex m, 3-H, 4-H, 5-H and 6-H masked by *E* isomer); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 21.4 (Me), 61.4 (OMe), 71.6 (C-1'), 112.5 (C-3), 117.5 (C-3'), 121.3 (C-5), 125.4 (C-1), 126.6 (C-2'), 128.3 (C-4), 129.6 (C-6), 152.8 (C=N) and 153.4 (C-2).

2-(2-*Bromoallyloxy*)*phenyl Methyl Ketone* O-*Benzyloxime* **2e**.—2-(2-Bromoallyloxy)phenyl methyl ketone **1b** (2.00 g, 7.84 mmol) and *O*-benzylhydroxylamine hydrochloride (1.50 g, 9.40 mmol) were stirred at room temperature in pyridine (20 cm^3) for 24 h. Work-up as for compound **2a** followed by chromatography on silica gel with dichloromethane–light petroleum (3:2, v/v) as the eluent gave a 7:1 mixture of *E* to *Z* isomers of the *oxime ether* **2e** (2.10 g, 5.83 mmol, 74%) as needles, m.p. 53–53.5 °C (from light petroleum) (Found: C, 60.0; H, 5.1; N, 4.0. $C_{18}H_{18}BrNO_2$ requires C, 60.01; H, 5.04; N, 3.89%); R_f (diethyl ether–light petroleum, 3:7, v/v) 0.47; ν_{max}(film)/cm^{-1} 3060m, 3013m, 2980–2905s, 2860s, 1640–1630w (C=N), 1595s, 1575w, 1482s and 1440s.

Major isomer (*E*): δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.27 (3 H, s, Me), 4.58 (2 H, dd, $J_{1',3'Z}$ 1.2 and $J_{1',3'E}$ 1.6, 1'-H), 5.22 (2 H, s, PhCH_2), 5.62 (1 H, dt, $J_{3'Z,3'E}$ 2.1, 3'*Z*-H), 5.92 (1 H, dt, 3'*E*-H), 6.79 (1 H, dd, $J_{3,5}$ 1.0 and $J_{3,4}$ 7.8, 3-H), 6.94 (1 H, td, $J_{5,4} = J_{5,6}$ 7.5, 5-H) and 7.22–7.41 (7 H, complex m, 4-H, 6-H, and H_o, H_m and H_p in *Ph*CH_2); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 16.5 (Me), 71.9 (C-1'), 75.8 (Ph*C*H_2), 112.5 (C-3), 117.9 (C-3'), 121.5 (C-5), 126.6 (C-1), 127.4 (C-2'), 127.5 (C_p in *Ph*CH_2), 127.8 (C_o or C_m in *Ph*CH_2), 128.2 (C_o or C_m in *Ph*CH_2), 129.8 (C-4), 130.0 (C-6), 138.1 (C-1 in *Ph*CH_2), 155.4 (C=N) and 156.4 (C-2); *m*/*z* (CI^+) 360/362 (M^+, 100%), 280 (4), 224 (10), 174 (10), 159 (10) and 91 (16) (Found: MH^+, 360.0599. $C_{18}H_{18}NO_2Br$ requires *M*, 360.0599).

Minor isomer (*Z*): δ_H(360 MHz; $CDCl_3$; Me_4Si) 2.16 (3 H, s, Me), 4.57 (2 H, dd, $J_{1',3'Z}$ 1.4 and $J_{1',3'E}$ 1.6, 1'-H), 5.05 (2 H, s, PhCH_2), 5.57 (1 H, dt, $J_{3'Z,3'E}$ 2.1, 3'*Z*-H), 5.90 (1 H, m, 3'*E*-H masked by *E* isomer) and 6.75–7.50 (complex m, masked by *E* isomer); δ_C(75.5 MHz; $CDCl_3$; TMS) 21.5 (Me), 71.6 (C-1'), 75.3 (Ph*C*H_2), 112.5 (C-3), 117.5 (C-3'), 121.3 (C-5), 126.6 (C-1), 127.27 (C_p in *Ph*CH_2 or C-2'), 127.34 (C-2' or C_p in *Ph*CH_2), 128.1 (C_o or C_m in *Ph*CH_2), 128.3 (C_m or C_o in *Ph*CH_2), 129.5 (C-4) and 130.0 (C-6); peaks due to C-2, C=N and C' were too small to be assigned.

4-*Methoxyamino*-3-*methylidenechromane* **3a**.—*Method A for radical cyclisation.* A solution of 2-(2-bromoallyloxy) benzaldehyde *O*-methyloxime **2a** (2.00 g, 7.37 mmol) and tributyltin hydride (2.59 g, 8.90 mmol) in benzene (370 cm^3, 0.02 mol dm^{-3} **2a**) was degassed by bubbling nitrogen through the solution for 1 h. The reaction mixture was heated at reflux under a nitrogen atmosphere and a solution of AIBN (240 mg, 1.46 mmol) in degassed benzene (10 cm^3) was added over 18 h *via* a syringe pump. Heating was continued for 24 h and benzene evaporated under reduced pressure. Chromatography of the residue on silica gel with diethyl ether–light petroleum (1:4, v/v) as the eluent yielded the *title compound* **3a** as a pale yellow oil (1.07 g, 76%); R_f [diethyl ether–light petroleum (b.p. 60–80 °C), 1:9, v/v] 0.27; δ_H(360 MHz; $CDCl_3$, Me_4Si) 3.50 (3 H, s, OMe), 4.43 (1 H, s, 4-H), 4.52 (1 H, d, $J_{2ax,2eq}$ 11.8, 2-H_{ax}), 4.84 (1 H, dd, $J_{2eq,Z}$ 1.2, 2-H_{eq}), 5.29 (1 H, s, H-*E*), 5.35 (1 H, d, H-*Z*), 5.57 (1 H, br s, NH), 6.83 (1 H, dd, $J_{8,6}$ 0.6 and $J_{8,7}$ 7.5, 8-H), 6.89 (1 H, td, $J_{6,5} = J_{6,7}$ 7.5, 6-H), 7.18 (1 H, td, $J_{7,5}$ 1.6, 7-H) and 7.22 (1 H, dd, 5-H); δ_C(90.5 MHz; $CDCl_3$; Me_4Si) 60.3 (C-4), 62.8 (OMe), 67.4 (C-2), 115.9 (C=*C*H_2), 117.0 (C-8), 120.1 (C-4a), 120.7 (C-6), 129.5 (C-7), 130.11 (C-5), 139.4 (C-3) and 155.2 (C-8a).

Anhydrous hydrogen chloride gas was passed through a solution of the hydroxylamine **3a** in anhydrous diethyl ether to give the hydrochloride salt as a powder (1.05 g, 82%), m.p. 131–134 °C (from chloroform–methanol) (Found: C, 56.9; H, 6.2; N, 5.7. $C_{11}H_{14}ClNO_2 \cdot \frac{1}{4}H_2O$ requires C, 56.90; H, 6.29; N, 6.03%); ν_{max}(CH_2Cl_2)/cm^{-1} 3940w, 3045s, 2980m, 2690w, 2300m, 1650m, 1580m, 1570m, 1040w and 895s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.91 (3 H, s, OMe), 4.60 (1 H, d, $J_{2ax,2eq}$ 12.8, 2-H_{ax}), 4.76 (1 H, s, 4-H), 5.11 (1 H, dd, $J_{2eq,E}$ 1.1, 2-H_{eq}), 5.61 (1 H, s, H-*E*), 5.66 (1 H, d, H-*Z*), 6.87 (1 H, dd, $J_{8,6}$ 1.1 and $J_{8,7}$ 8.3, 8-H), 6.95 (1 H, ddd, $J_{6,5}$ 7.7 and $J_{6,7}$ 8.6, 6-H), 7.23 (1 H, ddd, $J_{7,5}$ 1.4, 7-H), 7.77 (1 H, dd, 5-H) and 12.01 (2 H, br s, NH_2); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 58.8 (C-4), 62.7 (OMe), 67.6 (C-2), 112.2 (C-4a), 117.6 (C-8), 120.9 (C-6), 123.4 (C=*C*H_2), 131.5 (C-7), 131.71 (C-3), 132.0 (C-5) and 155.9 (C-8a); *m*/*z* (EI^+) 160 (2%), 145 (100), 115 (20), 91 (8) and 77 (2) (Found: $M^+ - Cl$, 192.1025. $C_{11}H_{14}ClNO_2$ requires *M*, 192.1025).

4-*Benzyloxyamino*-3-*methylidenechromane* **3b**.—Following method A, 2-(2-bromoallyloxy)benzaldehyde *O*-benzyloxime **2b** (300 mg, 0.87 mmol) was treated with tributyltin hydride (303 mg, 1.04 mmol). Chromatography on silica gel with diethyl ether–light petroleum (1:4, v/v) as eluent afforded the *hydroxylamine* **3b** as a pale yellow oil (176 mg, 0.66 mmol, 76%); R_f (diethyl ether–light petroleum, 1:4, v/v) 0.39; ν_{max}(film)/cm^{-1} 3080w, 3005w, 2960–2900m, 2805w, 1640m, 1610m, 1570w, 1485s and 1240s; δ_H(360 MHz; $CDCl_3$; Me_4Si) 4.43 (1 H, d, $J_{4,NH}$ 4.8, 4-H), 4.47 (1 H, d, $J_{2ax,2eq}$ 11.7, 2-H_{ax}), 4.65 and 4.72 (2 H, AB quartet, *J* 11.7, PhCH_2), 4.78 (1 H, dd, $J_{2eq,Z}$ 1.2, 2-H_{eq}), 5.28 (1 H, s, H-*E*), 5.35 (1 H, d, H-*Z*), 5.54 (1 H, d, NH), 6.83 (1 H, dd, $J_{8,6}$ 1.1 and $J_{8,7}$ 8.1, 8-H), 6.87 (1 H, td, $J_{6,5} = J_{6,7}$ 7.4, 6-H), 7.15 (1 H, dd, $J_{5,7}$ 1.7, 5-H), 7.18 (1 H, ddd, 7-H) and 7.25–7.34 (5 H, complex m, H_o, H_m and H_p in *Ph*CH_2); δ_C(90.5 MHz; $CDCl_3$; Me_4Si) 60.4 (C-4), 67.4 (C-2), 77.1 (Ph*C*H_2), 116.0 (C=*C*H_2), 117.0 (C-8), 120.1 (C-4a), 120.6 (C-6), 127.9 (C_p in *Ph*CH_2), 128.3 (C_m in *Ph*CH_2), 128.8 (C_o in *Ph*CH_2), 129.5 (C-7), 130.2 (C-5), 137.7 (C-1 in *Ph*CH_2), 139.5 (C-3) and 155.3 (C-8a).

The hydrochloride salt of the hydroxylamine **3b**, prepared as for compound **2a**, was obtained as a hygroscopic powder (164 mg, 0.54 mmol, 82%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 4.58 (1 H, d, $J_{2ax,2eq}$ 12.7, 2-H_{ax}), 4.80 (1 H, s, 4-H), 5.04 (1 H, d, *J* 9.1, PhCH_2), 5.15 (1 H, d, PhCH_2), 5.17 (1 H, d, 2-H_{eq}), 5.58 (1 H, s, H-*E*), 5.61 (1 H, s, H-*Z*), 6.81 (1 H, dd, $J_{8,6}$ 1.0 and $J_{8,7}$ 8.3, 8-H), 6.87 (1 H, ddd, $J_{6,5}$ 7.2 and $J_{6,7}$ 7.5, 6-H), 7.06 (1 H, ddd, $J_{7,5}$ 1.4, 7-H), 7.24–7.40 (5 H, complex m, H_o, H_m and H_p in *Ph*CH_2) and 7.78 (1 H, dd, 5-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 59.2 (C-4), 67.5 (C-2), 77.0 (Ph*C*H_2), 112.3 (C-4a), 117.5 (C-8), 120.9 (C-6), 123.3 (C=*C*H_2), 128.5 (C_m in *Ph*CH_2), 129.2 (C_p in *Ph*CH_2), 129.6 (C_o in *Ph*CH_2), 131.6 (C-7), 131.9 (C-1 in *Ph*CH_2), 132.0 (C-5), 132.8 (C-3) and 155.8 (C-8a); *m*/*z* (CI^+) 268 ($M - Cl$, 8%), 160 (12), 145 (100), 131 (2), 115 (6), 91 (21) and 77 (2) (Found: $M^+ - Cl$, 268.1337. $C_{17}H_{18}ClNO_2$ requires *M*, 268.1337).

4-tert-*Butoxyamino*-3-*methylidenechromane* **3c**.—Following method A, 2-(2-bromoallyloxy)benzaldehyde *O*-*tert*-butyloxime **2c** (400 mg, 1.28 mmol) was treated with tributyltin hydride (450 mg, 1.54 mmol). Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) gave the *hydroxylamine* **3c** as a pale yellow oil (242 mg, 1.04 mmol, 81%); R_f (diethyl ether–light petroleum, 1:4, v/v) 0.43; δ_H(360 MHz; $CDCl_3$; Me_4Si) 1.07 [9 H, s, $C(CH_3)_3$], 4.25 (1 H, s, 4-H), 4.41 (1 H, d, $J_{2ax,2eq}$ 11.7, 2-H_{ax}), 4.70 (1 H, dd, $J_{2eq,Z}$ 1.2, 2-H_{eq}), 4.85 (1 H, br s, NH), 5.19 (1 H, s, H-*E*), 5.23 (1 H, d, H-*Z*), 6.75 (1 H, dd, $J_{8,6}$ 1.0 and $J_{8,7}$ 8.9, 8-H), 6.82 (1 H, td, $J_{6,5} = J_{6,7}$ 7.6, 6-H), 7.10 (1 H, ddd, $J_{7,5}$ 1.5, 7-H) and 7.21 (1 H, dd, 5-H).

The hydrochloride salt of **3c**, prepared as for the hydroxylamine was obtained as a powder (238 mg, 0.88 mmol, 85%), m.p. 129–131 °C (from ethyl acetate–light petroleum) (Found: C, 61.3; H, 7.75; N, 5.15. $C_{14}H_{20}ClNO_2 \cdot \frac{1}{4}H_2O$ requires C, 61.31; H, 7.45; N, 5.11%); ν_{max}(CH_2Cl_2)/cm^{-1} 3940w, 3045s, 2980–2860s, 2690w, 2300m, 1720w, 1605m, 1580m, 1570m, 1040m and 895m; δ_H(360 MHz; $CDCl_3$; Me_4Si) 1.37 [9 H, s, $C(CH_3)_3$], 4.62 (1 H, d, $J_{2ax,2eq}$ 12.4, 2-H_{ax}), 4.97 (1 H, d, 2-H_{eq}), 5.05 (1 H, s, 4-H), 5.67 (1 H, s, H-*E*), 5.95 (1 H, s, H-*Z*), 6.88 (d, $J_{8,7}$ 8.2, 8-H), 6.99 (1 H, dd, $J_{6,7}$ 7.2 and $J_{6,5}$

7.7, 6-H), 7.24 (dd, 1 H, 7-H), 8.17 (d, 1 H, 5-H) and 11.69 (br s, 2 H, NH_2); δ_C(63.5 MHz; $CDCl_3$; Me_4Si) 27.0 (Me_3C), 58.2 (C-4), 69.2 (C-2), 84.5 (Me_3C), 113.6 (C-4a), 117.3 (C=CH_2), 121.3 (C-8), 123.8 (C-6), 131.3 (C-7), 131.9 (C-5), 132.8 (C-3) and 156.4 (C-8a); *m/z* 177 (5%), 160 (5), 145 (100), 115 (15), 91 (5) and 77 (2) (Found: $M^+ - Cl$, 234.1494. $C_{14}H_{20}ClNO_2$ requires *M*, 234.1494).

4-*Methoxyamino*-4-*methyl*-3-*methylidenechromane* **3d**.—*Method B for radical cyclisation.* A degassed solution of 2-(2-bromoallyloxy)phenyl methyl ketone *O*-methyloxime **2d** (265 mg, 0.93 mmol), tributyltin hydride (330 mg, 1.12 mmol) and AIBN (150 mg, 1.93 mmol) in benzene (47 cm^3, 0.02 mol dm^{-3} **2d**) was heated at reflux under a nitrogen atmosphere for 3 h, after which the mixture was evaporated under reduced pressure. Chromatography of the residue on silica gel with diethyl ether–light petroleum (1:4 v/v) gave the *hydroxylamine* **3d** as a pale yellow oil (135 mg, 71%).

The hydrochloride salt of **3d**, prepared as for the hydroxylamine **3a**, was obtained as a powder (137 mg, 86%), m.p. 120–123 °C (ethyl acetate–light petroleum) (Found: C, 58.2; H, 6.9; N, 5.6. $C_{12}H_{16}ClNO_2 \cdot \frac{1}{4}H_2O$ requires C, 58.53; H, 6.76; N, 5.69%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3940w, 3045s, 2980–2860s, 2690w, 2300m, 1710w, 1605w, 1580m, 1560m, 1320–1300s, 1040w and 895s; δ_H(360 MHz; $CDCl_3$; Me_4Si) 1.98 (3 H, s, Me), 3.99 (3 H, s, OMe), 4.58 (1 H, d, $J_{2ax,2eq}$ 12.6, 2-H_{ax}), 4.87 (1 H, d, 2-H_{eq}), 5.66 (1 H, s, H-*E*), 5.94 (1 H, s, H-*Z*), 6.90 (1 H, dd, $J_{8,6}$ 0.7 and $J_{8,7}$ 7.7, 8-H), 7.05 (1 H, ddd, $J_{6,7}$ 7.0 and $J_{6,5}$ 7.8, 6-H), 7.25 (1 H, ddd, $J_{7,5}$ 1.1, 7-H), 8.09 (1 H, dd, 5-H) and 12.47 (2 H, br s, NH_2); δ_C(63.5 MHz; $CDCl_3$; Me_4Si) 23.61 (Me), 62.67 (C-4), 63.11 (OMe), 69.55 (C-2), 117.93 (C=CH_2), 119.35 (C-4a), 119.92 (C-8), 122.00 (C-6), 128.71 (C-7), 130.84 (C-5), 137.84 (C-3) and 155.95 (C-8a); *m/z* (EI^+) 159 (100%), 144 (15), 131 (14), 115 (12), 91 (8) and 77 (20) (Found: $M^+ - Cl$, 206.1181. $C_{12}H_{16}ClNO_2$ requires *M*, 206.1181).

4-*Benzyloxyamino*-4-*methyl*-3-*methylidenechromane* **3e**.—Following method B, 2-(2-bromoallyloxy)phenyl methyl ketone *O*-benzyloxime **2e** (660 mg, 1.9 mmol) was treated with tributyltin hydride (660 mg, 2.3 mmol) and AIBN (310 mg, 1.9 mmol). Chromatography on silica gel with diethyl ether–light petroleum (1:4, v/v) gave the title compound **3e** as a pale yellow oil (360 mg, 71%); R_f (diethyl ether–light petroleum, 1:4, v/v) 0.38.

The hydrochloride salt of **3e**, prepared as for **3a**, was obtained as a hygroscopic powder (335 mg, 86%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3045s, 2990s, 2690m, 2300m, 1710br, 1605–1570w, 1480–1420m, 1260s and 895m; δ_H(360 MHz; $CDCl_3$; Me_4Si) 1.97 (3 H, s, CH_3), 4.56 (1 H, d, $J_{2ax,2eq}$ 12.5, 2-H_{ax}), 4.83 (1 H, d, 2-H_{eq}), 5.07 (1 H, d, *J* 9.8, PhCH_2O), 5.31 (1 H, d, PhCH_2O), 5.60 (1 H, s, H-*E*), 5.75 (1 H, s, H-*Z*), 6.69 (1 H, d, $J_{8,7}$ 7.3, 8-H), 7.06 (1 H, dd, $J_{6,5}$ 7.0 and $J_{6,7}$ 7.2, 6-H), 7.20–7.30 (6 H, complex m, 7-H, and H_o, H_m, H_p in *Ph*CH_2), 8.05 (1 H, d, 5-H) and 12.30 (2 H, br s, NH_2); δ_C(63.5 MHz; $CDCl_3$; Me_4Si) 22.6 (CH_3), 61.7 (C-4), 69.9 (C-2), 76.8 (PhCH_2), 117.6 (C-8), 119.5 (C-4a), 121.6 (C-6), 128.5–130.6 (C-3, C-5, C-7, R_2C=CH_2, and C-1, C_o, C_m and C_p in *Ph*CH_2) and 155.7 (C-8a); *m/z* (EI^+) 174 (M − HCl and $PhCH_2OH$, 4%), 159 (100), 144 (6), 131 (7), 115 (6), 91 (29) and 77 (6) (Found: $M^+ - Cl$, 282.1494. $C_{18}H_{20}ClNO_2$ requires *M*, 282.1494).

2-(*Prop*-2-*ynyloxy*)*benzaldehyde* **4**.—A solution of 3-bromopropyne (1.17 g, 9.84 mmol, 80 wt% in toluene) and 2-hydroxybenzaldehyde (1.00 g, 8.20 mmol) in acetone (20 cm^3) was heated at reflux with anhydrous potassium carbonate (2.26 g, 1.64 mmol) for 5 h after which it was diluted with water (50 cm^3) and extracted with diethyl ether. The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography of the residue on silica gel with dichloromethane–light petroleum (1:1 v/v) as eluent gave the product **4** as rhombic crystals (1.11 g, 85%), m.p. 68 °C [light petroleum (b.p. 60–80 °C)] (Found: C, 74.8; H, 4.8. $C_{10}H_8O_2$ requires C, 74.99; H, 5.03%); R_f (dichloromethane–light petroleum, 1:1 v/v) 0.30; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3300s, 3070–3015w, 2915w, 2870m, 1685s (C=O), 1600s, 1580m, 1480s and 1450s; δ_H(360 MHz; $CDCl_3$; Me_4Si) 2.58 (1 H, t, $J_{3',2'}$ 2.3, 3'-H), 4.83 (2 H, d, 1'-H), 7.07 (1 H, dd, $J_{3,5}$ 1.7 and $J_{3,4}$ 7.0, 3-H), 7.12 (1 H, ddd, $J_{5,6}$ 7.7 and $J_{5,4}$ 9.0, 5-H), 7.56 (1 H, ddd, $J_{4,6}$ 1.8, 4-H), 7.85 (1 H, dd, 6-H) and 10.47 (1 H, s, CHO); δ_C(90.5 MHz; $CDCl_3$; Me_4Si) 56.4 (C-1'), 76.5 (C-3'), 77.7 (C-2'), 113.2 (C-3), 121.7 (C-5), 125.5 (C-1), 128.5 (C-6), 135.7 (C-4), 159.7 (C-2) and 189.4 (CHO); *m/z* (CI^+) 178 ([M + NH_4]$^+$, 10%), 161 (MH^+, 100) 132 (3), 58 (3), 44 (7) and 36 (11) [Found: $(M + NH_4)^+$, 178.0868. $C_{10}H_8O_2$ requires *M*, 178.0868].

2-(*Prop*-2-*ynyloxy*)*benzaldehyde* O-*Methyloxime* **5a**.—2-(Prop-2-ynyloxy)benzaldehyde **4** (270 mg, 1.69 mmol), *O*-methylhydroxylamine hydrochloride (225 mg, 2.70 mmol) and pyridine (293 mg, 3.71 mmol) were stirred in methanol (5 cm^3) at room temperature for 4 h. Methanol was evaporated under reduced pressure and the residue dissolved in diethyl ether and the solution was washed with water. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue on silica gel with dichloromethane–light petroleum (1:1, v/v) afforded the title compound **5a** (173 mg, 54%) as prisms, m.p. 47–48 °C (from light petroleum) (Found: C, 69.6; H, 6.0; N, 7.25. $C_{11}H_{11}NO_2$ requires C, 69.82; H, 5.86; N, 7.40%); R_f (dichloromethane–light petroleum, 7:3, v/v) 0.63; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3300s, 2940s, 2900w, 2860w, 1600m, 1570m, 1480s and 1450s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.50 (1 H, t, $J_{3',1'}$ 2.4, 3'-H), 3.95 (3 H, s, OCH_3), 4.68 (2 H, d, 1'-H), 6.95 (1 H, dd, $J_{3,5}$ 1.1 and $J_{3,4}$ 8.4, 3-H), 6.98 (1 H, ddd, $J_{5,6}$ 8.0 and $J_{5,4}$ 7.4, 5-H), 7.31 (1 H, ddd, $J_{4,6}$ 1.7, 4-H), 7.80 (1 H, dd, 6-H) and 8.45 (1 H, s, HC=N); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 56.3 (C-1'), 61.9 (OCH_3), 75.9 (C-2'), 78.2 (C-3'), 112.8 (C-3), 121.5 (C-1), 121.7 (C-5), 126.5 (C-4), 130.8 (C-6), 144.4 (HC=N) and 155.4 (C-2); *m/z* (EI^+) 189 (M^+, 22%), 158 (22), 143 (100), 130 (15), 115 (22), 103 (15), 91 (33) and 77 (21) (Found: M^+, 189.0790. $C_{11}H_{11}NO_2$ requires *M*, 189.0790).

2-(*Prop*-2-*ynyloxy*)*benzaldehyde* O-*Benzyloxime* **5b**.—In the same way as for compound **5a**, 2-(prop-2-ynyloxy)benzaldehyde **4** (1.00 g, 6.24 mmol), *O*-benzylhydroxylamine hydrochloride (1.59 g, 9.99 mmol) and pyridine (1.09 g, 13.70 mmol) were stirred in methanol (20 cm^3) at room temperature overnight. Chromatography on silica gel with dichloromethane–light petroleum (7:3 v/v) as eluent gave the title compound **5b** as prisms (1.03 g, 62%), m.p. 54 °C (from light petroleum) (Found: C, 76.9; H, 5.8; N, 5.2. $C_{17}H_{15}NO_2$ requires C, 76.96; H, 5.70; N, 5.28%); R_f (dichloromethane–light petroleum, 7:3, v/v) 0.69; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3300s, 2940s, 2910w, 2860w, 1600m, 1570m and 1450s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.44 (1 H, t, $J_{3',1'}$ 2.4, 3'-H), 4.60 (2 H, d, 1'-H), 5.18 (2 H, s, $PhCH_2$), 6.91 (1 H, d, $J_{3,4}$ 8.3, 3-H), 6.93 (1 H, t, $J_{5,6} = J_{5,4}$ 7.7, 5-H), 7.23–7.41 (6 H, complex m, 4-H and H_o, H_m and H_p in $PhCH_2O$), 7.82 (1 H, dd, $J_{6,4}$ 1.6, 6-H) and 8.54 (1 H, s, HC=N); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 56.2 (C-1'), 75.8 (C-2'), 76.2 (PhCH_2), 78.1 (C-3'), 112.7 (C-3), 121.5 (C-1), 121.6 (C-5), 126.5 (C-4), 127.8 (C_p in $PhCH_2O$), 128.23 and 128.28 (C_o and C_m in $PhCH_2O$), 130.8 (C-6), 137.6 (C-1 in $PhCH_2O$), 144.4 (HC=N) and 155.4 (C-2); *m/z* (CI^+) 266 (MH^+, 100%), 175 (2), 160 (5), 122 (2), 108 (5) and 91 (8) (Found: MH^+, 266.1181. $C_{17}H_{15}NO_2$ requires *M*, 266.1181).

4-*Methoxyamino*-3-*methylidenechromane* **3a** *from* 2-(*Prop*-2-*ynyloxy*)*benzaldehyde* O-*Methyloxime* **5a**.—The oxime **5a** (200 mg, 1.06 mmol) was dissolved in benzene (0.02 mol dm^{-3} **5a**; 53 cm^3) and the solution degassed by bubbling a steady stream of nitrogen through it for 30 min. The solution was heated at reflux under a nitrogen atmosphere and a solution of tributyltin hydride (369 mg, 1.27 mmol) and AIBN (35 mg, 0.21 mmol) in benzene (10 cm^3) was added to it over 6 h. Heating was continued for a further 6 h. Benzene was removed under reduced pressure and the residue was diluted with methanol (2 cm^3). A few drops of glacial acetic acid were added to the reaction mixture which was then heated at reflux for 12 h, before it was concentrated under reduced pressure. Chromatography of the residue on silica gel with diethyl ether–light petroleum (1:4, v/v) as eluent afforded the chromane **3a** (105 mg, 52%) as a pale yellow oil, R_f (diethyl ether–light petroleum, 1:9, v/v) 0.27.

4-*Benzyloxyamino*-3-*methylidenechromane* **3b** *from* 2-(*Prop*-2-*ynyloxy*)*benzaldehyde* O-*Methyloxime* **5b**.—In the same way as for the reaction of compound **5a**, the oxime **5b** (320 mg, 1.26 mmol)was treated with tributyltin hydride (442 mg, 1.52 mmol) and AIBN (40 mg, 0.25 mmol) in benzene, followed by glacial acetic acid in methanol. Chromatography of the residue on silica gel with diethyl ether–light petroleum (1:4, v/v) yielded the chromane **3b** (188 mg, 56%) as a pale yellow oil, R_f (diethyl ether–light petroleum, 1:9, v/v) 0.39.

2-(2-*Bromobenzyloxy*)*benzaldehyde* **6**.—As for the preparation of compound **1a**, 2-hydroxybenzaldehyde (1.00 g, 8.19 mmol), 2-bromobenzyl bromide (2.46 g, 9.83 mmol) and anhydrous potassium carbonate (2.26 g, 16.4 mmol) were heated at reflux in dry acetone (30 cm^3) for 3 h. Chromatography on silica gel with dichloromethane–light petroleum (1:1, v/v) as eluent yielded the title compound **6** (2.22 g, 93%) as rhomboids, m.p. 91–92 °C [from light petroleum (b.p. 60–80 °C)] (Found: C, 57.7; H, 3.8. $C_{14}H_{11}BrO_2$ requires C, 57.75; H, 3.81%); R_f (dichloromethane–light petroleum, 1:1, v/v) 0.43; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3050w, 2890–2860w, 1735s (C=O) 1600s, 1580w and 1480s and 765s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 5.23 (2 H, s, OCH_2), 7.03–7.08 (2 H, complex m, 3-H and 5-H), 7.20 (1 H, ddd, $J_{4',6'}$ 1.7, $J_{4',5'}$ 7.5 and $J_{4',3'}$ 7.9, 4'-H), 7.35 (1 H, dt, $J_{5',3'}$ 1.2 and $J_{5',6'}$ 7.5, 5'-H), 7.51–7.57 (2 H, complex m, 6'-H and 4-H), 7.59 (1 H, dd, 3'-H), 7.87 (1 H, dd, $J_{6,4}$ 1.6 and $J_{6,5}$ 7.6, 6-H) and 10.58 (1 H, s, ArC*H*=O); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 69.9 (CH_2O), 113.03 (C-3), 121.2 (C-5), 122.3 (C-2'), 125.3 (C-1), 127.7 (C-5'), 128.7 (C-6'), 128.8 (C-4'), 129.6 (C-6), 132.8 (C-3'), 135.3 (C-1'), 135.9 (C-4), 160.6 (C-2) and 189.4 (C=O); *m/z* (CI^+) 290/292 (MH^+, 100%), 262/264 (8), 211 (8), 185/187 (79), 168/170 (12), 121 (9), 106 (2) and 89 (3) (Found: MH^+, 291.0021. $C_{14}H_{11}BrO_2$ requires *M*, 291.0021).

2-(2-*Bromobenzyloxy*)*benzaldehyde* O-*Methyloxime* **7a**.—As for the preparation of compound **2a**, 2-(2-bromobenzyloxy)-benzaldehyde **6** (1.00 g, 3.43 mmol) was stirred overnight at room temperature in pyridine (10 cm^3) with *O*-methylhydroxylamine hydrochloride (0.46 g, 5.50 mmol). Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) as eluent gave a mixture of the *E* and *Z* isomers of the *oxime ether* **7a** (0.96 g, 87%) as needles, m.p. 75.5–76 °C [from light petroleum (b.p. 60–80 °C)] (Found: C, 56.0; H, 4.4; N, 4.3. $C_{15}H_{14}BrNO_2$ requires C, 56.21; H, 4.40; N, 4.37%); R_f (diethyl ether–light petroleum, 1:9, v/v) 0.46 and 0.35; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3000w, 2940m, 2810m, 1605s (C=N), 1595s, 1570m and 1485s.

Major isomer (R_f 0.46): δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.96 (3 H, s, OMe), 5.10 (2 H, s, CH_2O), 6.90 (1 H, d, $J_{3,4}$ 8.2, 3-H), 6.95 (1 H, t, $J_{5,6} = J_{5,4}$ 7.6, 5-H), 7.14 (1 H, ddd, $J_{4',6'}$ 1.7, $J_{4',5'}$ 7.5 and $J_{4',3'}$ 7.9, 4'-H), 7.26–7.32 (2 H, complex m, 4-H and 5'-H), 7.49 (1 H, dd, $J_{6',5'}$ 7.7, 6'-H), 7.54 (1 H, dd, $J_{3',5'}$ 1.1, 3'-H), 7.81 (1 H, dd, $J_{6,4}$ 1.7, 6-H), 8.54 (1 H, s, HC=N); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 61.8 (OMe), 72.5 (OCH_2), 112.5 (C-3), 121.1 (C-2'), 121.3 (C-5), 122.2 (C-1), 126.6 (C-5'), 127.5 (C-6'), 128.7 (C-4'), 129.3 (C-6), 131.0 (C-3'), 132.6 (C-4), 135.8 (C-1'), 144.5 (C=N) and 156.2 (C-2); *m/z* (EI^+) 287/289 (10%), 272/274 (5), 168/170 (100), 119 (4), 91 (98) and 77 (7) (Found: MH^+, 320.0286. $C_{15}H_{14}BrNO_2$ requires *M*, 320.0286).

2-(2-*Bromobenzyloxy*)*benzaldehyde* O-tert-*Butyloxime* **7b**.—As for the preparation of compound **2a**, 2-(2-bromobenzyloxy)-benzaldehyde **6** (1.00 g, 3.43 mmol) and *O*-*tert*-butylhydroxylamine hydrochloride (0.52 g, 4.12 mmol) were stirred overnight at room temperature in pyridine (10 cm^3). Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) as eluent afforded the *oxime ether* **7b** (1.04 g, 84%) as needles, m.p. 53–56 °C [from light petroleum (b.p. 60–80 °C)] (Found: C, 59.25; H, 5.5; N, 3.9. $C_{18}H_{20}BrNO_2$ requires C, 59.67; H, 5.57; N, 3.87%); R_f (diethyl ether–light petroleum, 1:9, v/v) 0.48; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3060w, 2960m, 2920m, 2890w, 1600m (C=N), 1565w, 1480m, 1445m and 1230s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.37 [9 H, s $(CH_3)_3C$], 5.11 (2 H, s, OCH_2), 6.90 (1 H, d, $J_{3,4}$ 8.3, 3-H), 6.96 (1 H, t, $J_{5,4} = J_{5,6}$ 7.5, 5-H), 7.16 (1 H, dd, $J_{4',5'}$ 7.4 and $J_{4',3'}$ 8.0, 4'-H), 7.26 (1 H, dd, 4-H), 7.31 (1 H, dd, $J_{5',6'}$ 7.6, 5'-H), 7.50 (1 H, d, 6'-H), 7.55 (1 H, d, 3'-H), 7.88 (1 H, d, 6-H) and 8.52 (1 H, s, HC=N); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 27.6 [$(CH_3)_3C$], 69.6 (OCH_2), 78.9 [$(CH_3)_3C$], 112.4 (C-3), 121.1 (C-5), 122.1 (C-2'), 122.1 (C-1), 126.4 (C-5'), 127.5 (C-6'), 128.8 (C-4'), 129.2 (C-6), 130.4 (C-3'), 132.5 (C-4), 135.9 (C-1'), 142.8 (C=N) and 156.0 (C-2); *m/z* (CI^+) 361/363 (M^+, 100%), 287/289 (5), 226 (2), 210 (4), 194 (10) and 169 (1) (Found: MH^+, 362.0756. $C_{18}H_{20}BrNO_2$ requires *M*, 362.0755).

11-*Methoxyamino*-6,11-*dihydrobenzo*[b,e]*oxepine* **8a**.—*Method C for radical cyclisation.* A degassed solution of the 2-(2-bromobenzyloxy)benzaldehyde *O*-methyloxime **7a** (300 mg, 0.94 mmol) in benzene (95 cm^3, 0.01 mol dm^{-3} **7a**) was heated at reflux under a nitrogen atmosphere. A solution of tributyltin hydride (327 mg, 1.12 mmol) and AIBN (30 mg, 0.19 mmol) in benzene (10 cm^3) was added to the reaction mixture *via* a syringe pump over 12 h. Heating was continued for a further 12 h. Benzene was removed under reduced pressure. Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) as eluent afforded the *hydroxylamine* **8a** (111 mg, 49%) and the reduction product **9a** (66 mg, 29%) as pale yellow oils.

Data for compound **8a**: R_f (diethyl ether–light petroleum, 1:9, v/v) 0.31; ν_{max}(film)/cm^{-1} 3240w, 3040w, 2950s, 2920s, 2890m, 2800w, 1600m, 1540m, 1480s and 1440s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.24 (3 H, s, OCH_3), 4.83 (1 H, d, $J_{2x,2y}$ 12.8, 6-H_x), 4.92 (1 H, s, 11-H), 5.90 (1 H, br s, NH), 6.28 (1 H, d, 6-H_y), 6.89 (1 H, dd, $J_{4,2}$ 1.2, $J_{4,3}$ 8.2, 4-H), 6.92 (1 H, td, $J_{2,1} = J_{9,10}$ 7.4, 2-H) and 7.16–7.36 (6 H, complex m, 7-H, 8-H, 9-H, 10-H, 1-H and 3-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 62.5 (OCH_3), 70.6 (C-11), 71.0 (C-6), 120.5 (C-3), 121.5 (C-4), 124.1 (C-11a), 128.4 (C-8 and C-1), 129.8 (C-7), 130.4 (C-10), 132.9 (C-9), 136.4 (C-6a), 138.0 (C-10a) and 158.1 (C-4a); *m/z* (CI^+) 240 ($[M - H]^+$, 38%), 225 (2), 210 (8) and 195 (100) [Found: $(M - H)^+$, 240.1025. $C_{15}H_{15}NO_2$ requires *M*, 240.1025].

2-*Benzyloxybenzaldehyde* O-*methyloxime* **9a**. R_f (diethyl ether–light petroleum, 1:4, v/v) 0.26; ν_{max}(film)/cm^{-1} 3040w, 3000w, 2960s, 2940s, 2900m, 2820m, 1600s, 1590m, 1570m, 1480s, 1450s and 1380s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.95 (3 H, s, OCH_3), 5.05 (2 H, s, OCH_2), 6.91 (1 H, d, $J_{3,4}$ 8.6, 3-H), 6.94 (1 H, t, $J_{5,4} = J_{5,6}$ 7.6, 5-H), 7.25–7.41 (6 H, complex m, 4-H and H_o, H_m and H_p in $PhCH_2$), 7.82 (1 H, dd, $J_{6,4}$ 1.8, $J_{6,5}$ 7.7, 6-H) and 8.52 (1 H, s, RHC=N); δ_C(75.5 MHz; $CDCl_3$; Me_4Si)

61.8 (OCH_3), 70.2 (OCH_2), 112.4 (C-3), 121.0 (C-1 and C-5), 126.4 (C_p), 127.2 (C_o), 127.9 (C-6), 128.5 (C_m), 131.0 (C-4), 136.5 (C-1 in *Ph*CH_2), 144.6 (HC=N) and 156.6 (C-2); *m/z* (EI^+) 241 (M^+, 3%), 210 (48), 195 (15) and 91 (100) (Found: M^+, 241.1100. $C_{15}H_{15}NO_2$ requires *M*, 241.1103).

11-(tert-*Butoxyamino*)-6,11-*dihydrodibenzo*[b,e]*oxepine* **8b**. —2-(2-Bromobenzyloxy)benzaldehyde *O*-*tert*-butyloxime **7b** (250 mg, 0.69 mmol) was treated with tributyltin hydride (400 mg, 1.37 mmol) and AIBN (25 mg, 0.14 mmol) in dry benzene according to method C. Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) as eluent gave the cyclised product **8b** (92 mg, 47%) as a clear colourless oil and the reduction product **9b** (70 mg, 36%) as needles, m.p. 88–89 °C (from light petroleum).

Data for compound **8b**: R_f (diethyl ether–light petroleum, 1:9, v/v) 0.33; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3010w, 2980s, 2910m, 2890m, 1600m, 1570m, 1480s, 1360s, 1310m and 1230s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.88 [9 H, s, $C(CH_3)_3$], 4.81 (1 H, d, $J_{6x,6y}$ 12.4, 6-H_x), 4.86 (1 H, s, 11-H), 5.27 (1 H, br s, NH), 6.34 (1 H, d, 6-H_y), 6.85 (1 H, dd, $J_{4,2}$ 1.3 and $J_{4,3}$ 8.4, 4-H), 6.90 (1 H, td, $J_{2,1} = J_{2,3}$ 7.5, 2-H) and 7.15–7.33 (6 H, complex m, 7-H, 8-H, 9-H, 2-H, 1-H and 3-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 26.8 [$C(CH_3)_3$], 70.68 (C-11), 70.72 (C-6), 76.9 [$C(CH_3)_3$], 120.3 (C-3), 121.1 (C-4), 123.3 (C-11a), 128.2 (C-8), 128.4 (C-1), 129.8 (C-7), 130.6 (C-2), 133.7 (C-9), 136.4 (C-6a), 138.7 (C-10a) and 158.2 (C-4a); *m/z* (EI^+) 284 (MH^+, 2%), 210 (3), 195 (100) and 90 (7) (Found: MH^+, 284.1651. $C_{18}H_{21}NO_2$ requires *M*, 284.1650).

2-*Benzyloxybenzaldehyde* O-tert-*butyloxime* **9b**. (Found: C, 76.4; H, 7.7; N, 5.05. $C_{18}H_{20}BrNO_2$ requires C, 76.29; H, 7.47; N, 4.94%); R_f (diethyl ether–light petroleum, 1:4, v/v) 0.40; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3020w, 2960m, 2910w, 2860w, 1600m, 1570w, 1480m and 1360m; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.35 [9 H, s, $(CH_3)_3C$], 5.00 (2 H, s, CH_2O), 6.87 (1 H, d, $J_{3,4}$ 8.4, 3-H), 6.92 (1 H, t, $J_{5,4} = J_{5,6}$ 7.7, 5-H), 7.23 (1 H, ddd, $J_{4,6}$ 1.8, 4-H), 7.27–7.38 (5 H, complex m, H_o, H_m, H_p in *Ph*CH_2), 7.88 (1 H, dd, 6-H) and 8.50 (1 H, s, RCH=N); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 27.6 (CH_3), 70.2 (OCH_2), 78.8 (Me_3C), 112.3 (C-3), 120.9 (C-5), 122.0 (C-1), 126.2 (C_p), 127.3 (C_o), 128.5 (C_m), 130.4 (C-4), 136.6 (C-1 in *Ph*CH_2), 142.9 (C=N) and 156.4 (C-2); *m/z* (CI^+), 284 (MH^+, 100%), 242 (24), 228 (5), 210 (14), 194 (5), 122 (22), 108 (12) and 91 (18) (Found: MH^+, 284.1651. $C_{18}H_{21}NO_2$ requires *M*, 284.1651).

3-(2-*Bromophenyl*)*propanal* O-*Methyloxime* **11a**.—3-(2-Bromophenyl)propanal **10a** (0.49 g, 2.32 mmol) and *O*-methylhydroxylamine hydrochloride (0.23 g, 2.78 mmol) were stirred in pyridine (5 cm^3) at room temperature for 24 h. Pyridine was removed under reduced pressure and the residue was diluted with diethyl ether, washed with water and the organic layer dried ($MgSO_4$). The organic layer was concentrated under reduced pressure and chromatography of the residue on silica gel with diethyl ether–light petroleum (3:7, v/v) afforded a 1:1 mixture of *E* and *Z* isomers of the title compound **11a** (0.47 g, 84%) as a clear colourless oil, R_f (diethyl ether–light petroleum, 3:7, v/v) 0.54 and 0.49; ν_{max}(film)/cm^{-1} 3050m, 2930s, 2900s, 2810m, 1630w (C=N), 1590w, 1565m, 1470s, 1440s, 1280–1020s and 750s; *m/z* (CI^+) 241/243 (MH^+, 100%), 211/213 (3), 181/183 (2), 162 (25), 132 (20) and 117 (2) (Found: MH^+, 242.011. $C_{10}H_{12}BrNO$ requires *M*, 242.0180).

E Isomer: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.49 (2 H, td, $J_{2,1}$ 5.9, $J_{2,3}$ 8.8, 2-H), 2.91 (2 H, t, 3-H), 3.80 (3 H, s, OCH_3), 7.04 (1 H, ddd overlapping with *Z* isomer, 4'-H), 7.21 (2 H, complex overlapping with *Z* isomer, 5'-H and 6'-H), 7.39 (1 H, t, 1-H) and 7.51 (1 H, d, $J_{3',4'}$ 7.7, 3'-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 29.6 (C-2), 33.2 (C-3), 61.2 (OCH_3), 127.3 (C-2'), 127.5 (C-5'), 127.9 (C-4'), 130.3 (C-6'), 132.8 (C-3'), 139.8 (C-1') and 149.3 (C-1).

Z Isomer: δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.64 (2 H, dt, $J_{2,1}$ 5.4, $J_{2,3}$ 8.8, 2-H), 2.89 (2 H, t, 3-H), 3.85 (3 H, s, OCH_3), 6.67 (1 H, t, 1-H), 7.04 (1 H, ddd overlapping with *E* isomer, 4'-H), 7.21 (2 H, complex overlapping with *E* isomer, 5'-H and 6'-H), 7.39 (1 H, t, 1-H) and 7.51 (1 H, d, $J_{3',4'}$ 7.7, 3'-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 25.5 (C-2), 32.4 (C-3), 61.6 (OCH_3), 127.3 (C-2'), 127.5 (C-5'), 127.9 (C-4'), 130.1 (C-6'), 132.6 (C-3'), 139.8 (C-1') and 150.0 (C-1).

4-(2-*Bromophenyl*)*butan-2-one* O-*Methyloxime* **11b**.—As for compound **10a**, 4-(2-bromophenyl)butan-2-one **10b** (3.00 g, 13.22 mmol) and *O*-methylhydroxylamine hydrochloride (1.65 g, 19.82 mmol) were stirred at room temperature in pyridine (10 cm^3) for 24 h. Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) as eluent yielded a mixture of *E* and *Z* isomers of **11b** as a clear, colourless oil (3.11 g, 92%), R_f (diethyl ether–light petroleum, 1:9, v/v) 0.36 and 0.31; ν_{max}(film)/cm^{-1} 3050w, 2980w, 2930s, 2890m, 2810m, 1640w (C=N), 1560w, 1470s, 1440s and 750s; *m/z* (CI^+) 256/258 (MH^+, 100%), 226/228 (10), 176 (18), 162 (3), 146 (15) and 131 (20) (Found: MH^+, 256.0337. $C_{11}H_{14}BrNO$ requires *M*, 256.0337).

E Isomer (R_f 0.36): δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.68 (3 H, s, 1-H), 2.45 (2 H, m, 3-H), 2.93 (2 H, m, 4-H), 3.83 (3 H, s, OCH_3), 7.04 (1 H, ddd overlapping with *Z* isomer, 4'-H), 7.21 (2 H, complex m overlapping with *Z* isomer, 5'-H and 6'-H) and 7.51 (1 H, d, $J_{3',4'}$ 8.1, 3'-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 14.1 (C-1), 33.2 (C-3), 36.0 (C-4), 61.0 (OCH_3), 124.2 (C-2'), 127.4 (C-5'), 127.7 (C-4'), 130.3 (C-6'), 132.7 (C-3'), 140.3 (C-1') and 156.2 (C-2).

Z Isomer (R_f 0.31): δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.23 (3 H, s, 1-H), 2.58 (2 H, m, 3-H), 2.93 (2 H, m, 4-H), 3.80 (3 H, s, OCH_3), 7.04 (1 H, ddd overlapping with *E* isomer, 4'-H), 7.21 (2 H, complex m overlapping with *E* isomer, 5'-H and 6'-H) and 7.51 (1 H, d, $J_{3',4'}$ 8.1, 3'-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 20.1 (C-1), 29.4 (C-3), 31.9 (C-4), 61.0 (OCH_3), 124.2 (C-2'), 127.4 (C-5'), 127.7 (C-4'), 130.2 (C-6'), 132.6 (C-3'), 140.2 (C-1') and 156.8 (C-2).

1-*Methoxyaminoindane* **12a**.—3-(2-Bromophenyl)propanal *O*-methyloxime **11a** (100 mg, 0.41 mmol) was treated with tributyltin hydride (240 mg, 0.83 mmol) and AIBN (80 mg, 0.08 mmol) in benzene according to method C. Chromatography of the residue on silica gel with diethyl ether–light petroleum ether (3:7, v/v) as eluent gave the title compound **12a** as a colourless oil (93 mg, 69%), R_f (diethyl ether–light petroleum, 3:7, v/v) 0.34; ν_{max}(film)/cm^{-1} 3010m, 2940s, 2890m, 2840m, 1450s and 1210s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.02 (1 H, dddd, $J_{2x,1x}$ 4.8, $J_{2x,3x}$ 5.4, $J_{2x,3y}$ 8.8 and $J_{2x,2y}$ 13.3, 2-H_x), 2.32 (1 H, dddd, $J_{2y,3y}$ 6.5, $J_{2y,1}$ 7.3 and $J_{2y,3x}$ 8.8, 2-H_y), 2.84 (1 H, ddd, $J_{3x,3y}$ 15.1, 3-H_x), 3.04 (1 H, ddd, 3-H_y), 3.55 (3 H, s, OCH_3), 4.59 (1 H, dd, 1-H), 5.05 (1 H, br s, N*H*OCH_3), 7.15–7.24 (3 H, complex m, 5-H, 6-H and 7-H) and 7.40 (1 H, d, $J_{4,5}$ 6.5, 4-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 30.2 (C-2 or C-3), 30.4 (C-3 or C-2), 62.1 (OCH_3), 65.6 (C-1), 124.8 (C-6), 124.9 (C-7), 126.2 (C-5), 127.9 (C-4), 142.1 (C-3a) and 144.3 (C-7a); *m/z* (CI^+) 164 (MH^+, 100%), 132 (21), 117 (67) and 91 (2) (Found: MH^+, 164.1075. $C_{10}H_{13}NO$ requires *M*, 164.1075).

1-*Methoxyamino*-1-*methylindane* **12b**.—4-(2-Bromophenyl)-butan-2-one *O*-methyloxime **11b** (1.70 g, 6.66 mmol) was treated with tributyltin hydride (3.87 g, 13.31 mmol) and AIBN (0.11 g, 0.67 mmol) according to method C. Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) as eluent afforded the title compound **12b** as a clear, colourless oil (0.87 g, 74%), R_f (diethyl ether–light petroleum, 1:4, v/v) 0.17;

ν_{max}(film)/cm^{-1} 3230br w, 3060w, 3010w, 2960s, 2910s, 2880s, 2840m, 2800m, 1600w, 1580w, 1450s, 1370m and 750s; δ_H(300 MHz; $CDCl_3$; Me_3Si) 1.43 (3 H, s, CH_3), 1.93 (1 H, ddd, $J_{2x,3x}$ 6.6, $J_{2x,3y}$ 8.6 and $J_{2x,2y}$ 13.1, 2-H_x), 2.27 (1 H, ddd, $J_{2y,3y}$ 5.0 and $J_{2y,3x}$ 8.4, 2-H_y), 2.82 (1 H, ddd, $J_{3x,3y}$ 15.9, 3-H_x), 2.97 (1 H, ddd, 3-H_y), 3.47 (3 H, s, OCH_3), 5.26 (1 H, br s, N*H*OCH_3), 7.13–7.19 (3 H, complex m, 5-H, 6-H and 7-H) and 7.28 (1 H, m, 4-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 23.9 (CH_3), 29.7 (C-2 or C-3), 36.6 (C-3 or C-2), 62.9 (OCH_3), 69.3 (C-1), 123.3 (C-6), 124.7 (C-7), 126.2 (C-5), 127.7 (C-4), 143.6 (C-3a) and 146.2 (C-7a); *m/z* (CI$^+$) 178 (MH$^+$, 12%), 146 (15) and 131 (100) (Found: MH$^+$, 178.1232. $C_{11}H_{15}NO$ requires *M*, 178.1232).

Ethyl 1-(2-*Bromobenzyl*)-2-*oxocyclopentanecarboxylate* **13a**.—Ethyl 2-oxocyclopentanecarboxylate (2.00 g, 12.82 mmol) in tetrahydrofuran (THF) (10 cm^3) was added dropwise to sodium hydride (370 mg, 15.42 mmol, 80% dispersion in mineral oil) suspended in a solution of 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU) (1.97 g, 15.42 mmol) and THF (20 cm^3). After the mixture had been stirred at room temperature for 1 h, 2-bromobenzyl bromide (3.85 g, 15.42 mmol) in dry THF (10 cm^3) was added in one portion to it and the whole heated at reflux for 4 h. The reaction mixture was then poured into water and the product was extracted with diethyl ether. The organic phase was dried ($MgSO_4$) and diethyl ether removed under reduced pressure. Chromatography of the residue on silica gel with ethyl acetate–light petroleum (1:9, v/v) as eluent gave the title compound **13a** as a clear colourless oil (3.01 g, 72%); R_f (ethyl acetate–light petroleum, 1:3, v/v) 0.48; ν_{max}(film)/cm^{-1} 3025w, 2980–2860s, 1740s (C=O), 1720s (CO_2Et, C=O), 1560w, 1465s, 1435s, 1230s and 750m; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.25 (3 H, t, *J* 7.1, OCH_2CH_3), 1.66–2.08 (4 H, complex m, 4-H and 5-H), 2.31–2.53 (2 H, complex m, 3-H), 3.31 (1 H, d, *J* 14.2, ArCH_a), 3.54 (1 H, d, ArCH_b), 4.17 [1 H, dq (AB system), *J* 11.8, OCH_a], 4.21 [1 H, dq (AB system), OCH_b], 7.02–7.09 (1 H, complex m, 4′-H), 7.10–7.24 (2 H, complex m, 5′-H and 6′-H) and 7.53 (1 H, d, $J_{3',4'}$ 7.8, 3′-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 14.0 (CH_3), 19.7 (C-4), 31.7 (ArCH_2), 37.5 (C-5), 38.2 (C-3), 61.4 (C-1), 61.6 (OCH_2), 126.3 (C-2′), 127.5 (C-5′), 128.4 (C-4′), 131.4 (C-6′), 132.9 (C-3′), 136.7 (C-1′), 170.8 (CO_2Et) and 214.7 (C-2); *m/z* (CI$^+$) 341/343 [(M + NH_3)$^+$, 100%], 324/326 (M$^+$, 78), 295/297 (2), 278/280 (5), 261/263 (3), 245 (27), 185/187 (2), 172 (31) 155, (27), 128 (3) and 91 (2) (Found: M$^+$, 325.0439. $C_{15}H_{17}BrO_3$ requires *M*, 325.0439).

Ethyl 1-(2-*Bromobenzyl*)-2-*oxocyclohexanecarboxylate* **13b**.—As for the preparation of compound **13a**, ethyl 2-oxocyclohexanecarboxylate (4.94 g, 29.02 mmol) was successively treated with sodium hydride (80% dispersion in mineral oil; 0.84 g, 34.83 mmol) in a solution of dry THF (50 cm^3) and DMPU (4.46 g, 34.83 mmol) and 2-bromobenzyl bromide (7.98 g, 31.92 mmol) in dry THF (10 cm^3). Chromatography on silica gel with diethyl ether–light petroleum (1:4, v/v) as eluent afforded the title compound **13b** (7.77 g, 79%) as prisms, m.p. 47.5–48.5 °C (from aqueous methanol) (Found: C, 56.65; H, 5.7. $C_{16}H_{19}BrO_3$ requires C, 56.65; H, 5.65%); R_f (diethyl ether–light petroleum, 1:4, v/v) 0.33; ν_{max}(CH_2Cl_2)/cm^{-1} 3030w, 2980m, 2940s, 2860m, 1760–1700s (C=O and CO_2Et), 1560w, 1465s and 1430s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.20 (3 H, t, *J* 7.1, CH_3), 1.52–1.80 (4 H, complex m, 4-H and 5-H), 2.00 (1 H, complex m, 6-H_a), 2.41–2.52 (3 H, complex m, 3-H and 6-H_b), 3.28 (1 H, d, *J* 14.3, ArCH_aH_b), 3.46 (1 H, d, ArCH_aH_b), 4.13 [1 H (ABX$_3$ system), dq, *J* 10.8, OCH_xH_y], 4.17 [1 H (ABX$_3$ system), dq, OCH_xH_y], 7.05 (1 H, ddd, $J_{4',6'}$ 2.8, $J_{4',5'}$ 6.0 and $J_{4',3'}$ 8.0, 4′-H), 7.14–7.28 (2 H, complex m, 5′-H and 6′-H) and 7.50 (1 H, d, 3′-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 13.9 (CH_3), 22.5 (C-5), 27.5 (ArCH_2), 35.3 (C-4), 38.6 (C-6), 41.1 (C-3), 61.4 (OCH_2), 61.9 (C-1), 125.9 (C-2′), 127.0 (C-5′), 128.2 (C-4′), 132.0 (C-6′), 132.8 (C-3′), 136.5 (C-1′), 170.8 ($CO_2CH_2CH_3$) and 206.9 (C-2); *m/z* (CI$^+$) 356/358 [(M + NH_4)$^+$, 11%], 339/341 (MH$^+$, 100), 259 (25), 232 (2), 185 (13) and 169 (13) (Found: MH$^+$, 339.0596. $C_{16}H_{19}BrO_3$ requires *M*, 339.0596).

Ethyl 1-(2-*Bromobenzyl*)-2-*oxocyclopentanecarboxylate* O-*Methyloxime* **14a**.—As for the preparation of compound **2a**, ethyl 1-(2-bromobenzyl)-2-oxocyclopentanecarboxylate **13a** (2.80 g, 8.94 mmol) and *O*-methylhydroxylamine hydrochloride (0.90 g, 10.73 mmol) were stirred at room temperature in pyridine (10 cm^3) for 24 h. Chromatography on silica gel with ethyl acetate–light petroleum (1:3, v/v) as eluent gave the title compound **14a** as a clear, colourless oil (2.57 g, 84%); R_f (ethyl acetate–light petroleum, 1:3, v/v) 0.53; ν_{max}(film)/cm^{-1} 3060w, 2980–2810s, 1725s (C=O), 1645w (C=N), 1565w, 1465m, 1440s, 1230s and 750m; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.24 (3 H, t, *J* 7.1, CH_3), 1.56–2.56 (6 H, complex m, 3-H, 4-H and 5-H), 3.36 (1 H, d, *J* 14.2, ArCH_a), 3.62 (1 H, d, ArCH_b), 3.91 (3 H, s, OCH_3), 4.17 [1 H, dq (ABX$_3$ system), *J* 11.7, OCH_xH_y], 4.20 [1 H, dq (ABX$_3$ system), OCH_xH_y], 7.03 (1 H, ddd, $J_{4',6'}$ 1.7, $J_{4',5'}$ 7.7 and $J_{4',3'}$ 8.0, 4′-H), 7.17 (1 H, td, $J_{5',3'}$ 1.3 and $J_{5',6'}$ 7.7, 5′-H), 7.36 (1 H, dd, 6′-H) and 7.51 (1 H, dd, 3′-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_3), 22.0 (C-4), 27.9 (ArCH_2), 34.1 (C-5), 39.4 (C-3), 57.3 (C-1), 61.2 (OCH_2), 61.9 (OCH_3), 126.5 (C-2′), 127.1 (C-5′), 128.1 (C-4′), 131.7 (C-6′), 132.7 (C-3′), 137.5 (C-1′), 164.6 (C-2) and 173.2 ($CO_2CH_2CH_3$); *m/z* (CI$^+$) 353/355 (M$^+$, 100%), 339/341 (8), 323/325 (2), 274 (27), 260 (2), 244 (15), 170 (11) and 128 (2) (Found: M$^+$, 354.0704. $C_{16}H_{20}BrNO_3$ requires *M*, 374.0704).

Ethyl 1-(2-*Bromobenzyl*)-2-*oxocyclohexanecarboxylate* O-*Methyloxime* **14b**.—As for the preparation of compound **2a**, ethyl 1-(2-bromobenzyl)-2-oxocyclohexanecarboxylate **13b** (1.00 g, 2.95 mmol) and *O*-methylhydroxylamine hydrochloride (0.30 g, 3.54 mmol) were stirred at room temperature for 24 h in pyridine (10 cm^3). Chromatography on silica gel with diethyl ether–light petroleum (1:4, v/v) as eluent gave the title compound **14b** (0.73 g, 67%) as a clear, colourless oil; R_f (diethyl ether–light petroleum, 1:4, v/v) 0.47; ν_{max}(film)/cm^{-1} 3050w, 2930s, 2895m, 2880m, 2810w, 1720s (C=O), 1645w (C=N), 1460s, 1430s and 750s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.18 (3 H, t, *J* 7.1, CH_3), 1.23–1.78 (6 H, complex m, 4-H, 5-H and 6-H), 2.30 (1 H, ddd, 3-H_a), 3.31 (1 H, ddd, 3-H_b), 3.35 (1 H, d, *J* 14.3, ArCH_aH_b), 3.53 (1 H, d, ArCH_aH_b), 4.10 [1 H (ABX$_3$ system), dq, *J* 15.6, OCH_xH_y], 4.13 [1 H (ABX$_3$ system), dq, OCH_xH_y], 7.03 (1 H, ddd, $J_{4',6'}$ 2.3, $J_{4',5'}$ 6.8 and $J_{4',3'}$ 7.9, 4′-H), 7.19 (2 H, complex m, 5′-H and 6′-H) and 7.51 (1 H, dd, $J_{3',5'}$ 1.1, 3′-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 14.0 (CH_3), 22.8 (C-5), 24.0 (ArCH_2), 25.6 (C-4), 35.1 (C-6), 39.4 (C-3), 54.7 (C-1), 61.0 (OCH_2), 61.5 (CH_3), 126.2 (C-2′), 126.7 (C-5′), 127.9 (C-4′), 132.1 (C-6′), 132.7 (C-3′), 137.3 (C-1′), 158.8 (C-2) and 172.6 (C=O); *m/z* (CI$^+$), 368/370 (M$^+$, 100%), 338/340 (4), 228 (15), 258 (15), 243 (8), 217 (3) and 184 (8) (Found: MH$^+$, 368.0861. $C_{17}H_{22}BrNO_3$ requires *M*, 368.0861).

Ethyl 3a-*Methoxyamino*-1,2,3,3a,8,8a-*hexahydrocyclopent*-[a]*indene*-8a-*carboxylate* **15a**.—According to method A, ethyl 1-(2-bromobenzyl)-2-oxocyclopentanecarboxylate *O*-methyloxime **14a** (200 mg, 0.56 mmol) was treated with tributyltin hydride (330 mg, 0.56 mmol) and AIBN (20 mg, 0.11 mmol) in benzene (37 cm^3). Chromatography on silica gel with ethyl acetate–light petroleum (1:9, v/v) as eluent gave the *hydroxylamine* **15a** as a single diastereoisomer as a clear colourless oil (105 mg, 0.38 mmol, 68%); R_f (ethyl acetate–light petroleum, 1:9, v/v) 0.39; ν_{max}(CH_2Cl_2)/cm^{-1} 3010w, 2960s, 2900m, 2860m,

2810w, 1710s (C=O), 1590w, 1470–1430m and 1230w; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.29 (3 H, t, *J* 7.1, CH_3), 1.33–1.42 (1 H, complex m, 2-H_x), 1.70–1.84 (2 H, complex m, 3-H_x and 2-H_y), 1.95–2.09 (2 H, complex m, 1-H_x and 3-H_y), 2.27–2.37 (1 H, m, 1-H_y), 2.84 (1 H, d, $J_{8x,8y}$ 16.2, 8-H_x), 3.74 (1 H, d, 8-H_y), 4.21 (2 H, q, *J* 7.1, OCH_2), 6.49 (1 H, br s, NH), 7.14–7.26 (3 H, complex m, 4-H, 7-H and 5-H or 6-H), 7.33–7.38 (1 H, complex m, 6-H or 5-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 14.2 (CH_3), 23.3 (C-2), 37.3 (C-3), 41.0 (C-1), 43.9 (C-8), 58.8 (C-8a), 60.7 (OCH_2), 62.4 (OCH_3), 84.4 (C-3a), 124.2 (C-6), 124.5 (C-7), 126.8 (C-5), 128.1 (C-4), 142.3 (C-3b), 144.5 (C-7a) and 176.3 (C=O); *m/z* (CI^+) 276 (MH^+, 100%), 244 (37), 229 (40), 170 (4) and 155 (11) (Found: MH^+, 276.1600. $C_{16}H_{21}NO_3$ requires *M*, 276.1600).

Ethyl 4a-*Methoxyamino*-1,2,3,4,4a,9a-*hexahydrofluorene*-9a-*carboxylate* **15b**.—Ethyl 1-(2-bromobenzyl)-2-oxocyclohexanecarboxylate *O*-methyloxime **14b** (300 mg, 0.82 mmol) was treated with tributyltin hydride (475 mg, 1.63 mmol) and AIBN (30 mg, 0.18 mmol) according to method A. Chromatography on silica gel with diethyl ether–light petroleum (1:4, v/v) as eluent afforded the *hydroxylamine* **15b** as a clear, colourless oil (214 mg, 0.74 mmol, 90%), R_f (diethyl ether–light petroleum, 1:4, v/v) 0.32; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3262w, 3010w, 2920s, 2850s, 2800w, 1710s (C=O), 1600w, 1560w, 1500m, 1480–1440s and 1230m; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.07 (1 H, qt, $J_{3ax,3eq} = J_{3ax,4ax} = J_{3ax,2ax}$ 13.6 and $J_{3ax,4eq} = J_{3ax,2eq}$ 3.7, 3-H_{ax}), 1.27 (1 H, td, $J_{4ax,4eq}$ 13.6 and $J_{4ax,3eq}$ 4.0, 4-H_{ax}), 1.31 (3 H, t, CH_3), 1.37 (1 H, m, 2-H_{eq}), 1.48 (1 H, qt, $J_{2ax,2eq} = J_{2ax,1ax}$ 13.6 and $J_{2ax,1eq} = J_{2ax,3eq}$ 4.0, 2-H_{ax}), 1.67 (1 H, br m, 3-H_{eq}), 1.84 (1 H, td, $J_{1ax,1eq}$ 13.6 and $J_{1ax,2eq}$ 4.2, 1-H_{ax}), 1.93 (1 H, ddd, $J_{4eq,3eq}$ 4.8, 4-H_{eq}), 2.39 (1 H, br ddd, 1-H_{eq}), 2.61 (1 H, d, $J_{9x,9y}$ 15.3, 9-H_x), 2.90 (1 H, s, OCH_3), 3.67 (1 H, d, 9-H_y), 4.23 (2 H, q, OCH_2), 6.27 (1 H, br, NH), 7.16–7.34 (4 H, complex m, 5-H, 6-H, 7-H and 8-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_3), 21.8 (C-3), 21.9 (C-2), 28.4 (C-4), 35.7 (C-1), 42.8 (C-9), 54.7 (C-9a), 60.2 (OCH_2), 62.3 (OCH_3), 70.9 (C-4a), 124.2 (C-7), 125.0 (C-8), 126.1 (C-6), 127.8 (C-5), 142.2 (C-4b), 142.8 (C-8a) and 175.0 (C=O); *m/z* (EI^+) 290 (MH^+, 80%), 260 (32), 243 (100), 199 (3) and 169 (36) (Found: MH^+, 290.1756. $C_{17}H_{23}NO_3$ requires *M*, 290.1756).

2-(2-*Bromobenzyl*)*cyclohexanone* **16**.—Pyrrolidin-1-ylcyclohex-1-ene (2.57 g, 17.00 mmol) and 2-bromobenzyl bromide (4.25 g, 17.00 mmol) were heated at reflux temperature in benzene (30 cm^3) for 6 h. A solution of sodium acetate–acetic acid–water (1:2:2; 25 cm^3) was added to the reaction mixture which was then heated at reflux for 2 h. The mixture was then diluted with water and extracted with diethyl ether. The organic extracts were dried and evaporated under reduced pressure. Chromatography of the residue on silica gel with diethyl ether–light petroleum (1:4, v/v) as eluent afforded the product **16** as a clear colouress oil (3.16 g, 11.84 mmol, 70%); R_f (diethyl ether–light petroleum, 1:4, v/v) 0.34; ν_{max}(film)/cm^{-1} 3025w, 2930s, 2860s, 1700s (C=O), 1560w, 1465s, 1440s and 745s; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.39 (1 H, complex dddd, $J_{3ax,2ax} = J_{3ax,4ax} = J_{3ax,4eq}$ 3.6 and $J_{3ax,3eq}$ 12.0, 3-H_{ax}), 1.60 (2 H, complex m, 4-H_{ax} and 5-H_{ax}), 1.80 (1 H, complex dddd, 2-H_{ax}), 2.04 (2 H, complex m, 5-H_{eq} and 3-H_{eq}), 2.30 (1 H, complex ddd, $J_{6ax,5ax}$ 10.2, $J_{6ax,5eq}$ 5.8 and $J_{6ax,6eq}$ 12.9, 6-H_{ax}), 2.39 (1 H, complex m, 4-H_{eq}), 2.54 (dd, 1 H, $J_{a,2ax}$ 8.1 and $J_{a,b}$ 13.7, $ArCH_aH_b$), 2.66 (1 H, complex m, 6-H_{eq}), 3.34 (1 H, dd, $J_{b,2ax}$ 5.2, $ArCH_aH_b$), 7.03 (1 H, ddd, $J_{4',6'}$ 2.1, $J_{4',5'}$ 7.0 and $J_{4',3'}$ 7.9, 4'-H), 7.18 (1 H, ddd, $J_{5',3'}$ 1.1 and $J_{5',6'}$ 7.6, 5'-H), 7.23 (1 H, dd, 6'-H) and 7.49 (1 H, dd, 3'-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 25.2 (C-5), 28.1 (C-4), 33.6 (C-3), 35.6 ($ArCH_2$), 42.2 (C-6), 50.5 (C-2), 124.6 (C-2'), 127.1 (C-5'), 127.7 (C-4'), 131.7 (C-6'), 132.6 (C-3'), 139.6 (C-1') and 211.8 (C-1); *m/z* (CI^+) 284/286 [$(M + NH_4)^+$, 100%], 267/269 (MH^+, 31), 187 (53) and 169/171 (2) [Found: $(M + NH_4)^+$, 284.0650. $C_{13}H_{15}BrO$ requires $(M + NH_4)^+$, 284.0650].

2(2-*Bromobenzyl*)*cyclohexanone* O-*Methyloxime* **17**.—As for compound **2a**, 2-(2-bromobenzyl)cyclohexanone **16** (1.00 g, 3.75 mmol) and *O*-methylhydroxylamine hydrochloride (0.47 g, 5.62 mmol) were stirred overnight at room temperature in pyridine (10 cm^3). Chromatography on silica gel with diethyl ether–light petroleum ether (1:9, v/v) as eluent gave a mixture of isomers of the *oxime ether* **17** as a clear colourless oil (0.86 g, 2.93 mmol, 78%); R_f (diethyl ether–light petroleum, 1:4, v/v) 0.31 and 0.28; ν_{max}(film)/cm^{-1} 3030w, 2980w, 2930s, 2880s, 2805w, 1650w (C=N), 1560w, 1465s, 1440s, 1050s, 1020s and 750s.

Major isomer (R_f = 0.31): δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.26–1.79 (6 H, complex m, 2-H_{ax}, 3-H_{ax}, 3-H_{eq}, 4-H_{ax}, 5-H_{ax} and 5-H_{eq}), 2.04 (1 H, ddd, $J_{6ax,5eq}$ 4.4, $J_{6ax,5ax}$ 9.9 and $J_{6ax,6eq}$ 14.0, 6-H_{ax}), 2.56 (1 H, br m, 4-H_{eq}), 2.74 (1 H, dd, $J_{x,2ax}$ 8.7 and $J_{x,y}$ 13.7, $ArCH_xH_y$), 2.91 (1 H, m overlapping with minor isomer, 6-H_{eq}), 3.26 (1 H, dd, $J_{y,2ax}$ 5.5, $ArCH_xH_y$), 3.82 (3 H, s, OCH_3), 7.03 (1 H, ddd, $J_{4',6'}$ 2.3, $J_{4',5'}$ 6.9 and $J_{4',3'}$ 7.8, 4'-H), 7.16–7.23 (2 H, m, 5'-H and 6'-H), 7.50 (1 H, d, 3'-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 24.3 (C-5), 24.5 (C-4), 26.2 (C-3), 32.4 ($ArCH_2$), 37.1 (C-6), 42.2 (C-2), 61.0 (OCH_3), 124.9 (C-2'), 126.9 (C-5'), 127.5 (C-4'), 131.7 (C-6'), 132.7 (C-3'), 140.2 (C-1') and 160.9 (C-1).

Minor isomer (R_f = 0.28): δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.26–1.79 (6 H, complex m, 2-H_{ax}, 3-H_{ax}, 3-H_{eq}, 4-H_{ax}, 5-H_{ax} and 5-H_{eq}), 1.96 (1 H, m, 6-H_{ax}), 2.30 (2 H, dd, $ArCH_2$), 2.90 (2 H, m, 4-H_{eq} and 6-H_{eq}), 3.56 (3 H, s, OCH_3), 7.03 (1 H, ddd, $J_{4',6'}$ 2.3, $J_{4',5'}$ 6.9 and $J_{4',3'}$ 7.8, 4'-H), 7.16–7.23 (2 H, m, 5'-H and 6'-H) and 7.50 (1 H, d, 3'-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 21.0 (C-5), 26.8 (C-4), 28.8 (C-3), 28.9 ($ArCH_2$), 33.6 (C-2), 36.4 (C-6), 60.6 (OCH_3), 124.9 (C-2'), 127.0 (C-5'), 127.7 (C-4'), 130.9 (C-6'), 132.5 (C-3'), 139.2 (C-1') and 161.4 (C-1); *m/z* (CI^+) 296/298 (MH^+, 100%), 266 (5), 216 (45), 186 (12), 171 (5) (Found: MH^+, 296.0650. $C_{14}H_{18}BrNO$ requires *M*, 296.0650).

9b-*Methoxyamino*-1,2,3,3a,8,8a-*hexahydrocyclopent*[a]-*indene* **18**.—2-(2-Bromobenzyl)cyclohexanone *O*-methyloxime **17** (300 mg, 1.01 mmol) was treated with tributyltin hydride (590 mg, 2.03 mmol) and AIBN (33 mg, 0.02 mmol) in benzene (51 cm^3, 0.02 mol dm^{-3} **17**) according to method A. Chromatography on silica gel with diethyl ether–light petroleum (1:9, v/v) yielded the *hydroxylamine* **18** (127 mg, 0.59 mmol, 58%) as a pale yellow oil; R_f (diethyl ether–light petroleum, 1:9, v/v) 0.31; ν_{max}(film)/cm^{-1} 3400br (H_2O), 3210br w, 3030w, 2910s, 2850s, 2800m, 1630–1580w, 1450m and 760s; δ_H(400 MHz and COSY; $CDCl_3$; Me_4Si) 1.15 (1 H, m, 4-H_{ax}), 1.20 (1 H, m, 2-H_{ax}), 1.36 (1 H, dtt, $J_{3ax,4eq} = J_{3ax,2eq}$ 3.5, $J_{3ax,4ax} = J_{3ax,2ax}$ 9.4, $J_{3ax,3eq}$ 13.0, 3-H_{ax}), 1.47 (1 H, dtt, $J_{3eq,2eq} = J_{3eq,4eq}$ 3.4, $J_{3eq,4ax} = J_{3eq,2ax}$ 6.7, 3-H_{eq}), 1.60 (1 H, m, 2-H_{eq}), 1.79 (1 H, m, 4-H_{eq}), 1.88 (1 H, ddd, $J_{1ax,2eq}$ 4.1, $J_{1ax,2ax}$ 9.6, $J_{1ax,1eq}$ 13.9, 1-H_{ax}), 1.96 (1 H, ddd, $J_{1eq,2eq}$ 4.2, $J_{1eq,2ax}$ 6.8, 1-H_{eq}), 2.48 (1 H, m, 4-H_a), 2.52 (dd, 1 H, $J_{5x,4a}$ 4.5, $J_{5x,5y}$ 15.0, 5-H_x), 3.09 (1 H, dd, $J_{5y,4a}$ 6.1, 5-H_y), 3.48 (3 H, s, OCH_3), 5.47 (1 H, br s, NH), 7.17–7.30 (4 H, complex m, 6-H, 7-H, 8-H and 9-H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 22.1 (C-3), 23.3 (C-4), 28.3 (C-2), 30.2 (C-1), 36.0 (C-5), 41.0 (C-4a), 62.9 (OCH_3), 70.5 (C-9b), 123.1 (C-7), 125.7 (C-6), 126.1 (C-8), 127.6 (C-9), 143.4 (C-9a) and 145.3 (C-5a); *m/z* (CI^+) 218 (MH^+, 15%), 186 (15), 171 (100) and 129 (12) (Found: MH^+, 218.1545. $C_{14}H_{19}NO$ requires *M*, 218.1545).

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