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Efficient Routes to Cyclic 2,3-Epoxyalcohols from Cycloalkenyl Ketones, *via* Cycloalkenyl Alcohols

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Abstract: *The minimising of torsional strain and non-bonding interactions is proposed as the explanation of high diastereoselectivity observed in the epoxidation of cycloalkenyl alcohols, reported for twenty three examples The resulting 2,3-epoxyalcohols are key intermediates in the synthesis of tricyclic 1, 2-diols and β-hydroxy ketones*

Background

In recent years, 2,3-epoxyalcohols have been shown to be highly versatile intermediates in organic synthesis.[1] Their accessibility by epoxidation of the corresponding allylic alcohols is enhanced by the stereoselectivity of the Katsuki-Sharpless reaction.[2,3] Considerably less attention has been given to the epoxidation of alicyclic unsaturated alcohols such as **1-4** (*Figure 1*). Such epoxidations would be expected to show appreciable diastereoselection and this has been demonstrated for **1**,[4,5] **2**[6] and **3**.[7,8,9] In the latter case, the epoxyketoalcohols serve as key precursors in stereocontrolled syntheses of hydroxylated tricyclic systems.[7,9] Accordingly, we sought expeditious routes to the analogous but less structurally intricate epoxides derived from cycloalkenyl alcohols **4**. In the following paper we show that such epoxides are crucial precursors for an efficient and highly diastereoselective synthesis of tricyclic diols.

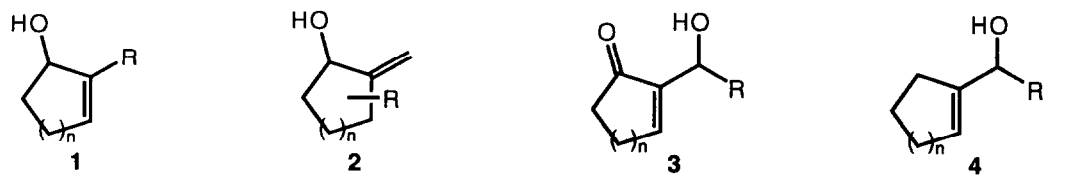
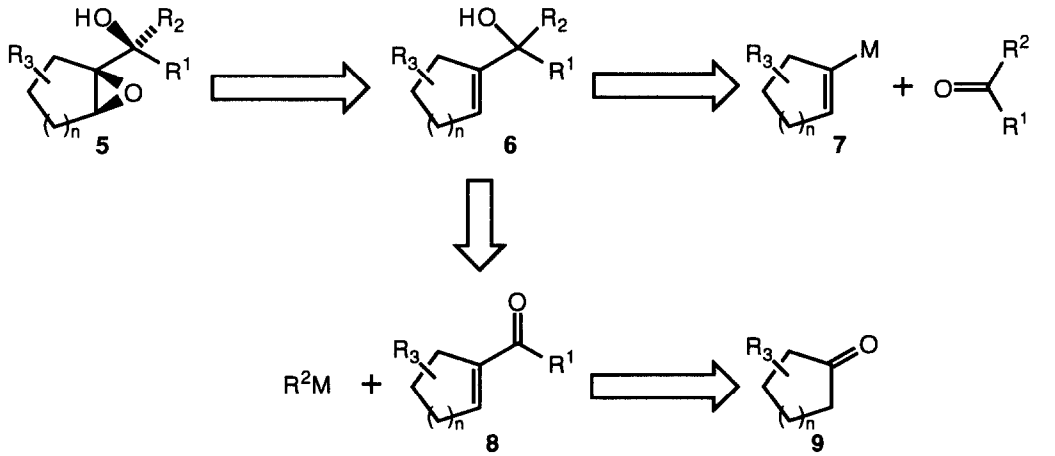


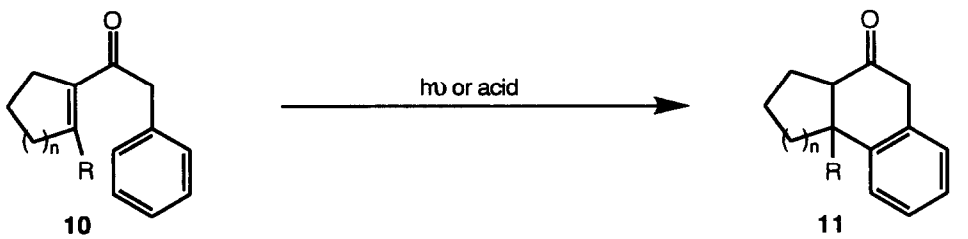
Figure 1. Alicyclic Unsaturated Alcohols

Additionally, we have shown that such epoxides can undergo a remarkable variety of 1, 2-migrations from one carbon atom to another carbon atom.[10] The present paper reports the preparation of an extensive range of alicyclic epoxyalcohols of the form **5** (*Scheme 1*), together with efficient routes to the corresponding allylic alcohols **6**. We also show that the latter can frequently be prepared from cycloalkanones **9** *via* the cycloalkenyl ketones **8**.



Scheme 1: Synthetic Strategy

The cycloalkenyl ketones **8** are themselves valuable intermediates in the synthesis of angularly fused polycyclic systems (*e.g.* **11** n=1 the BCD skeleton of the steroids, *Scheme 2*). For example both acid catalysed[11] and photochemical[12] ring closures of **10** (R=H, CH_3 n=2) have been reported.



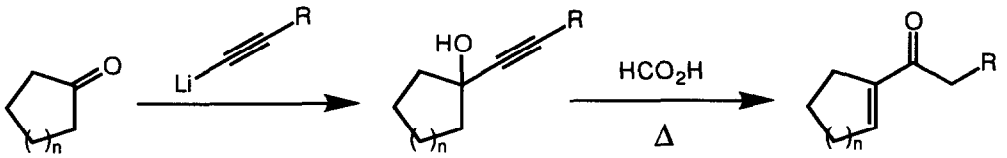
Scheme 2: Cyclisation of Cycloalkenyl Ketones

Results and Discussion

The most convergent approach to the allylic alcohols **6** involves the addition of a cycloalkenyl metal species **7** (M=Li or MgX) to a ketone or aldehyde. This route is satisfactory for some unsubstituted cycloalkenyllithiums (**3**, R^3=H, n=1,[14] **2**[15,16] and **3**[17]) which have been prepared by reaction of lithium with the appropriate 1-chloro-1-cycloalkene. However, the

yields rarely exceed 50%. An alternative is the Shapiro reaction,[18] but this employs costly reagents and is not usually amenable to multigram scales.

An alternative approach employs a 1, 2-addition of an organometallic reagent to an enone **8**. Although cycloalkenyl ketones such as **8** are useful intermediates in synthesis, early attempts to prepare them were not synthetically viable, and in many cases efficient routes to them are still lacking. Friedel-Crafts acylation[19] of cycloalkenes usually affords mixtures of ketones (including chloroketones and deconjugated ketones). In a recent modification, 1-acetyl-1-cycloalkenes were obtained in good yields[19c] but the success of other acylating reagents has yet to be demonstrated. Since cycloalkanones **9** are available in quantity, an attractive possibility was the synthesis of the ketones **8** by a Rupe reaction[20-24] of propargylic alcohols **12** prepared by a Nef reaction[25] between a cycloalkanone **9** and an alkynyllithium (*Scheme 3*).



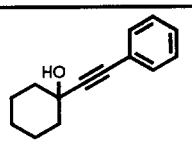
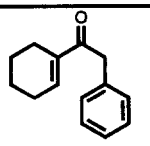
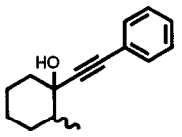
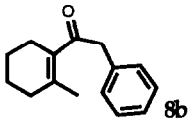
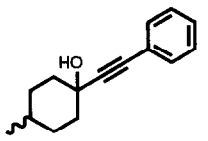
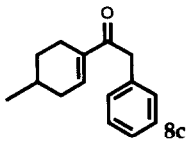
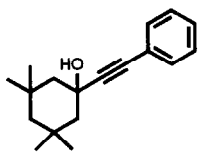
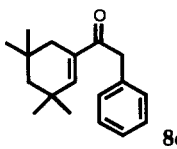
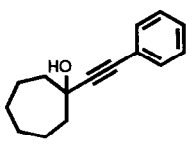
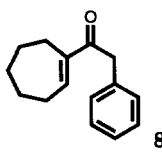
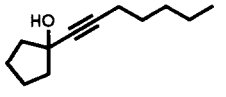
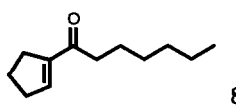
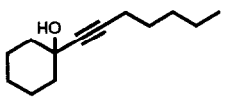
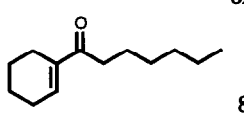
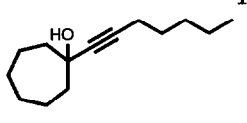
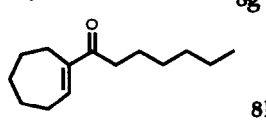
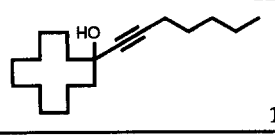
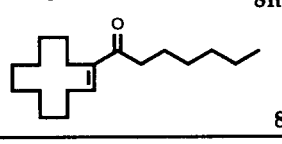
9 **12** **8**

Scheme 3: Formation of Cycloalkenyl Ketones *via* a Rupe Rearrangement

This approach provided an effective preparation of a considerable variety of cycloalkenyl ketones (*Table 1*). Entry 2 shows the preference for the thermodynamically stable ketone; no other regioisomer was detected. The reaction proceeds with a variety of substituted cycloalkanes, including the severely hindered ketone in entry 4. Entries 5, 6 and 8 show that the Rupe reaction proceeds on a variety of different sizes of the cycloalkane ring. Interestingly, entries 6-9 show that alkyl cycloalkenyl ketones can also be prepared. The procedure is attractive in its simplicity (typically reflux in formic acid for 4 h) and amenability to large scale (multigram quantities of enones can readily be prepared). It can be expected to be of particular value (*e.g.* entry 3) where a corresponding Friedel-Crafts reaction (acylation of 4-methylcyclohexene) would give regioisomers.

The apparent 1,2-transposition of the hydroxy group in the Rupe reaction[20,21] has been shown in several cases to proceed through the enyne formed by dehydration of the carbinol.[21,22] The alternative 1,3-transposition of the hydroxy group, the Meyer-Schuster rearrangement,[22,23] proceeding by means of an allenic rearrangement was not a major side-reaction in the examples investigated. Although 1-ethynylcyclohexan-1-ol has been shown to undergo the Rupe reaction,[24] the present study is, to our knowledge, the first to show that the reaction proceeds both with an internal alkyne with an aliphatic chain *and* with cycloalkyl rings other than cyclohexane.

Table 1: Cycloalkenyl Ketones Prepared by Rupe Rerrangement

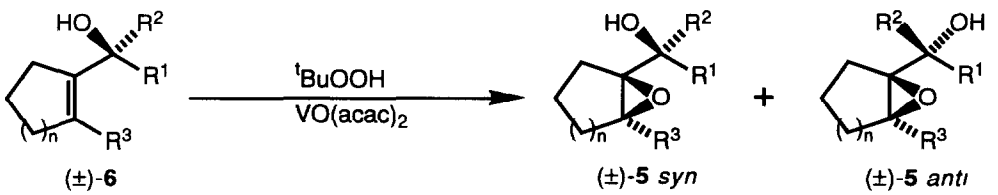
Entry	Carbinol[a]	Yield (%)[b]	Enone[a]	Yield(%)[b]
1.	 **12a**	92	 **8a**	52
2.	 **12b**	68	 **8b**	55
3.	 **12c**	79	 **8c**	68
4.	 **12d**	60	 **8d**	34
5.	 **12e**	45	 **8e**	40
6.	 **12f**	87	 **8f**	50
7.	 **12g**	99	 **8g**	53
8.	 **12h**	89	 **8h**	32
9.	 **12i**	75	 **8i**	64

[a]All new compounds were fully characterised by spectroscopic means.
[b]Isolated yield of pure material, judged by TLC and ^{1}H NMR.

Synthesis and Epoxidation of 1-Cycloalkenyl Alcohols

The secondary 1-cycloalkenyl alcohols **6a-j** were prepared by addition of organometallic reagents to cyclopentene-1-carboxaldehyde. 1-Cycloalkenyl alcohols **6k-w** were prepared from the 1-cycloalkenyl ketones **8** either by addition of an appropriate organometallic reagent R^2M (M=MgX or Li), to give a tertiary alcohol; or by reduction with lithium aluminium hydride in ether, to give a secondary alcohol. In no case was 1,4-addition realised to an inconvenient extent. A number of alkynic alcohols have been shown to display immunosuppressant activity;[26] thereby validating methods of preparing alcohols such as **6k** and **6u** and enones **8**, from which such alkynic alcohols can be prepared.

All the cycloalkenyl alcohols examined reacted smoothly with *t*-butylhydroperoxide[1c] in the presence of a catalytic amount of vanadyl acetylacetonate to give predominantly the *syn*-isomer[13] of the corresponding epoxide (*scheme 4*).



(±)-**6** (±)-**5** *syn* (±)-**5** *anti*

Scheme 4: Preparation of 2,3-Epoxyalcohols (R^1 Bulkier than R^2)

The results are summarised in *Table 2*; in almost every case a strong preference for the *syn*-isomer was observed. Only in entry 14 was a poor diastereoselectivity noted, all other examples showing a predominance of at least 3:1 in favour of the *syn*-epoxide. In Katsuki-Sharpless asymmetric epoxidation, the predominance of the *erythro*-epoxide has been stated in the form of an empirical rule.[2b,5,27] The present study, however, provides strong confirmation of the rationale of the diastereoselectivity of such epoxidations in terms of a simple model based essentially (or exclusively) on steric interactions.[7] The rationale previously proposed[6] was that minimisation of torsional strain and non-bonding interactions can account for the formation of exclusively *syn*-epoxides when α-(hydroxyalkyl)cycloalkenones are treated with *t*-butylhydroperoxide and vanadyl acetylacetonate.

One isolated example[5] of the epoxidation of a cycloalkenyl alcohol has also been shown to be *syn*-diastereoselective. The present work (*Table 2*) shows the diastereoselectivity of epoxidation using *t*-butylhydroperoxide and vanadyl acetylacetonate to be generally about 10:1, notably higher *syn*-diastereoselection than with acyclic allylic alcohols.[5]

Table 2: Diastereosective Epoxidation of 1-Cycloalkenyl Alcohols

Entry	Allylic alcohol[a]	R^1	R^2	R^3	n	Conditions	Epoxy-alcohol[a]	*Syn:anti* ratio[b]	Yield (%)[c]
1.	**6a**	CH_3	H	H	1	20°C, 2h	**5a**	79:21	34
2.	**6b**	$(CH_2)_3CH_3$	H	H	1	80°C, 24h	**5b**	83:17	73
3.	**6c**	C≡CH	H	H	1	20°C, 16h	**5c**	91:9	76
4.	**6d**	C≡CPh	H	H	1	20°C, 2h	**5d**	75:25	63
5.	**6e**	$CH=CH_2$	H	H	1	80°C, 4h	**5e**	81:19	90
6.	**6f**	$CH_2CH=CH_2$	H	H	1	20°C, 2.5h	**5f**	92:8	52
7.	**6g**	1-naphthyl	H	H	1	0°C, 3h	**5g**	91:9	70
8.	**6h**	Ph	H	H	1	80°C, 1h	**5h**	88:12	63
9.	**6i**	CH_2Ph	H	H	1	20°C, 0.5h	**5i**	92:8	97
10.	**6j**	CH_2CH_2Ph	H	H	1	20°C, 16h	**5j**	79:21	98
11.	**6k**	$(CH_2)_5CH_3$	C≡CPh	H	1	20°C, 5h	**5k**	82:18	45
12.	**6l**	$CH_2CH=CH_2$	CH_3	H	2	20°C, 3h	**5l**	78:22	86
13.	**6m**	$CH_2C(CH_3)=CH_2$	CH_3	H	2	20°C, 3h	**5m**	98:2	61
14.	**6n**	$C\equiv CCH_2OSiPh_2Bu^t$	CH_3	H	2	20°C, 7h	**5n**	57:43	23
15.	**6o**	Ph	H	H	2	80°C, 0.2h	**5o**	87:13	99
16.	**6p**	CH_2Ph	H	H	2	20°C, 1h	**5p**	86:14	98
17.	**6q**	CH_2Ph	CH_3	H	2	20°C, 3h	**5q**	94:6	64
18.	**6r**	CH_2Ph	H	CH_3	2	20°C, 8h	**5r**	87:13	76
19.	**6s**	CH_2Ph	CH_3	CH_3	2	20°C, 2h	**5s**	92:8	50
20.	**6t**	$CHPhCH_2CH=CH_2$	H	H	2	20°C, 16h	**5t**	90:10	66
21.	**6u**	$CHPhCH_2CH=CH_2$	C≡CPh	H	2	20°C, 16h	**5u**	97:3	81
22.	**6v**	Ph	H	H	3	20°C, 12h	**5v**	90:10	89
23.	**6w**	CH_2Ph	H	H	3	20°C, 5h	**5w**	96:4	91

[a]All new compounds were purified by chromatography on silica and fully characterised by spectroscopic means.
[b]Calculated from ratio of integration of ^1H NMR signals. See ref 13 for use of *'syn'* and *'anti'*.
[c]Isolated yield.

Conclusion

Efficient routes to 1-cycloalkenyl ketones, 1-cycloalkenyl carbinols and to the corresponding epoxides have been established. The *syn*-diastereoselection of epoxidation using *t*- butylhydroperoxide and vanadyl acetylacetonate is typically ≥9:1 and is crucial to the synthesis of tricyclic diols reported in the following paper, and also to the construction of alicyclic systems with two adjacent (quaternary) centres.[10]

Experimental

All melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Chemical shifts for NMR spectra are quoted in ppm downfield from internal tetramethylsilane, and the line separations (*J*) are expressed in Hertz. The following abbreviations are used to describe NMR signals: s, singlet; d, doublet; dd double doublet; t, triplet; q, quartet; m, multiplet; b, broad. ^{13}C and ^{1}H NMR spectra were determined on a Bruker AM-250 NMR spectrometer operating at 68.8 and 250 MHz respectively. Mass spectra were obtained on a Kratos MS-25 instrument, operating in chemical ionisation (CI) or electron impact (EI) mode, as specified in the text. Microanalytical data were obtained on a Perkin-Elmer 2400 CHN elemental analyser. Infra-red spectra were obtained on Perkin-Elmer 684 or 157G instruments, state as specified. Yields are for material assessed as homogeneous by TLC and ^{1}H NMR. Thin-layer chromatography was performed on Merck 0.2 mm aluminum-backed silica plates and visualised using ultra-violet light or developed using cerium (IV) sulphate spray. Column chromatography was performed using Merck silica gel 60 (230-400 mesh) under gravity. Petroleum ether (40-60 fraction) and ethyl acetate were distilled prior to use. Evaporation refers to the removal of solvent under reduced pressure, unless otherwise stated.

The following compounds were prepared according to known literature procedures: **cyclopentene-1-carboxaldehyde,**[28] **1-acetylcyclohexene,**[24b,29] **(1-cyclohexenyl)phenylmethanol (6o),**[15] **(1-cycloheptenyl)phenylmethanol (6v).**[17]

Formation of Tertiary Propargylic Alcohols; Typical Procedure:

1-(Phenylethynyl)cyclohexan-1-ol (12a)

A solution of phenylacetylene (10.72g, 0.105mol) in dry tetrahydrofuran (200ml) was treated dropwise at 0°C with a solution of *n*-butyllithium (75.0ml, 0.12mol, 1.6M). The reaction mixture was stirred at 0°C for 75min, then treated dropwise with a solution of cyclohexanone (9.82g, 0.1mol) in dry tetrahydrofuran (50ml). The mixture was allowed to warm to room temperature over 3.5h, then poured into ice-water (100ml). The layers were separated, and the aqueous layer was extracted with ether (3 x 100ml). the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The oily residue was purified by distillation under reduced pressure (air condenser) to give **12a** as a white solid (18.45g, 92%); bp 176-178°C/10mm Hg ; mp 55-56°C (literature[30] mp 59-60°C); found C, 83.95; H, 8.32% ($C_{14}H_{16}O$ requires C, 83.96; H, 8.05%); R_F=0.48 (10% ethyl acetate: petroleum ether); υ_{max} (solution) 3480, 2940, 2860, and 1600 cm^{-1}; δ_H ($CDCl_3$) 7.42 (2H, m), 7.27 (3H, m), 2.30 (1H, bs) and 2.05-1.12 (10H, m); δ_C ($CDCl_3$) 131.7 (d), 128.2 (d), 128.1 (d), 123.0 (s), 93.0 (s), 84.4 (s), 69.1 (s), 40.1 (t), 25.1 (t) and 23.5 (t) and M/Z(%)+EI: 201 (M+1, 25), 200 (M, 45), 172 (20), 158 (100), 145 (25), 130 (50), 116 (32), 103 (24), 82 (20) and 55 (70).

1-(Phenylethynyl)-2-methylcyclohexan-1-ol (12b)[31]

Following the typical procedure (above), 1-phenylacetylene (18.3g, 0.17mol) in tetrahydrofuran (200ml) when treated sequentially with *n*-butyllithium (68ml, 2.5M solution in hexanes) and 4-methylcyclohexane (14g , 0.12mol) afforded a residue which was distilled under reduced pressure to give **12b** as a 50:50 mixture of two diastereoisomers. The isomers were separated by column chromatography on silica using 10% ethyl acetate in petroleum ether as eluent to give a colourless oil (DIASTEREOMER 'A', 9.05g, 34%); found C, 83.88; H, 8.37% ($C_{15}H_{18}O$ requires C, 84.07; H, 8.47%); R_F=0.38 (10% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 7.43 (2H, m), 7.20 (3H, m), 2.10 (1H, m), 2.00 (1H, bs), 1.20-1.85 (8H, m), 1.12 (2H, d, *J*=5.9Hz); δ_C ($CDCl_3$) 131.7 (d) 128.3 (d) 128.3 (d) 123.0 (s) 94.1 (s) 83.1 (s) 70.0 (s) 40.8 (t) 39.3 (d) 29.3 (t) 25.1 (t) 21.2 (t) 16.3 (q); and a colourless oil (DIASTEREOMER 'B', 9.05g, 34%); R_f=0.27 (10% ethyl acetate: petroleum ether); δ_C ($CDCl_3$) 128.5 (d) 128.2 (d) 128.1 (d) 122.9 (s) 90.1 (s) 86.3 (s) 73.6 (s) 42.8 (d) 40.8 (t) 32.3 (t) 25.5 (t) 24.3 (t) 16.2 (q); M/Z (%)+EI: 214 (M, 49), 197 (74), 157 (100), 129 (80), 102, (50), 95 (30), 77 (20).

1-(Phenylethynyl)-4-methylcyclohexan-1-ol (12c)

Following the typical procedure (above), phenylacetylene (9 83g, 96.3mmol) in tetrahydrofuran (100ml) when treated sequentially with *n*-butyllithium (65.1ml, 1.6M in hexanes) and 4-methylcyclohexane (9.00g, 80.24mmol) afforded a residue which was distilled under reduced pressure behind a protective shield to give **12c** as a white solid (13.6g, 79%); b.p. 94-96°C/2mm Hg; found C, 83.92; H, 8.31% ($C_{15}H_{18}0$ requires C, 84.07; H, 8.47%); υ_{max} (KBr disc) 3300, 1598, 1572, 1490. 754, and 679 cm^{-1}; δ_H ($CDCl_3$) 7.55 (2H, m), 7.35 (3H, m), 1.34-2.22 (10H, m), 0.95 (3H, d, *J*=6Hz); δ_C ($CDCl_3$) 131.5 (d), 128.1 (d), 128.0 (d), 122.8 (s), 92.4 (s), 84.8 (s), 69.5 (s), 39.9 (t), 38.0 (t), 32.4 (t), 31.6 (d), 29.4 (t) and 21.7 (q); M/Z (%)+EI: 213 (M-1, 53), 157 (85), 129 (48), 115 (57), 102 (36), 77 (19), 55 (100).

3, 3, 5, 5-Tetramethyl-1-(phenylethynyl)cyclohexan-1-ol (12d)

Following the typical procedure (above), phenylacetylene (3.48g, 15.6mmol) in tetrahydrofuran (25ml) when treated sequentially with *n*-butyllithium (15.6ml, 38.9mol, 2.5M in hexane) and 3,3,5,5-tetramethylcyclohexan-1-one (5.0g, 32.4mmol) afforded a residue which was purified by column chromatography on silica using 5% ethyl acetate: petroleum ether as eluent to give **12d** as a white solid (4.95g, 60%); mp 97.5-98.5°C (di-*iso*-propyl ether); found C, 84.02; H, 9.32% ($C_{18}H_{24}O$ requires C, 84.32; H, 9.44%); R_F=0.55 (10% ethyl acetate: petroleum ether); υ_{max} (KBr disc) 3390, 2960, 2215 and 1600 cm^{-1}; δ_H ($CDCl_3$) 7.46-7.16 (5H, m), 2.08 (1H, s), 1.82 (1H, m), 1.52 (1H, m), 1.12 (2H, m), 1.00 (6H, s), 0.96 (6H, s) and 0.81 (2H, s); δ_C ($CDCl_3$) 131.4 (d), 128.3 (d), 128.2 (d), 123.0 (s), 95.1 (s), 83.7 (s), 68.3 (s), 33.3 (t), 32.0 (q), 31.4 (t) and 30.5 (t); M/Z(%)+EI: 256 (M, 45), 255 (M-1, 35), 239 (M-17, 100), 223 (15), 185 (70), 129 (40) and 97 (96).

1-(Phenylethynyl)cycloheptan-1-ol (12e)

Following the typical procedure (above), phenylacetylene (11.8g, 116.0mmol) in tetrahydrofuran (40ml) when treated sequentially with *n*-butyllithium (84.0ml, 134.0mmol, 1.6M in hexane) and cycloheptanone (10.0g, 89.2mmol) afforded a residue which was purified by reduced pressure distillation to give **12e** as a colourless oil (8.5g, 45%); bp 175-180°C/5 mm Hg; M^+ 214.1351 ($C_{15}H_{18}O$ requires 214.1358); υ_{max} (liquid film) 3380, 2940, 1600, 1560, 1500 and1450 cm^{-1}; δ_H ($CDCl_3$) 7.5-7.2 (5H, m), 2.2-1.4 (13H, m); δ_C ($CDCl_3$) 131.6 (d), 128.2 (d), 128.1 (s), 94.0 (s), 89.0 (s), 72.3 (s), 43.2 (t), 27.9 (t), 22.3 (t); M/Z(%)+CI: 214 (M^+, 40), 197 (17), 185 (29), 171 (43), 157 (100).

1-(1-Heptynyl)cyclopentan-1-ol (12f)

Following the typical procedure (above), 1-heptyne (5.0g, 52.0mmol) in tetrahydrofuran (20ml) when treated sequentially with a solution of *n*-butyllithium (37.1ml, 0.0594mol, 1.6M in hexane) and cyclopentanone (4.17g, 49.5,mmol) was found to give **12f** as a colourless oil (7.75g, 87%); M^+ 180.1506 ($C_{12}H_{20}O$ requires 180.1510) R_F=0.65 (20% ethyl acetate: petroleum ether); υ_{max} (liquid film) 3350, 2940, 2860, 2235 and 1465 cm^{-1}; δ_H 2.02 (1H, bs), 1.96-1.22 (16H, m) and 0.90 (3H, m); δ_C 84.1 (s), 83.4 (s), 74.5 (s), 42.5 (t), 31.0 (t), 28.4 (t), 28.4 (t), 23.3 (t), 22.2 (t), 18.6 (t) and 13.9 (q); M/Z(%)+EI: 180 (M, 3), 151 (62), 137 (57), 124 (32), 109 (35), 95 (54), 81 (59), 67 (88), 55 (100) and 41 (69).

1-(1-Heptynyl)cyclohexan-1-ol (12g)

Following the typical procedure (above), 1-heptyne (12.7g, 0.13mol) in tetrahydrofuran (100ml) when treated sequentially with a solution of *n*-butyllithium (95.5ml, 0.15mol, 1.6M in hexane) and cyclohexanone (10.0g, 0.10mol) was found to give **12g** as a colourless oil (19.6g, 99%); M^+ 194.1679 ($C_{13}H_{22}O$ requires 194.1671); υ_{max} (liquid film) 3380, 2940, 2860, 2215 and 1450 cm^{-1}; δ_H ($CDCl_3$) 2.20 (2H, t, *J*=8Hz), 1.95-1.00 (16H, m), 0.90 (3H, t, *J*=7Hz); δ_C ($CDCl_3$) 84.8 (s), 83.9 (s), 68.8 (s), 40.3 (t), 40.3 (t), 31.0 (t), 28.5 (t), 25.3 (t), 23.5 (t), 23.5 (t), 22.2 (t), 18.6 (t), 14.0 (q); M/Z(%)+EI 194 (8), 179 (10), 165 (8), 151 (100), 138 (15), 123 (17), 95 (25), 81 (43).

1-(1-Heptynyl)cycloheptan-1-ol (12h)

Following the typical procedure (above), 1-heptyne (10.0g, 0.104mol) in tetrahydrofuran (100ml) when treated sequentially with a solution of *n*-butyllithium (75.0ml, 0.120mol, 1.6M in hexane) and cycloheptanone (9.0g, 0.080mol) was found to give **12h** as a colourless oil (14.9g, 89%); M^+ 208.1819 ($C_{14}H_{24}O$ requires 208.1827); υ_{max} (liquid film) 3390, 2930, 2240 and 1460 cm^{-1}; δ_H ($CDCl_3$) 2.15 (2H, t, *J*=8Hz), 1.9 (2H, dd, *J*=7 and 14Hz), 1.7 (2H, m), 1.5 (9H, m), 1.3 (6H, m), 0.8 (3H, *J*=7Hz); δ_C ($CDCl_3$) 84.9 (s), 84.1 (s), 71.9 (s), 43.4 (t), 43.4 (t), 31.0 (t), 28.5 (t), 27.9 (t), 22.5 (t), 22.3 (t), 22.2 (t), 18.6 (t), 14.0 (q); M/Z(%)+EI: 208 (5), 190 (3), 179 (27), 165 (25), 151 (100), 137 (32), 123 (52), 113 (48).

1-(1-Heptynyl)cyclododecan-1-ol (12i)

Following the typical procedure (above), 1-heptyne (7.50g, 78.0mmol) in tetrahydrofuran (75ml) when treated sequentially with a solution of *n*-butyllithium (35.6ml, 89.0mmol, 2.5M in hexane) and cyclododecanone (13.5g, 74.0mmol) was found to give **12i** as a colourless oil (15.4g, 75%); M^+ 278.2615 ($C_{19}H_{34}O$ requires 278.2609); υ_{max} (liquid film) 3360, 2920, 2845, and 2220 cm^{-1}; δ_H ($CDCl_3$) 2.17 (2H, t, *J*=7Hz), 1.30-1.90 (29H, m), 0.88 (3H, t, *J*=7Hz); δ_C ($CDCl_3$) 84.6 (s), 83.9 (s), 70.8 (s), 36.2 (t), 30.9 (t), 28.4 (t), 26.0 (t), 25.8 (t), 22.4 (t), 22.1 (t), 19.7 (t), 18.5 (t), 13.8 (q); M/Z(%)+EI: 278 (M, 32), 260 (36), 151 (46), 139 (58), 98 (82) 81 (100), 67 (95).

Preparation of Cycloalkenyl Ketones **8** by the Rupe Rearrangement of Tertiary Propargylic Alcohols; Typical Procedure:

1-(1-Oxo-2-phenylethyl)cyclohexene (8a)

1-(Phenylethynyl)cyclohexanol (53.0g, 0.265mol) and aqueous formic acid (500ml, 90%) were heated together under vigorous reflux for 3h. The mixture was allowed to cool, brine (400ml) and benzene (250ml) were added and the mixture was neutralised by portionwise addition of solid sodium carbonate (approximately 300g). The layers were separated, and the aqueous layer was extracted with benzene (3 x 200ml). The combined organic extracts were washed with saturated sodium hydrogen carbonate solution (400ml) and brine (500ml), then dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by distillation under reduced pressure to give **8a** as a greasy white solid (27.5g, 52%); bp 166-167°C/10mm Hg; mp 37-40°C (literature[32] mp 46-48°C); found C, 84.24; H, 8.05% ($C_{14}H_{16}O$ requires C, 83.96; H, 8.05%); M^+ 200.1217 ($C_{14}H_{16}O$ requires 200.1201); R_F=0.33 (20% ethyl acetate: petroleum ether); υ_{max} (solution) 3090, 3030, 3020, 2930, 2860, 1750, 1675, 1640, 1605 and 1590 cm^{-1}; δ_H 7.22 (5H, m), 7.03 (1H, m), 3.94 (2H, s), 2.25 (4H, m) and 1.61 (4H, m); δ_C 198.6 (s), 141.2 (d), 139.0 (s), 135.5 (s), 129.3 (d), 128.5 (d), 126.6 (d), 44.0 (t), 26.2 (t), 23.3 (t), 21.9 (t) and 21.4 (t) and M/Z(%)+EI: 201 (M, 65), 109 (100), 91 (22) and 81 (70).

1-(1-Oxo-2-phenylethyl)-2-methyl-1-cyclohexene (8b)

Following the typical procedure (above), 1-(phenylethynyl)-2-methylcyclohexan-1-ol (17.2g, 80.3mmol) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate in petroleum ether as eluent to give **8b** as a pale yellow oil (9.4g, 55%); R_F=0.61 (10% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 7.40-7.20 (5H, m), 3.80 (2H, s), 2.25 (2H, m), 2.05 (2H, m), 1.80 (3H, s) and 1.55 (4H, m); δ_C ($CDCl_3$) 204.2 (s), 140.5 (s), 134.7 (s), 132.9 (s), 129.5 (d), 128.5 (d), 126.7 (d), 48.4 (t), 32.7 (t), 26.7 (t), 22.3 (t), 22.2 (t) and 21.5(q); M/Z (%)+EI: 214 (M, 22), 123 (72), 95 (62) and 91 (100).

1-(1-Oxo-2-phenylethyl)-4-methyl-1-cyclohexene (8c)

Following the typical procedure (above), 1-(phenylethynyl)-4-methylcyclohexan-1-ol (3.0g, 14.0mmol) afforded a residue which was distilled under reduced pressure to give **8c** as a pale yellow oil (2.03g, 68%); bp 170-172°C/6mm Hg); υ_{max} (liquid film) 2930, 2875, 1712, 1680, 1605, 1585 and 1500 cm^{-1}; δ_H ($CDCl_3$) 7.10-7.30 (5H, m), 7.01 (1H, m), 3.95 (2H, s), 1.10-2.50 (8H, m), 1.00 (3H, d, *J*=8.5Hz); δ_C ($CDCl_3$) 198.5 (s), 140.7 (d), 138.7 (s), 135.6 (s), 129.3 (d), 128.5 (d), 126.6 (d), 44.1 (t), 37.6 (t), 31.1 (t), 27.7 (d), 23.4 (t), 21.1 (q); M/Z (%)+EI: 214 (M, 2), 129 (3), 123 (100), 109 (18), 96

(60) 77 (19), 67 (37); 2,4-dinitrophenylhydrazone mp 187.5-188.5°C; found C, 63.82; H, 5.68; N, 14.27% ($C_{21}H_{22}N_4O_4$ requires C, 63.94; H, 5.62; N, 14.21%).

1-(1-Oxo-2-phenylethyl)-3, 3, 5, 5-tetramethyl-1-cyclohexene (8d)

Following the typical procedure (above), 1-(phenylethynyl)-3,3,5,5-tetramethylcyclohexan-1-ol (4.5g, 0.0176mol) afforded a residue which was recystallised from di-*iso*-propyl ether/petroleum ether to give **8d** as white crystals (1.54g, 34%); mp 77-80°C; found C, 84.27; H, 9.41% ($C_{18}H_{24}O$ requires C, 84.32; H, 9.44%); δ_H 7.22 (5H, m), 6.68 (1H, m), 4.00 (2H, s), 2.01 (2H, s), 1.38 (2H, s), 1.10 (6H, s) and 0.93 (6H, s).

1-(1-Oxo-2-phenylethyl)cyclohept-1-ene (8e)

Following the typical procedure (above), 1-(phenylethynyl)cycloheptan-1-ol (7.0g, 32.7mmol) afforded a residue which was purified by reduced pressure distillation to give **8e** as a colourless oil (2.8 g, 40%); 185-186°C/10 mm Hg; M^+ 214.1348 ($C_{15}H_{18}O$ requires 214.1358); υ_{max} (liquid film) 2920, 2850, 1660, 1500 and1450 cm^{-1}; δ_H ($CDCl_3$) 7.35-7.20 (6H, m), 3.95 (2H, s), 2.50 (2H, m), 2.45-2.20 (2H, m), 1.80-1.30 (6H, m); δ_C ($CDCl_3$) 198.7 (s), 145.9 (s), 145.7 (d), 135.8 (s), 129.2 (d), 128.5 (d), 126.6 (d), 44.1 (t), 32.2 (t), 29.2 (t), 26.0 (t), 25.8 (t), 25.8 (t); M/Z(%)+CI: 214 (M, 100), 200 (14), 186 (28), 157 (57), 139 (75), 136 (78).

1-(1-Oxoheptyl)-1-cyclopentene (8f)

Following the typical procedure (above), 1-(1-heptynyl)cyclopentan-1-ol (7.0g, 38.8mmol) afforded a residue which was distilled under reduced pressure to give **8f** as a colourless oil (3.50g, 50%); bp 122-124°C/10mm Hg; R_F=0.65 (20% ethyl acetate: petroleum ether); υ_{max} (liquid film) 2920, 1720, 1665 and 1615 cm^{-1}; δ_H 6.65 (1H, m), 2.58 (2H, t, *J*=7Hz), 2.49 (4H, m), 1.86 (2H, m), 1.53 (2H, m), 1.24 (6H, m) and 0.82 (3H, t, *J*=6Hz); δ_C 199.5 (s), 145.7 (s), 143.0 (d), 39.1 (t), 33.9 (t), 31.6 (t), 30.7 (t), 29.1 (t), 24.7 (t), 22.8 (t), 22.5 (t) and 14.0 (q); M/Z(%)+CI: 195 (32), 179 (M-1, 28), 113 (68), 99 (80), 95 (30), 85 (60), 71 (68), 60 (32), 55 (70) and 43 (100); 2,4-dinitrophenylhydrazone mp 98-99°C (ethanol); found C, 60.01; H, 6.51; N, 15.45% ($C_{18}H_{24}N_4O_4$ requires C, 59.99; H, 6.71; N, 15.55%).

1-(1-Oxoheptyl)-1-cyclohexene (8g)

Following the typical procedure (above), 1-(1-heptynyl)cyclohexan-1-ol (8.0g, 41.24mmol) was found to give **8g** as a colourless oil (4.20g, 53%); M^+ 194.1662 ($C_{13}H_{22}O$ requires 194.1671); υ_{max} (liquid film) 2940, 2360 and1670 cm^{-1}; δ_H ($CDCl_3$) 6.9 (1H, m), 2.6 (2H, t, *J*=9Hz), 2.2 (4H, m), 1.6 (6H, m), 1.25 (6H, m), 0.9 (3H, t, *J*=7Hz); δ_C ($CDCl_3$) 201.8 (s), 139.4 (d), 139.2 (s), 37.0 (t), 31.7 (t), 29.1 (t), 26.0 (t), 24.9 (t), 23.1 (t), 22.5 (t), 22.0 (t), 21.6 (t), 14.0 (q); M/Z (%)+EI: 194 (10), 137 (5), 124 (58), 109 (100), 81 (85).

1-(1-Oxoheptyl)-1-cycloheptene (8h)

Following the typical procedure (above), 1-(1-heptynyl)cycloheptan-1-ol (10.0g, 48.1mmol) afforded a residue which was distilled under reduced pressure to give **8h** as a colourless oil (3.2g, 32%); υ_{max} (liquid film) 2930, 1710 and1460 cm^{-1}; δ_H ($CDCl_3$) 7.05 (1H, t, *J*=7Hz), 2.65 (1H, t, *J*=9Hz), 2.50 (1H, m), 2.35 (1H, m), 1.85-1.20 (17H, m), 0.85 (3H, t, *J*=7Hz); δ_C ($CDCl_3$) 201.8 (s), 146.2 (s), 144.0 (d), 37.2 (t), 32.3 (t), 31.7 (t), 29.1 (t), 26.2 (t), 25.9 (t), 25.6 (t), 25.2 (t), 22.5 (t), 14.1 (q); M/Z(%)+EI: 208 (44),137 (6),122 (17),112 (38), 95 (28), 85 (16), 67 (12), 55 (38) and 43 (100).

1-(1-Oxoheptyl)-1-cyclododecene (8i)

Following the typical procedure (above), 1-(1-heptynyl)cyclododecan-1-ol (12.0g, 43.1mmol) afforded a residue which was distilled under reduced pressure to give **8i** as a colourless oil (7.71g, 64%); M^+ 278.2599 ($C_{19}H_{34}O$ requires 278.2609); υ_{max} (liquid film) 3420, 3350, 1710, 1670, and 1630 cm^{-1}; δ_H ($CDCl_3$) 6.51 (1H, t, *J*=8Hz), 2.51 (2H, t, *J*=7.5Hz), 2.30 (2H, t, *J*=7Hz), 2.23 (2H, m), 1.10-1.60 (24H, m), 0.82 (3H, t, *J*=6.5Hz); d_C ($CDCl_3$) 202.4 (s), 142.1 (d), 141.8 (s), 37.6 (t), 31.6 (t),

28.9 (t), 26.2 (t), 26.1 (t), 26.1 (t), 25.1 (t), 24.9 (t), 24.9 (t), 23.7 (t), 22.9 (t), 22.8 (t), 22.7 (t), 22.4 (t) 22.1 (t), 13.9 (q); M/Z(%)+EI: 278 (M, 20), 193 (54), 95 (39), 83 (72), 67 (52), 55 (100).

1-(1-Oxo-2-phenyl-4-pentenyl)-1-cyclohexene (8j)

A stirred solution of 1-(1-oxo-2-phenylethyl)cyclohexene (9.6g, 48.0mmol) and allyl bromide (6.4g, 52.8mmol) in toluene (120ml) was treated dropwise at 0°C with a solution of sodium *t*-pentoxide (5.44g, 49.0mmol) in toluene (120ml). The resulting mixture was stirred for 30min at 0°C and then heated at reflux for 4h. The mixture was allowed to cool, then transferred to a separating funnel and washed with water (3 x 50ml). The combined aqueous layers were extracted with ether and the combined organic layers were dried ($MgSO_4$). Concentration of the dried extracts *in vacuo* afforded a residue which was distilled under reduced pressure to afford **8j** as a colourless oil (7.65g, 66%); bp 178-182°C / 18mm Hg; M^+ 240.1519 ($C_{17}H_{20}O$ requires 240.1514); υ_{max} (liquid film); 1665, 1635 and 1600 cm^{-1}; δ_H ($CDCl_3$); 7.15-7.35 (5H, m), 7.01 (1H, m), 5.69 (1H, m), 5.00 (1H, m, *J*=17Hz, 1.5Hz), 4.93 (1H m, *J*=10Hz, 1.5Hz), 4.38 (1H, t, *J*=7.5Hz), 2.88-2.73 (1H, m), 2.52-2.39 (1H, m), 2.31 (4H, m), 1.41-1.62 (4H, m); δ_C ($CDCl_3$); 200.0 (s), 140.5 (d), 139.8 (s), 138.7 (s), 136.1 (d), 128.5 (d), 127.8 (d), 126.6 (d), 116.2 (t), 51.6 (d), 38.2 (t), 25.9 (t), 23.3 (t), 21.7 (t), 21.3 (t); M/Z (%)+EI; 240 (M, 13) , 109 (100), 128 (67), 81 (82).

Preparation of Cycloalkenyl Alcohols **6**; Typical Procedure 'A':

1-(1-Cyclopentenyl)-2-phenylethan-1-ol (6i)

A solution of cyclopentene-1-carboxaldehyde (2.0g, 20.8mmol) in dry ether (40ml) was treated dropwise at 0°C with a solution of phenylmagnesium chloride (41.6ml, 41.6mmol, 1.0M in ether). The mixture was stirred at room temperature overnight, then poured into ice-cold saturated ammonium chloride solution (50ml). The aqueous layer was separated and extracted with ether (2 x 50ml). The combined organic extracts were washed with water (80ml), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica using 20% ethyl acetate: petroleum ether as eluent to give **6i** as a colourless oil (2.68g, 68%); M^+ 188.1206 ($C_{13}H_{16}O$ requires 188.1201); υ_{max} (liquid film) 3350, 2960, 2850, 1610, 1600, 1500 and 1455 cm^{-1}; δ_H ($CDCl_3$) 7.38-7.18 (5H, m), 5.61 (1H, m), 4.47 (1H, m), 2.95 (1H, dd, *J*=14 and 4.5Hz), 2.78 (1H, dd, *J*=14 and 9Hz), 2.36 (4H, m), 1.91 (2H, ttd, *J*=7, 7 and 1Hz); δ_C ($CDCl_3$) 146.2 (s), 138.4 (s), 129.3 (d), 128.9 (d), 126.3 (d), 125.6 (d), 72.0 (d), 42.5 (t), 32.1 (t), 31.5 (t), 23.3 (t); M/Z(%)+EI: 188 (33), 170 (100), 155 (49), 142 (81), 128 (80), 115 (88), 103 (77).

1-(1-Cyclopentenyl)ethanol (6a)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (2.0g, 21.0mmol) when treated with methyllithium (26.25ml, 36.75mmol, 1.4M in ether) was found to give **6a** as a colourless oil (1.60g, 69%); found C, 74.72; H, 10.77% ($C_7H_{12}O$ requires C, 74.95; H, 10.78%); R_F=0.26 (10% ethyl acetate: petroleum ether); υ_{max} (liquid film) 3350, 2920, 2840 and 1650 cm^{-1}; δ_H ($CDCl_3$) 5.56 (1H,s), 4.40 1H,q,J=5Hz), 2.45 (1H,bs), 2.30 (4H,m), 1.87 (2H,m) and 1.25 (3H,m).

1-(1-Cyclopentenyl)pentan-1-ol (6b)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (4.0g, 41.6mmol) when treated with *n*-butyllithium (64.0ml, 83.2mmol, 1.3M in hexane) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **6b** as a pale yellow oil (5.30g, 83%); found C, 77.59; H, 11.61% ($C_{10}H_{18}O$ requires C, 77.86; H, 11.79%); R_F=0.43 (20% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 5.58 (1H, s), 4.23 (1H, t, *J*=9Hz), 2.31 (4H, m), 1.83 (2H, m), 1.50 (2H, m), 1.25 (4H, m) and 0.89 (3H, t, *J*=10Hz); δ_C ($CDCl_3$) 147.2 (s), 124.9 (d), 71.0 (d), 35.1 (t), 30.1 (t), 27.6 (t), 23.2(t), 22.5 (t) and 13.8 (q); M/Z(%)+CI: 196 (M+16, 15), 194 (20), 178 (30), 112 (51), 108 (28), 98 (45), 55 (78) and 41 (100).

1-(1-Cyclopentenyl)-2-propyn-1-ol (6c)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (1.50g, 15.6mmol) when treated with ethynylmagnesium bromide (65ml, 31.2mmol, 0.5M in tetrahydrofuran) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **6c** as a pale yellow oil (1.68g, 88%); R_F=0.26 (10% ethyl acetate: petroleum ether); M^+ 122.0732 ($C_8H_{10}O$ requires 122.0736); υ_{max} (liquid film) 3320, 2120, 1050, and 960 cm^{-1}; δ_H ($CDCl_3$) 5.85 (1H, m), 5.00 (1H, m), 2.55 (1H, d, *J*=2Hz), 2.35-2.50 (4H, m), 2.30 (1H, d, *J*=6Hz), 1.95 (2H, m); δ_C ($CDCl_3$) 142.8 (s), 128.2 (d), 83.1 (s), 73.3 (d), 61.4 (d), 32.3 (t), 31.4 (t), 23.4 (t); M/Z(%)+EI: 122 (M, 18), 103 (10), 81 (100), 67 (39), 41 (51).

1-(1-Cyclopentenyl)-3-phenyl-2-propyn-1-ol (6d)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (1.55g, 15.6mmol) when treated with phenylethynyllithium {prepared from phenylacetylene (2.55g, 25.0mmol) and *n*-butyllithium (10ml, 25.0mmol, 2.5M in hexane)} afforded a residue which was purified by column chromatography on silica using 11% ethyl acetate in petroleum ether as eluent to give **6d** as a colourless oil (2.4g, 80%); M^+ 198.1038 ($C_{14}H_{14}0$ requires 198.1045); R_F=0.33 (20% ethyl acetate: petroleum ether); υ_{max} (liquid film) 3400, 2900, 2200, and 1640 cm^{-1}; δ_H ($CDCl_3$) 7.45 (2H, m), 7.25 (3H,m), 5.85 (1H, m), 5.20 (1H, m), 2.45 (5H, m), 1.95 (2H,m); δ_C ($CDCl_3$) 143.3 (s), 131.7 (d), 128.4 (d), 128.3 (d), 128.0 (d), 88.4 (s), 85.2 (s), 62.0 (d), 32.4 (t), 31.6 (t), 23.4 (t); M/Z(%)+EI: 196 (67), 167 (55), 129 (100).

1-(1-Cyclopentenyl)-2-propen-1-ol (6e)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (2.3g, 23.9mmol) when treated with vinylmagnesium bromide (32ml, 32mmol, 1.0M in tetrahydrofuran) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **6c** as a colourless oil (2.56g, 89%); M^+ 124.0888 ($C_8H_{12}O$ requires 124.0890); υ_{max} (liquid film) 3340, 2940, 2840, 1440, and 915 cm^{-1}; δ_H ($CDCl_3$) 5.92 (1H, ddd, *J*=17Hz, *J*=10Hz, *J*=6Hz), 5.65 (1H, dd, *J*=3.5Hz, *J*=2.5Hz), 5.27 (1H, ddd, *J*=17Hz, *J*=2Hz, *J*=2Hz), 5.15 (1H, ddd, *J*=10Hz, *J*=1Hz, *J*=1Hz), 4.73 (1H, d, *J*=6Hz), 2.30-2.40 (5H, m), 1.70-2.00 (2H, m); δ_C ($CDCl_3$) 145.4 (s), 139.1 (d), 125.6 (d), 114.7 (t), 72.3 (d), 32.2 (t), 31.4 (t), 23.1 (t); M/Z(%)+EI: 124 (M, 49), 105 (38), 97 (83), 95 (100), 67 (98), 55 (49).

1-(1-Cyclopentenyl)-3-buten-1-ol (6f)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (4.7g, 49.0mmol) when treated with allylmagnesium bromide (85.6ml, 85.6mmol, 1.0M in ether) was found to give **6f** as a colourless oil (6.3g, 93%); M^+ 138.1051 ($C_9H_{14}O$ requires 138.1045); υ_{max} 3400 and 2915 cm^{-1}; δ_H ($CDCl_3$) 5.80 (1H, m), 5.62 (1H, s), 5.13 (2H, m), 4.29 (1H, t, *J*=6Hz), 2.30 (6H, m) and 1.87 (3H, m); δ_C ($CDCl_3$) 146.4 (s), 134.6 (d), 125.4 (d), 117.5 (d), 70.2 (d), 40.2 (t), 32.1 (t), 31.4 (t) and 23.3 (t).

(1-Cyclopentenyl)naphthylmethanol (6g)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (2.5g, 26.0mmol) when treated with 1-naphthylmagnesium bromide {from 1-bromonaphthalene (16.2g, 78.0mmol) and magnesium (1.90g, 78.0mmol)} afforded a residue which was purified by column chromatography on silica using 5% ethyl acetate: petroleum ether as eluent to give **6g** as a clear, viscous oil (5.74g, 98%); M^+ 224.1206 ($C_{16}H_{16}O$ requires 224.1201); R_F=0.18 (5% ethyl acetate: petroleum ether); υ_{max} (liquid film) 3430, 3030, 2930, 2830, 1590 and 1505 cm^{-1}; δ_H ($CDCl_3$) 8.13 (1H, m), 7.90-7.76 (2H, m), 7.60 (1H, d, *J*=9Hz), 7.46 (3H, m), 6.01 (1H, s), 5.74 (1H, s), 2.68 (1H, bs), 2.35 (2H, m), 2.21 (2H, m) and 1.83 (2H, m); δ_C ($CDCl_3$) 145.9 (s), 137.9 (s), 133.8 (s), 130.8 (s), 128.6 (d), 128.1 (d), 127.0 (d), 125.8 (d), 125.4 (d), 125.3 (d), 123.9 (d), 123.7 (d), 70.9 (d), 32.32 (t), 32.27 (t) and 23.3 (t); M/Z(%)+EI: 225 (M+1, 50), 224 (M, 90), 223 (M-1, 65), 207 (100), 195 (40), 178 (60), 166 (65), 155 (65) and 141 (50).

(1-Cyclopentenyl)phenylmethanol (6h)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (2.0g, 0.021mol) when treated with phenylmagnesium bromide (11.0ml, 0.033mol, 3.0M in ether) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **6h** as a colourless oil (2.4g, 66%); found C, 83.01; H, 7.98% ($C_{12}H_{14}O$ requires C, 82.72; H, 8.10%); R_F=0.74 (20% ethyl acetate: petroleum ether); υ_{max} (liquid film) 3340, 3015, 2935, 2830, 1590 and 1505 cm^{-1}; δ_H ($CDCl_3$) 7.31 (5H, m), 5.69 (1H,m), 5.31 (1H,s), 2.34 (2H,m), 2.19 (2H,m), 2.10 (1H,s) and 1.86 (2H,m); δ_C ($CDCl_3$) 146.4 (s), 142.5 (s), 128.2 (d), 127.3 (d), 126.3 (d), 126.0 (d), 73.8 (d), 32.2 (t), 31.5 (t) and 23.2 (t).

1-(1-Cyclopentenyl)-3-phenylpropan-1-ol (6j)

Following typical procedure 'A' (above), cyclopentene-1-carboxaldehyde (2.00g, 20.8mmol) when treated with 2-phenylethylmagnesium bromide {prepared from 1-phenyl-2-bromoethane (1.55g, 62.4mmol) and magnesium turnings (0.56g, 22.9mmol)} afforded a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **6j** as a colourless oil (3.65 g, 87%); M^+ 202.1349 ($C_{14}H_{18}O$ requires 202.1350); υ_{max} (liquid film) 3400, 2920, 1700, 1600 and 1500 cm^{-1}; δ_H ($CDCl_3$) 7.32-7.14 (5H, m), 5.62 (1H, m), 4.29 (1H, td, *J*=6 and 1Hz), 2.80-2.48 (2H, m), 2.40-2.26 (3H, m+brs), 1.96-1.82 (5H, m); δ_C ($CDCl_3$) 146.8 (s), 142.0 (s), 128.3 (d), 128.2 (d), 125.7 (d), 125.5 (d), 70.6 (d), 37.1 (t), 32.1 (t), 31.8 (t), 31.0 (t), 23.3 (t); M/Z(%)+EI: 202 (37), 185 (100), 104 (17). 91 (82), 67 (30).

1-(1-Cyclopentenyl)-1-(phenylethynyl)heptan-1-ol (6k)

Following typical procedure 'A' (above), 1-(1-oxoheptyl)-1-cyclopentene (3.65g, 20.2mmol) when treated with phenylethynyllithium {prepared from phenylacetylene (2.17g, 21.3mmol) and *n*-butyllithium (25.3ml, 25.3mmol, 1.0M in hexane)} afforded a residue which was purified by column chromatography on silica using 6% ethyl acetate in petroleum ether as eluent to give **6k** as a colourless oil (2.85g, 50%); M^+ 282.1991 ($C_{20}H_{26}O$ requires 282.1984); R_F=0.47 (10% ethyl acetate. petroleum ether); δ_H ($CDCl_3$) 7.41 (2H, m), 7.28 (3H, m), 5.92 (1H, t, *J*=1Hz), 2.40 (4H, m), 2 22 (1H, bs), 1.89 (4H, m), 1.45 (2H, m), 1.29 (6H, m) and 0.87 (3H, m); δ_C ($CDCl_3$) 146.7 (s), 131.7 (d), 128.2 (d), 128.2 (d), 126.9 (d), 122.9 (s), 91 5 (s), 84.5 (s), 71.3 (s), 40.7 (t), 32.3 (t), 31.8 (t), 31.1 (t), 29.4 (t), 24.5 (t), 23.8 (t), 22.6 (t) and 14.1 (q); M/Z(%)+EI: 283 (M+1, 50), 282 (M, 54), 197 (100) and 129 (20).

2-(1-Cyclohexenyl)-4-penten-2-ol (6l)

Following the typical procedure 'A' (above), 1-acetylcyclohexene (5.0g, 40.3mmol) when treated with allylmagnesium bromide (60.4ml, 60.4mmol, 1.0M in tetrahydrofuran) afforded a residue which was purified by column chromatography on silica using 8% ethyl acetate: petroleum ether as eluent to give **6l** as a colourless oil (4.51g, 67%); found C, 79.31; H, 11.01% ($C_{11}H_{18}O$ requires C, 79.46; H, 10.91%); R_F=0.47 (10% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 5.70 (2H, m), 5.11 (1H, s), 5.06 (1H,m), 2.42 (1H, m), 2.24 (1H, m), 2.03 (4H, m), 1.68 (1H, bs), 1.56 (4H, m) and 1.29 (3H, s); δ_C ($CDCl_3$) 142.0 (s), 134 1 (d), 120 1 (d), 118.5 (t), 74.2 (s), 45.0 (t), 27.1 (q), 25 1 (t), 24.9 (t), 23.1 (t) and 22.3 (t); M/Z(%)+EI: 165 (M-1, 15), 157 (12), 149 (M-17, 11), 139 (100), 125 (90), 124 (76), 109 (82) and 105 (30).

2-(1-Cyclohexenyl)-4-methyl-4-penten-2-ol (6m)

Following typical procedure 'A' (above), 1-acetylcyclohexene (5.0g, 40.3mmol) when treated with 2-methyl-2-butenylmagnesium chloride {prepared from 3-chloro-2-methyl-1-propene (7.30g, 80.6mmol) and magnesium (1.96g, 80.6mmol)} afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **6m** as a colourless oil (3.45g, 48%); M-1 179.1436 ($C_{12}H_{20}O$-H requires 179.1414); R_F=0.6 (10% ethyl acetate. petroleum ether); υ_{max} (liquid film) 3440, 2910 and 1440 cm^{-1}; δ_H ($CDCl_3$) 5.73 (1H, m),

4.90 (1H, m), 4.73 (1H, m), 2.31 (2H, q_{AB}, *J*=15Hz), 2.04 (4H, m), 1.98 (1H, s), 1.75 (3H, s), 1.57 (4H, m) and 1.30 (3H, s); δ_C ($CDCl_3$) 142.9 (s), 142.3 (s), 119.7 (d), 114.8 (t), 73.8 (s), 48.2 (t), 27.8 (q), 25.2 (t), 25.1 (t), 24.2 (q), 23.0 (t) and 22.3 (t); M/Z(%)+EI: 163 (M-17, 2), 147 (2), 139 (22), 125 (100) and 111 (12).

1-(*t*-Butyldiphenylsilyloxy)-4-(1-cyclohexenyl)-2-pentyn-4-ol (6n)

Following the typical procedure (above), 1-acetylcyclohexene (0.89g, 7.13mmol) when treated with 1-(*t*-butyldiphenylsilyloxy)-2-propynyllithium {prepared from 1-(*t*-butyldiphenylsilyloxy)-2-propyne (1.75g, 5.94mmol) and *n*-butyllithium (3.57ml, 7.13mmol, 2.0M in hexane)} afforded a residue which was purified by column chromatography on silica using 5% ethyl acetate: petroleum ether as eluent to give **6n** as a colourless oil (0.65g, 26%); found C, 77.16; H, 8.01%; ($C_{27}H_{34}O_2Si$ requires C, 77.46; H, 8.19%); R_F=0.74 (20% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 7.72 (4H, m), 7.41 (6H, m), 5.92 (1H, m), 4.38 (2H, s), 2.05 (4H, m), 1.76 (1H, s), 1.57 (4H, m), 1.44 (3H, s) and 1.05 (9H, s); δ_C ($CDCl_3$) 140.0 (s), 135.7 (d), 133.3 (s), 129.8 (d), 127.7 (d), 121.5 (d), 88.4 (s), 82.4 (s), 70.4 (s), 52.8 (t), 28.6 (q), 26.7 (q), 25.0 (t), 23.8 (t), 22.9 (t), 22.2 (t) and 19.2 (s); M/Z(%)+EI: 223 (43), 199 (100), 181 (12), 139 (20), 123 (15), 91 (12), 77 (22), 57 (12) and 43 (35); M/Z(%)+CI: 417 (M-1, 20), 401 (100), 383 (20), 374 (29), 355 (31), 339 (26), 323 (30), 295 (32), 279 (22), 255 (45) and 237 (24).

2-(1-Cyclohexenyl)-1-phenylpropan-2-ol (6q)

Following typical procedure 'A' (above), 1-acetylcyclohexene (6.0g, 0.0483mol) when treated with a solution of benzylmagnesium chloride (36.2ml, 0.0725mol, 2.0M in ether) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **6q** as a colourless oil (4.6g, 44%); found C, 83.11; H, 9.21% ($C_{15}H_{20}O$ requires C, 83.29; H, 9.32%); R_F=0.70 (20% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 7.30-7.12 (5H, m), 5.51 (1H, m), 2.83 (2H, q, *J*=14Hz), 2.22 (2H, m), 2.07 (2H, m), 1.65 (4H, m) and 1.26 (3H, s); δ_C ($CDCl_3$) 141.6 (s), 137.3 (s), 130.4 (d), 127.7 (d), 126.2 (d), 120.5 (d), 74.8 (s), 46.8 (t). 26.9 (q), 25.0 (t), 22.9 (t), 22.8 (t) and 22.2 (t).

2-(2-Methyl-1-cyclohexyl)-1-phenylpropan-2-ol (6s)

Following typical procedure 'A' (above), 2-methyl-1-(1-oxo-2-phenylethyl)-1-cyclohexene (2.0g, 9.35mmol) when treated with methylmagnesium iodide (9.33ml, 28.0mmol, 3.0M in ether) afforded a residue which was purified by column chromatography on silica using 5% ethyl acetate: petroleum ether as eluent to give **6s** as a colourless oil (1.0g, 47%); M^+ 212.1517 ($C_{16}H_{22}O$-H_2O requires 212.1565); R_F= 0.55 (10% ethyl acetate: petroleum ether); υ_{max} (liquid film) 3400, 3030, 2900, 1605 and 1495 cm^{-1}; δ_H ($CDCl_3$) 7.40-7.15 (5H, m), 2.95 (2H, q_{AB}, *J*=18Hz), 2.03 (2H, m), 1.81 (3H, s), 1.79-1.29 (7H, m) and 1.27 (3H, s); δ_C ($CDCl_3$) 137.7 (s), 134.2 (s), 130.6 (d), 129.5 (s), 127.9 (d), 126.4 (d), 76.5 (s), 47.2 (t), 34.4 (t), 28.0 (q), 28.0 (t), 23.4 (t), 22.8 (t) and 21.6 (q); M/Z(%)+EI: 213 (M-17, 4), 197 (3), 139 (70), 123 (4), 95 (12), 91 (23), 81 (16), 65 (8), 55 (8) and 43 (100).

1-(1-Cyclohexenyl)-1-(1-phenylethynyl)-2-phenyl-4-penten-1-ol (6u)

Following typical procedure 'A' (above), 1-(1-oxo-2-phenyl-4-pentenyl)cyclohexene (0.4g, 1.6mmol) when treated with a solution of phenylethynyllithium {prepared from 1-phenylacetylene (0.22g, 2.2mmol) and *n*-butyllithium (1.46ml, 1.6M solution in hexanes)} afforded a residue which was purified by column chromatography on silica gel using 5% ethyl acetate in petroleum ether as eluent to give **6u** as a colourless oil (0.52g, 89%); M^+ 324.1876 ($C_{25}H_{26}O$-H_2O requires 324.1878); υ_{max} (liquid film) 3400, 2920, 2850, 1595, 1578, 1489, 750, and 730 cm^{-1}; δ_H ($CDCl_3$) 7.60-7.30 (10H, m), 6.35 (1H, bt , *J*=3.2Hz), 5.65 (1H, m), 5.05 (1H, dd *J*=17Hz, 2Hz), 4.95 (1H m, *J*=10Hz, 2Hz), 3.21 (1H, dd, *J*=11Hz, 4Hz), 2.60-2.90 (2H, m), 1.50-2.35 (9H, m); δ_C ($CDCl_3$) 138.6 (s), 137.4 (s), 136.9 (d), 131.6 (d), 130.6 (d), 128.4 (d), 128.4 (d), 128.0 (d), 127.4 (d), 126.2

(d), 122.9 (s), 116.0 (t) 90.0 (s), 88.4 (s), 77.7 (s), 53.1 (d), 35.1 (t), 25.9 (t), 25.1 (t), 22.8 (t), 22.3 (t); M/Z(%)+CI: 325 (28), 283 (52), 241 (11), 211 (100), 207 (12).

Preparation of Cycloalkenyl Alcohols **6**: Typical procedure 'B'

1-(1-Cyclohexenyl)-2-phenylethan-1-ol (6p)

A solution of 1-(1-oxo-2-phenylethyl)-1-cyclohexene (5.0g, 24.96mmol) in dry ether (25ml) was added dropwise at room temperature to a stirred suspension of lithium aluminium hydride (0.48g , 12.48 mmol) in dry ether (75ml). The mixture was stirred at room temperature for 3 hours and the reaction quenched by the cautious addition of wet ether. The resulting aluminate salt was removed by filtration under reduced pressure through a pad of celite. The celite was washed with ether (2 x 20ml) and the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give **6p** as a colourless oil (4.62g, 92%); M^+ 202.1313 ($C_{14}H_{18}O$ requires 202.1358); υ_{max} (liquid film) 3350, 2920, 1650 and 1600 cm^{-1}; δ_H ($CDCl_3$) 7.4-7.1 (5H, m), 5.6 (1H, m), 4.2 (1H, m), 3.0-2.6 (2H, m), 2.2-1.9 (4H, m), 1.8-1.4 (4H, m + OH); δ_C ($CDCl_3$) 139.3 (s), 138.7 (s), 129.3 (d), 128.4 (d), 126.3 (d), 123.2 (d), 77.2 (d), 42.2 (t), 25.0 (t), 24.2 (t), 22.7 (t), 22.6 (t); M/Z(%)+EI: 185 (18), 111 (100), 91 (55), 81 (18), 67 (62).

1-(2-Methyl-1-cyclohexenyl)-2-phenylethan-1-ol (6r)

Following typical procedure 'B' (above), 1-(1-oxo-2-phenylethyl)-2-methylcyclohex-1-ene (1.60g, 7.84mmol) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **6r** as a colourless oil (1.45g, 90%); M-18: 198.1416 ($C_{15}H_{20}O$-H_2O requires 198.1408); υ_{max} (liquid film) 3320, 3420, 1600, and 1490 cm^{-1}; δ_H ($CDCl_3$) 7.15-7.40 (5H, m), 4.75 (1H, dd, *J*=8Hz, *J*=6Hz), 2.85 (1H, dd, *J*=13Hz, 8Hz), 2.75 (1H, dd, *J*=13Hz, 6Hz), 1.50-2.30 (8H, m), 1.45 (3H, s); δ_C ($CDCl_3$) 138.9 (s), 130.9 (s), 129.5 (s), 129.3 (s), 128.3 (d), 126.3 (d), 72.1 (d), 41.7 (t), 32.3 (t), 23.0 (t), 23.0 (t), 22.9 (t), 18.8 (q); M/Z(%)+CI: 215 (M-1, 10), 199 (88), 183 (15), 125 (72), 91 (28), 41 (100).

1-(1-Cyclohexenyl)-2-phenyl-4-penten-1-ol (6t)

Following typical procedure 'B' (above), 1-(1-oxo-2-phenyl-4-pentenyl)-1-cyclohexene (0.8g, 3.33mmol) afforded a residue which was recrystallised from light petroleum to give **6t** as a white solid (0.75g, 93%), a single diastereoisomer; found C, 84.64; H, 9.26% ($C_{17}H_{22}O_2$ requires C, 84.25; H, 9.08%); υ_{max} (KBr disc) 3324, 1665, 1640, 1602, 1584 and 1495 cm^{-1}; δ_H ($CDCl_3$) 7.15-7.35 (5H, m), 5.18 (1H, m), 5.06 (1H, m), 4.92 (2H, m), 4.13 (1H, d, *J*=9Hz), 2.80 (1H, ddt, *J*=10.5Hz, 9Hz, 5Hz), 1.30-2.42 (11H, m) ; δ_C ($CDCl_3$) 141.1 (s), 137.8 (s), 136.6 (d), 128.9 (d), 128.6 (d), 127.9 (d), 126.1 (d), 115.8 (t), 80.5 (d), 49.7 (d), 37.0 (t), 25.5 (t), 23.3 (t), 22.7 (t), 22.5 (t); M/Z(%)+EI: 242 (M, 3), 225 (8), 201 (4), 183 (100), 155 (10).

1-(1-Cycloheptenyl)-3-phenylethan-1-ol (6w)

Following typical procedure 'B' (above), 1-(1-oxoheptyl)cycloheptene (2.00g, 9.34mmol) was found to give **6w** as a colourless oil (1.73g, 86%); M^+ 198.1410 ($C_{15}H_{20}O$ requires 198.1408); υmax (liquid film) 3360, 2920, 1600, 1500 and 1450 cm^{-1}; δ_H ($CDCl_3$) 7.38-7.14 (5H, m), 5.78 (1H, td, *J*=6 and 1Hz), 4.20 (1H, dd, *J*=9 and 4Hz), 2.85 (1H, dd, *J*=4 and 13Hz), 2.73 (1H, dd, *J*=9 and 13Hz), 2.28-1.96 (3H, m), 1.85-1.38 (8H, m); δ_C ($CDCl_3$) 145.6 (s), 136.7 (s), 129.4 (d), 128.4 (d), 128.0 (d), 126.4 (d), 78.6 (d), 42.2 (t), 32.6 (t), 28.4 (t), 28.2 (t), 27.2 (t), 26.9 (t); M/Z(%)+EI: 216 (10), 199 (100), 198 (55), 125 (25), 91 (22), 81 (22).

Preparation of 2,3-Epoxyalcohols **5**; Typical Procedure:

***Syn/anti*-1-(1,2-Epoxycyclopentyl)-2-phenylethan-1-ol (5i)**

A solution of 1-(1-cyclopentenyl)-2-phenylethan-1-ol (2.00g, 10.6mmol) and vanadyl acetyl acetonate (5mg) in benzene (80ml) was treated dropwise at room temperature with an aqueous solution of *t*-butylhydroperoxide (2.05g, 15.9mmol, 70%). The mixture was stirred at room temperature, and judged complete after 0.5h (monitored by TLC). The mixture was washed with

saturated sodium sulphite solution (50ml), dried ($MgSO_4$) and concentrated *in vacuo* to give **5i** as a colourless oil (2.10g, 97%); M^+ 204.1158 ($C_{13}H_{16}O_2$ requires 204.1150); υ_{max} (liquid film) 3450, 2960, 1600 and 1500 cm^{-1}; δ_H ($CDCl_3$) 7.35-7.18 (5H, m), 4.12 (1H, dd J = 8 and 3 Hz), 3.33 (1H, s), 3.02 (1H, dd J = 14 and 3 Hz), 2.76 (1H, dd J = 14 and 8 Hz), 2.13 (1H, brs), 2.20-1.36 (6H, m); δ_C ($CDCl_3$) 37.9 (s), 129.3 (d), 128.2 (d), 126.3 (d), 70.5 (d), 69.9 (s), 61.4 (d), 39.5 (t), 27.1 (t), 26.1 (t), 19.0 (t); M/Z(%)+CI: 205 (M+1), 187 (M-17), 169 (M-35, 100).

***Syn/anti*-1-(1,2-Epoxycyclopentyl)ethanol (5a)**

Following the typical procedure (above), 1-(1-cyclopentenyl)ethanol (1.30g, 11.7mmol) afforded a residue which was purified by column chromatography on silica using 15% ethyl acetate: petroleum ether as eluent to give **5a** as a colourless oil (0.51g, 34%); found C, 65.40; H, 9.32% ($C_7H_{12}O_2$ requires C, 65.60; H, 9.44%); R_F=0.08 (10% ethyl acetate: petroleum ether) υ_{max} 3395 and 2950 cm^{-1}; δ_H ($CDCl_3$) 4.10 (1H, m), 3.48 (1H, s) and 2.40-1.21 (10H, m); δ_C ($CDCl_3$) 71.1 (s), 65.6 (d), 61.0 (d), 27.2 (t), 26.1 (t), 19.1 (t) and 18.9(q).

***Syn/anti*-1-(1,2-Epoxycyclopentyl)pentan-1-ol (5b)**

Following the typical procedure (above), 1-(1-cyclopentenyl)pentan-1-ol (5.2g, 34.0mmol) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **5b** as a mixture of diastereoisomers (4.2g, 73%); M^+ 170.1298 ($C_{10}H_{18}O_2$ requires 170.1307); R_F=0.39 (20% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 3.87 (1H, m), 3.49 (1H, s), 2.12 (1H, s), 2.08-1.22 (12H, m) and 0.94 (3H, t, J=8Hz); δ_C ($CDCl_3$) 70.6 (s), 69.4 (d), 61.1 (d), 33.0 (t), 27.5 (t), 27.2 (t), 26.1 (t), 22.7 (t), 19.1 (t) and 13.9 (q); M/Z(%)+CI: 171 (M+1, 20), 153 (M-17, 40), 135 (18), 99 (22) and 85 (100).

***Syn/anti*-1-(1,2-Epoxycyclopentyl)-2-propyn-1-ol (5c)**

Following the typical procedure (above), 1-(1-cyclopentenyl)-2-propyn-1-ol (1.0g, 7.16mmol) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **5c** as a colourless oil (845mg, 76%); M^+ 138.0677 ($C_9H_{10}O_2$ requires 138.0681); υ_{max} (liquid film) 3420, 2970 and 2125 cm^{-1}; δ_H ($CDCl_3$) 4.62 (1H, d, J=2Hz), 3.57 (1H, s), 3.00 (1H, bs), 2.47 (1H, d, J=2Hz), 1.40-2.10 (6H, m); δ_C ($CDCl_3$) 81.5 (s), 81.0 (s), 74.1 (d), 73.9 (d), 69.9 (s), 69.4 (s), 62.1 (d), 61.7 (d), 61.6 (d), 61.5 (d), 27.6 (t), 27.0 (t), 26.5 (t), 26.0 (t), 19.4 (t) and 19.3 (t); M/Z (%)+EI; 137 (M-1, 7), 121 (5), 94 (37), 81 (32), 55 (100).

***Syn/anti*-1-(1,2-Epoxycyclopentyl)-3-phenyl-2-propyn-1-ol (5d)**

Following the typical procedure (above), 1-(1-cyclopentenyl)-3-phenyl-2-propyn-1-ol (0.65g, 3.28mmol) afforded a residue which was purified by column chromatography on silica using 15% ethyl acetate: petoleum ether as eluent to give **5d** as a colourless oil (0.44g, 63%); M^+ 214.1003 ($C_{14}H_{14}O_2$ requires 214.0994); υ_{max} (liquid film) 3400, 2940, 1600, and 1490 cm^{-1}; δ_H ($CDCl_3$) 7.35 (2H, m), 7.20 (3H, m), 4.80 (1H, m), 3.60 (1H, s), 3.2 (1H, s), 2.00-1.50 (6H, m); δ_C ($CDCl_3$) 131.8 (d), 128.6 (d), 128.3 (d), 122.3 (s), 86.4 (s), 85.8 (s), 69.9 (s), 62.4 (d), 62.3 (d), 27.1 (t), 26.7 (t), 19.6 (t); M/Z (%)+CI; 215(14), 197 (60), 157 (40), 141 (45), 129 (95), 118 (80), 105 (100).

***Syn/anti*-1-(1,2-Epoxycyclopentyl)-2-propen-1-ol (5e)**

Following the typical procedure (above), 1-(1-cyclopentenyl)-2-penten-1-ol (0.7g, 5.64mmol) afforded a residue which was purified by column chromatography on silica using 15% ethyl acetate: petroleum ether as eluent to give **5e** as a colourless oil (0.71g, 90%); found C, 68.28; H, 8.49% ($C_8H_{12}O_2$ requires C, 68.55: H, 8.63%); M^+ 140.0829 ($C_8H_{12}O_2$ requires 140.0837); υ_{max} (liquid film) 3400, 2945, 1420, and 985 cm^{-1}; δ_H ($CDCl_3$) 5.75-5.90 (1H, m), 5.20-5.45 (2H, m), 5.44 (1H, d, J=7Hz), 3.51 (1H, s), 2.45 (1H, bs), 1.40-2.10 (6H, m); δ_C ($CDCl_3$) 136.9 (d), 136.4 (d), 117.2 (t), 116.1 (t), 71.8 (d), 71.2 (d), 69.9 (s), 69.8 (s), 61.2 (d), 60.8 (d), 27.1 (t0, 27.0 (t), 26.2 (t), 25.9 (t), 19.2 (t), 19.0 (t); M/Z(%)+CI: 141 (M+1, 12), 123 (50), 95 (60), 55, (100), 41 (52).

***Syn/anti*-1-(1,2-Epoxycyclopentyl)-3-buten-1-ol (5f)**

Following the typical procedure (above), 1-(1-cyclopentenyl)-3-buten-1-ol (6.0g, 43.4mmol) afforded a residue which was purified by column chromatography on silica using 12% ethyl acetate: petroleum ether as eluent to give **5f** as a colourless oil (3.51g, 52%); M^+ 154.0986 ($C_9H_{14}O_2$ requires 154.0994); R_F=0.13 (10% ethyl acetate: petroleum ether); υ_{max} (liquid film) 3325, 2900, 1715 and 1615 cm^{-1}; δ_H ($CDCl_3$) 5.89 (1H,m), 5.12 (2H,m), 4.0-3.78 (1H,m), 3.47 (1H,s), 2.54-2.09 (3H,m) and 2.08-1.36 (6H,m); δ_C ($CDCl_3$) 134.3 (d), 134.1 (d), 117.8 (t), 117.5 (t), 70.4 (s), 70.0 (s), 69.9 (d), 68.9 (d), 61.5 (d), 61.3 (d), 38.7 (t), 37.7 (t), 27.1(t), 26.9 (t), 26.2 (t), 26.0 (t), 19.4 (t) and 19.1 (t); M/Z(%)+EI: 154 (M, 3), 139 (12), 121 (22), 113 (40), 95 (29), 85 (12), 67 (100), 57 (21) and 55 (48).

***Syn/anti*-(1,2-Epoxycyclopentyl)(1-naphthyl)methanol (5g)**

Following the typical procedure (above), (1-cyclopentenyl)(1-naphthyl)methanol (2.0g, 8.92mmol) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **5g** as a viscous, colourless oil (1.5g, 70%). The compound solidified after standing for 28 weeks; mp 95-95.5°C (di-*iso*-propyl ether); found C, 80.11; H, 6.70% ($C_{16}H_{16}O_2$ requires C, 79.97: H, 6.71%); R_F=0.22 (20% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 8.12 (1H, d, *J*=11Hz), 7.89 (2H, m), 7.63 (1H, d, *J*=11Hz), 7.51 (3H, m), 5.82 (1H, s), 3.69 (1H, s), 2.78 (1H, s), 2.06-1.81 (2H, m) and 1.64-1.37 (4H, m); δ_C ($CDCl_3$) 136.0 (s), 133.4 (s), 131.0 (s), 128.5 (d), 128.1 (d), 125.8 (d), 125.3 (d), 125.1 (d), 124.3 (d), 123.3 (d), 71.2 (s), 68.5 (d), 61.8 (d), 26.9 (t), 26.7 (t) and 19.1 (t); M/Z(%)+EI: 240 (M, 100), 223 (80), 205 (70), 165 (45), 155 (35) and 128 (30).

***Syn/anti*-(1,2-Epoxycyclopentyl)phenylmethanol (5h)**

Following the typical procedure (above), (1-cyclopentenyl)phenylmethanol (0.8g, 4.59mmol) afforded a residue which was purified by column chromatography on silica using 15% ethyl acetate: petroleum ether as eluent to give **5h** as a viscous yellow oil (0.55g, 63%); M^+ 190.0971 ($C_{12}H_{14}O_2$ requires 190.0969); R_F=0.66 (20% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 7.35 (5H,m), 4.99-4.79 (1H,m), 3.67 (1H,m), 2.78-2.60 (1H,m) and 2.07-1.38 (6H,m); δ_C ($CDCl_3$) 140.2 (s), 128.2 (d), 127.9 (d), 127.6 (d), 126.9 (d), 126.4 (d), 73.1 (d), 72.2 (d), 71.1 (s), 61.6 (d), 60.9 (d), 27.1 (t), 26.3 (t), 25.8 (t), 19.2 (t) and 19.1 (t).

***Syn/anti*-1-(1,2-Epoxycyclopentyl)-3-phenylpropan-1-ol (5j)**

Following the typical procedure (above), 1-(1-cyclopentenyl)-3-phenylpropanol (1.00g, 4.95mmol) was found to give **5j** as a colourless oil, a mixture of diastereoisomers (1.06g, 98%); M^+ 218.1306 ($C_{14}H_{18}O_2$ requires 218.1307); υ_{max} (liquid film) 3440, 2950, 1600, 1500 and 1450 cm^{-1}; δ_H ($CDCl_3$) 7.4-7.1 (5H, m), 3.95 (1H, dd, J=3 and 8Hz), 3.5 (1H, s), 3.0-2.6 (2H, m), 2.3 (1H, brs), 2.1-1.4 (8H, m); δ_C ($CDCl_3$) 141.8 (s), 128.4 (d), 128.3 (d), 125.8 (d), 70.6 (s), 68.6 (d), 60.9 (d), 35.1 (t), 31.7 (t), 27.2 (t), 26.3 (t), 19.1 (t); M/Z(%)+EI: 200 (3), 129 (10), 114 (17), 104 (48), 91 (100).

***Syn*- and *anti*-1-(1,2-Epoxycyclopentyl)-1-(phenylethynyl)heptan-1-ol (5k)**

Following the typical procedure (above), 1-(1-cyclopentenyl)-1-(phenylethynyl)heptan-1-ol (1.30g, 4.60mmol) afforded a residue which was purified by column chromatography on silica using 6% ethyl acetate in petroleum ether as eluent to give **5k** as a colourless oil (DIASTEREOMER 'A', 0.50g, 37%); υ_{max} (liquid film) 3350, 2875, 2175, 1595 and 1560 cm^{-1}; δ_H ($CDCl_3$) 7.40 (2H, m), 7.25 (3H, m), 3.57 (1H, s), 2.63 (1H, s), 2.15-1.17 (16H, m) and 0.87 (3H, m); δ_C ($CDCl_3$) 131.9 (d), 128.4 (d), 128.3 (d), 122.8 (s), 90.3 (s), 84.6 (s), 72.7 (s), 69.4 (s), 61.5 (d), 38.7 (t), 31.9 (t), 29.6 (t), 27.4 (t), 26.6 (t), 23.9 (t), 22.7 (t), 19.6 (t) and 14.2 (q); and a colourless oil (DIASTEREOMER 'B', 0.11g, 8%); M-85 213.0913 ($C_{20}H_{26}O_2$-C_6H_{11} requires 213.0915); υ_{max} (liquid film) 3350, 2880, 2190, 1595 and 1560 cm^{-1}; δ_H ($CDCl_3$) 7.40 (2H, m), 7.28 (3H, m), 3.64 (1H, s), 2.70 (1H, s), 2.07-1.18 (16H, m) and 0.85 (3H, m); δ_C (CDCl3) 131.8 (d), 128.4 (d), 128.2 (d), 122.6 (s), 89.1 (s), 84.9 (s), 72.4 (s), 70.3 (s), 61.9 9d), 39.9 (t), 31.7 (t), 29.4 (t), 27.0 (t), 26.2 (t), 23.9 (t), 22.6 (t), 19.9 (t)

and 14.1 (q); M/Z(%)+EI: 298 (M, 14), 280 (M-18, 12), 264 (12), 213 (22), 181 (36), 167 (18), 147 (13), 129 (100), 111 (20), 91 (12) and 55 (48).

***Syn/anti*-2-(1,2-Epoxycyclohexyl)-4-penten-2-ol (5l)**

Following the typical procedure (above), 2-(1-cyclohexenyl)-4-penten-2-ol (3.0g, 18.0mmol) was found to give **5l** as a colourless oil (2.82g, 86%); M^+ 182.1307 ($C_{11}H_{18}O_2$ requires 182.1307); R_F=0.37 (10% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 5.90 (1H, m), 5.10 (2H, m), 3.39 (1H, m), 2.34 (2H, m), 2.12 (1H, bs), 1.80 (4H, m), 1.45 (4H, m) and 1.23 (3H, m), δ_C ($CDCl_3$) 133.9 (d), 133.4 (d), 118.5 (t), 117.4 (t), 71.9 (s), 71.2 (s), 64.5 (s), 63.9 (s), 56.3 (d), 53.9 (d), 43.1 (t), 42.8 (t), 24.7 (t), 24.6 (t), 24.3 (q), 23.5 (q), 20.8 (t), 20.5 (t) and 19.1 (t); M/Z(%)+EI: 165 (M-17, 28), 147 (20), 139 (50), 123 (22), 98 (62), 81 (64), 69 (82) and 55 (100).

***Syn*-2-(1,2-Epoxycyclohexyl)-4-methyl-4-penten-2-ol (5m)**

Following the typical procedure (above), 2-(1-cyclohexenyl)-4-methyl-4-penten-2-ol (3.00g, 16.6mmol) afforded a residue which was purified by column chromatography on silica using 8% ethyl acetate: petroleum ether as eluent to give **5m** as colourless plates (1.98g, 61%); mp 44-45°C; found C, 73.58; H, 10.44% ($C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27%); M-15 181.1220 ($C_{12}H_{20}O_2$-CH_3 requires 181.1228); R_F=0.51 (10% ethyl acetate: petroleum ether); υ_{max} (KBr disc) 3480, 3085, 2960, 1650, 1460 and 1445 cm^{-1}; δ_H ($CDCl_3$) 4.81 (1H, m), 4.64 (1H, m), 3.30 (1H, t, *J*=1Hz), 2.23 (2H, s), 2.12 (1H, s), 2.04-1.57 (4H, m), 1.78 (3H, s), 1.48-1.18 (4H, m) and 1.16 (3H, s); δ_C ($CDCl_3$) 142.8 (s), 114.3 (t), 72.7 (s), 63.9 (s), 56.1 (d), 45.6 (t), 25.0 (q), 24.8 (t), 24.6 (t), 24.4 (q), 20.5 (t) and 18.8 (t); M/Z(%)+EI: 181 (M-15, 50), 169 (28), 153 (30), 139 (39), 123 (90), 115 (50), 111 (67), 98 (100), 83 (98), 67 (32) and 55 (60).

***Syn*- and *anti*-1-(*t*-Butyldiphenylsilyloxy)-4-(1,2-epoxycyclohexyl)-2-pentyn-4-ol (5n)**

Following the typical procedure (above), 1-(*t*-butyldiphenylsilyloxy)-4-(1,2-epoxycyclohexyl)-2-pentyn-4-ol (0.65g, 1.55mmol) afforded a residue which was purified by column chromatography on silica using 5% ethyl acetate: petroleum ether as eluent to give **5n** as a colourless oil (DIASTEREOMER 'A', 0.090g, 13%); M-77 377.1581 ($C_{27}H_{34}O_3Si$-C_6H_5 requires 377.1573); δ_H ($CDCl_3$) 7.70 (4H, m), 7.40 (6H, m), 4.37 (2H, s), 3.30 (1H, m), 2.54 (1H, s), 2.03-1.64 (4H, m), 1.52-1.19 (4H, m), 1.40 (3H, s) and 1.06 (9H, s); δ_C ($CDCl_3$) 135.6 (d), 133.2 (s), 129.8 (d), 127.7 (d), 85.6 (s), 82.7 (s), 68.4 (s), 63.8 (s), 56.0 (d), 52.7 (t), 26.7 (q), 25.7 (q), 24.5 (t), 24.3 (t), 20.6 (t), 19.2 (t) and 19.0 (s); M/Z(%)+EI: 391 (10), 299 (10), 249 (12), 221 (10), 199 (100), 181 (13), 161 (10) and 139 (25); and a colourless oil (DIASTEREOMER 'B', 0.071g, 10%); υ_{max} (liquid film) 3370, 3005, 2905, 2200 and 1590 cm^{-1}; δ_H ($CDCl_3$) 7.71 (4H, m), 7.42 (6H, m), 4.36 (2H, s), 3.42 (1H, m), 2.21 (1H, s), 1.95 (2H, m), 1.74 (2H, m), 1.54-1.10 (4H, m), 1.42 (3H, s) and 1.04 (9H, s); δ_C ($CDCl_3$) 135.6 (d), 133.2 (s), 129.8 (d), 127.7 (d), 85.6 (s), 82.7 (s), 68.4 (s), 63.8 (s), 56.0 (d), 52.7 (t), 26.7 (q), 25.7 (q), 24.5 (t), 24.3 (t), 20.6 (t), 19.2 (t) and 19.0 (s).

***Syn/anti*-(1,2-Epoxycyclohexyl)phenylmethanol (5o)**

Following the typical procedure (above), 1-(1-cyclohexenyl)phenylmethanol (1.92g, 10.2mmol) was found to give **5o** as a white solid (2.07 g, 99%). Recrystallisation afforded the pure *syn*-epoxide mp 114-115°C (diethyl ether); found C, 76.09; H, 7.77% ($C_{13}H_{16}O_2$ requires C, 76.44; H, 7.90%); υ_{max} (KBr disc) 3420, 2940 and 1500 cm^{-1}; δ_H ($CDCl_3$) 7.5-7.2 (5H, m), 4.6 (1H, s), 3.5 (1H, m), 2.6 (1H, bs), 2.1-1.0 (8H, m); δ_C ($CDCl_3$) 135.7 (s), 128.0 (d), 127.3 (d), 126.2 (d), 70.5 (d), 68.4 (s), 58.7 (d), 33.2 (t), 27.0 (t), 24.4 (t), 23.7 (t); M/Z(%)+EI: 204 (M), 187 (M-17), 157 (M-47), 105 (M-99), 98 (M-106, 100).

***Syn/anti*-1-(1,2-Epoxycyclohexyl)-2-phenylethan-1-ol (5p)**

Following the typical procedure (above), 1-(1-cyclohexenyl)-2-phenylethan-1-ol (3.50g, 17.33mmol) was found to give **5p** as a white solid (3.70g, 98%). Recrystallisation afforded the pure *syn*-isomer; mp 62-63°C (diethyl ether-petroleum ether); M^+ 218.1312 ($C_{14}H_{18}O_2$ requires

218.1307); υ_{max} (KBr disc) 3410, 2940, 1600, 1500 and 1455 cm^{-1}; δ_H ($CDCl_3$) 7.35-7.20 (5H, m), 3.79 (1H, dd, *J*=4 and 8Hz), 3.04 (1H, m), 2.90 (1H, dd, *J*=4 and 14Hz), 2.75 (1H, dd, *J*=8 and 14Hz), 2.22 (1H, bs), 1.98-1.74 (3H, m), 1.69-1.60 (1H, m), 1.55-1.34 (2H, m); 1.34-1.20 (2H, m) δ_C ($CDCl_3$) 138.1 (s), 129.6 (d), 128.3 (d), 126.5 (d), 73.1 (d), 61.7 (s), 56.1 (d), 39.0 (t), 24.9 (t), 24.4 (t), 20.3 (t), 19.5 (t); M/Z(%)+EI: 218 (37), 200 (100), 171 (97), 127 (27), 109 (30).

***Syn-* and *anti*-2-(1,2-Epoxycyclohexyl)-1-phenylpropan-2-ol (5q)**

Following the typical procedure above, 2-(1-cyclohexenyl)-1-phenylpropan-2-ol (5.0g, 0.023mol) afforded a residue which was purified by column chromatography on silica using 7% ethyl acetate: petroleum ether as eluent to give **5q** as a white solid (DIASTEREOMER 'A', 3.20g, 60%); mp 84-85°C (recrystallised from di-*iso*-propyl ether); found C, 77.25; H, 8.78% ($C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%); R_F=0.46 (10% ethyl acetate: petroleum ether); δ_H ($CDCl_3$)7.22 (5H, m), 2.88 (2H, dd, *J*=30Hz, *J*=17Hz), 2.17 (1H, s), 1.99-1.39 (8H, m) and 1.27 (3H, s); δ_C ($CDCl_3$) 137.1 (s), 130.7 (d), 127.8 (d), 126.3 (d), 72.4 (s), 63.4 (s), 56.4 (d), 44.0 (t), 25.1 (q), 24.6 (t), 24.4 (t), 20.5 (t) and 18.6 (t); M/Z(%)+EI: 214 (M-18, 10), 203 (10), 175 (8), 158 (14), 141 (30), 123 (28), 105 (100), 91 (85), 77 (25) and 43 (32); and a colourless, greasy solid (DIASTEREOMER 'B', 0.22g, 4%); found C, 77.32; H, 8.53% ($C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%); R_F=0.25 (10% ethyl acetate: petroleum ether); δ_H ($CDCl_3$) 7.22 (5H, m), 2.88 (2H, dd, *J*=30Hz, *J*=17Hz), 2.17 (1H, s), 1.99-1.39 (8H, m) and 1.27 (3H, s); δ_C ($CDCl_3$) 136.9 (s), 130.8 (d), 128.0 (d), 126.4 (d), 72.2 (s), 64.9 (s), 54.3 (d), 43.7 (t), 25.1 (t), 24.6 (t), 23.1 (q), 21.0 (t) and 19.1 (t); M/Z(%)+EI: 232 (M, 3), 215 (M-17, 10), 197 (8), 141 (21), 123 (28), 91 (62), 81 (22) and 43 (100).

***Syn/anti*-1-(1,2-Epoxy-2-methylcyclohexyl)-2-phenylethan-1-ol (5r)**

Following the typical procedure (above), 1-(2-methyl-1-cyclohexenyl)-2-phenylethan-1-ol (1.50g, 6.94mmol) afforded a residue which was purified by column chromatography on silica using 10% ethyl acetate: petroleum ether as eluent to give **5r** as a white solid (1.22g, 76%); mp 92-94°C; found C, 77.36; H, 8.54% ($C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%); υ_{max} (KBr disc) 3470, 2930, 2860, 1610, 1500, and 1455 cm^{-1}; δ_H ($CDCl_3$) 7.20-7.40 (5H, m), 3.78 (1H, ddd, *J*=10Hz, *J*=3Hz, *J*=0.8Hz), 2.98 (1H, dd, *J*=13.5Hz, 3Hz), 2.82 (1H, dd, *J*=13.5Hz, *J*=10Hz), 1.21-2.10 (9H, m), 1.45 (3H, s); δ_C ($CDCl_3$) 138.6 (s), 129.4 (d), 128.6 (d), 126.5 (d), 74.2 (d), 65.8 (s), 63.6 (s), 38.7 (t), 32.4 (t), 24.2 (t), 24.2 (t), 21.3 (t), 19.9 (q), 19.8 (t); M/Z(%)+EI: 232 (M, 2), 214 (6), 141 (30), 95 (100), 91 (77), 77 (13).

***Syn/anti*-2-(1,2-Epoxy-2-methylcyclohexyl)-1-phenylpropan-2-ol (5s)**

Following the typical procedure (above), 2-(2-methyl-1-cyclohexenyl)-1-phenylpropan-2-ol (1.84g, 8.05mmol) afforded a residue which was purified by column chromatography on silica using 5% ethyl acetate: petroleum ether as eluent to give **5s** as a white solid (1.0g, 50%); mp 29-31°C; found C, 77.80; H, 8.86% ($C_{16}H_{22}O_2$ requires C, 78.01; H, 9.00%); R_F=0.50 (10% ethyl acetate: petroleum ether); υ_{max} (KBr disk) 3490, 2940, 1600 and 1490 cm^{-1}; δ_H ($CDCl_3$) 7.40-7.15 (5H, m), 2.90 (2H, q_{AB}, *J*=18Hz), 2.50 (1H, s), 1.69-1.10 (8H, m) and 1.12 (6H, s); δ_C ($CDCl_3$) 137.3 (s), 130.6 (d), 127.9 (d), 126.3 (d), 74.0 (s), 68.7 (s), 64.9 (s), 43.9 (t), 34.1 (t), 27.0 (t), 26.1 (q), 21.7 (t), 20.4 (q) and 19.4 (t); M/Z(%)+EI: 246 (M, 10), 185 (52), 155 (38), 146 (18), 137 (33), 113 (42), 91 (100), 84 (25), 77 (11), 65 (28) and 55 (38).

***Syn/anti*-1-(1,2-Epoxycyclohexyl)-2-phenyl-4-penten-1-ol (5t)**

Following the typical procedure (above), 1-(1-cyclohexenyl)-2-phenyl-4-penten-1-ol (5.79g, 23.9mmol) afforded a residue which was purified by column chromatography on silica gel using 5% ethyl acetate in petroleum ether as eluent to give **5t** as a colourless oil (4.1g, 66%), a mixture of diastereoisomers; M^+ 240.1522 ($C_{17}H_{22}O_2$-H_2O requires 240.1514); υ_{max} (liquid film) 3470, 2940, 2880 and 1640 cm^{-1}; δ_H ($CDCl_3$) 7.15-7.3 (5H, m), 5.71 (1H, m), 5.07 (1H, m, *J*=17Hz, 1.5Hz), 4.95 (1H, m, *J*=10.5Hz, 1.5Hz), 3.85 (1H, d, *J*=3.5Hz), 2.92 (1H, ddd, *J*=8.5Hz, 6.8Hz, 3.5Hz), 2.73 (2H, m), 2.41 (1H, t, *J*=1.5Hz), 2.27 (1H, bs), 1.00-2.00 (8H, m); δ_C ($CDCl_3$) 140.5 (s), 136.8 (d), 129.5 (d), 127.8

(d), 126.7 (d), 116.4 (t), 73.1 (d), 61.0 (s), 55.7 (d), 47.6 (d), 37.2 (t), 26.7 (t), 25.2 (t), 20.1 (t), 19.3 (t); M/Z(%)+CI: 259 (M+1, 38), 241 (100), 223 (82), 171 (45), 131 (83), 91 (49).

***Syn*-1-(1,2-Epoxycyclohexyl)-1-(1-phenylethynyl)-2-phenyl-4-penten-1-ol (5u)**

Following the typical procedure (above), 1-(1-cyclohexenyl)-1-phenylacetylenyl-2-phenyl-4-penten-1-ol (3.90g, 11.4mmol) afforded a residue which was recrystallised from a mixture of light petroleum and ethyl acetate to give **5u** as a white solid (3.49g, 81%) as a single diastereoisomer; found C, 83.67; H, 7.40% ($C_{25}H_{26}O_2$ requires C, 83.76%; H, 7.31%); υ_{max} (KBr disc) 3400, 2110, 1638, 1600 , 1575 and 1480 cm^{-1}; δ_H ($CDCl_3$) 7.50 (2H, m), 7.23 (8H, m), 5.66 (1H, m), 4.95 (1H, ddt, *J*=17Hz, 2.3Hz, 1.5Hz), 4.85 (1H, m, *J*=10Hz, 2.3Hz), 3.15 (2H, m), 2.85 (1H, m), 2.75 (1H, d, *J*=1.8Hz), 2.58 (1H, t, *J*=2.4Hz), 2.10 (2H, m), 0.70-1.70 (6H, m); δ_C ($CDCl_3$) 139.1 (s), 137.1 (d), 131.8 (d), 130.2 (d), 128.4 (d), 128.3 (d), 127.8 (d), 127.0 (d), 122.7 (s), 116.0 (t), 90.2 85.1 (s), 74.2 (s), 62.9 (s), 56.9 (d), 52.4 (d), 35.7 t 24.9 (t), 24.0 (t), 20.2 (t), 18.6 (t); M/Z (%)+EI: 358 (12), 300 (9), 253 (12), 227 (100), 209 (28).

***Syn/anti*-(1,2-Epoxycycloheptyl)phenylmethanol (5v)**

Following the typical procedure (above), 1-(1-cycloheptenyl)phenylmethanol (0.77g, 3.81mmol) was found to give **5v** as a colourless oil (0.74 g, 89%); M^+ 218.1296 ($C_{14}H_{18}O_2$ requires 218.1307); M-18 200.1211 ($C_{14}H_{18}O_2$-H_2O requires 200.1201); υ_{max} (liquid film) 3430, 2920, 1600, 1500 and 1450 cm^{-1}; δ_H ($CDCl_3$) 7.4-7.2 (5H, m), 4.6 (1H, m), 3.5 (1H, dd, *J* = 6.5 and 2.5 Hz), 3.2 (1H, bs), 2.2-1.0 (10H, m); δ_C ($CDCl_3$) 140.2 (s), 128.4 (d), 128.0 (d), 127.4 (d), 76.1 (d), 65.8 (s), 58.0 (d), 30.8 (t), 30.1 (t), 28.3 (t), 24.4 (t), 24.0 (t); M/Z(%)+EI: 218 (M), 200 (M-18), 183 (M-35), 171 (M-47), 164 (M-54, 100), 156 (M-162).

***Syn/anti*-1-(1,2-Epoxycycloheptyl)-2-phenylethan-1-ol (5w)**

Following the typical procedure (above), 1-(1-cycloheptenyl)-2-phenylethan-1-ol (1.20g, 5.56mmol) was found to give **5w** as a colourless oil (1.17g, 91%), a mixture of diastereoisomers; M^+ 232.1468 ($C_{15}H_{20}O_2$ requires 232.1463); υ_{max} (KBr disc) 3400, 2930, 1600, 1500 and 1400 cm^{-1}; δ_H ($CDCl_3$) 7.4-7.1 (5H, m), 3.79 (1H, dd, *J*=4 and 8Hz), 3.03 (1H, m), 2.99 (1H, dd, *J*=14 and 4Hz), 2.74 (1H, dd, *J*=14 and 8Hz), 2.2 (1H, bs), 2.00-1.15 (10H, m); δ_C ($CDCl_3$) 138.2 (s), 129.5 (d), 128.3 (d), 126.4 (d), 74.4 (d), 64.7 (s), 58.1 (d), 38.9 (t), 30.8 (t), 30.0 (t), 27.9 (t), 24.3 (t), 23.8 (t); M/Z(%)+CI: 235 (8), 215 (100), 197 (48), 185 (25), 141 (37), 123 (45), 105 (49).

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(13) The assignment of the major diastereoisomer of the epoxide as *'syn'* (see definition below) follows from the configuration of the tricyclic diols formed by Lewis acid cyclisation of the epoxides, as discussed in the following paper.
Upon orienting the cycloalkenyl group and the bulkier of the other groups attached to the carbinol carbon atom to approximate co-planarity, the epoxide and hydroxyl groups then reside on the same or opposite faces, respectively referred to here as *'syn'* and *'anti'*. These correspond to *'erythro'* and *'threo'*, respectively, as applied to substituted epoxyalcohols, with reference to the relative configuration of the allylic hydroxy group to the vicinal epoxide oxygen bond. We prefer to avoid the the terms *'erythro'* and *'threo'*, which cannot be applied to highly substituted epoxides of type **4**. Although our use of *'syn'* and *'anti'* refers to a particular orientation as defined above, and differs from *'syn'* and *'anti'* as applied to substituents on a chain, we believe prediction of the major diastereoisomer and understanding of the stereoselection to be facilitated by the use of *'syn'* and *'anti'* as defined herein.

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