Carotenoids and related polyenes. Part 5.[1] Lewis acid-promoted stereoselective rearrangement of 5,6-epoxy carotenoid model compounds

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The novel acyclic tetrasubstituted olefinic end group and the cyclopentyl end group of carotenoids were obtained by Lewis acid-promoted stereoselective rearrangement of the epoxide end group of 5,6-epoxy carotenoids. The scope and limitation of this rearrangement were investigated.

Introduction

Crassostreaxanthin B **1** (Scheme 1), a marine carotenoid having the novel tetrasubstituted olefinic end group, was isolated from the viscera of *Crassostrea gigas* and its stereostructure was determined by Matsuno's group in 1992.[2] However, the absolute configuration in the new end group has remained undetermined. It is conceivable that this end group is formed in nature from the epoxide end group of 5,6-epoxy carotenoids† such as halocynthiaxanthin **2**[3] by opening of the C-6-oxygen bond of the oxirane ring and subsequent migration of the methyl group at the C-1 position (route *a*). Thus, the absolute configuration at C-3′ in crassostreaxanthin B **1** is considered to be *S*, since chiralities at C-3 in most of the known natural epoxy carotenoids are *R*. On the other hand, mytiloxanthin **3**[3b,4] is also believed[5] to arise from 5,6-epoxy carotenoids by cleavage of the oxirane ring at the C-5 position and successive ring contraction (a pinacolic rearrangement) (Scheme 1, route *b*). In a previous communication,[6] we reported that treatment of the epoxide **5a**, having the partial structure of the epoxy carotenoids, with Lewis acids gave the cyclopentyl ethyl ketone **8** possessing the same configuration as mytiloxanthin **3**, and the acyclic tetrasubstituted olefinic methyl ketone **10** including the partial structure of crassostreaxanthin B **1** (Scheme 2). It supported the proposed metabolic pathway of the 5,6-epoxy carotenoids.

In order to accomplish the biomimetic synthesis of **2** and **3**, we investigated the reaction of epoxides having various substituents at the C-6 position with Lewis acids. The present paper is concerned with a full account of these experiments.

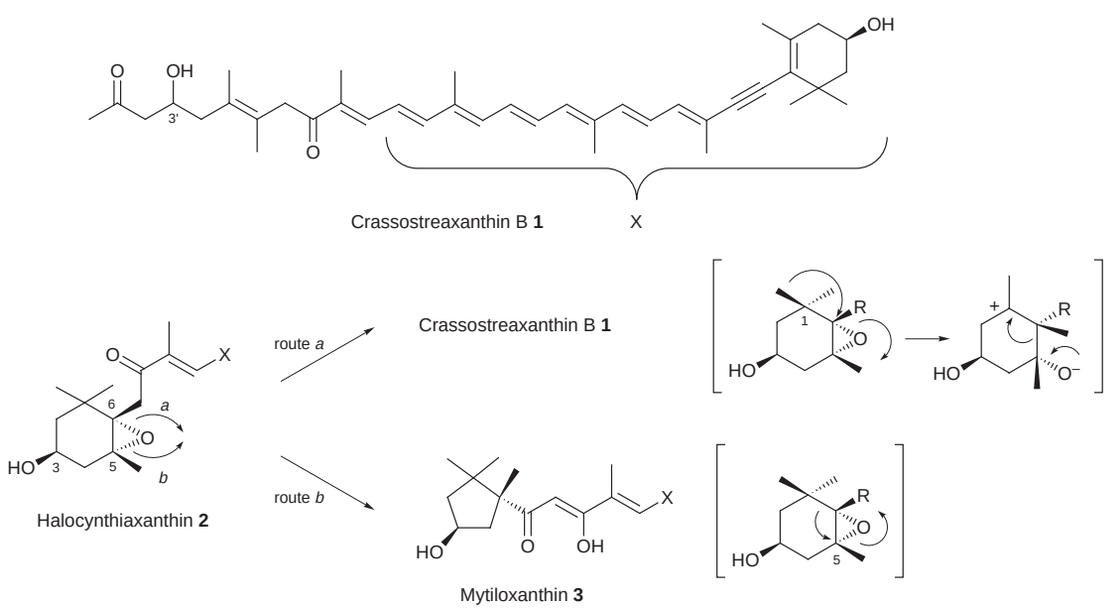
† We have employed the numbering system used in carotenoids.

Results and discussion

Rearrangement of epoxides 5a,b

It was reported[7] by Rüttimann that reaction of epoxides **4a**,**b** (Scheme 2) with $BF_3{\cdot}OEt_2$ followed by hydrolysis gave cyclopentyl methyl ketones **6** and **11**, respectively, each as a single product in up to 70% yield. Then he proposed the possible intermediates I and II deriving from 'axial' cleavage of the respective epoxides. However, the mechanism for the formation of the methyl ketone **6** from *anti*-epoxide **4a** is in conflict with the proposed biosynthetic mechanism[5] for mytiloxanthin **3** formation. Since substituents at the C-5 and C-6 positions of these epoxides are both methyl groups, the direction of the oxirane ring opening cannot be proved. Thus, epoxides **5a**,**b** having an ethyl group at C-6 were treated with $BF_3{\cdot}OEt_2$.

Epoxides **5a**,**b** were synthesized from the known[8] optically active ketone **15** as shown in Scheme 3. Treatment of ketone **15**

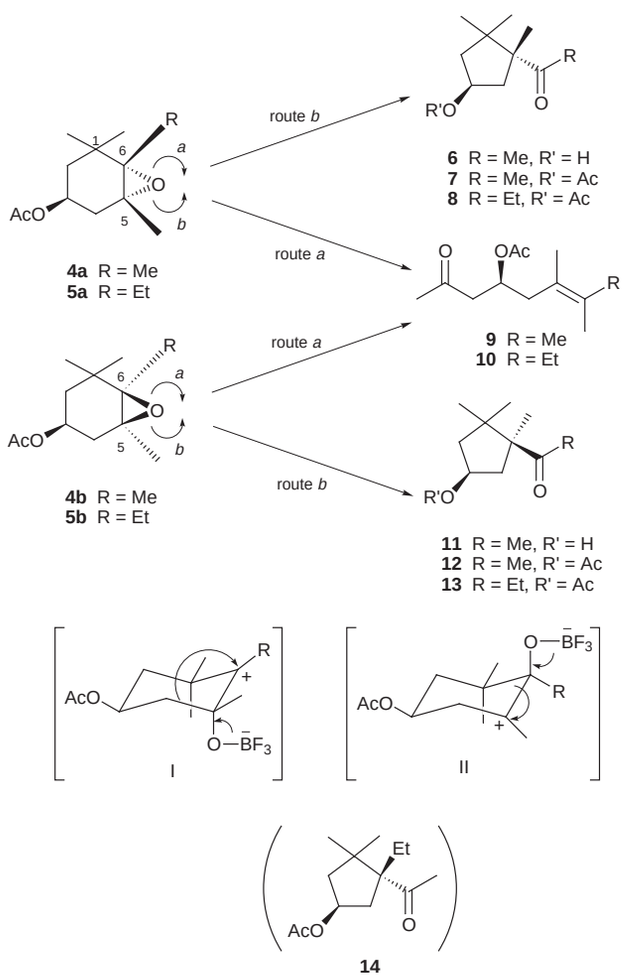


Scheme 1

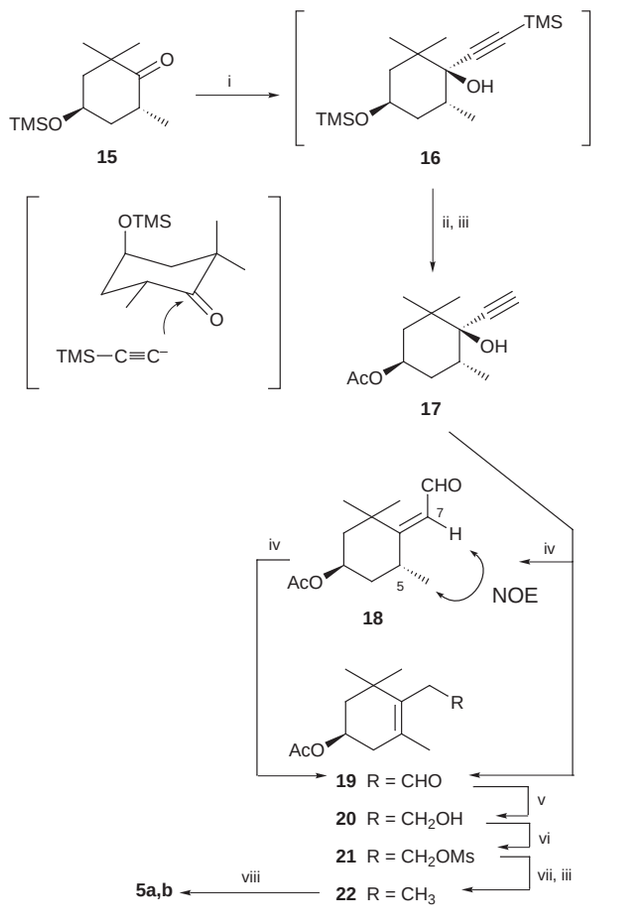
Table 1 Rearrangement of the α-acetylenic alcohol **17** and the α,β-unsaturated aldehyde **18** by a silyl vanadate catalyst[a]

		Catalyst (molar equiv.)			Reaction	Isolated yield (%)	
Entry	Substrate	TPSV	TPS	$PhCO_2H$	time (h)	**18**	**19**
1	**17**	0.02	0.15	0.02	23	43	48
2	**17**	0.02	—	0.02	6	—	96
3	**17**	0.02	—	—	24	—	76
4	**18**	0.02	—	0.02	6.5	—	95
5	**18**	0.02	—	—	5.5	—	85

[a] All reactions were carried out in refluxing xylenes.

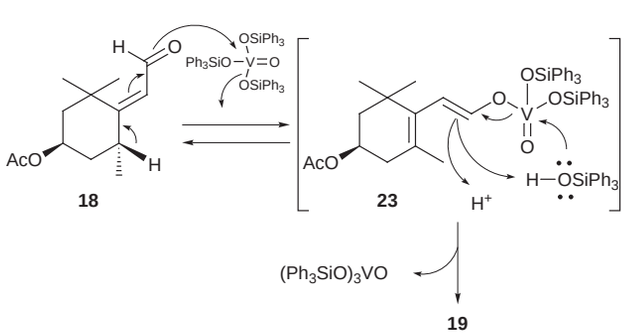


Scheme 2



Scheme 3 *Reagents and conditions*: i, LiC≡CTMS; ii, 10% aq. KOH; iii, Ac_2O, Py; iv, see Table 1; v, $NaBH_4$; vi, MsCl, Py; vii, $LiAlH_4$, THF, reflux; viii, MCPBA

with lithium trimethylsilylacetylide gave the hydroxy compound **16** which, without purification, was deprotected and then acetylated to afford the acetate **17** as a single product in 94% yield from **15**. Its stereochemistry was deduced from mechanistic considerations[8] as shown in Scheme 3. The β,γ-unsaturated aldehyde **19** was obtained by rearrangement of the α-acetylenic alcohol **17** using tris(triphenylsilyl)vanadate (TPSV) catalyst.[9,10] According to the literature,[9] the α-acetylenic alcohol **17** was treated with TPSV (0.02 molar equiv.), triphenylsilanol (TPS; 0.15 molar equiv.) and benzoic acid (0.02 molar equiv.) in refluxing xylenes to give the α,β- and β,γ-unsaturated aldehydes **18** (43%) and **19** (48%) (Table 1, entry 1). Although under these reaction conditions, much of the α,β-unsaturated aldehyde **18** remained unchanged, it was found to be converted efficiently into the desired aldehyde **19** under the conditions either without TPS (entry 4) or with TPSV only (entry 5). Thus, alcohol **17** was treated under these two conditions (entries 2 and 3). Aldehyde **19** was effectively obtained in a shorter time by the coupled use of TPS and benzoic acid (entry 2). This reaction may be envisaged to proceed *via* the vanadate



Scheme 4

ester **23** as shown in Scheme 4. It is considered that the transesterification reaction (**18** + TPSV ⟶ **23**) would be inhibited by the presence of an excess of TPS, resulting in the α,β-unsaturated aldehyde **18** remaining, even after a long reaction time (entry 1).

The structures of products **18** and **19** were confirmed on the basis of their spectral data (see Experimental section). In the IR

Table 2 Rearrangement of epoxides **5a**,**b**

Entry	Substrate	Conditions (equiv.)	Isolated yield (%) **8**	**10**	**13**
1	**5a**	$BF_3{\cdot}Et_2O$ (3)/CH_2Cl_2 −78 °C, 3 h to 0 °C, 1 h	31	54	—
2	**5a**	$SnCl_4$ (2)/CH_2Cl_2 −25 °C, 2.5 h to 0 °C, 2.5 h	trace	70	—
3	**5a**	(p-$BrC_6H_4)_3NSbCl_6$ (0.1) CH_2Cl_2/rt, 1.5 h	12	71	—
4	**5b**	$BF_3{\cdot}Et_2O$ (2)/CH_2Cl_2 −78 °C, 1.25 h to −25 °C, 1.5 h	—	49	44
5	**5b**	$SnCl_4$ (2)/CH_2Cl_2 −78 °C, 2 h	—	59	14
6	**5b**	$TiCl_4$ (3)/CH_2Cl_2 −78 °C, 30 min	—	15	—
7	**5b**	$ZnCl_2$ (2)/toluene rt, 60 h	—	50	12
8	**5b**	(p-$BrC_6H_4)_3NSbCl_6$ (0.1) CH_2Cl_2/rt, 1.5 h	—	62	23

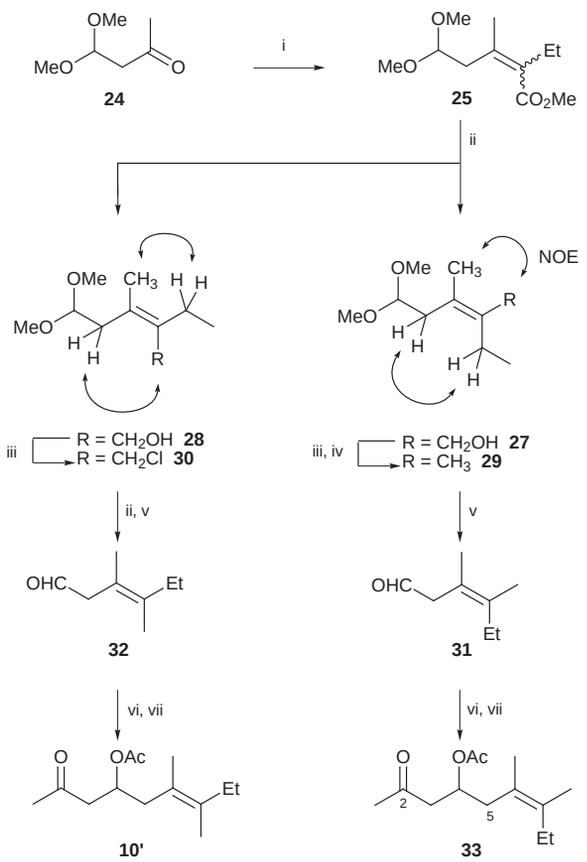
spectrum, compound **18** showed an absorption (1660 cm^{-1}) due to an α,β-unsaturated aldehyde, whereas an absorption (1720 cm^{-1}) due to a saturated aldehyde appeared in compound **19**. The ylidene double bond in compound **18** was determined to be the *Z*-form from ^1H NMR spectroscopy including 2D nuclear Overhauser enhancement spectroscopy (NOESY) experiments (cross-peaks between 5-CH_3 and 7-H).

Reduction of the formyl group in **19** with $NaBH_4$ followed by mesylation gave the mesylate **21** (86% from **19**), which was refluxed with $LiAlH_4$ in THF and then reacetylated to afford compound **22** (90%). Treatment of compound **22** with MCPBA led to a mixture of the *anti*-epoxide **5a** (34%) and the *syn*-epoxide **5b** (61%). The relative configurations between the acetoxy and epoxy groups in the two isomers were confirmed by their ^1H NMR data.[8]

Reaction of the *anti*-epoxide **5a** with $BF_3{\cdot}OEt_2$ (Table 2, entry 1) gave the acyclic tetrasubstituted olefinic methyl ketone **10** (54%) and the cyclopentyl ethyl ketone **8** (31%) (Scheme 2). In this reaction, the cyclopentyl methyl ketone **14** arising through the intermediate **I**[7] was not obtained. Thus, it was found that for epoxide **5a**, cleavage of the oxirane ring at C-6 (route *a*) did not induce the skeletal transformation into compound **14**, but rather caused the migration of the methyl group at C-1 to give compound **10**. On the other hand, the five membered ethyl ketone **8** was formed in the same pathway as the proposed biosynthetic mechanism[5] of mytiloxanthin **3** (route *b*). Then, the same treatment (entry 4) of the *syn*-epoxide **5b** provided the cyclopentyl ethyl ketone **13** (44%) and compound **10** (49%). In addition, a variety of Lewis acids were also examined as shown in Table 2. Predominant formation of the novel olefinic methyl ketone **10** was found by treatment of both epoxides **5a**,**b** with $SnCl_4$ (entries 2 and 5) and tris(4-bromophenyl)aminium hexachloroantimonate[11] (entries 3 and 8). In these cases, the *anti*-epoxide **5a** showed a tendency to give compound **10** more selectively than the *syn*-epoxide **5b**. Rearrangement of the *syn*-epoxide **5b** tends to proceed more rapidly than that of the *anti*-epoxide **5a**.

The stereostructures of the cyclopentyl ethyl ketones **8** and **13** were determined by the comparison of their ^1H NMR data with those of the known[12] five membered methyl ketones **7** and **12** (Scheme 2). The structure of the novel compound **10** was confirmed on the basis of its spectral data (see Experimental section), which failed to prove the geometry of the tetrasubstituted double bond. Thus, it was chemically determined by the synthesis of both isomers **10′** and **33** as shown in Scheme 5.

Reaction of the ketone **24** with phosphorothioate **26** prepared according to the literature[13] and following reduction of the products gave an isomeric mixture of alcohols **27** and **28**



Scheme 5 *Reagents and conditions*: i, $(EtO)_2P(O)SCH(Et)CO_2Me$ **26**, LDA; ii, $LiAlH_4$; iii, MsCl, Py; iv, $Py{\cdot}SO_3$, $LiAlH_4$; v, PTSA; vi, LDA, acetone; vii, Ac_2O, Py

(34% from **24**; **27** : **28** = *ca.* 3 : 2), which was cleanly separated by column chromatography. Stereochemistries of these alcohols were determined by their NOESY measurements as shown in Scheme 5. Each of them was transformed into their respective acyclic methyl ketones **33** and **10′** *via* the aldehydes **31** and **32** by modification of a reported[6] method. Spectral properties of the *E*-olefinic methyl ketone **10′** derived from the alcohol **28** were in good agreement with those of compound **10** obtained from rearrangement of epoxides **5a**,**b**. In the NOESY spectra of the *Z*-isomer **33**, cross-peaks between the methylene protons of the ethyl group and the methylene protons at the C-5 position were observed. Hence, the stereoselective formation of compound **10** from both the *anti*- and *syn*-epoxides **5a** and **5b** could be accounted for through a concerted antiperiplanar pathway.

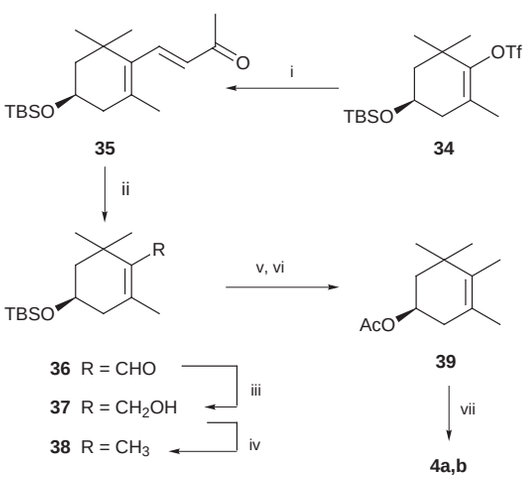
Rearrangement of epoxides 4a,b

Rüttimann reported[7] that only ring-contracted products **6** and **11** (Scheme 2) were obtained by treatment of epoxides **4a**,**b** with $BF_3{\cdot}OEt_2$ followed by hydrolysis. On the other hand, in the case of epoxides **5a**,**b**, the ring contraction competed with migration of the methyl group at the C-1 position as mentioned in the preceding section. Thus, reaction of epoxides **4a**,**b** with $BF_3{\cdot}OEt_2$ was reinvestigated.

Epoxides **4a**,**b** were effectively synthesized from the known[8] triflate **34** as shown in Scheme 6. A coupling reaction[8,14] of the triflate **34** with methyl vinyl ketone in the presence of a palladium catalyst gave the dienone **35** (81%). Ozonolysis of the dienone **35** provided the enal **36** which, without purification, was reduced with $NaBH_4$ to give the alcohol **37** (79% from **35**). Deoxygenation[15] of the alcohol **37** was attained by treatment with a pyridine–sulfur trioxide complex and by subsequent reduction with $LiAlH_4$ to provide the compound **38** (94%), which was deprotected and then acetylated to afford the acetate **39** (88%). Treatment of the compound **39** with MCPBA led to a mixture of *anti*-epoxide **4a** (23%) and *syn*-epoxide **4b** (51%).

Table 3 Epoxidation of **40**, **43**, **45**, **47**, **49**, **51** and **54**

Substrate	Amount of MCPBA Conditions	Purification method Eluents, proportions	Products (Yield)
40	1.2 equiv. 0 °C, 3 h	*p*-HPLC MeOH–Et_2O–hexane, 0.3 : 30 : 70	**41a** 34% **41b** 54%
43	1.1 equiv. 0 °C, 1 h	*p*-HPLC Et_2O–hexane, 9 : 41	**44a** 17% **44b** 44%
45	1.5 equiv. 0 °C, 20 min ⟶ rt, 30 min	short CC Et_2O–hexane, 3 : 17	**46a** 16% **46b** 68%
47	2 equiv. 0 °C, 1 h ⟶ rt, 3 h	low-pressure CC acetone–hexane, 1 : 4	**48a** 23% **48b** 63%
49	2 equiv. 0 °C, 2 h	short CC Et_2O–hexane, 1 : 39	**50a** 31% **50b** 48%
51	2 equiv. 0 °C, 30 min ⟶ rt, 1 h	CC Et_2O–CH_2Cl_2, 1 : 19	**52a** 22% **52b** 63%
54	1.3 equiv. 0 °C, 2 h	short CC Et_2O–hexane, 1 : 9	**55a** 26% **55b** 61%

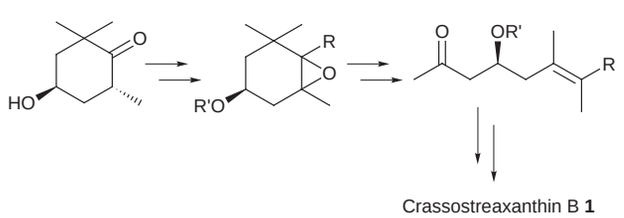


Scheme 6 *Reagents and conditions*: i, methyl vinyl ketone, $PdCl_2(PPh_3)_2$, Et_3N, DMF, 85 °C; ii, O_3, −20 °C; then Zn, AcOH, −20 °C to 0 °C; iii, $NaBH_4$; iv, SO_3·Py; then $LiAlH_4$; v, 47% aq. HF; vi, Ac_2O, Py; vii, MCPBA

Reaction of *syn*-epoxide **4b** with BF_3·OEt_2 provided only the five-membered methyl ketone **12** (63%) in accordance with the results reported[7] by Rüttimann. On the contrary, the same treatment of *anti*-epoxide **4a** was found to give the olefinic ketone **9** together with compound **7** (63%; **9** : **7** = *ca.* 1 : 1).

Rearrangement of other epoxides

From the results in the preceding sessions, it is expected that this rearrangement reaction should provide an effective synthesis of optically active crassostreaxanthin B **1** as shown in Scheme 7, in which the absolute stereochemistry of the β-hydroxy group has not been confirmed. Thus, the reaction of epoxides (**41**, **44**, **46**, **48**, **50**, **52**, **55** and **58**) having several substituents at the C-6 position with BF_3·OEt_2 was next studied towards the biomimetic synthesis of crassostreaxanthin B **1** as shown in Scheme 8.



Scheme 7

(a) Preparation of epoxides 41, 44, 46, 48, 50, 52, 55 (Table 3) and 58. Treatment of compound **40**[10] with MCPBA, which was a key intermediate for the synthesis of halocynthiaxanthin **2**, afforded *anti*-epoxide **41a** (34%) and *syn*-epoxide **41b** (54%).

Epoxides **44a**,**b** were obtained from the known[8] dienoate **42** by deprotection, acetylation and subsequent epoxidation (**44a**: 12% from **42**; **44b**: 31% from **42**).

Epoxides **46a**,**b** were synthesized from siloxy ketone **15** by reaction with phenyllithium, deprotection, acetylation, dehydration and then epoxidation (**46a**: 13% from **15**; **46b**: 54% from **15**).

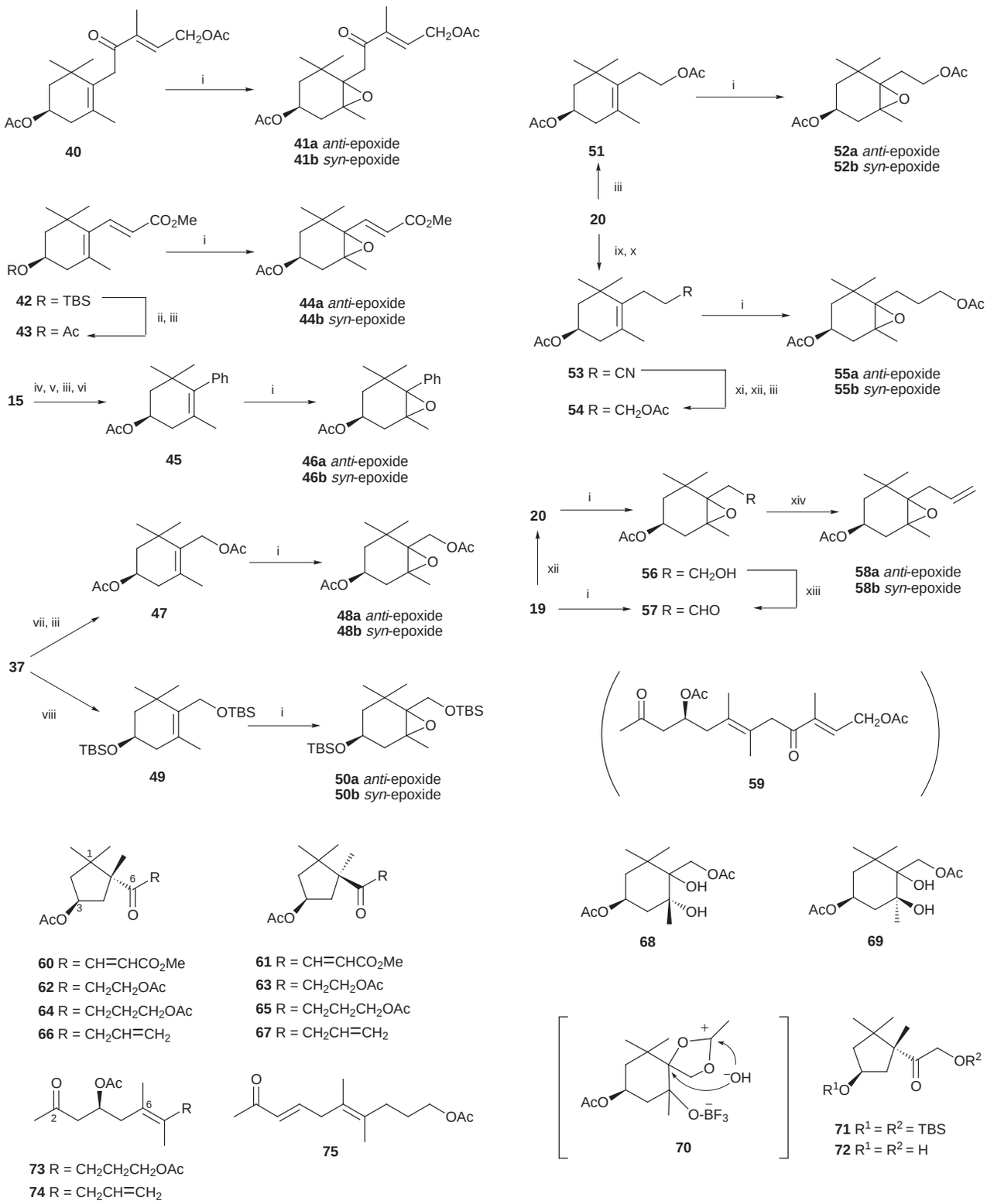
Epoxides **48a**,**b**, **50a**,**b**, **52a**,**b** and **55a**,**b** were prepared either from the alcohol **37** or the alcohol **20** as shown in Scheme 8.

Epoxides **58a**,**b** were synthesized through the epoxy aldehyde **57** as follows. Direct preparation of **57** by treatment of the aldehyde **19** with MCPBA resulted in a low yield (46%) because of competition with the Baeyer–Villiger reaction. Thus, **57** was prepared from alcohol **20** by epoxidation with MCPBA followed by oxidation[16] with tetrapropylammonium perruthenate (TPAP) and NMO in 87% yield for the two steps. Then, compound **57** was treated with the Wittig reagent derived from methyltriphenylphosphonium bromide and *n*-butyllithium to afford compounds **58a** (14%) and **58b** (35%).

(b) Rearrangement of epoxides 41, 44, 46, 48, 50, 52, 55 and 58 (Table 4). Initially, rearrangement of epoxides **41a**,**b** with BF_3·OEt_2 was examined. However, this reaction did not afford the desired olefinic compound **59** but gave a complicated mixture.

Nicolaou and his co-workers reported[17] that a π-orbital placed adjacent to the epoxide unit acts as an activator of the C–O bond cleavage in the oxirane ring. Thus, the reaction of epoxides **44a**,**b** and **46a**,**b** was next examined in order to obtain the olefinic compounds mainly. Against expectation, epoxides **44a**,**b** provided exclusively the five-membered compounds **60** (20% from **44a**: 18% from **44b**) and **61** (67% from **44b**) formed through cleavage of the oxirane ring at the C-5 position, whereas epoxides **46a**,**b** gave a complicated mixture.

As rearrangement of epoxides **4** and **5** afforded the olefinic compounds **9** and **10** (Scheme 2), the reaction of epoxides **48**, **52** and **55**, whose substituents at the C-6 position are alkyl groups having an oxygen functional group, was next examined. Treatment of epoxides **48a**,**b** with BF_3·OEt_2 provided the diols **68** (98% from **48a**) and **69** (12% from **48b**), which were considered to be formed through the dioxenium ion intermediate[18] **70**. Thus, epoxide **50a** was treated with BF_3·OEt_2 to provide the five-membered compounds **71** (62%) and **72** (28%) by regioselective cleavage of the epoxide at the C-5 position and successive skeletal rearrangement. Epoxides **52a**,**b** also afforded the five-membered compounds **62** and **63**. However, *anti*-epoxide **52a** did not provide the expected *anti*-compound **62** but the *syn*-



Scheme 8 *Reagents and conditions*: i, MCPBA; ii, TBAF; iii, Ac_2O, Py; iv, PhLi; v, PTSA; vi, $POCl_3$, Py, reflux; vii, 47% aq. HF; viii, TBSCl, DMAP, Et_3N; ix, MsCl, Py; x, KCN, 18-crown-6, DMSO, 120 °C; xi, DIBAL-H; xii, $NaBH_4$; xiii, NMO, mol. sieves 4 Å, TPAP; xiv, $MePPh_3Br$, BuLi

compound **63** in low yield (14%), whereas *syn*-epoxide **52b** gave a mixture of compounds **62** and **63** (*ca.* 3:1) in 86% yield. Low stereoselectivity in the rearrangement of these epoxides **52a**,**b** cannot at present be explained. On the other hand, the tetrasubstituted olefinic compound **73** (51% from **55a**; 26% from **55b**) was obtained accompanied with five-membered compounds **64** (16% from **55a**) and **65** (29% from **55b**), and the conjugated enone **75** (16% from **55a**; 13% from **55b**) formed through compound **73**. These results show that decreasing the electron-withdrawing inductive effect of the oxygen atom on the C-6 carbon atom has a tendency to cause cleavage of the oxirane ring at the C-6 position, thus providing the olefinic compounds.

Rearrangement of epoxides **58a**,**b** with $BF_3{\cdot}OEt_2$ provided the tetrasubstituted olefinic compound **74** as a minor product (13% from **58a**; 12% from **58b**) and the five-membered compounds **66** (16% from **58a**) and **67** (77% from **58b**).

In summary, Lewis acid-catalysed rearrangement of 5,6-epoxy carotenoid model compounds possessing the appropriate substituents provides stereoselectively the novel tetrasubsti-

Table 4 Rearrangement of other epoxides with $BF_3{\cdot}Et_2O$

Substrate	Conditions	Purification method Eluents, Proportion	Products (Yield)
41a	−78 °C, 1 h	short CC acetone–hexane, 15 : 85	complex mixture
41b	−78 °C, 1 h	short CC acetone–hexane, 15 : 85	complex mixture
44a	−78 °C, 1 h ⟶ 0 °C, 4 h	*p*-TLC Et_2O–hexane, 1 : 1	**60** 20%
44b	−78 °C, 1 h ⟶ 0 °C, 1.5 h ⟶ rt, 1.5 h	*p*-TLC Et_2O–hexane, 1 : 1	**60** 18% **61** 67%
46a	0 °C, 3 h	short CC Et_2O–hexane, 1 : 9	complex mixture
46b	−78 °C, 1 h ⟶ 0 °C, 1.5 h ⟶ rt, 1.5 h	short CC Et_2O–hexane, 1 : 9	complex mixture
48a	−78 °C, 5 h	short CC acetone–hexane, 3 : 7	**68** 98%
48b	−78 °C, 4 h	short CC acetone–hexane, 1 : 4	**69** 12%
50a	−78 °C, 4 h	short CC Et_2O–hexane, 1 : 19 ⟶ 1 : 4	**71** 62% **72** 28%
50b	−78 °C, 2 h	short CC Et_2O–hexane, 1 : 19	complex mixture
52a	−78 °C, 2 h ⟶ 0 °C, 6 h ⟶ rt, 15 h	short CC Et_2O–hexane, 2 : 3	**63** 14%
52b	−78 °C, 1 h ⟶ 0 °C, 4 h	short CC Et_2O–hexane, 1 : 3	**62** : **63** = 3 : 1 86%
55a	−78 °C, 2 h	short CC Et_2O–hexane, 3 : 7	**64** 16% **73** 51% **75** 16%
55b	−78 °C, 2 h ⟶ 0 °C, 2 h	short CC acetone–hexane, 1 : 4	**65** 29% **73** 26% **75** 13%
58a	−78 °C, 2 h ⟶ 0 °C, 6 h ⟶ rt, 15 h	*p*-TLC Et_2O–hexane, 3 : 7	**66** 16% **74** 13%
58b	−78 °C, 2 h	short CC Et_2O–hexane, 1 : 4	**67** 77% **74** 12%

tuted olefinic compounds as the major products. Work is in progress on a biomimetic synthesis of crassostreaxanthin B **1** using this rearrangement.

Experimental

Mps were measured on a micro melting point apparatus (Yanagimoto) and are uncorrected. UV–VIS spectra were recorded on a JASCO Ubest-55 instrument. IR spectra were measured on a Shimadzu IR-27G spectrometer, or on a Shimadzu FT-IR 4000 spectrometer or a Perkin-Elmer FT-IR spectrometer, model Paragon 1000, for chloroform solutions unless otherwise stated. ^{1}H NMR spectra at 200, 300 or 500 MHz were determined on a Varian XL-200, a Varian Gemini-200, a Varian Gemini-300 or a Varian VXR-500 superconducting FT-NMR spectrometer, respectively, for deuteriochloroform solutions (tetramethylsilane as internal reference). ^{13}C NMR spectrum at 125 MHz was measured on a Varian VXR-500 superconducting FT-NMR spectrometer in a deuteriochloroform solution using tetramethylsilane as an internal standard. *J* Values are given in Hz. Mass spectra were taken on a Hitachi M-4100 spectrometer. Optical rotations were measured on a JASCO DIP-181 polarimeter ($[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}).

Column chromatography (CC) was performed on silica gel (Merck Art. 7734). Short column chromatography (short CC) was performed on silica gel (Merck Art. 7739) under reduced pressure. Low-pressure column chromatography was conducted on a Yamazen Low pressure Liquid Chromatography System using a Lobar column (Merck LiChroprep Si 60). Preparative TLC (PLC) was performed on silica gel plates (Merck silica gel $60F_{254}$ precoated plates, 0.5 mm thickness). Analytical and preparative HPLCs were carried out on Shimadzu LC-5A and 6A instruments with a UV–VIS detector, using a LiChrosorb Si-60 (7 μm), 1.0 × 30 cm column.

Standard work-up means that the organic layers were finally washed with brine, dried over anhydrous sodium sulfate (Na_2SO_4), filtered and concentrated *in vacuo* below 30 °C using a rotary evaporator. All operations were carried out under nitrogen or argon. Hexane refers to *n*-hexane.

(1*R*,4*R*,5*R*)-4-Ethynyl-4-hydroxy-3,3,5-trimethylcyclohexyl acetate 17

BuLi (1.63 mol dm^{-3} in hexane; 40.4 cm^3, 66 mmol) was added to a solution of TMS acetylene (9.3 cm^3, 66 mmol) in dry THF (60 cm^3) at 0 °C and the mixture was stirred for a further 20 min. To this mixture was added dropwise a solution of the ketone **15**[8] (10.0 g, 44 mmol) in dry THF (80 cm^3) at 0 °C and the mixture was stirred at 0 °C for 1 h. The reaction was quenched with saturated aq. NH_4Cl. After evaporation off of the THF, the residue was extracted with Et_2O. The extracts were washed with brine, dried and evaporated to give the crude hydroxy compound **16** which, without purification, was dissolved in MeOH (100 cm^3) and aq. 10% KOH (50 cm^3) was added to this solution and the reaction mixture was stirred at room temperature for 30 min. After evaporation off of the MeOH, the residue was extracted with AcOEt. The extracts were washed with brine, dried and evaporated to afford the diol which, without purification, was dissolved in a mixture of dry pyridine (Py) (77.5 cm^3) and Ac_2O (29 cm^3). After being stirred at room temperature for 16 h, the reaction mixture was poured into ice–water and extracted with Et_2O. The extracts were

washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (acetone–hexane, 1:4) to afford the *acetylenic alcohol* **17** (9.27 g, 94%) as colourless crystals; mp 63.5–64.5 °C (from Et_2O–hexane); $[\alpha]_D^{27}$ −28.0 (*c* 1.00, MeOH); ν_{max}/cm^{-1} 3600 and 3450 (OH), 3320 (C≡CH), 1720 (OAc); δ_H(300 MHz) 1.08 (3H, d, *J* 6.5, 5-Me), 1.12 and 1.13 (each 3H, s, *gem*-Me), 2.04 (3H, s, OAc), 2.22 (1H, m, 5-H), 2.51 (1H, s, 8-H), 4.96 (1H, quint., *J* 3, 3-H) (Found: C, 69.31; H, 9.26. $C_{13}H_{20}O_3$ requires C, 69.61; H, 8.99%).

Rearrangement of the α-acetylenic alcohol 17 and the α,β-unsaturated aldehyde 18 by a silyl vanadate catalyst (Table 1)

General procedure. The reaction was conducted in the conditions shown in Table 1 and continued until a change in the TLC spots of each product was not observed. After evaporation off of the solvent, the residue was purified by short CC (acetone–hexane, 3:17) to give the *α,β-unsaturated aldehyde* **18** or *β,γ-one* **19** in the yield as shown in Table 1.

Compound 18. $[\alpha]_D^{25}$ −115.7 (*c* 1.59, MeOH); λ_{max}(EtOH)/nm 243; ν_{max}/cm^{-1} 1725 (OAc), 1660 (conj. CHO), 1605 (C=C); δ_H(500 MHz) 1.10 (3H, d, *J* 6.5, 5-Me), 1.43 (3H, s, 1-Me_{ax}), 1.48 (3H, s, 1-Me_{eq}), 1.68 (1H, ddd, *J* 15, 12.5 and 7, 4-H_{ax}), 1.76 (1H, dd, *J* 14 and 5.5, 2-H_{eq}), 1.88 (1H, dd, *J* 14 and 8.5, 2-H_{ax}), 1.88 (1H, ddd, *J* 15, 5.5 and 3.5, 4-H_{eq}), 2.07 (3H, s, OAc), 2.82 (1H, m, 5-H), 5.06 (1H, m, 3-H), 5.80 (1H, dd, *J* 8 and 1.5, 7-H), 10.38 (1H, d, *J* 8, CHO) (Found: M^+, 224.1413. $C_{13}H_{20}O_3$ requires M, 224.1413).

Compound 19. $[\alpha]_D^{28}$ −74.3 (*c* 1.01, MeOH); ν_{max}/cm^{-1} 1735 (OAc), 1720 (CHO); δ_H(200 MHz) 1.03 and 1.06 (each 3H, s, *gem*-Me), 1.60 (3H, s, 5-Me), 1.61 (1H, t, *J* 12, 2-H_{ax}), 1.80 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.04 (3H, s, OAc), 2.14 (1H, ddd-like, *J* 17, 9.5 and 1, 4-H_{ax}), 2.42 (1H, br dd, *J* 17 and 5, 4-H_{eq}), 3.13 (2H, br s, 7-H_2), 5.04 (1H, m, 3-H), 9.53 (1H, t, *J* 2, CHO) (Found: M^+, 224.1403. $C_{13}H_{20}O_3$ requires M, 224.1413).

(1*R*)-4-[2-(Methanesulfonyloxy)ethyl]-3,5,5-trimethylcyclohex-3-enyl acetate 21

$NaBH_4$ (0.51 g, 13.4 mmol) was added to an ice-cooled solution of the aldehyde **19** (6.0 g, 26.8 mmol) in MeOH (50 cm^3). The mixture was stirred at 0 °C for 20 min and then poured into ice–water, and extracted with Et_2O. The organic layer was washed with brine and dried. Evaporation of the extracts gave a residue which, without purification, was dissolved in dry Py (10 cm^3) and dry CH_2Cl_2 (20 cm^3). MsCl (4.15 cm^3, 53.6 mmol) was added to this solution at 0 °C for 1 h and at room temperature for 2 h. The mixture was poured into ice–water and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (acetone–hexane, 1:4) to afford the *mesylate* **21** (6.98 g, 86%) as a colourless oil; $[\alpha]_D^{27}$ −34.0 (*c* 1.00, MeOH); ν_{max}/cm^{-1} 1725 (OAc), 1355 and 1170 (OSO_2); δ_H(300 MHz) 1.08 (6H, s, *gem*-Me), 1.54 (1H, t, *J* 12, 2-H_{ax}), 1.68 (3H, s, 5-Me), 1.75 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.03 (3H, s, OAc), 2.04 (1H, ddd-like, *J* 16.5, 9.5 and 1, 4-H_{ax}), 2.34 (1H, br dd, *J* 16.5 and 5.5, 4-H_{eq}), 2.53 (2H, m, 7-H_2), 3.01 (3H, s, OSO_2Me), 4.14 (2H, m, 8-H_2), 4.98 (1H, m, 3-H) (Found: M^+, 244.1121. $C_{12}H_{20}O_3S$ requires M, 244.1134).

(1*R*)-4-Ethyl-3,5,5-trimethylcyclohex-3-enyl acetate 22

A solution of the mesylate **21** (6.80 g, 22.4 mmol) in dry THF (30 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (2.55 g, 67 mmol) in dry THF (20 cm^3) at 0 °C and the mixture was stirred at 0 °C for 10 min and refluxed for 1 h. After cooling, the excess of $LiAlH_4$ was decomposed by dropwise addition of water. The mixture was extracted with Et_2O and the extracts were washed with brine and dried. Evaporation off of the solvent gave the hydroxy compound which, without purification, was dissolved in dry Py (60 cm^3). Ac_2O (20 cm^3) was added to this solution and the mixture was stirred at room temperature for 16 h, poured into ice–water, and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts afforded a residue, which was purified by short CC (Et_2O–hexane, 1:4) to yield the *diacetate* **22** (4.23 g, 90%) as a colourless oil; $[\alpha]_D^{26}$ −66.3 (*c* 1.01, MeOH); ν_{max}/cm^{-1} 1725 (OAc); δ_H(300 MHz) 1.08 (6H, s, *gem*-Me), 1.54 (1H, t, *J* 12, 2-H_{ax}), 1.68 (3H, s, 5-Me), 0.98 (3H, t, *J* 7.5, 8-H_3), 1.06 (6H, s, *gem*-Me), 1.53 (1H, t, *J* 12, 2-H_{ax}), 1.61 (3H, s, 5-Me), 1.71 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.91–2.14 (3H, m, 4-H_{ax} and 7-H_2), 2.03 (3H, s, OAc), 2.29 (1H, br dd, *J* 16 and 5.5, 4-H_{eq}), 5.00 (1H, m, 3-H) [Found: $(M - AcOH)^+$, 150.1407. $C_{11}H_{18}$ requires M − AcOH, 150.1409].

Epoxidation of the acetate 22

A solution of MCPBA (70%, 5.77 g, 23.5 mmol) in dry CH_2Cl_2 (80 cm^3) was added to an ice-cooled solution of the diacetate **22** (4.10 g, 19.5 mmol) in dry CH_2Cl_2 (50 cm^3). After being stirred at 0 °C for 3 h, the reaction mixture was diluted with CH_2Cl_2 and washed successively with aq. 1% $Na_2S_2O_3$, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solvent gave a residue, which was purified by short CC (Et_2O–hexane, 1:4) followed by low-pressure CC (Et_2O–hexane, 1:4) to afford the anti-*epoxide* **5a** (1.50 g, 34%) and the syn-*epoxide* **5b** (2.70 g, 61%) as oils.

***anti*-Epoxide 5a.** $[\alpha]_D^{29}$ −23.0 (*c* 1.00, MeOH); ν_{max}/cm^{-1} 1735 (OAc); δ_H(300 MHz) 1.02 (3H, t, *J* 7.5, 8-H_3), 1.07 and 1.17 (each 3H, s, *gem*-Me), 1.29 (1H, dd, *J* 13 and 8.5, 2-H_{ax}), 1.33 (3H, s, 5-Me), 1.57 and 1.86 (each 1H, dq, *J* 15 and 7.5, 7-H_2), 1.59 (1H, br dd, *J* 14.5 and 3, 2-H_{eq}), 1.74 (1H, dd, *J* 14.5 and 7, 4-H_{ax}), 2.00 (3H, s, OAc), 2.33 (1H, br dd, *J* 14.5 and 6, 4-H_{eq}), 4.85 (1H, m, 3H) (Found: M^+, 226.1557. $C_{13}H_{22}O_3$ requires M, 226.1570).

***syn*-Epoxide 5b.** $[\alpha]_D^{29}$ −33.0 (*c* 1.00, MeOH); ν_{max}/cm^{-1} 1725 (OAc); δ_H(200 MHz) 0.87 (3H, t, *J* 7.5, 8-H_3), 0.99 and 1.06 (each 3H, s, *gem*-Me), 1.15 (1H, ddd, *J* 12.5, 4 and 1.5, 2-H_{eq}), 1.21 (3H, s, 5-Me), 1.43–1.78 (2H, m, 7-H_2), 1.56 (1H, t, *J* 12.5, 2-H_{ax}), 1.73 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 1.93 (3H, s, OAc), 2.18 (1H, ddd, *J* 15, 7.5 and 1.5, 4-H_{eq}), 4.77 (1H, m, 3H) (Found: M^+, 226.1570. $C_{13}H_{22}O_3$ requires M, 226.1570).

Rearrangement of epoxides 5a and 5b (Table 2)

General procedure. Epoxides **5a** or **5b** were treated with Lewis acid under the conditions shown in Table 2 and the reaction mixture was diluted with either CH_2Cl_2 or Et_2O and the organic layer was washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solution gave a residue which was purified by short CC (Et_2O–hexane, 3:7).

Entry 2. To a solution of **5a** (340 mg, 1.5 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise a solution of 1 M $SnCl_4$ in CH_2Cl_2 (3 cm^3, 3.0 mmol) at −25 °C and the mixture was stirred at −25 °C for 2.5 h and at 0 °C for 2.5 h. The mixture was followed by the general work-up procedure to give the anti-*cyclopentyl ethyl ketone* **8** (trace) and the *tetrasubstituted olefinic methyl ketone* **10** (246 mg, 70%) as oils.

Entry 3. To a solution of **5a** (340 mg, 1.5 mmol) in CH_2Cl_2 (15 cm^3) was added $(p\text{-}BrC_6H_4)_3NSbCl_6$ (123 mg, 0.1 mmol) at room temperature and the mixture was stirred at room temperature for 1.5 h. Evaporation of the reaction mixture gave a residue, which was purified by short CC (Et_2O–hexane, 3:7) to afford the anti-*cyclopentyl ethyl ketone* **8** (40 mg, 12%) and the *tetrasubstituted olefinic methyl ketone* **10** (242 mg, 71%) as oils.

Entry 8. To a solution of **5b** (340 mg, 1.5 mmol) in CH_2Cl_2 (15 cm^3) was added $(p\text{-}BrC_6H_4)_3NSbCl_6$ (123 mg, 0.1 mmol) at room temperature and the mixture was stirred at room temperature for 40 min. Evaporation of the reaction mixture gave a residue, which was purified by short CC (Et_2O–hexane, 3:7) to afford the syn-*cyclopentyl ethyl ketone* **13** (77 mg, 23%) and the *tetrasubstituted olefinic methyl ketone* **10** (211 mg, 62%) as oils.

***anti*-Cyclopentyl ethyl ketone 8.** $[\alpha]_D^{21}$ −6.54 (*c* 0.92, MeOH); ν_{max}/cm^{-1} 1725 (OAc), 1700 (C=O); δ_H(500 MHz) 0.83, 1.14 and 1.26 (each 3H, s, Me × 3), 1.01 (3H, t, *J* 7, 8-H_3), 1.54 (1H, dd, *J* 14.5 and 8.5, 4-H_β), 1.71 (1H, dd, *J* 14.5 and 4.5, 2-H_β), 2.02 (3H, s, OAc), 2.06 (1H, dd, *J* 14.5 and 8.5, 2-H_α), 2.45 (2H, qd-like, *J* 7 and 1.5, 7-H_2), 2.86 (1H, dd, *J* 15 and 8.5, 4-H_α), 5.22 (1H, m, 3H) (Found: M^+, 226.1568. $C_{13}H_{22}O_3$ requires M, 226.1570).

Tetrasubstituted olefinic methyl ketone 10. $[\alpha]_D^{25}$ −1.69 (*c* 1.18, MeOH); ν_{max}/cm^{-1} 1730 (OAc); δ_H(500 MHz) 0.92 (3H, t, *J* 7.5, CH_2CH_3), 1.67 [3H, d-like, *J* 1, =C(Et)*Me*], 1.69 [3H, d-like, *J* 1, *Me*(CH_2)C=], 1.98 (3H, s, OAc), 2.10 (2H, q, *J* 7.5, CH_2CH_3) 2.16 [3H, s, $CH_2C(O)CH_3$], 2.19 (1H, dd, *J* 13.5 and 6) and 2.42 (1H, dd, *J* 13.5 and 8) [Me(CH_2)C=], 2.60 (1H, dd, *J* 16.5 and 4.5) and 2.70 (1H, dd, *J* 16.5 and 8) [$CH_2C(O)CH_3$], 5.40 (1H, tdd, *J* 8, 6 and 4.5, CHOAc); δ_C(125 MHz) 12.3 (CH_2CH_3), 18.1 [=C(CH_3)Et], 18.3 [$CH_2(CH_3)$C=], 21.0 (CH_3CO_2), 27.6 (CH_2CH_3), 30.3 [$CH_2C(O)CH_3$], 39.2 [$CH_2(CH_3)$C=], 47.8 [$CH_2C(O)CH_3$], 69.3 [CH_2(OAc)CH], 122.7 [$CH_2(CH_3)C$=], 134.1 [=C(CH_3)Et], 170.1 (CH_3CO_2), 205.7 [$CH_2C(O)CH_3$] (Found: M^+, 226.1566. $C_{13}H_{22}O_3$ requires M, 226.1570).

***syn*-Cyclopentyl ethyl ketone 13.** $[\alpha]_D^{21}$ −25.0 (*c* 1.00, MeOH); ν_{max}/cm^{-1} 1725 (OAc), 1700 (C=O); δ_H(500 MHz) 0.94, 1.10, 1.14 (each 3H, s, Me × 3), 1.03 (3H, t, *J* 7, 8-H_3), 1.64 (1H, dd, *J* 14.5 and 3.5, 2-H_β), 2.04 (3H, s, OAc), 2.06 (1H, dd, 14.5 and 8.5, 4-H_α), 2.12 (1H, dd, *J* 14.5 and 9, 2-H_α), 2.43 and 2.52 (each 1H, dq, *J* 18.5 and 7, 7-H_2), 2.55 (1H, dd, *J* 14.5 and 6, 4-H_β), 5.15 (1H, m, 3H) (Found: M^+, 226.1570. $C_{13}H_{22}O_3$ requires M, 226.1570).

(*S*)-Methyl 2-[(diethoxyphosphoryl)sulfanyl]butanoate 26

To a solution of diethyl phosphite (5.0 g, 0.36 mol) in dry benzene (250 cm^3) was added sodium metal (8.5 g, 0.37 mol), and the mixture was stirred at room temperature for 2 h. After sulfur (11.6 g, 0.36 mol) was added to it, the reaction mixture was stirred at room temperature overnight. To the reaction mixture was added, over a 20 min period, a solution of methyl 2-bromobutyrate (65.16 g, 0.36 mol) in benzene (50 cm^3), and then the mixture was refluxed for 3 h and the resulting precipitate filtered. Evaporation and distillation under reduced pressure of the filtrate gave *butanoate* **26** (48.5 g, 50%) as a pale yellow oil; bp 119–121 °C/1 mmHg; ν_{max}/cm^{-1} 1737 (C=O), 1252 (P=O); δ_H(300 MHz), 1.03 (3H, t, *J* 7.5, $CHCH_2CH_3$), 1.37 (6H, t-like, *J* 7, OCH_2CH_3 × 2), 1.82–2.07 (2H, m, $CHCH_2CH_3$), 3.76 (3H, s, CO_2Me), 3.81 (1H, ddd, *J* 13, 7.5 and 6.5, $CHCH_2CH_3$), 4.11–4.26 (4H, m, OCH_2CH_3 × 2) (Found: M^+, 270.0691. $C_9H_{19}O_5SP$ requires M, 270.0689).

(2*E*/*Z*)-2-Ethyl-5,5-dimethoxy-3-methylpent-2-enol 27 and 28

BuLi (1.68 mol dm^{-3} in hexane; 35.7 cm^3, 0.06 mol) was added to diisopropylamine (8.41 cm^3, 0.06 mol) at 0 °C and the mixture was diluted with dry THF (25 cm^3) at 0 °C. To this LDA solution was added dropwise a solution of the butanoate **26** (12.96 g, 0.048 mol) in dry THF (30 cm^3) at −78 °C, and the solution was stirred at −78 °C for 30 min. A solution of the ketone **24** (5.28 g, 0.04 mol) in dry THF (15 cm^3) was added to the reaction mixture at −78 °C, and the solution was stirred at −78 °C for 1 h and at room temperature for 30 min. After being quenched with saturated aq. NH_4Cl, the mixture was extracted with Et_2O. The extracts were washed with brine, dried and evaporated to give a residue which was purified by CC (Et_2O–hexane, 1:4) to afford the conjugated ester **25** (3.83 g, 43%). Subsequently, a solution of **25** (3.36 g, 15 mmol) in dry Et_2O (15 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (0.68 g, 18 mmol) in dry Et_2O (30 cm^3) at 0 °C and the mixture was stirred at 0 °C for 20 min. The excess of $LiAlH_4$ was decomposed by the dropwise addition of water. The mixture was extracted with Et_2O and the extracts were washed with brine. Evaporation of the dried extracts gave a residue which was purified by short CC (acetone–hexane, 1:9) to afford the E-*alcohol* **27** (1.26 g, 45%) and the Z-*alcohol* **28** (1.04 g, 37%) as colourless oils, respectively.

***E*-Alcohol 27.** ν_{max}/cm^{-1} 3611 and 3465 (OH); δ_H(500 MHz; C_6D_6) 1.00 (3H, t, *J* 7.5, CH_2CH_3), 1.71 [3H, s, =C(CH_3)CH_2], 2.21 (2H, q, *J* 7.5, CH_2CH_3), 2.43 [2H, d, *J* 5.5, =C(CH_3)CH_2], 3.14 (6H, s, OMe × 2), 3.99 (2H, br s-like, CH_2OH), 4.43 [1H, t, *J* 5.5, CH(OMe)$_2$] (Found: M^+, 188.1400. $C_{10}H_{20}O_3$ requires M, 188.1413).

***Z*-Alcohol 28.** ν_{max}/cm^{-1} 3455 (OH); δ_H(500 MHz; C_6D_6) 0.99 (3H, t, *J* 7.5, CH_2CH_3), 1.58 [3H, s, =C(CH_3)CH_2], 2.18 (2H, q, *J* 7.5, CH_2CH_3), 2.39 [2H, d, *J* 5.5, =C(CH_3)CH_2], 3.02 (6H, s, OMe × 2), 4.10 [2H, br s, CH_2OH], 4.24 [1H, t, *J* 5.5, CH(OMe)$_2$] (Found: M^+, 188.1408. $C_{10}H_{20}O_3$ requires M, 188.1413).

(3*Z*)-4-Chloromethyl-1,1-dimethoxy-3-methylhex-3-ene 30

MsCl (0.62 cm^3, 8.0 mmol) was added to a solution of the *Z*-alcohol **28** (1.00 g, 5.3 mmol) in dry Py (3 cm^3) at 0 °C and the mixture was stirred at 0 °C for 30 min. The mixture was poured into ice–water and extracted with Et_2O. The extracts were washed with diluted aq. oxalic acid, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (acetone–hexane, 6:94) to afford the Z-*chloride* **30** (681 mg, 62%) as an oil; δ_H(300 MHz; C_6D_6) 0.86 (3H, t, *J* 7.5, CH_2CH_3), 1.59 [3H, s, =C(CH_3)-CH_2], 2.10 (2H, q, *J* 7.5, CH_2CH_3), 2.41 [2H, d, *J* 5.5, =C(CH_3)-CH_2], 3.09 (6H, s, OMe × 2), 4.04 (2H, s, CH_2Cl), 4.37 [1H, t, *J* 5.5, CH(OMe)$_2$] [Found: $(M - OMe)^+$, 175.0883. $C_9H_{16}O^{35}Cl$ requires M − OMe, 175.0889] [Found: $(M - OMe)^+$, 177.0872. $C_9H_{16}O^{37}Cl$ requires M − OMe, 177.0859].

(3*Z*)-1,1-Dimethoxy-3,4-dimethylhex-3-ene 29

Py·SO_3 (1.80 g, 11.3 mmol) was added to a solution of the *E*-alcohol **27** (1.06 g, 5.64 mmol) in THF (15 cm^3) at 0 °C and the mixture was stirred at 0 °C for 2.5 h. After dry THF (25 cm^3) was added to the reaction solution, $LiAlH_4$ (0.86 g, 22.6 mmol) was added to this solution at 0 °C. The mixture was stirred at room temperature for 4 h. The excess of $LiAlH_4$ was decomposed by the dropwise addition of water. The mixture was extracted with Et_2O and the extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (Et_2O–hexane, 1:9) to afford the Z-*reduction product* **29** (340 mg, 35%) as a colourless oil; δ_H(300 MHz; C_6D_6) 0.95 (3H, t, *J* 7.5, CH_2CH_3), 1.65 and 1.68 [each 3H, s, =C(CH_3)CH_2 × 2], 2.07 (2H, q, *J* 7.5, CH_2CH_3), 2.36 (2H, d, *J* 5.5, $CHCH_2$), 3.33 (6H, s, OMe × 2), 4.39 [1H, t, *J* 5.5, CH(OMe)$_2$] (Found: M^+, 172.1466. $C_{10}H_{20}O_2$ requires M, 172.1464).

(3*E*)-3,4-Dimethylhex-3-enal 32

To a solution of the *Z*-chloride **30** (681 mg, 3.3 mmol) in dry THF (30 cm^3) was added $LiAlH_4$ (250 mg, 6.6 mmol) at 0 °C and the mixture was refluxed for 1 h. After cooling, the excess of $LiAlH_4$ was decomposed by wet silica gel, and the reaction mixture was filtered through Celite. Evaporation of the filtrates gave the crude products which, without purification, were dissolved in THF (8 cm^3) and a solution of PTSA (60 mg) in THF (3 cm^3) was added to it. After being stirred at room temperature for 5 h, the reaction mixture was diluted with Et_2O and washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave the E-*aldehyde* **32** (113 mg, 27%) as a colourless oil; ν_{max}/cm^{-1} 1718 (CHO); δ_H(300 MHz; C_6D_6) 0.83 (3H, t, *J* 7.5, CH_2CH_3), 1.41 and 1.47 [each 3H, br s, =C(CH_3)CH_2 × 2], 1.89 (2H, q, *J* 7.5, CH_2CH_3), 2.67 (2H, br d, *J* 2.5, CH_2CHO), 9.24 (1H, t, *J* 2.5, CHO).

(3*Z*)-3,4-Dimethylhex-3-enal 31

A solution of PTSA (90 mg) in THF (5 cm^3) was added to a solution of the *Z*-reduction product **29** (340 mg, 2.0 mmol) in

THF (1 cm^3) and the mixture was stirred at room temperature for 5 h. The mixture was diluted with Et_2O and washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave the *Z-aldehyde* **31** (79.7 mg, 32%) as a colourless oil; ν_{max}/cm^{-1} 1719 (CHO); δ_H(300 MHz, C_6D_6) 0.79 (3H, t, *J* 7.5, CH_2CH_3), 1.46 and 1.49 [each 3H, br s, $=C(CH_3)CH_2$ × 2], 1.79 (2H, qd, *J* 7.5, CH_2CH_3), 2.70 (2H, dd-like, *J* 2.5 and 1, CH_2CHO), 9.27 (1H, t, *J* 2.5, CHO).

(6*E*)-4-Acetoxy-6,7-dimethylnon-6-en-2-one 10′

BuLi (1.68 mol dm^{-3} in hexane; 0.62 cm^3, 1.04 mmol) was added to diisopropylamine (0.15 cm^3, 1.04 mmol) at 0 °C. To this LDA solution was added acetone (0.07 cm^3, 0.96 mmol) at −78 °C and the solution was stirred at −78 °C for 20 min. To the reaction solution was added the *E*-aldehyde **32** (101 mg, 0.8 mmol) at −78 °C and the reaction mixture was stirred at −78 °C for 1 h. After being quenched with saturated aq. NH_4Cl, the mixture was extracted with AcOEt. The extracts were washed with brine, dried and evaporated to give an oil which was dissolved in dry Py (2 cm^3). Ac_2O (1 cm^3) was added to this solution and the reaction mixture was stirred at room temperature for 2 h, poured into ice–water and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (Et_2O–hexane, 1:1) to afford the E-*acetate* **10′** (37 mg, 21%) as a colourless oil. Spectral properties of this acetate were in good agreement with those of the tetrasubstituted olefinic methyl ketone **10** in the rearrangement; ν_{max}/cm^{-1} 1733 (OAc); δ_H(300 MHz) 0.92 (3H, t, *J* 7.5, CH_2CH_3), 1.67 and 1.68 [each 3H, br s, $=C(CH_3)CH_2$ × 2], 1.98 (3H, s, OAc), 1.94–2.09 (2H, m, CH_2CH_3), 2.15 [3H, s, $C(O)CH_3$], 2.18 (1H, dd, *J* 13.5 and 6) and 2.42 (1H, dd, *J* 13.5 and 7.5) [$CH(OAc)CH_2C(Me)=$], 2.59 (1H, dd, *J* 16 and 5) and 2.70 (1H, dd, *J* 16 and 8) [$C(O)CH_2$], 5.40 (1H, m, CHOAc) (Found: M^+, 226.1591. $C_{13}H_{22}O_3$ requires M, 226.1570).

(6*Z*)-4-Acetoxy-6,7-dimethylnon-6-en-2-one 33

In the same manner as described for the synthesis of the *E*-acetate **10′** from the *E*-aldehyde **32**, the *Z*-aldehyde **31** (75 mg, 0.6 mmol) was reacted with acetone followed by acetylation to give the *Z-acetate* **33** (61 mg, 45%) as a colourless oil; ν_{max}/cm^{-1} 1733 (OAc); δ_H(500 MHz) 0.95 (3H, t, *J* 7.5, CH_2CH_3), 1.62 and 1.67 [each 3H, br s, $=C(CH_3)CH_2$ × 2], 1.98 (3H, s, OAc), 2.02–2.13 (2H, m, CH_2CH_3), 2.15 (3H, s, CH_3CO), 2.21 (1H, dd, *J* 14 and 6.5) and 2.42 (1H, dd, *J* 14 and 7.5) [$CH(OAc)CH_2C(Me)=$], 2.60 (1H, dd, *J* 16 and 4.5) and 2.70 (1H, dd, *J* 16 and 8) [$C(O)CH_2$], 5.37 (1H, m, CHOAc) (Found: M^+, 226.1579. $C_{13}H_{22}O_3$ requires M, 226.1570).

(*E*)-4-[(4*R*)-4-*tert*-Butyldimethylsilyloxy-2,6,6-trimethylcyclohex-1-enyl]but-3-en-2-one 35

$PdCl_2(PPh_3)_2$ (489 mg, 0.70 mmol) was added to a solution of the enol triflate **34**[8] (9.35 g, 23 mmol), methyl vinyl ketone (9.4 cm^3, 116 mmol) and Et_3N (11.4 cm^3, 81 mmol) in dry DMF (65 cm^3). The mixture was heated and stirred at 85 °C for 20 h. After cooling, the reaction mixture was diluted with Et_2O and washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solution gave a residue which was purified by CC (Et_2O–hexane, 1:3) to afford the 3-*silyloxy-β-ionone* **35** (6.03 g, 81%) as a pale yellow oil; $[\alpha]_D^{21}$ −45.6 (*c* 1.14, MeOH); λ_{max}(EtOH)/nm 216, 291; ν_{max}/cm^{-1} 1666 (conj. C=O), 1604 (C=C); δ_H(200 MHz) 0.08 (6H, s, SiMe × 2), 0.90 (9H, s, $SiBu^t$), 1.09 and 1.11 (each 3H, s, *gem*-Me), 1.50 (1H, t, *J* 12, 2-H_{ax}), 1.68 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 1.76 (3H, s, 5-Me), 2.10 (1H, br dd, *J* 18 and 9, 4-H_{ax}), 2.29 (3H, s, CH_3CO), 2.30 (1H, br dd, *J* 18 and 6, 4-H_{eq}), 3.95 (1H, m, 3-H), 6.11 (1H, d, *J* 16, 8-H), 7.22 (1H, br d, *J* 16, 7-H) (Found: M^+, 322.2314. $C_{19}H_{34}O_2Si$ requires M, 322.2330).

***tert*-Butyldimethylsilyl (1*R*)-4-hydroxymethyl-3,5,5-trimethylcyclohex-3-enyl ether 37**

Ozone gas was introduced into a stirred solution of **35** (6.00 g, 18.6 mmol) in MeOH (50 cm^3) at −20 °C until the spot for compound **35** disappeared on TLC. Nitrogen gas was bubbled into the reaction solution for 10 min to remove the excess ozone gas. Aq. AcOH (15 cm^3) and Zn powder (2.5 g) were added to the solution at −20 °C and then the reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was filtered off, then the filtrate was concentrated to give a residue which was diluted with Et_2O, washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave **36** as an oil which, without purification, was dissolved in MeOH (50 cm^3). $NaBH_4$ (496 mg, 13 mmol) was added to this solution at 0 °C and the reaction mixture was stirred at 0 °C for 30 min. This mixture was poured into ice–water and extracted with Et_2O. The organic layer was washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by CC (Et_2O–hexane, 1:1) to afford the *alcohol* **37** (4.19 g, 79% from **35**) as a colourless oil; $[\alpha]_D^{28}$ −49.0 (*c* 1.00, MeOH); ν_{max}/cm^{-1} 3615 and 3480 (OH); δ_H(200 MHz) 0.07 (6H, s, SiMe × 2), 0.90 (9H, s, $SiBu^t$), 1.05 and 1.10 (each 3H, s, *gem*-Me), 1.47 (1H, t, *J* 12, 12-H_{ax}), 1.64 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 1.76 (3H, s, 5-Me), 2.04 (1H, br dd, *J* 17 and 9, 4-H_{ax}), 2.19 (1H, br dd, *J* 17 and 5.5, 4-H_{eq}), 3.92 (1H, m, 3-H), 4.08 and 4.17 (each 1H, d, *J* 12, 7-H_2) (Found: M^+, 284.2169. $C_{16}H_{32}O_2Si$ requires M, 284.2173).

***tert*-Butyldimethylsilyl (1*R*)-3,4,5,5-tetramethylcyclohex-3-enyl ether 38**

$Py{\cdot}SO_3$ (5.60 g, 35.0 mmol) was added to a solution of the alcohol **37** (5.00 g, 17.6 mmol) in THF (50 cm^3) at 0 °C and the mixture was stirred at 5 °C for 45 h. After dry THF (50 cm^3) was added to the reaction solution, $LiAlH_4$ (4.01 g, 105 mmol) was added to this solution at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 4 h. The excess of $LiAlH_4$ was decomposed by the dropwise addition of water. The mixture was extracted with Et_2O and the extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (Et_2O–hexane, 3:97) to afford the *silyl ether* **38** (4.43 g, 94%) as a colourless oil; $[\alpha]_D^{28}$ −55.4 (*c* 1.01, MeOH); δ_H(300 MHz) 0.07 (6H, s, SiMe × 2), 0.90 (9H, s, $SiBu^t$), 0.99 and 1.01 (each 3H, s, *gem*-Me), 1.44 (1H, t, *J* 12, 2-H_{ax}), 1.54 and 1.58 (each 3H, br s, 5-Me and 6-Me), 1.62 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.99–2.20 (2H, m, 4-H_2), 3.90 (1H, m, 3-H) (Found: M^+, 268.2204. $C_{16}H_{32}OSi$ requires M, 268.2224).

(1*R*)-3,4,5,5-Tetramethylcyclohex-3-enyl acetate 39

Aq. 47% HF (15 cm^3) was added to a solution of the silyl ether **38** (4.34 g, 16.5 mmol) in THF (50 cm^3). The mixture was stirred at room temperature for 10 min and then neutralized with saturated aq. $NaHCO_3$. The organics were extracted with AcOEt and washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solution gave the alcohol, which without purification was dissolved in dry Py (30 cm^3). Ac_2O (10 cm^3) was added to this solution and the reaction mixture was stirred at room temperature for 16 h, poured into ice–water and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (Et_2O–hexane, 5:95) to afford the *acetate* **39** (2.85 g, 88%) as a colourless oil; $[\alpha]_D^{23}$ −61.4 (*c* 0.88, EtOH); ν_{max}/cm^{-1} 1719 (OAc); δ_H(300 MHz) 1.03 and 1.06 (each 3H, s, *gem*-Me), 1.53 (1H, t, *J* 12, 2-H_{ax}), 1.57 and 1.59 (each 3H, s, 5-Me and 6-Me), 1.74 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 2.02 (1H, m, 4-H_{ax}), 2.03 (3H, s, OAc), 2.31 (1H, br dd, *J* 16.5 and 6, 4-H_{eq}), 5.01 (1H, m, 3-H) [Found: $(M - AcOH)^+$, 136.1230. $C_{10}H_{16}$ requires M − AcOH, 136.1253].

Epoxidation of acetate 39

In the same manner as described for MCPBA oxidation of **22**, the acetate **39** (1.94 g, 9.9 mmol) was treated with MCPBA to give oxidation products which were purified by short CC (Et_2O–CH_2Cl_2–hexane, 1:3:6) to afford the anti-*epoxide* **4a** (0.49 g, 23%) and the syn-*epoxide* **4b** (1.06 g, 51%) as colourless oils, respectively.

***anti*-Epoxide 4a.** $[\alpha]_D^{20}$ −27.5 (*c* 1.02, EtOH); ν_{max}/cm^{-1} 1730 (OAc); δ_H(300 MHz) 1.07 and 1.08 (each 3H, s, *gem*-Me), 1.26 and 1.33 (each 3H, s, 5-Me and 6-Me), 1.29 (1H, dd, *J* 13 and 9, 2-H_{ax}), 1.61 (1H, ddd, *J* 13, 3 and 1, 2-H_{eq}), 1.72 (1H, dd, *J* 15 and 7, 4-H_{ax}), 2.00 (3H, s, OAc), 2.35 (1H, br dd, *J* 15 and 6, 4-H_{eq}), 4.87 (1H, m, 3-H) (Found: M^+, 212.1439. $C_{12}H_{20}O_3$ requires M, 212.1413).

***syn*-Epoxide 4b.** $[\alpha]_D^{20}$ −22.7 (*c* 1.10, EtOH); ν_{max}/cm^{-1} 1729, 1713 (split) (OAc); δ_H(300 MHz) 1.08 and 1.10 (each 3H, s, *gem*-Me), 1.23 and 1.30 (each 3H, s, 5-Me and 6-Me), 1.27 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 1.62 (1H, t, *J* 12, 2-H_{ax}), 1.83 (1H, dd, *J* 15 and 10, 4-H_{ax}), 2.00 (3H, s, OAc), 2.25 (1H, ddd, *J* 15, 8 and 2, 4-H_{eq}), 4.84 (1H, m, 3H) [Found: $(M - AcOH)^+$, 152.1225. $C_{10}H_{16}O$ requires M − AcOH, 152.1202].

Rearrangement of the *anti*-epoxides 4a

To a solution of **4a** (212 mg, 1.0 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise 47% $BF_3{\cdot}Et_2O$ (906 mg, 3 mmol) at −25 °C and the mixture was stirred at −25 °C for 4 h and at 0 °C for 3 h. The reaction mixture was diluted with CH_2Cl_2 and the organic layer was washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solution gave a residue which was purified by short CC (Et_2O–hexane, 3:17) to afford a mixture of the anti-*cyclopentyl methyl ketone* **7** and *tetrasubstituted olefinic methyl ketone* **9** (134 mg, 63%; **7**:**9** = *ca.* 1:1) as colourless oils. Spectral properties of the *anti*-cyclopentyl methyl ketone **7** were in agreement with those reported.[12]

***anti*-Cyclopentyl methyl ketone 7.** δ_H(300 MHz) 0.88, 1.15 and 1.28 (each 3H, s, Me × 3), 1.53 (1H, dd, *J* 15 and 3, 4-H_β), 1.72 (1H, br dd, *J* 14.5 and 4.5, 2-H_β), 2.02 (3H, s, OAc), 2.08 (1H, dd, *J* 14 and 8, 2-H_α), 2.13 (3H, s, CH_3CO), 2.86 (1H, dd, *J* 15 and 9, 4-H_α), 5.14 (1H, m, 3H).

Tetrasubstituted olefinic methyl ketone 9. δ_H(300 MHz) 1.64 (3H, s) and 1.68 (6H, s) (=CMe × 3), 1.99 (3H, s, OAc), 2.15 [3H, s, $CH_2C(O)CH_3$], 2.23 (1H, br dd, *J* 13.5 and 6.5) and 2.42 (1H, br dd, *J* 13.5 and 7) (2-H_2), 2.59 (1H, dd, *J* 16.5 and 5) and 2.70 (1H, dd, *J* 16.5 and 8) (4-H_2), 5.37 (1H, m, 3-H).

Rearrangement of the *syn*-epoxide 4b

In the same manner as described above, **4b** (212 mg, 1.0 mmol) was treated with 47% $BF_3{\cdot}Et_2O$ (906 mg, 3.0 mmol) at −78 °C for 4 h and at −25 °C for 1 h to provide the syn-*cyclopentyl methyl ketone* **12** (134 mg, 63%) as a colourless oil. Spectral properties of the *syn*-cyclopentyl methyl ketone **12** were in agreement with those reported;[12] δ_H(300 MHz) 0.99, 1.11 and 1.15 (each 3H, s, Me × 3), 1.64 (1H, dd, *J* 14.5 and 3.5, 2-H_β), 2.03 (3H, s, OAc), 2.04 (1H, dd, *J* 14.5 and 8.5, 4-H_α), 2.14 (1H, dd, *J* 14.5 and 9, 2-H_α), 2.16 (3H, s, CH_3CO), 2.55 (1H, dd, *J* 14.5 and 6, 4-H_β), 5.14 (1H, m, 3H).

(*E*)-Methyl 3-[(4*R*)-acetoxy-2,6,6-trimethylcyclohex-1-enyl]-prop-2-enoate 43

A solution of TBAF (1 mol dm^{-3} in THF; 3 cm^3, 3 mmol) was added to a solution of **42**[8] (1.7 g, 5.0 mmol) in dry THF (20 cm^3) and the mixture was stirred at room temperature for 2 h and at 80 °C for 2 h. The reaction mixture was diluted with AcOEt and washed with brine. Evaporation of the dried solvent gave a residue which was purified by short CC (acetone–hexane, 1:9) to afford the hydroxy compound. This was dissolved in dry Py (10 cm^3) and Ac_2O (5 cm^3) was added to it. The reaction mixture was stirred at room temperature for 16 h, poured into ice–water and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (Et_2O–hexane, 1:4) to afford **43** (0.81 g, 71% from **42**) as a colourless oil; ν_{max}/cm^{-1} 1718 (OAc and CO_2Me); δ_H(300 MHz) 1.10 and 1.14 (each 3H, s, *gem*-Me), 1.59 (1H, t, *J* 12, 2-H_{ax}), 1.76 (3H, s, 5-Me), 1.79 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.05 (3H, s, OAc), 2.14 (1H, br dd, *J* 17.5 and 9.5, 4-H_{ax}), 2.49 (1H, br dd, *J* 17.5 and 6, 4-H_{eq}), 3.77 (3H, s, CO_2Me), 5.04 (1H, m, 3-H), 5.83 (1H, d, *J* 16, 8-H), 7.36 (1H, d, *J* 16, 7-H) (Found: M^+, 266.1519. $C_{15}H_{22}O_4$ requires M, 266.1519).

(1*R*)-3,5,5-Trimethyl-4-phenylcyclohex-3-enyl acetate 45

Phenyllithium (1.8 mol dm^{-3} in cyclohexane–Et_2O; 7:3; 3.33 cm^3, 6 mmol) was added to a solution of **15** (1.14 g, 5 mmol) in dry THF (20 cm^3) at −78 °C and the reaction mixture was stirred for 2 h at −78 °C. The reaction was quenched with saturated aq. NH_4Cl and the mixture was extracted with Et_2O. The extracts were washed with brine, dried and evaporated to give a residue, which was dissolved with MeOH (10 cm^3). PTSA (10 mg) was added to this solution and the mixture was stirred at room temperature for 1 h. After evaporation off of the MeOH, the residue was extracted with AcOEt. The extracts were washed with saturated aq. $NaHCO_3$ and brine, dried and evaporated to give the diol, which was dissolved in dry Py (7 cm^3). Ac_2O (5 cm^3) was added to this solution and the reaction mixture was stirred at room temperature for 16 h, poured into ice–water, and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (Et_2O–hexane, 1:4) to afford the acetoxy compound (quant.). The acetoxy compound (1.15 g, 4.17 mmol) was dissolved in dry Py (15 cm^3). Phosphorus oxychloride (2.33 cm^3) was added slowly to the stirred reaction mixture and the mixture was stirred at 75 °C for 16 h. After cooling, the reaction mixture was cautiously poured into ice–water and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (Et_2O–hexane, 1:4) to afford **45** (0.86 g, 80% from **15**); ν_{max}/cm^{-1} 1725 (OAc), 1600 (Ph); δ_H(300 MHz) 0.89, 1.10 and 1.30 (each 3H, s, Me × 3), 1.71 (1H, t, *J* 12, 2-H_{ax}), 1.86 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 2.08 (3H, s, OAc), 2.16 (1H, ddd-like, *J* 16.5, 9.5 and 1, 4-H_{ax}), 2.48 (1H, ddd, *J* 16.5, 6 and 1.5, 4-H_{eq}), 5.19 (1H, m, 3-H), 6.98 (2H, m) and 7.28 (3H, m) (Ar-H) [Found: $(M + H)^+$, 259.1672. $C_{17}H_{23}O_2$ requires M + H, 259.1699].

(1*R*)-3,5,5-Trimethyl-4-acetoxymethylcyclohex-3-enyl acetate 47

Aq. 47% HF (7 cm^3) was added to a solution of the silyl alcohol **37** (1.1 g, 3.87 mmol) in THF (20 cm^3). The mixture was stirred at room temperature for 1 h and neutralized with saturated aq. $NaHCO_3$. The organics were extracted with AcOEt and washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solution gave the diol, which without purification was dissolved in dry Py (10 cm^3). Ac_2O (4 cm^3) was added to the reaction and the mixture was stirred at room temperature for 16 h, poured into ice–water and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (Et_2O–hexane, 15:85) to afford the *diacetate* **47** (0.41 g, 42%) as a colourless oil; $[\alpha]_D^{27}$ −50.0 (*c* 1.02, MeOH); ν_{max}/cm^{-1} 1726 (OAc); δ_H(300 MHz) 1.06 and 1.08 (each 3H, s, *gem*-Me), 1.59 (1H, t, *J* 12, 2-H_{ax}), 1.70 (3H, s, 5-Me), 1.76 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 2.04 and 2.05 (each 3H, s, OAc × 2), 2.11 (1H, ddd, *J* 17, 9 and 1, 4-H_{ax}), 2.43 (1H, ddd, *J* 17, 6 and 1, 4-H_{eq}), 4.59 (2H, s, CH_2OAc), 5.04 (1H, m, 3-H).

***tert*-Butyldimethylsilyl (1*R*)-4-*tert*-butyldimethylsilyloxymethyl-3,5,5-trimethylcyclohex-3-enyl ether 49**

TBSCl (0.79 g, 5.25 mmol) was added to a stirred solution of the alcohol **37** (1.42 g, 5 mmol), Et_3N (0.76 cm^3, 5.5 mmol) and DMAP (0.61 g, 5 mmol) in dry CH_2Cl_2 (15 cm^3) at room temperature. The mixture was stirred at room temperature for 3 h, poured into ice–water and extracted with Et_2O. The extracts were washed successively with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue which was purified by short CC (Et_2O–hexane, 1:9) to afford **49** (1.56 g, 78%) as a colourless oil; δ_H(200 MHz) 0.07 (12H, s, $SiMe_2$ × 2), 0.90 (18H, s, SiBu′ × 2), 1.04 and 1.06 (each 3H, s, *gem*-Me), 1.45–1.70 (2H, m, 2-H_2), 1.68 (3H, s, 5-Me), 1.95–2.25 (2H, m, 4-H_2), 3.93 (1H, m, 3-H), 4.09 (2H, br s, 7-H_2).

(1*R*)-4-(2-Acetoxyethyl)-3,5,5-trimethylcyclohex-3-enyl acetate 51

Ac_2O (1 cm^3) was added to a solution of **20** (96 mg, 0.42 mmol) in dry Py (1 cm^3) and the reaction mixture was stirred at room temperature for 1 h, poured into ice–water, and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (acetone–hexane, 1:4) to afford **51** (114 mg, quantitatively) as a colourless oil; ν_{max}/cm^{-1} 1728 (OAc); δ_H(300 MHz) 1.08 (6H, s, *gem*-Me), 1.53 (1H, t, *J* 12, 2-H_{ax}), 1.68 (3H, s, 5-Me), 1.74 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.03 (1H, br dd, *J* 16 and 10, 4-H_{ax}), 2.03 and 2.05 (each 3H, s, OAc × 2), 2.26–2.47 (3H, m, 4-H_{eq} and 7-H_2), 4.01 (2H, t, *J* 8.5, 8-H_2), 4.99 (1H, m, 3-H) [Found: $(M + H)^+$, 269.1736. $C_{15}H_{25}O_4$ requires M + H, 269.1754].

3-[(4*R*)-4-Acetoxy-2,6,6-trimethylcyclohex-1-enyl]propionitrile 53

MsCl (0.23 cm^3, 3.0 mmol) was added to a solution of **20** (337 mg, 1.5 mmol) in dry Py (3 cm^3) at 0 °C and the mixture was stirred at room temperature for 2 h, poured into ice–water, and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (Et_2O–hexane, 2:3) to afford the mesylate (quantitatively). KCN (3.24 g, 50 mmol) was added to a solution of the mesylate (3.79 g, 12.5 mmol) and 18-crown-6 (330 mg, 1.25 mmol) in dry DMSO (30 cm^3) at room temperature and the mixture was stirred vigorously and warmed at 80 °C for 16 h. Then the mixture was poured into ice–water carefully and extracted with Et_2O. The extracts were washed with brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (Et_2O–hexane, 3:7) to afford **53** (2.34 g, 80%) as a colourless oil; ν_{max}/cm^{-1} 2247 (CN), 1731 (OAc); δ_H(300 MHz) 1.08 (6H, s, *gem*-Me), 1.54 (1H, t, *J* 12, 2-H_{ax}), 1.67 (3H, s, 5-Me), 1.74 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.03 (3H, s, OAc), 2.05 (1H, br dd, *J* 16.5 and 9, 4-H_{ax}), 2.30–2.53 (5H, m, 4-H_{eq}, 7-H_2 and 8-H_2), 4.98 (1H, m, 3-H) [Found: $(M + H)^+$, 236.1628. $C_{14}H_{22}O_2N$ requires M + H, 236.1652].

(1*R*)-4-(3-Acetoxypropyl)-3,5,5-trimethylcyclohex-3-enyl acetate 54

A solution of DIBAL-H (2.44 cm^3, 13.7 mmol) in dry hexane (5 cm^3) was added to a solution of **53** (805 mg, 3.43 mmol) in dry Et_2O (10 cm^3) at 0 °C and the mixture was stirred at 0 °C for 1 h. The excess DIBAL-H was destroyed by an addition of moist silica gel (SiO_2–H_2O, 5:1) and the mixture was filtered through Celite. Evaporation of the dried filtrate gave a residue, which was dissolved in MeOH (10 cm^3). $NaBH_4$ (127 mg, 3.34 mmol) was added to the solution at 0 °C and this was stirred at 0 °C for 30 min. After evaporation of MeOH, the residue was purified by short CC (acetone–hexane, 1:4) to afford the diol and then this compound was dissolved in dry Py (10 cm^3). Ac_2O (5 cm^3) was added to the reaction mixture at room temperature and the mixture was stirred at room temperature for 16 h, poured into ice–water, and extracted with Et_2O. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (Et_2O–hexane, 1:4) to afford **54** (448 mg, 46%) as a colourless oil; ν_{max}/cm^{-1} 1728 (OAc); δ_H(300 MHz) 1.05 and 1.06 (each 3H, s, *gem*-Me), 1.53 (1H, t, *J* 12, 2-H_{ax}), 1.61 (3H, s, 5-Me), 1.62–1.76 (3H, m, 2-H_{eq} and 8-H_2), 1.94–2.14 (3H, m, 4-H_{ax} and 7-H_2), 2.03 and 2.06 (each 3H, s, OAc × 2), 2.31 (1H, br dd, *J* 17 and 6, 4-H_{eq}), 4.06 (2H, t, *J* 6.5, 9-H_2), 5.00 (1H, m, 3-H) [Found: $(M + H)^+$, 283.1914. $C_{16}H_{27}O_4$ requires M + H, 283.1911].

Epoxidation of compounds 40, 43, 45, 47, 49, 51 and 54

In the same manner as described for MCPBA oxidation of **22**, the compounds **40**,[10] **43**, **45**, **47**, **49**, **51** and **54** were treated with MCPBA to give oxidation products. Reaction conditions, purification methods and yields of products are listed in Table 3.

***anti*-Epoxide 41a.** λ_{max}(EtOH)/nm 230; ν_{max}/cm^{-1} 1730 (OAc), 1677 (conj. C=O); δ_H(200 MHz) 0.94 and 1.05 (each 3H, s, *gem*-Me), 1.20 (3H, s, 5-Me), 1.38 (1H, dd, *J* 13 and 11, 2-H_{ax}), 1.55 (1H, ddd, *J* 13, 3.5 and 2, 2-H_{eq}), 1.82 (3H, d, *J* 1.5, 9-Me), 1.86 (1H, dd, *J* 14 and 9, 4-H_{ax}), 2.02 and 2.13 (each 3H, s, OAc × 2), 2.37 (1H, br dd, *J* 14 and 5, 4-H_{eq}), 2.58, 3.62 (each 1H, d, *J* 18.5, 7-H_2), 4.82 (2H, d, *J* 6, 11-H_2), 4.86 (1H, m, 3-H), 6.58 (1H, td-like, *J* 6 and 1.5, 10-H) (Found: M^+, 352.1895. $C_{19}H_{28}O_6$ requires M, 352.1884).

***syn*-Epoxide 41b.** λ_{max}(EtOH)/nm 234; ν_{max}/cm^{-1} 1730 (OAc), 1680 (conj. C=O); δ_H(200 MHz) 0.97 and 1.05 (each 3H, s, *gem*-Me), 1.17 (3H, s, 5-Me), 1.30 (1H, ddd, *J* 12.5, 4 and 2, 2-H_{eq}), 1.55 (1H, t, *J* 12.5, 2-H_{ax}), 1.82 (3H, d, *J* 1, 9-Me), 1.82 (1H, dd, *J* 14.5 and 10, 4-H_{ax}), 2.00 and 2.12 (each 3H, s, OAc × 2), 2.34 (1H, ddd, *J* 14.5, 8.5 and 2, 4-H_{eq}), 2.70 and 3.47 (each 1H, d, *J* 18.5, 7-H_2), 4.81 (2H, d, *J* 6, 11-H_2), 4.97 (1H, m, 3-H), 6.56 (1H, td-like, *J* 6 and 1, 10-H) (Found: M^+, 352.1880. $C_{19}H_{28}O_6$ requires M, 352.1884).

***anti*-Epoxide 44a.** λ_{max}(EtOH)/nm 218; ν_{max}/cm^{-1} 1722 (C=O); δ_H(200 MHz) 0.99, 1.20 and 1.21 (each 3H, s, Me × 3), 1.38 (1H, dd, *J* 13.5 and 8, 2-H_{ax}), 1.67 (1H, ddd, *J* 13.5, 3.5 and 1, 2-H_{eq}), 1.79 (1H, dd, *J* 15 and 5, 4-H_{ax}), 2.02 (3H, s, OAc), 2.41 (1H, br dd, *J* 15 and 5, 4-H_{eq}), 3.76 (3H, s, CO_2Me), 4.73 (1H, m, 3-H), 6.05 (1H, d, *J* 15.5, 8-H), 7.20 (1H, d, *J* 15.5, 7-H) [Found: $(M + H)^+$, 283.1560. $C_{15}H_{23}O_5$ requires M + H, 283.1546].

***syn*-Epoxide 44b.** λ_{max}(EtOH)/nm 219; ν_{max}/cm^{-1} 1723 (C=O); δ_H(200 MHz) 0.99, 1.18 and 1.26 (each 3H, s, Me × 3), 1.36 (1H, ddd, *J* 12.5, 4.5 and 1.5, 2-H_{eq}), 1.66 (1H, t, *J* 12.5, 2-H_{ax}), 1.87 (1H, dd, *J* 15 and 11, 4-H_{ax}), 2.02 (3H, s, OAc), 2.35 (1H, ddd, *J* 15, 7.5 and 1, 4-H_{eq}), 3.76 (3H, s, CO_2Me), 4.91 (1H, m, 3-H), 6.03 (1H, d, *J* 15.5, 8-H), 7.13 (1H, d, *J* 15.5, 7-H) [Found: $(M + H)^+$, 283.1534. $C_{15}H_{23}O_5$ requires M + H, 283.1546].

***anti*-Epoxide 46a.** ν_{max}/cm^{-1} 1729 (OAc); δ_H(300 MHz) 0.94, 0.99 and 1.05 (each 3H, s, Me × 3), 1.48 (1H, dd, *J* 13.5 and 8, 2-H_{ax}), 1.77 (1H, ddd, *J* 13.5, 3.5 and 1, 2-H_{eq}), 1.90 (1H, dd, *J* 15 and 6.5, 4-H_{ax}), 2.06 (3H, s, OAc), 2.46 (1H, ddd, *J* 15, 6 and 1, 4-H_{eq}), 5.03 (1H, m, 3-H), 7.13–7.38 (5H, m, Ph) (Found: M^+, 274.1584. $C_{17}H_{22}O_3$ requires M, 274.1570).

***syn*-Epoxide 46b.** ν_{max}/cm^{-1} 1728 (OAc); δ_H(300 MHz) 0.94, 0.96 and 1.12 (each 3H, s, Me × 3), 1.40 (1H, ddd, *J* 12, 4 and 1.5, 2-H_{eq}), 1.82 (1H, t, *J* 12, 2-H_{ax}), 1.94 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 2.04 (3H, s, OAc), 2.40 (1H, ddd, *J* 15, 7.5 and 1.5, 4-H_{eq}), 5.03 (1H, m, 3-H), 7.07–7.36 (5H, m, Ph) (Found: M^+, 274.1595. $C_{17}H_{22}O_3$ requires M, 274.1570).

***anti*-Epoxide 48a.** $[a]_D^{27}$ −21.4 (*c* 1.03, MeOH); ν_{max}/cm^{-1} 1734 (OAc); δ_H(300 MHz) 1.13 and 1.15 (each 3H, s, *gem*-Me), 1.32 (1H, dd, *J* 13 and 10.5, 2-H_{ax}), 1.39 (3H, s, 5-Me), 1.59 (1H, ddd, *J* 13, 3.5 and 2, 2-H_{eq}), 1.77 (1H, dd, *J* 14.5 and 8, 4-H_{ax}),

2.01 and 2.09 (each 3H, s, OAc × 2), 2.39 (1H, ddd, *J* 14.5, 5.5 and 1.5, 4-H_{eq}), 4.03 and 4.41 (each 1H, d, *J* 12, 7-H_2), 4.85 (1H, m, 3-H) [Found: $(M + H)^+$, 271.1549. $C_{14}H_{23}O_5$ requires (M + H), 271.1546].

***syn*-Epoxide 48b.** $[\alpha]_D^{27}$ −18.6 (*c* 1.18, MeOH); ν_{max}/cm^{-1} 1733 (OAc); δ_H(200 MHz), 1.11 and 1.14 (each 3H, s, *gem*-Me), 1.29 (1H, ddd, *J* 12.5, 4 and 2, 2-H_{eq}), 1.36 (3H, s, 5-Me), 1.59 (1H, t, *J* 12.5, 2-H_{ax}), 1.82 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 2.02 and 2.07 (each 3H, s, OAc × 2), 2.29 (1H, ddd, *J* 15, 7 and 1.5, 4-H_{eq}), 3.95 and 4.52 (each 1H, d, *J* 12.5, 7-H_2), 4.87 (1H, m, 3-H) [Found: $(M + H)^+$, 271.1544. $C_{14}H_{23}O_5$ requires (M + H), 271.1546].

***anti*-Epoxide 50a.** δ_H(300 MHz) 0.03 (12H, s, $SiMe_2$ × 2), 0.87 and 0.89 (each 9H, s, SiBu^t × 2), 1.05 and 1.20 (each 3H, s, *gem*-Me), 1.22 (1H, dd, *J* 12.5 and 11, 2-H_{ax}), 1.35 (3H, s, 5-Me), 1.39 (1H, ddd, *J* 12.5, 3.5 and 2, 2-H_{eq}), 1.61 (1H, dd, *J* 14 and 9, 4-H_{ax}), 2.18 (1H, ddd, *J* 14, 5 and 2, 4-H_{eq}), 3.55 and 3.88 (each 1H, d, *J* 11, 7-H_2), 3.75 (1H, dddd, *J* 11, 9, 5 and 3.5, 3-H) [Found: $(M + H)^+$, 415.3086. $C_{22}H_{47}O_3Si_2$ requires (M + H), 415.3066].

***syn*-Epoxide 50b.** δ_H(300 MHz) 0.04 (12H, s, $SiMe_2$ × 2), 0.87 and 0.89 (each 9H, s, SiBu^t × 2), 1.05 and 1.14 (each 3H, s, *gem*-Me), 1.12 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.35 (3H, s, 5-Me), 1.46 (1H, t, *J* 12, 2-H_{ax}), 1.80 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 2.00 (1H, ddd, *J* 15, 7 and 2, 4-H_{eq}), 3.41 and 4.04 (each 1H, d, *J* 11, 7-H_2), 3.79 (1H, dddd, *J* 12, 9.5, 7 and 3.5, 3-H) [Found: $(M + H)^+$, 415.3051. $C_{22}H_{47}O_3Si_2$ requires M + H, 415.3066].

***anti*-Epoxide 52a.** ν_{max}/cm^{-1} 1732 (OAc); δ_H(300 MHz) 1.07 and 1.16 (each 3H, s, *gem*-Me), 1.32 (1H, dd, *J* 14 and 6, 2-H_{ax}), 1.35 (3H, s, 5-Me), 1.62 (1H, ddd, *J* 13.5, 3.5 and 2, 2-H_{eq}), 1.77 (1H, dd, *J* 15 and 6, 4-H_{ax}), 1.92–2.14 (2H, m, 7-H_2), 2.00 and 2.05 (each 3H, s, OAc × 2), 2.36 (1H, br dd, *J* 15 and 7.5, 4-H_{eq}), 4.15 (2H, t, *J* 7.5, 8-H_2), 4.86 (1H, m, 3-H) [Found: $(M + H)^+$, 285.1687. $C_{15}H_{25}O_5$ requires M + H, 285.1703].

***syn*-Epoxide 52b.** ν_{max}/cm^{-1} 1732 (OAc); δ_H(300 MHz) 1.09 and 1.12 (each 3H, s, *gem*-Me), 1.27 (1H, ddd, *J* 12, 4 and 1.5, 2-H_{eq}), 1.30 (3H, s, 5-Me), 1.62 (1H, t, *J* 12, 2-H_{ax}), 1.82 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 1.99 (2H, q, *J* 7, 7-H_2), 2.00 and 2.04 (each 3H, s, OAc × 2), 2.27 (1H, ddd, *J* 15, 7.5 and 1.5, 4-H_{eq}), 4.07 and 4.09 (each 1H, dd, *J* 7 and 2, 8-H_2), 4.83 (1H, m, 3-H) [Found: $(M + H)^+$, 285.1704. $C_{15}H_{25}O_5$ requires M + H, 285.1703].

***anti*-Epoxide 55a.** ν_{max}/cm^{-1} 1731 (OAc); δ_H(300 MHz) 1.07 and 1.16 (each 3H, s, *gem*-Me), 1.30 (1H, dd, *J* 13.5 and 7.5, 2-H_{ax}), 1.57 (3H, s, 5-Me), 1.60 (1H, ddd, *J* 13.5, 3.5 and 1.5, 2-H_{eq}), 1.75 (1H, dd, *J* 15 and 6.5, 4-H_{ax}), 1.66–1.86 (4H, m, 7-H_2 and 8-H_2), 2.00 and 2.04 (each 3H, s, OAc × 2), 2.35 (1H, ddd, *J* 15, 6 and 1, 4-H_{eq}), 4.03 (2H, td-like, *J* 6 and 2.5, 9-H_2), 4.86 (1H, m, 3-H) [Found: $(M + H)^+$, 299.1854. $C_{16}H_{27}O_5$ requires M + H, 299.1860].

***syn*-Epoxide 55b.** ν_{max}/cm^{-1} 1731 (OAc); δ_H(300 MHz) 1.06 and 1.13 (each 3H, s, *gem*-Me), 1.20–1.30 (1H, m, 2-H_{eq}), 1.27 (3H, s, 5-Me), 1.63 (1H, t, *J* 12, 2-H_{ax}), 1.58–1.72 (4H, m, 7-H_2 and 8-H_2), 1.81 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 2.00 and 2.05 (each 3H, s, OAc × 2), 2.26 (1H, ddd, *J* 15, 7.5 and 1, 4-H_{eq}), 4.04 (2H, m, 9-H_2), 4.83 (1H, m, 3-H) [Found: $(M + H)^+$, 299.1864. $C_{16}H_{27}O_5$ requires M + H, 299.1860].

Preparation of epoxides 58a and 58b

According to the procedure described for the epoxidation of **22**, compound **20** was treated with MCPBA to give the crude oxidation products, which were purified by short CC (acetone–hexane, 1:4) to afford the epoxy alcohols **56** (1.57 g, 97%) as colourless oils. A solution of a part of the epoxy alcohol (860 mg, 3.6 mmol) in dry CH_2Cl_2 (28 cm^3) was added to a solution of NMO (620 mg, 5.3 mmol) and molecular sieves 4 Å (1.78 g) in dry CH_2Cl_2 (34 cm^3) at room temperature and the mixture was stirred at room temperature for 10 min. Then TPAP (62 mg, 0.18 mmol) was added to the reaction and the mixture was stirred at room temperature for 2 h. The mixture was filtered through Celite and the filtrate was diluted with CH_2Cl_2 and washed with aq. Na_2SO_3, brine and aq. $CuSO_4$. Evaporation of the dried extracts gave a residue, which was purified by short CC (acetone–hexane, 1:4) to afford **57** (0.77 g, 90%) as colourless oils. BuLi (1.63 mol dm^{-3} in hexane; 2.17 cm^3, 1.33 mmol) was added to a solution of methyltriphenylphosphonium bromide (1.38 g, 3.86 mmol) in dry THF (10 cm^3) at 0 °C and the mixture was stirred at 0 °C for 1 h. A solution of **57** (0.77 g, 3.21 mmol) in dry THF (10 cm^3) was added to the reaction mixture at 0 °C and the mixture was stirred at 0 °C for 2 h and quenched with saturated aq. NH_4Cl. The mixture was extracted with Et_2O and the extracts were washed with brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (Et_2O–hexane, 1:9) and then low pressure column chromatography (Et_2O–hexane, 3:17) to afford **58a** (107 mg, 14%) and **58b** (267 mg, 35%) as colourless oils, respectively.

***anti*-Epoxide 58a.** ν_{max}/cm^{-1} 1729 (OAc); δ_H(300 MHz) 1.08 and 1.14 (each 3H, s, *gem*-Me), 1.29 (1H, dd, *J* 13.5 and 9, 2-H_{ax}), 1.36 (3H, s, 5-Me), 1.58 (1H, ddd, *J* 13.5, 3.5 and 1.5, 2-H_{eq}), 1.75 (1H, dd, *J* 14.5 and 7.5, 4-H_{ax}), 2.00 (3H, s, OAc), 2.31 (1H, ddt, *J* 16, 6 and 2, 7-H), 2.36 (1H, ddd, *J* 14, 6.5 and 1, 4-H_{eq}), 2.67 (1H, br dd, *J* 16 and 6.5, 7-H), 4.87 (1H, m, 3-H), 5.03 (1H, m) and 5.10 (1H, m) (9-H_2), 5.86 (1H, ddt, *J* 17.5, 10 and 6.5, 8-H) [Found: $(M + H)^+$, 239.1646. $C_{14}H_{23}O_3$ requires M + H, 239.1648].

***syn*-Epoxide 58b.** ν_{max}/cm^{-1} 1730 (OAc); δ_H(300 MHz) 1.09 and 1.13 (each 3H, s, *gem*-Me), 1.23 (1H, ddd, *J* 12, 4 and 1.5, 2-H_{eq}), 1.32 (3H, s, 5-Me), 1.62 (1H, t, *J* 12.5, 2-H_{ax}), 1.82 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 2.00 (3H, s, OAc), 2.26 (1H, ddd, *J* 14.5, 7.5 and 1.5, 4-H_{eq}), 2.34 (1H, ddt, *J* 16, 6 and 2) and 2.64 (1H, br dd, *J* 16 and 7.5) (7-H_2), 4.84 (1H, m, 3-H), 5.00 (1H, t, *J* 1.5) and 5.07 (1H, dt, *J* 4.5 and 1.5) (9-H_2), 5.78 (1H, m, 8-H) [Found: $(M + H)^+$, 239.1625. $C_{14}H_{23}O_3$ requires M + H, 239.1648].

Rearrangement of other epoxides

General procedure. In the same manner as described for the rearrangement of the *anti*-epoxide **4a**, epoxides **41**, **44**, **46**, **48**, **50**, **52**, **55** and **58** were treated with 47% $BF_3{\cdot}Et_2O$ (3 equiv.) to provide each product. Reaction conditions, purification methods and yields of products are listed in Table 4.

Compound 60. λ_{max}(EtOH)/nm 219; ν_{max}/cm^{-1} 1723 (OAc and C=O); δ_H(300 MHz) 0.87, 1.18 and 1.33 (each 3H, s, Me × 3), 1.58 (1H, dd, *J* 15 and 3, 4-H_β), 1.76 (1H, br dd, *J* 14.5 and 4.5, 2-H_β), 2.03 (3H, s, OAc), 2.06 (1H, dd, *J* 14.5 and 8, 2-H_α), 2.92 (1H, dd, *J* 15 and 8.5, 4-H_α), 3.81 (3H, s, CO_2Me), 5.23 (1H, m, 3-H), 6.71 (1H, d, *J* 15.5, 8-H), 7.40 (1H, d, *J* 15.5, 7-H) [Found: $(M + H)^+$, 283.1559. $C_{15}H_{23}O_5$ requires M + H, 283.1546].

Compound 61. λ_{max}(EtOH)/nm 223; ν_{max}/cm^{-1} 1727 (OAc), 1688 (conj. C=O); δ_H(300 MHz) 0.96, 1.13 and 1.21 (each 3H, s, Me × 3), 1.67 (1H, dd, *J* 14.5 and 3.5, 2-H_β), 2.05 (3H, s, OAc), 2.09 (1H, dd, *J* 14.5 and 8.5, 4-H_α), 2.17 (1H, dd, *J* 14.5 and 8.5, 2-H_α), 2.60 (1H, dd, *J* 14.5 and 6, 4-H_β), 5.18 (1H, m, 3-H), 6.73 (1H, d, *J* 15.5, 8-H), 7.45 (1H, d, *J* 15.5, 7-H) [Found: $(M + H)^+$, 283.1553. $C_{15}H_{23}O_5$ requires M + H, 283.1546].

Compound 62. ν_{max}/cm^{-1} 1732 (OAc and C=O); δ_H(500 MHz) 0.87, 1.15 and 1.28 (each 3H, s, Me × 3), 1.54 (1H, dd, *J* 15 and 3, 4-H_β), 1.73 (1H, br dd, *J* 14 and 5, 2-H_β), 2.01 and 2.02 (each 3H, s, OAc × 2), 2.08 (1H, dd, *J* 14 and 8, 2-H_α), 2.77 (each 1H, td, *J* 6 and 1, 7-H_2), 2.87 (1H, dd, *J* 15 and 8.5, 4-H_α), 4.31 and 4.35 (each 1H, dt, *J* 11.5 and 6.5, 8-H_2), 5.21 (1H, m, 3-H) [Found: $(M + H)^+$, 285.1683. $C_{15}H_{25}O_5$ requires M + H, 285.1703].

Compound 63. ν_{max}/cm^{-1} 1733 (OAc and C=O); δ_H(500 MHz) 0.98, 1.11 and 1.15 (each 3H, s, Me × 3), 1.66 (1H, dd, *J* 14.5 and 3.5, 2-H_β), 2.02 and 2.04 (each 3H, s, OAc × 2), 2.05 (1H, dd, *J* 14.5 and 8.5, 4-H_α), 2.14 (1H, dd, *J* 14.5 and 8.5, 2-H_α),

2.55 (1H, dd, *J* 14.5 and 6, 4-H_β), 2.75 and 2.83 (each 1H, dt, *J* 18 and 6.5, 7-H_2), 4.33 and 4.37 (each 1H, dt, *J* 11.5 and 6.5, 8-H_2), 5.15 (1H, m, 3-H) [Found: $(M + H)^+$, 285.1701. $C_{15}H_{25}O_5$ requires M + H, 285.1703].

Compound 64. ν_{max}/cm^{-1} 1728 (OAc), 1698 (C=O); δ_H(200 MHz) 0.84, 1.15 and 1.27 (each 3H, s, Me × 3), 1.55 (1H, dd, *J* 14.5 and 3, 4-H_β), 1.72 (1H, dd, *J* 14.5 and 4.5, 2-H_β), 1.82–1.96 (2H, m, 8-H_2), 2.02 and 2.04 (each 3H, s, OAc × 2), 2.07 (1H, dd, *J* 14.5 and 8, 2-H_α), 2.52 (each 1H, td, *J* 7 and 2.5, 7-H_2), 2.86 (1H, dd, *J* 14.5 and 9, 4-H_α), 4.07 (2H, t, *J* 6.5, 9-H_2), 5.21 (1H, m, 3-H) [Found: $(M + H)^+$, 299.1842. $C_{16}H_{27}O_5$ requires M + H, 299.1860].

Compound 65. ν_{max}/cm^{-1} 1730 (OAc and C=O); δ_H(300 MHz) 0.95, 1.11 and 1.15 (each 3H, s, Me × 3), 1.65 (1H, dd, *J* 14.5 and 3.5, 2-H_β), 1.90 (2H, m, 8-H_2), 2.04 and 2.05 (each 3H, s, OAc × 2), 2.07 (1H, dd, *J* 14 and 8.5, 4-H_α), 2.13 (1H, dd, *J* 14.5 and 8.5, 2-H_α), 2.55 (1H, dd, *J* 14 and 7, 4-H_β), 2.41–2.65 (2H, m, 7-H_2), 4.07 (2H, t, *J* 6.5, 9-H_2), 5.15 (1H, m, 3H) [Found: $(M + H)^+$, 299.1852. $C_{16}H_{27}O_5$ requires (M + H), 299.1860].

Compound 73. ν_{max}/cm^{-1} 1732 (OAc and C=O); δ_H(200 MHz) 1.69 (6H, s, 6-Me and 7-Me), 1.98 and 2.05 (each 3H, s, OAc × 2), 1.98–2.18 (4H, m, 8-H_2 and 9-H_2), 2.16 [3H, s, $CH_2C(O)CH_3$], 2.20 (1H, dd, *J* 13.5 and 5.5) and 2.43 (1H, dd, *J* 13.5 and 7.5) (5-H_2), 2.58 (1H, dd, *J* 16.5 and 5) and 2.72 (1H, dd, *J* 16.5 and 7.5) (3-H_2), 4.02 (2H, t, *J* 6.5, 10-H_2), 5.39 (1H, m, 4-H) [Found: $(M + H)^+$, 299.1862. $C_{16}H_{27}O_5$ requires M + H, 299.1860].

Compound 75. λ_{max}(EtOH)/nm 220; ν_{max}/cm^{-1} 1729 (OAc), 1669 (conj. C=O); δ_H(300 MHz) 1.65 (6H, s, 6-Me and 7-Me), 1.65–1.77 (2H, m, 9-H_2), 2.06 (3H, s, OAc), 2.13 (2H, m, 8-H_2), 2.25 [3H, s, $CH_2C(O)CH_3$], 2.93 (1H, dd, *J* 6.5 and 1.5, 5-H_2), 4.04 (2H, t, *J* 6.5, 10-H_2), 6.03 (1H, dt, *J* 16 and 1.5, 3-H), 6.72 (1H, dt, *J* 16 and 6.5, 4-H) [Found: $(M + H)^+$, 239.1634. $C_{14}H_{23}O_3$ requires M + H, 239.1648].

Compound 66. ν_{max}/cm^{-1} 1725 (OAc), 1697 (C=O); δ_H(300 MHz) 0.87, 1.15 and 1.29 (each 3H, s, Me × 3), 1.55 (1H, dd, *J* 15 and 3.5, 4-H_β), 1.71 (1H, dd, *J* 14.5 and 4.5, 2-H_β), 2.02 (3H, s, OAc), 2.07 (1H, dd, *J* 14 and 8, 2-H_α), 2.87 (1H, dd, *J* 15 and 9, 4-H_α), 3.23 (2H, m, 7-H_2), 5.07 (1H, dq, *J* 17 and 1.5) and 5.16 (1H, dq, *J* 10 and 1.5) (9-H_2), 5.21 (1H, m, 3-H), 5.92 (1H, ddt, *J* 17, 10 and 6.5, 8-H) [Found: $(M + H)^+$, 239.1636. $C_{14}H_{23}O_3$ requires M + H, 239.1648].

Compound 67. ν_{max}/cm^{-1} 1725 (OAc), 1699 (C=O); δ_H(300 MHz) 0.98, 1.11 and 1.16 (each 3H, s, Me × 3), 1.65 (1H, dd, *J* 14.5 and 3.5, 2-H_β), 2.06 (3H, s, OAc), 2.06 (1H, dd, *J* 14.5 and 8.5, 4-H_α), 2.12 (1H, dd, *J* 14.5 and 8.5, 2-H_α), 2.55 (1H, dd, *J* 14.5 and 6, 4-H_β), 3.21 and 3.29 (each 1H, ddt, *J* 17, 6.5 and 1, 7-H_2), 5.09 (1H, dq, *J* 17 and 1) and 5.06 (1H, dq, *J* 10.5 and 1) (9-H_2), 5.17 (1H, m, 3-H), 5.94 (1H, ddt, *J* 17, 10.5 and 6.5, 8-H) [Found: $(M + H)^+$, 239.1636. $C_{14}H_{23}O_3$ requires M + H, 239.1648].

Compound 74. ν_{max}/cm^{-1} 1732 (OAc and C=O); δ_H(300 MHz) 1.67 and 1.70 (each 3H, s, 6-Me and 7-Me), 1.98 (3H, s, OAc), 2.15 [3H, s, $CH_2C(O)CH_3$], 2.22 (1H, dd, *J* 13.5 and 6) and 2.46 (1H, dd, *J* 13.5 and 8) (5-H_2), 2.60 (1H, dd, *J* 16.5 and 5) and 2.72 (1H, dd, *J* 16.5 and 8) (3-H_2), 2.71 and 2.80 (each 1H, br dd, *J* 15 and 6.5, 8-H_2), 4.97 (1H, dq, *J* 11 and 1.5) and 4.98 (1H, dq, *J* 16 and 1.5) (10-H_2), 5.40 (1H, tdd, *J* 8, 6 and 5, 4-H), 5.70 (1H, ddt, *J* 16, 11 and 6.5, 9-H) [Found: $(M + H)^+$, 239.1639. $C_{14}H_{23}O_3$ requires M + H, 239.1648].

Compound 68. ν_{max}/cm^{-1} 3608 and 3487 (OH), 1729 (OAc); δ_H(300 MHz) 1.06, 1.22 and 1.33 (each 3H, s, Me × 3), 1.48 (1H, ddd, *J* 12.5, 4.5 and 2.5, 2-H_{eq}), 1.76 (1H, t, *J* 12.5, 2-H_{ax}), 1.79 (1H, ddd, *J* 13, 4.5 and 2.5, 4-H_{eq}), 1.91 (1H, dd, *J* 13 and 11.5, 4-H_{ax}), 2.02 and 2.11 (each 3H, s, OAc × 2), 2.39 (1H, s, OH), 4.37 and 4.49 (each 1H, d, *J* 12, 7-H_2), 5.14 (1H, tt, *J* 12 and 4.5, 3-H) [Found: $(M + H)^+$, 289.1673. $C_{14}H_{25}O_6$ requires M + H, 289.1652].

Compound 69. ν_{max}/cm^{-1} 3588 (OH), 1737 (OAc); δ_H(300 MHz) 1.05, 1.22 and 1.27 (each 3H, s, Me × 3), 1.64 (1H, ddd, *J* 15, 3.5 and 2.5, 2-H_{eq}), 1.75 (1H, dt, *J* 15 and 3, 4-H_{eq}), 1.90 (1H, dd, *J* 15 and 3.5, 2-H_{ax}), 2.06 and 2.12 (each 3H, s, OAc × 2), 2.19 (1H, dd, *J* 15 and 4, 4-H_{ax}), 2.55 and 2.88 (each 1H, br s, OH), 4.47 and 4.59 (each 1H, d, *J* 12, 7-H_2), 5.18 (1H, quint., *J* 3.5, 3-H) [Found: $(M + H)^+$, 289.1635. $C_{14}H_{25}O_6$ requires M + H, 289.1652].

Compound 71. ν_{max}/cm^{-1} 1713 (C=O); δ_H(300 MHz) 0.01 (6H, s, SiMe × 2), 0.08 and 0.09 (each 3H, s, SiMe × 2), 0.87 and 0.91 (each 9H, s, SiBu′), 0.84, 1.14 and 1.26 (each 3H, s, Me × 3), 1.48 (1H, dd, *J* 14 and 3, 4-H_β), 1.63 (1H, dd, *J* 13.5 and 4.5, 2-H_β), 1.93 (1H, dd, *J* 13.5 and 7.5, 2-H_α), 2.66 (1H, dd, *J* 14 and 8, 4-H_α), 4.36 and 4.43 (each 1H, d, *J* 18, 7-H_2), 4.39 (1H, m, 3-H) [Found: $(M + H)^+$, 415.3053. $C_{22}H_{47}O_3Si_2$ requires M + H, 415.3066].

Compound 72. ν_{max}/cm^{-1} 1713 (C=O); δ_H(300 MHz) 0.02 (6H, s, SiMe × 2), 0.87 (9H, s, SiBu′), 0.80, 1.14 and 1.28 (each 3H, s, Me × 3), 1.51 (1H, dd, *J* 14 and 3, 4-H_β), 1.67 (1H, dd, *J* 13.5 and 4.5, 2-H_β), 1.96 (1H, dd, *J* 13.5 and 7.5, 2-H_α), 2.67 (1H, dd, *J* 14 and 8, 4-H_α), 4.23 and 4.32 (each 1H, d, *J* 19, 7-H_2), 5.21 (1H, m, 3-H) [Found: $(M + H)^+$, 301.2197. $C_{16}H_{33}O_3Si$ requires M + H, 301.2201].

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