Stereoselective synthesis of 24-alkyl-22-hydroxysterols based on chelation-controlled radical reactions

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We have shown that the diastereoselectivity in the radical-mediated reactions of steroidal 24-methylene-22-oxy-25-oic acid esters **6–11** with alkyl iodides performed in the presence of Lewis acid MgBr$_2$·OEt$_2$ depends on the bulk of the alkyl iodides, the oxy groups at C-22 and the configuration at C-22. The ethylation of **9** afforded the *syn*-adduct exclusively and the methylation of **6** and **7**, ethylation of **10** and isopropylation of **9** gave *syn*-adducts with high selectivities (*syn–anti* = 8.8–5.1 : 1). Other combinations, except for the *tert*-butyl radical addition to **6**, **7** and **10** predominantly yielding *anti*-adducts, showed lower *syn*-selectivities.

Introduction

There is great variety in the structures of side chains, as well as the tetracyclic nucleus, of brassinolides[1] and marine sterols[2] and they play important roles in their biological activities as growth-promoting plant hormones and possible cell membrane mechanical reinforcers, respectively. The stereochemical control at C-22, C-23 and C-24 in the construction of the side chains is therefore of particular interest and extensive efforts to synthesise side chains have been carried out.[3,4]
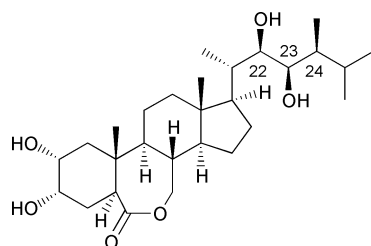

brassinolide
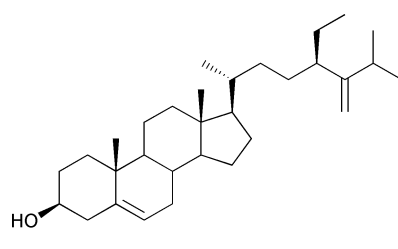
sutinasterol
isolated from a *Xestospongia* sp.

During the past decade radical reactions in acyclic systems have been shown to proceed with high stereoselectivity.[5] However, little is known about steroidal side chain construction based on radical C–C bond formation.[4] Koreeda and Wu have reported brassinolide side chain synthesis by the use of a stereoselective 5-*exo*-α-silyl radical cyclization–protodesilylation sequence.[4a] Recently we have reported the chelation-controlled 1,3-asymmetric induction in radical addition to γ-oxy-α-methylenecarboxylic acid esters **1** (Scheme 1) and the effects of substituents R^1, R^2 and R^3 and Lewis acids on the diastereoselectivity.[6] We applied the radical reaction to the construction of steroidal side chains with a variety of alkyl substituents at
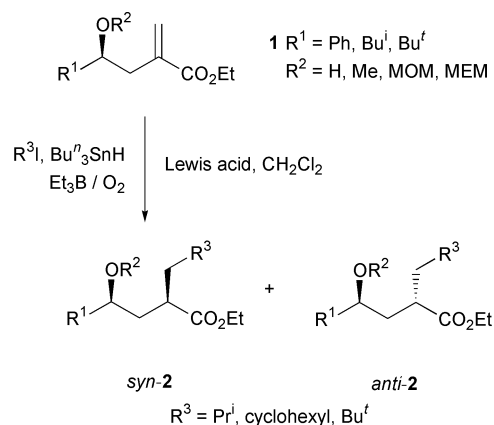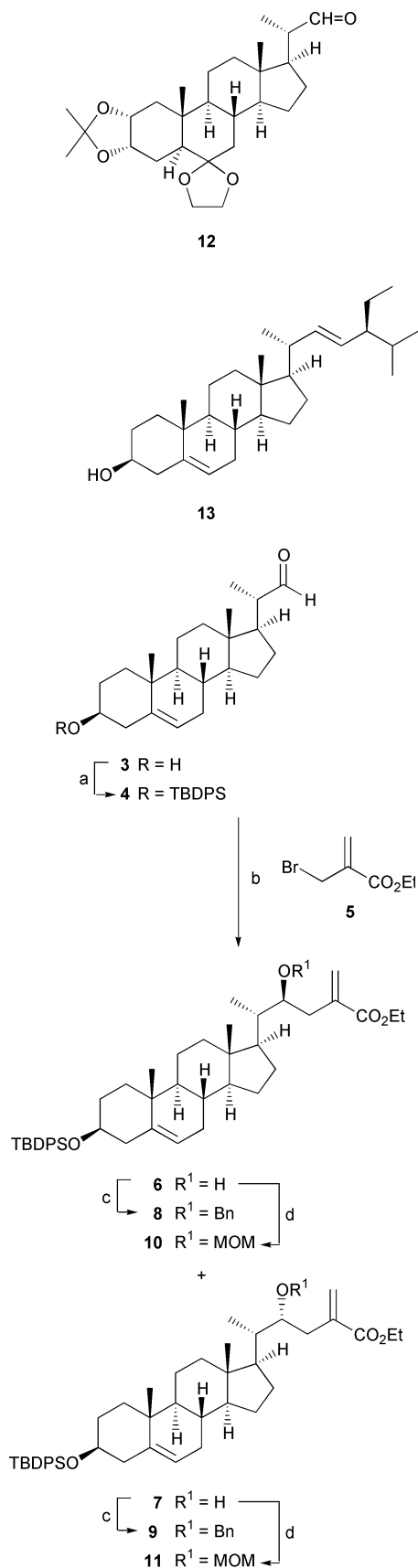

Scheme 1

C-24, and now report the effects of the bulk of alkyl halides, the oxy groups at C-22 and the configuration at C-22 on the diastereoselectivity in the radical reaction of the 24-methylene-22-oxy-25-oic acid esters **6–11**, prepared from 22-aldehyde **4**[7] through the Reformatsky reaction with ethyl α-bromomethylacrylate **5**[6,8] (Scheme 2). The 22-aldehyde **3** and the highly elaborated analogue **12**[9] have been prepared from stigmasterol **13** and used as the starting materials for the syntheses of brassinolides. Application of the radical reaction to the aldehyde **12** would afford brassinolide analogues with a variety of alkyl substituents at C-24 and oxygen functional groups at C-22 and C-25.

Results and discussion

In order to probe the effects of the oxy substituents at C-22 and their stereochemistry on the diastereoselectivity, compounds **6–11**[10] (for compound **6′**, see ref. 10) were prepared from 22-aldehyde **3**, which was obtained from stigmasterol **13** in four steps following the reported procedures (Scheme 2).[7] The Reformatsky reaction of *tert*-butyl(diphenyl)silyl (=TBDPS) ether of **3** (=**4**) with ethyl α-bromomethylacrylate **5**[6,8] gave a diastereomeric mixture of **6** (more polar Cram adduct) and **7** (less polar *anti*-Cram adduct) in a ratio of 2 : 1 and in 80% yield. The two diastereomers were separated by flash chromatography on silica gel, and the stereochemistry at C-22 was assigned by

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12

13

a ⌐ **3** R = H
⌐→ **4** R = TBDPS

b

5

c ⌐ **6** R¹ = H
  ⌐ **8** R¹ = Bn ⌐ d
    10 R¹ = MOM ←

+

c ⌐ **7** R¹ = H
  ⌐ **9** R¹ = Bn ⌐ d
    11 R¹ = MOM ←

**Scheme 2** *Reagents*: a TBDPSCl, imidazole, DMF; b **5**, Zn; c BnOC-(=NH)CCl₃, TfOH; d MOMCl, Pr$^i_2$NEt.

comparing their chemical shift values in ¹³C NMR spectra [**6** (22S): δ 52.6 (C-17), 41.0 (C-20) and 11.6 (C-21); **7** (22R): δ 53.1 (C-17), 42.7 (C-20) and 12.3 (C-21)] with those of (22R)- and (22S)-22-hydroxy steroids reported in literature.[11]

Treatment of the alcohols **6** and **7** with benzyl 2,2,2-trichloro-acetimidate in the presence of trifluoromethanesulfonic acid[12]

Table 1 Chelation-controlled 1,3-asymmetric induction in the radical reactions of α-methylene carboxylic esters **6–11** with alkyl iodides R²I

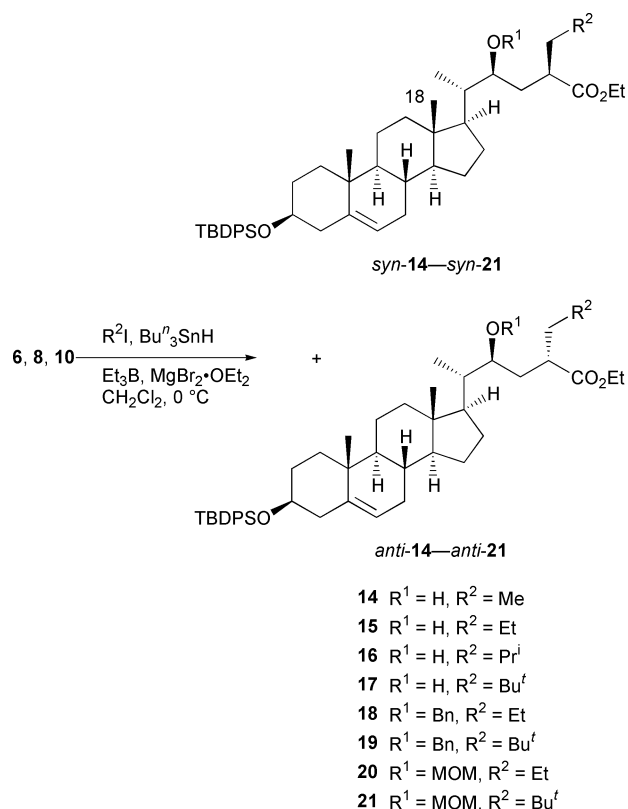| Entry	Substrate (R¹)	Product (R²)	Yield (%)	Diastereomer ratio *syn : anti*
1	**6** (H)	**14** (Me)	78	6.5 : 1
2	**6**	**15** (Et)	69[a]	1 : 1.2[a]
3	**6**	**15**	83	2.0 : 1
4	**6**	**16** (Pr^i)	95	3.2 : 1
5	**6**	**17** (Bu^t)	94	1 : 3.0
6	**8** (Bn)	**18** (Et)	84	1.4 : 1
7	**8**	**19** (Bu^t)	84	2.0 : 1
8	**10** (MOM)	**20** (Et)	67[a]	1 : 2.0[a]
9	**10**	**20**	84	6.1 : 1
10	**10**	**21** (Bu^t)	83	1 : 3.2
11	**7** (H)	**22** (Me)	87	5.1 : 1
12	**7**	**23** (Et)	66[a]	1 : 1.1[a]
13	**7**	**23**	95	3.4 : 1
14	**7**	**24** (Pr^i)	88	3.3 : 1
15	**7**	**25** (Bu^t)	99	1 : 3.2
16	**9** (Bn)	**26** (Me)	39	1 : 1.3
17	**9**	*syn*-**27** (Et)	73[b]	
18	**9**	**28** (Pr^i)	51	8.8 : 1
19	**9**	**29** (Bu^t)	68	3.7 : 1
20	**11** (MOM)	**30** (Et)	76	3.5 : 1

[a] The yield and diastereomer ratio in the reaction performed without Lewis acid. [b] Only one diastereomer was detected by ¹H NMR spectroscopy.
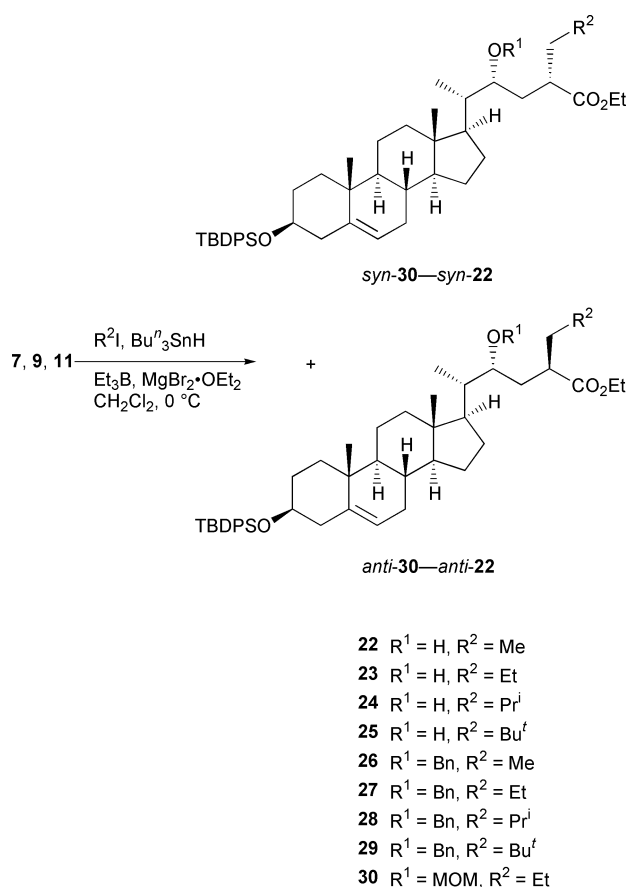

6'

16'
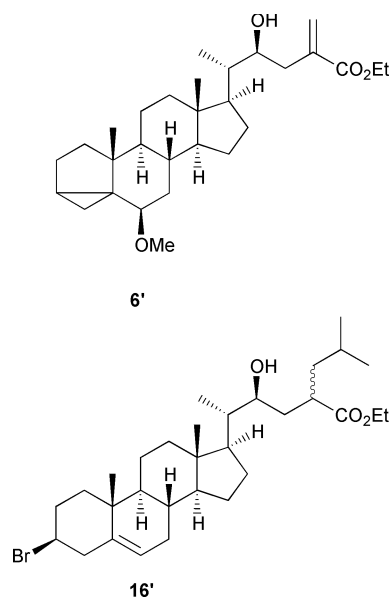
gave benzyl ethers **8** and **9**, respectively, in high yields without concomitance of the lactonisation of **6** and **7**.[13] The alcohols **6** and **7** were transformed into MOM ethers **10** and **11**, respectively, following standard procedures.

The radical reactions were performed following the procedure reported previously.[6a] After a 10 min complexation time, the alkylation reactions of the acrylates **6–11** were conducted with alkyl iodide R²I (3 equiv.), *n*-Bu₃SnH (2 equiv.) and Et₃B (1 equiv.) as a radical initiator[14] in CH₂Cl₂ at 0 °C (Schemes 3 and 4). The concentration of the acrylates was 0.04–0.05 mol dm^{-3} in all the reactions. A summary of the radical reactions is given in Table 1.

In the absence of Lewis acid, the radical reactions of hydroxy esters **6** and **7** and MOM ether **10** with ethyl iodide gave **15**, **23** and **20**, respectively, with poor diastereoselectivities (entries 2, 8 and 12). The use of 3 equiv. of MgBr₂·OEt₂ reversed the diastereoselectivity in the reaction of **6** with ethyl and iso-propyl iodides, but gave low diastereoselectivities (entries 3 and 4). However, compound **6** showed higher *syn*-selectivity

syn-**14**—syn-**21**

anti-**14**—anti-**21**

14 R^1 = H, R^2 = Me
15 R^1 = H, R^2 = Et
16 R^1 = H, R^2 = Pr^i
17 R^1 = H, R^2 = Bu^t
18 R^1 = Bn, R^2 = Et
19 R^1 = Bn, R^2 = Bu^t
20 R^1 = MOM, R^2 = Et
21 R^1 = MOM, R^2 = Bu^t

Scheme 3

syn-**30**—syn-**22**

anti-**30**—anti-**22**

22 R^1 = H, R^2 = Me
23 R^1 = H, R^2 = Et
24 R^1 = H, R^2 = Pr^i
25 R^1 = H, R^2 = Bu^t
26 R^1 = Bn, R^2 = Me
27 R^1 = Bn, R^2 = Et
28 R^1 = Bn, R^2 = Pr^i
29 R^1 = Bn, R^2 = Bu^t
30 R^1 = MOM, R^2 = Et

Scheme 4

in the reaction with methyl iodide (entry 1). The diastereoselectivity depends on the bulk of the alkyl iodide and in the case of bulky *tert*-butyl iodide, compound *anti*-**17** was yielded predominantly (entry 5).[6a] A similar trend was observed for the diastereoselectivity in the reaction of epimeric (22*R*)-22-

hydroxy ester **7** (entries 11–15). The *syn*-selectivity in methylation was higher than that of ethylation and isopropylation.

The ethylation of benzyl ethers **8** and **9** without Lewis acid gave complex mixtures. Lewis acids play two important roles, stereochemical control[4,5] and rate enhancement,[6b,15] in radical-mediated C–C bond forming reactions. The addition of the Lewis acid enhanced the reactions of benzyl ether **8** with ethyl and *tert*-butyl iodides and gave **18** and **19**, respectively, in high yields but with poor *syn*-selectivity (entries 6 and 7). The *syn*-selectivity of entries 7 and 19 is an exception for *tert*-butyl substituents (*cf*. entries 5, 10 and 15 and ref. 6*a*). The epimeric benzyl ether **9** was quite different in diastereoselectivitiy. In the reaction with ethyl iodide, *syn*-**27** was produced in high yield as a single diastereomer (entry 17). Entry 18 shows high *syn*-selectivity in the reaction with isopropyl iodide. However, contrary to our expectation, the methylation of **9** gave **26** in poor yield and selectivity (entry 16).

The ethylation of MOM ether **10** was superior in diastereoselectivity to that of hydroxy ester **6** (entry 9 *vs*. entry 3). The epimeric MOM ether **11** showed *syn*-selectivity similar to that of hydroxy ester **7**, but inferior to that of MOM ether **10** (entries 3, 8 and 20).

Thus we have found that in the radical reactions performed in the presence of MgBr$_2$·OEt$_2$ the diastereoselectivity was affected not only by the configuration at C-22 but also by the further remote stereogenic centre at C-20, and the careful combination of the oxy groups at C-22, their stereochemistry and the alkyl iodides would furnish the alkylation products with high diastereoselectivities.

The diastereomeric pairs of each of **16**, **17** and **24** were separated by silica gel column chromatography. The *syn* diastereomers were less polar than *anti* diastereomers. The other diastereomeric pairs obtained by the radical reactions could not be separated by flash chromatography on silica gel because of the differences in polarity being too small. The diastereomer ratios of the alcohols **14**–**17** and **22**–**25**, (22*R*)-benzyl ethers **26**, **28** and **29** were determined by the integrations of 24-H in their ^{1}H NMR spectra. However, in the case of (24*S*)-benzyl and MOM ethers **18**–**21** and **30** the 24-H signals overlapped. For the (22*S*)-benzyl ethers **18** and **19** the integrations of 13-Me (=18-H) were therefore used. The ratios of the MOM ethers **20**, **21** and **30** were obtained from the integrations of methyl signals of MOM groups.

The stereochemistry of **14** was firmly established by transforming it into the *tert*-butyl(diphenyl)silyl ether of (24*R*)-24-ethylcholesterol (=β-sitosterol) **35**, which was identical with an authentic sample of **35** derived from stigmasterol **13** in five steps (Scheme 5).[16] Treatment of **14** with 1,1′-thiocarbonyl-diimidazole gave **31**, which was then reduced with Bu^n$_3$SnH to give ester **32**. Methylation of the ester with methyllithium gave tertiary alcohol **33**. Dehydration of the alcohol by treatment with methanesulfonyl chloride in pyridine gave diene **34**. Finally, partial hydrogenation of **34** over 10% Pd–C was performed to give (24*R*)-24-ethylcholesterol **35**. The difference in chemical shift of C-29 in ^{13}C NMR spectra (observed in CDCl$_3$) of sitosterol acetate **36** (24*R*, δ 12.0) and clionasterol [=(24*S*)-24-ethylcholesterol] **37** (24*S*, δ 12.3) can be used to discriminate between 24*R*- and 24*S*-epimers.[17,18] Furthermore, the stereochemical assignment was supported by comparing the chemical shift values of C-27 (δ 18.2), C-28 (δ 26.1) and C-29 (δ 12.1) in the ^{13}C NMR spectrum of **34** with those of (24*S*)- and (24*R*)-stigmasta-5,25-dienes (=clerosterol) **38** and 24-epiclerosterol **39**.[19] The stereochemistry at C-24 of the other alcohols **15**–**17** and **22**–**25** was assigned by comparing the chemical shift values of 24-H. The methine protons resonating consistently at a lower field were assigned to *syn* products.[6a]

The hydrogenolysis of the benzyl ethers **19**, *syn*-**27** and **28** over 10% Pd–C gave the corresponding alcohols **17**, *syn*-**23** and **24**, respectively. The methine protons at C-24 (=methine proton α to ester carbonyl) of **26**, **28** and **29** resonating at a lower field
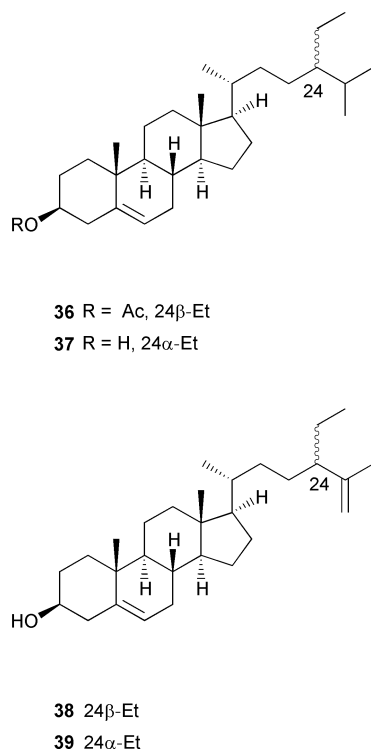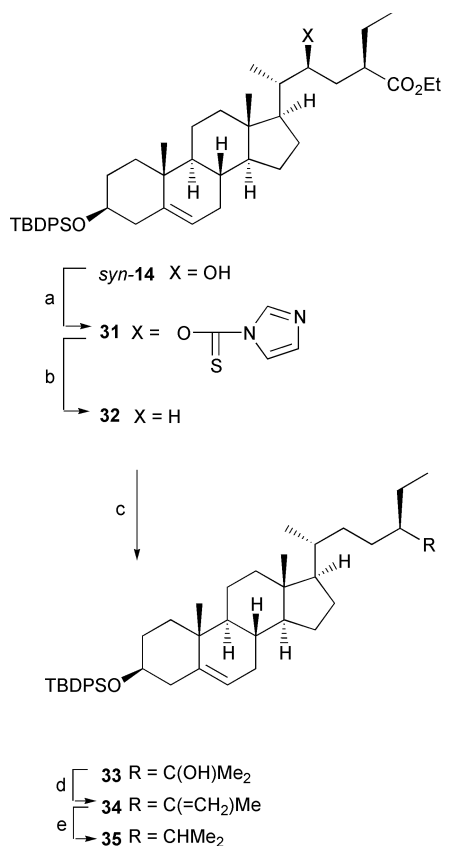
Scheme 5 *Reagents*: a 1,1′-thiocarbonyldiimidazole; b Bu$^n_3$SnH, AIBN; c MeLi; d MsCl, pyridine; e H$_2$, 10% Pd–C, ethanol–ethyl acetate.

were assigned to *syn* diastereomers. The stereochemistry of the benzyl ether **18** was assigned by comparing the chemical shift value of a single methyl at C-13 with that of the benzyl ether **19**. The methyl signals resonating at a lower field were assigned as *anti*.

Treatment of the alcohol **15** with methoxymethyl chloride and diisopropylethylamine gave **20**. The stereochemistry of the MOM ethers **21** and **30** was assigned by comparing the chemical shifts of methyl signals of MOM groups to that of **20**. The methyl groups resonating at lower field were assigned as *syn*.

Conclusions

We have shown that the ethylation of **9** afforded the *syn*-adduct exclusively and the methylation of **6** and **7**, ethylation of **10** and isopropylation of **9** gave *syn*-adducts with high selectivities (*syn*–*anti* = 8.8–5.1 : 1), but other combinations, except for the *tert*-butyl radical addition to **6**, **7** and **10** yielding *anti*-adducts predominantly, showed lower *syn*-selectivities.

Further transformation of the terminal oxygen function as shown in Scheme 5 would give various types of side chain.[20]

Experimental

IR spectra were taken on a Perkin-Elmer 2000 spectrometer. ^{1}H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) or GSX-400 (400 MHz) spectrometer with CDCl$_3$ as the solvent (unless otherwise stated) and tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on the instruments operating at 67.8 or 100.4 MHz with CDCl$_3$ as the solvent and internal standard (δ 77.0). Mass spectra (EI, 70 eV) were obtained on a JEOL JMS-700 mass spectrometer. Precoated Merck Kieselgel 60 F$_{254}$ and Wakogel C-300 were used for thin layer chromatography and flash column chromatography, respectively.

Aldehyde 4

To a solution of the aldehyde **3** (1.72 g, 5.20 mmol)[7] and imidazole (2.10 g, 30.8 mmol) in DMF (21 cm^3) cooled to 0 °C was added *tert*-butyl(diphenyl)silyl chloride (2.71 cm^3, 10.4 mmol). The solution was stirred at 0 °C for 30 min and then extracted with hexane. The organic layer was washed with water and saturated brine and then dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel [eluent: hexane–ethyl acetate (30 : 1)] to give **4** (2.05 g, 69%) as an oil; ν_{max} (film)/cm^{-1} 3076, 3048, 2800, 1718, 1590, 1258, 1113, 1046, 910, 821, 797 and 740; δ_H (270 MHz) 9.53 (1H, s, CH=O), 7.73–7.36 (10H, m, 2 × Ph), 5.13 (1H, s, 6-H), 3.56 (1H, m, 3-H), 1.08 (9H, s, CMe$_3$), 0.99 (3H, s, 10-Me) and 0.71 (3H, s, 13-Me); δ_C (67.8 MHz) 204.9, 141.0, 129.3, 127.4, 120.8, 73.1, 55.9, 50.9, 50.0, 49.4, 42.9, 42.5, 39.4, 37.2, 36.5, 31.8, 27.0, 26.6, 24.6, 21.0, 19.4, 19.2, 13.5 and 12.2.

Reformatsky reaction of 4

To a solution of the aldehyde **4** (2.05 g, 3.60 mmol) in THF (4.7 cm^3) were added the bromide **5** (821 mg, 4.24 mmol), saturated aqueous NH$_4$Cl (12 cm^3) and activated zinc powder (475 mg, 7.26 mmol). After stirring at 0 °C for 3 h, the mixture was extracted with ethyl acetate and the organic layer was washed with saturated brine and then dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel to give **6** and **7** (1.97 g, 80%) in a ratio of 2 : 1. The diastereomers were separated by flash chromatography on silica gel [eluent: benzene–ether (50 : 1)]. More polar, major diastereomer **6**, amorphous; ν_{max} (KBr)/cm^{-1} 3504, 3070, 3030, 1716, 1629, 1263, 1179, 1112, 1070, 1028, 960, 821, 799 and 741; δ_H (270 MHz) 7.66–7.36 (10H, m, 2 × Ph), 6.21 (1H, d, *J* 1.4, =CHH), 5.63 (1H, s, =CHH), 5.11 (1H, d, *J* 5.1, 6-H), 4.21 (2H, m, CH$_2$CH$_3$), 3.79 (1H, m, 22-H), 3.53 (1H, m, 3-H), 1.30 (3H, t, *J* 7.3, CH$_2$CH$_3$), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.93 (3H, d, *J* 6.0, 20-Me) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 167.5, 141.1, 138.4, 135.6, 134.7, 129.3, 127.3, 126.9, 121.0,

73.2, 72.6, 60.9, 56.6, 52.6, 50.0, 42.5, 42.3, 41.0, 39.8, 38.9, 37.2, 36.5, 32.0, 31.9, 27.8, 27.1, 24.3, 21.1, 19.5, 19.2, 14.3, 11.9 and 11.6; m/z 625 ($M^+ - C_4H_9$, 26), 579 (52), 525 (27), 499 (80) and 199 (100). m/z 625.3740 ($M^+ - C_4H_9$). $C_{40}H_{53}O_4Si$ requires 625.3713.

Less polar, minor diastereomer 7; mp 131.3–131.7 °C (from hexane–diethyl ether); v_{max} (KBr)/cm^{-1} 3515, 3070, 3030, 1714, 1630, 1261, 1179, 1112, 1071, 1030, 960, 821, 799 and 746; δ_H (270 MHz) 7.66–7.36 (10H, m, 2 × Ph), 6.23 (1H, s, =CHH), 5.65 (1H, s, =CHH), 5.13 (1H, s, 6-H), 4.21 (2H, q, J 7.0, CH_2CH$_3$), 3.76 (1H, m, 22-H), 3.53 (1H, m, 3-H), 1.30 (3H, t, J 7.0, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.95 (3H, d, J 7.0, 20-Me) and 0.68 (3H, s, 13-Me); δ_C (67.8 MHz) 167.7, 141.2, 138.6, 135.7, 134.7, 129.3, 127.3, 127.2, 120.9, 73.2, 72.4, 61.1, 56.5, 53.1, 50.1, 42.7, 42.5, 41.6, 39.8, 37.3, 36.6, 33.7, 32.0, 31.9, 27.4, 27.1, 24.5, 21.1, 19.5, 19.2, 14.3, 12.3 and 11.9; m/z 625 ($M^+ - C_4H_9$, 51), 579 (76), 525 (33), 499 (49) and 199 (100). m/z 625.3740 ($M^+ - C_4H_9$). $C_{40}H_{53}O_4Si$ requires 625.3713.

Benzyl ether 8

To a solution of the alcohol 6 (193 mg, 0.284 mmol) in cyclohexane–CH$_2$Cl$_2$ (2 : 1; 2.6 cm^3) were added benzyl 2,2,2-trichloroacetimidate (0.11 cm^3, 0.59 mmol) and trifluoromethanesulfonic acid (0.014 cm^3). The reaction mixture was stirred at room temperature for 1 h. After dilution with diethyl ether, the solution was washed successively with saturated aqueous NaHCO$_3$, water and brine, and dried over anhydrous sodium sulfate. The crude product was chromatographed on silica gel [eluent: hexane–ethyl acetate (40 : 1)] to afford the benzyl ether 8 (190 mg, 86%) as an oil; v_{max} (film)/cm^{-1} 3072, 3032, 1718, 1629, 1219, 1179, 1110, 1100, 1028, 821, 799 and 740; δ_H (270 MHz) 7.70–7.32 (15H, m, 3 × Ph), 6.17 (1H, s, =CHH), 5.57 (1H, s, =CHH), 5.10 (1H, br s, 6-H), 4.60 (1H, d, J 11.9, CHHPh), 4.47 (1H, d, J 11.9, CHHPh), 4.20 (2H, q, J 7.3, CH_2CH$_3$), 3.62 (1H, m, 22-H), 3.51 (1H, m, 3-H), 1.29 (3H, t, J 7.3, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.97 (3H, s, 10-Me) and 0.61 (3H, s, 13-Me); δ_C (67.8 MHz) 167.0, 141.2, 138.2, 135.6, 134.7, 129.3, 128.2, 127.4, 127.3, 127.0, 121.0, 79.9, 73.3, 72.0, 60.7, 56.7, 52.5, 50.1, 42.5, 42.4, 39.8, 39.0, 37.3, 36.5, 35.1, 32.0, 28.3, 27.1, 24.4, 21.1, 19.5, 19.2, 14.4, 12.9 and 11.7; m/z 715 ($M^+ - C_4H_9$, 12), 609 (13) and 199 (100). m/z 715.4130 ($M^+ - C_4H_9$). $C_{47}H_{59}O_4Si$ requires 715.4183.

Benzyl ether 9

Treatment of the alcohol 7 with benzyl 2,2,2-trichloroacetimidate and trifluoromethanesulfonic acid as described above gave 9, an oil, in 94% yield; v_{max} (film)/cm^{-1} 3072, 3030, 1715, 1636, 1219, 1167, 1100, 1069, 1020, 821, 799 and 746; δ_H (270 MHz) 7.70–7.32 (15H, m, 3 × Ph), 6.17 (1H, s, =CHH), 5.61 (1H, s, =CHH), 5.12 (1H, br s, 6-H), 4.57 (1H, d, J 11.6, CHHPh), 4.30 (1H, d, J 11.6, CHHPh), 4.12 (2H, q, J 7.0, CH_2CH$_3$), 3.55 (1H, m, 22-H), 3.51 (1H, m, 3-H), 1.28 (3H, t, J 7.0, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.97 (3H, s, 10-Me) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 167.2, 141.2, 138.9, 138.2, 135.7, 134.7, 129.6, 129.3, 128.0, 127.4, 127.3, 126.9, 121.0, 79.2, 73.2, 70.8, 60.5, 56.4, 52.8, 50.1, 42.8, 42.5, 39.8, 37.4, 37.3, 36.6, 31.9, 31.8, 27.1, 26.6, 24.5, 19.5, 19.2, 14.3, 12.6 and 11.9; m/z 715 ($M^+ - C_4H_9$, 11), 609 (6) and 199 (100). m/z 715.4120 ($M^+ - C_4H_9$). $C_{47}H_{59}O_4Si$ requires 715.4183.

MOM ether 10

To a solution of the alcohol 6 (122 mg, 0.178 mmol) in dry CH$_2$Cl$_2$ (1 cm^3) were successively added Pr$^i_2$NEt (0.363 cm^3, 2.13 mmol) and methoxymethyl (MOM) chloride (0.140 cm^3, 1.86 mmol) at 0 °C. The solution was stirred at this temperature for 4 h and then diluted with diethyl ether. After work-up as described above the crude product was submitted to flash chromatography on silica gel [eluent: hexane–ethyl acetate

[30 : 1]] to afford the MOM ether 10 (116 mg, 90%) as an oil; v_{max} (film)/cm^{-1} 3072, 3032, 1718, 1635, 1263, 1156, 1111, 1100, 1028, 822, 799 and 741; δ_H (270 MHz) 7.69–7.32 (10H, m, 2 × Ph), 6.18 (1H, s, =CHH), 5.57 (1H, s, =CHH), 5.10 (1H, d, J 4.9, 6-H), 4.62 (1H, d, J 13.8, OCHHO), 4.59 (1H, d, J 13.2, OCHHO), 4.20 (2H, q, J 7.0, CH_2CH$_3$), 3.78 (1H, m, 22-H), 3.54 (1H, m, 3-H), 3.34 (3H, s, OMe), 2.50 (2H, m, 23-H), 1.29 (3H, t, J 7.0, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.95 (3H, d, J 5.9, 20-Me) and 0.63 (3H, s, 13-Me); δ_C (67.8 MHz) 166.8, 141.1, 138.0, 135.6, 134.7, 129.3, 127.3, 127.0, 121.0, 96.4, 79.0, 73.2, 60.7, 56.8, 55.7, 52.3, 50.0, 42.6, 42.3, 39.8, 39.2, 37.2, 36.5, 36.0, 31.9, 31.7, 28.3, 27.1, 24.4, 21.1, 19.5, 19.2, 14.3, 12.8 and 11.7; m/z 669 ($M^+ - C_4H_9$, 37), 609 (5) and 199 (100). m/z 669.4037 ($M^+ - C_4H_9$). $C_{42}H_{57}O_5Si$ requires 669.3975.

MOM ether 11

Treatment of the alcohol 7 with Pr$^i_2$NEt and MOMCl as described above gave 11, an oil, in 82% yield; v_{max} (film)/cm^{-1} 3072, 3032, 1720, 1637, 1260, 1156, 1111, 1079, 1028, 821, 799 and 745; δ_H (270 MHz) 7.68–7.35 (10H, m, 2 × Ph), 6.19 (1H, s, =CHH), 5.63 (1H, s, =CHH), 5.11 (1H, br s, 6-H), 4.61 (1H, d, J 7.0, OCHHO), 4.42 (1H, d, J 7.0, OCHHO), 4.20 (2H, q, J 6.8, CH_2CH$_3$), 3.75 (1H, m, 22-H), 3.53 (1H, m, 3-H), 3.27 (3H, s, OMe), 1.29 (3H, t, J 6.8, CH$_2$CH_3), 1.06 (9H, s, CMe$_3$), 0.99 (3H, s, 10-Me), 0.95 (3H, d, J 6.5, 20-Me) and 0.68 (3H, s, 13-Me); δ_C (67.8 MHz) 167.1, 141.1, 138.3, 135.6, 134.7, 129.3, 127.3, 127.0, 121.0, 95.3, 77.7, 73.2, 60.6, 56.5, 55.5, 52.9, 50.1, 42.7, 42.5, 39.8, 39.0, 37.3, 36.5, 34.5, 31.9, 31.7, 27.6, 27.1, 24.4, 21.1, 19.5, 19.2, 14.3, 12.6 and 11.9; m/z 669 ($M^+ - C_4H_9$, 67) and 199 (100). m/z 669.3994 ($M^+ - C_4H_9$). $C_{42}H_{57}O_5Si$ requires 669.3975.

General procedure of the radical reactions performed in the presence of MgBr$_2$·OEt$_2$

To a solution of α-methylene esters 6–11 (0.06 mmol) in 1.5 cm^3 of dry CH$_2$Cl$_2$ was added MgBr$_2$·OEt$_2$ (0.18 mmol, 3 equiv.) and the mixture was stirred at room temperature for 10 min. To the suspension cooled to 0 °C were added alkyl iodide R^{2}I (0.18 mmol, 3 equiv.), Bu$^n_3$SnH (0.12 mmol, 2 equiv.) and Et$_3$B (1.06 mol dm^{-3} in hexane; 0.057 cm^3, 0.06 mmol, 1 equiv.). The mixture was stirred at 0 °C for 1 h. KF and water were added and the mixture was stirred at room temperature for 3 h. After filtration, the solvent was evaporated in $vacuo$. The residue was purified by flash chromatography on silica gel [eluent: hexane–ethyl acetate (20 : 1 or 10 : 1)] to give 14–30.

General procedure of the radical reactions performed in the absence of MgBr$_2$·OEt$_2$

The radical reaction was performed similarly as described above without Lewis acid.

Compounds 14. v_{max} (film)/cm^{-1} 3483, 3072, 3032, 1733, 1590, 1263, 1179, 1112, 1070, 1040, 1028, 960, 822, 799 and 741; δ_H (270 MHz) 7.68–7.37 (10H, m, 2 × Ph), 5.12 (1H, d, J 3.5, 6-H), 4.13 (2H, m, CH_2CH$_3$), 3.63 (1H, m, 22-H), 3.50 (1H, m, 3-H), 2.51 (syn) and 2.45 ($anti$) (1H, m each, 24-H), 1.27 (3H, t, J 7.3, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.91 (3H, d, J 6.2, 20-Me), 0.88 (3H, t, J 5.4, Me) and [0.66 ($anti$) and 0.65 (syn) (3H, s each, 13-Me)]; δ_H (270 MHz; C$_6$D$_6$) 7.86–7.16 (10H, m, 2 × Ph), 5.21 (1H, br s, 6-H), 4.00 (2H, m, CH_2CH$_3$), 3.76 (2H, m, 3-H and 22-H), 2.76 (1H, m, 24-H), 1.36 (9H, s, CMe$_3$) and 0.63 ($anti$) and 0.59 (syn) (3H, s each, 13-Me); δ_C (67.8 MHz) 176.6, 141.5, 136.0, 135.0, 129.6, 127.6, 121.2, 73.4, 72.8 ($anti$), 71.5 (syn), 61.1 ($anti$), 60.4 (syn), 56.8, 52.8, 50.2, 42.7, 42.4, 41.5, 40.9, 39.9, 38.1, 37.4, 36.7, 32.1, 32.0, 31.8, 27.8, 27.2, 26.1, 24.4, 22.9, 21.2, 19.6, 19.3, 14.6 (syn), 14.3 ($anti$), 12.0 (syn), 11.9 ($anti$) and 11.8; m/z 641 ($M^+ - C_4H_9$, 7), 595 (31), 499 (26) and 199 (100). m/z 641.4045 ($M^+ - C_4H_9$). $C_{41}H_{57}O_4Si$ requires 641.4026.

Compounds 15. ν_{max} (film)/cm^{-1} 3447, 3070, 3032, 1733, 1590, 1263, 1179, 1111, 1080, 1040, 1030, 960, 822, 799 and 740; δ_H (270 MHz) 7.69–7.32 (10H, m, 2 × Ph), 5.12 (1H, d, J 4.9, 6-H), 4.12 (2H, m, CH_2CH$_3$), 3.62 (1H, m, 22-H), 3.52 (1H, m, 3-H), 2.58 (*syn*) and 2.41 (*anti*) (1H, m each, 24-H), 1.25 (3H, t, J 7.0, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.91 (3H, d, J 7.0, 20-Me), 0.88 (3H, t, J 6.8, Me) and 0.66 (*anti*) and 0.64 (*syn*) (3H, s each, 13-Me); δ_H (270 MHz; C$_6$D$_6$) 7.83–7.23 (10H, m, 2 × Ph), 5.21 (1H, br s, 6-H), 4.03 (2H, m, CH_2CH$_3$), 3.76 (2H, m, 3H and 22-H), 2.78 (1H, m, 24-H), 1.36 (9H, s, CMe$_3$) and 0.63 (*anti*) and 0.59 (*syn*) (3H, s each, 13-Me); δ_C (67.8 MHz) 176.3, 141.0, 135.5, 134.5, 129.2, 127.2, 120.8, 73.1, 72.3 (*anti*), 71.2 (*syn*), 60.2 (*anti*), 60.1 (*syn*), 56.5, 52.5 (*syn*), 52.3 (*anti*), 49.9, 42.5, 42.1, 41.2, 40.6, 39.7, 38.2, 37.1, 36.4, 35.2, 35.0, 31.8, 31.7, 27.6, 27.0, 24.1, 21.0, 20.6, 20.5 (*syn*), 20.4 (*anti*), 19.4, 19.1, 14.4 (*syn*), 14.2 (*anti*), 12.1 (*anti*), 11.8 (*syn*) and 11.7; m/z 655 (M$^+$ − C$_4$H$_9$, 4), 609 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O, 31), 499 (24) and 199 (100). m/z 609.3798 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O). C$_{40}$H$_{53}$O$_3$Si requires 609.3764.

Compound syn-16. An oil; ν_{max} (film)/cm^{-1} 3737, 3064, 3044, 1724, 1612, 1259, 1177, 1104, 1085, 1027, 1007, 959, 823, 794 and 731; δ_H (270 MHz) 7.68–7.26 (10H, m, 2 × Ph), 5.11 (1H, d, J 4.9, 6-H), 4.13 (2H, q, J 7.3, CH_2CH$_3$), 3.60 (1H, m, 22-H), 3.52 (1H, m, 3-H), 2.64 (1H, m, 24-H), 1.25 (3H, t, J 7.3, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 1.00 (3H, s, 10-Me), 0.90 (3H, d, J 6.5, 20-Me), 0.88 (6H, t, J 6.2, CH(CH_3)$_2$) and 0.64 (3H, s, 13-Me); δ_C (67.8 MHz) 176.6, 141.2, 135.7, 134.7, 129.3, 127.3, 121.0, 73.2, 71.2, 60.2, 56.6, 52.6, 50.0, 42.5, 42.3, 41.3, 40.9, 39.8, 38.8, 37.2, 36.5, 32.0, 31.9, 27.7, 27.1, 26.2, 24.3, 23.1, 22.2, 21.1, 19.5, 19.2, 14.5, 11.9 and 11.8; m/z 669 (M$^+$ − C$_4$H$_9$, 4), 623 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O, 58), 499 (10) and 199 (100). m/z 623.3985 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O). C$_{41}$H$_{55}$O$_3$Si requires 623.3920.

Compound anti-16. ν_{max} (film)/cm^{-1} 3740, 3067, 3048, 1734, 1611, 1267, 1174, 1107, 1078, 1025, 1010, 956, 818, 791 and 734; δ_H (270 MHz) 7.69–7.32 (10H, m, 2 × Ph), 5.11 (1H, d, J 4.6, 6-H), 4.11 (2H, m, CH_2CH$_3$), 3.68 (1H, m, 22-H), 3.52 (1H, m, 3-H), 2.47 (1H, m, 24-H), 1.25 (3H, t, J 7.3, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.91 (3H, d, J 6.8, 20-Me), 0.88 (6H, t, J 6.2, CH(CH_3)$_2$) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 177.1, 141.3, 135.7, 134.8, 129.5, 127.4, 121.1, 73.4, 72.7, 60.5, 56.8, 52.6, 50.1, 42.7, 42.6, 41.9, 40.9, 39.9, 38.8, 37.4, 36.7, 32.1, 27.9, 27.2, 27.1, 26.3, 24.4, 23.2, 22.4, 21.3, 19.7, 19.4, 14.5, 12.0 and 11.9; m/z 669 (M$^+$ − C$_4$H$_9$, 6), 623 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O, 34), 499 (8) and 199 (100).

Compound syn-17. An oil; ν_{max} (film)/cm^{-1} 3689, 3072, 3048, 1730, 1616, 1241, 1186, 1111, 1094, 1026, 1003, 957, 820, 797 and 729; δ_H (270 MHz) 7.70–7.32 (10H, m, 2 × Ph), 5.11 (1H, d, J 4.9, 6-H), 4.15 (2H, m, CH_2CH$_3$), 3.56 (1H, m, 22-H), 3.50 (1H, m, 3-H), 2.63 (1H, m, 24-H), 1.26 (3H, t, J 7.3, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.88 (9H, s, CMe$_3$) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 177.3, 141.2, 135.6, 134.7, 129.3, 127.3, 120.9, 73.2, 70.9, 60.3, 56.6, 52.6, 50.1, 42.2, 41.1, 39.8, 39.2, 37.2, 36.5, 32.0, 31.9, 30.9, 27.7, 27.1, 24.3, 21.1, 19.5, 19.2, 14.4, 11.9 and 11.8; m/z 683 (M$^+$ − C$_4$H$_9$, 2), 637 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O, 33), 499 (11), 277 (51) and 199 (100). m/z 637.4130 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O). C$_{42}$H$_{57}$O$_3$Si requires 637.4077.

Compound anti-17. An oil; ν_{max} (film)/cm^{-1} 3478, 3074, 3045, 1734, 1590, 1241, 1193, 1108, 1085, 1028, 1005, 958, 821, 797 and 736; δ_H (270 MHz) 7.69–7.26 (10H, m, 2 × Ph), 5.11 (1H, d, J 5.1, 6-H), 4.16 (2H, m, CH_2CH$_3$), 3.67 (1H, m, 22-H), 3.51 (1H, m, 3-H), 2.45 (1H, m, 24-H), 1.25 (3H, t, J 7.3, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.88 (9H, s, CMe$_3$) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 177.6, 141.2, 135.6, 134.7, 129.3, 127.3, 121.0, 73.2, 72.0, 60.4, 56.7, 52.5, 50.0, 42.5, 42.3,

40.9, 40.7, 39.8, 37.2, 36.5, 32.0, 31.9, 30.9, 29.5, 27.7, 27.1, 24.3, 21.1, 19.5, 19.2, 14.2, 11.9 and 11.8; m/z 683 (M$^+$ − C$_4$H$_9$, 8), 637 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O, 45), 499 (9) and 199 (100). m/z 637.4100 (M$^+$ − C$_4$H$_9$ − C$_2$H$_6$O). C$_{42}$H$_{57}$O$_3$Si requires 637.4077.

Compounds 18. ν_{max} (film)/cm^{-1} 3071, 3032, 1734, 1590, 1263, 1176, 1111, 1108, 1029, 865, 799 and 740; δ_H (270 MHz) 7.69–7.31 (15H, m, 3 × Ph), 5.11 (1H, d, J 4.6, 6-H), 4.55 (1H, d, J 13.5, CHH), 4.41 (1H, d, J 13.5, CHH), 4.10 (2H, m, CH_2-CH$_3$), 3.55 (1H, m, 3-H), 3.35 (1H, m, 22-H), 2.52 (1H, m, 24-H), 1.25 (3H, t, J 7.3, CH$_2$CH_3), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.94 (3H, d, J 6.5, 20-Me), 0.88 (3H, t, J 7.3, Me) and 0.64 (3H, s, 13-Me); δ_H (270 MHz; C$_6$D$_6$) 7.86–7.39 (15H, m, 3 × Ph), 5.20 (1H, br s, 6-H), 4.64–4.43 (2H, m, CH$_2$), 4.01 (2H, m, CH_2CH$_3$), 3.77 (1H, m, 3-H), 3.52 (1H, m, 22-H), 2.73 (1H, m, 24-H), 1.24 (9H, s, CMe$_3$) and 0.69 (*anti*) and 0.65 (*syn*) (3H, s each, 13-Me); δ_C (67.8 MHz) 176.2, 141.0, 138.9, 135.5, 134.6, 129.2, 128.0, 127.3, 127.2, 120.9, 80.8 (*syn*), 79.0 (*anti*), 73.1 (*syn*), 72.6 (*anti*), 71.5 (*anti*), 71.0 (*syn*), 60.0, 56.5, 52.6, 49.9, 42.7, 42.5, 42.4, 42.3, 39.7, 38.2, 37.1, 36.4, 35.3, 33.5, 31.8, 28.2, 27.9, 27.0, 24.4, 21.0, 20.5, 19.4, 19.1, 14.4 (*anti*), 14.0 (*syn*), 13.0 and 11.6; m/z 745 (M$^+$ − C$_4$H$_9$, 13), 497 (42), 263 (75) and 199 (100). m/z 745.4700 (M$^+$ − C$_4$H$_9$). C$_{49}$H$_{65}$O$_4$Si requires 745.4652.

Compounds 19. ν_{max} (film)/cm^{-1} 3070, 3032, 1734, 1590, 1269, 1154, 1111, 1086, 1024, 822, 798 and 735; δ_H (270 MHz) 7.68–7.30 (15H, m, 3 × Ph), 5.11 (1H, br s, 6-H), 4.54 (2H, s, OCH_2Ph), 4.10 (2H, m, CH_2CH$_3$), 3.53 (1H, m, 3-H), 3.33 (1H, m, 22-H), 2.54 (1H, m, 24-H), 1.25 (3H, t, J 7.3, CH$_2$CH_3), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.93 (3H, d, J 6.2, 20-Me), 0.86 (9H, s, CMe$_3$) and 0.64 (3H, s, 13-Me); δ_H (270 MHz; C$_6$D$_6$) 7.86–7.41 (15H, m, 3 × Ph), 5.20 (1H, br s, 6-H), 4.54 (2H, m, CH$_2$), 4.00 (2H, m, CH_2CH$_3$), 3.78 (1H, m, 3-H), 3.53 (1H, m, 22-H), 2.81 (1H, m, 24-H), 1.24 (9H, s, CMe$_3$), 0.93 (9H, s, CMe$_3$) and 0.69 (*anti*) and 0.64 (*syn*) (3H, s each, 13-Me); δ_C (67.8 MHz) 177.3, 141.2, 139.2, 135.7, 134.7, 129.3, 128.0, 127.4, 127.2, 121.0, 80.5 (*anti*), 79.2 (*syn*), 73.2, 72.5, 60.1, 56.6, 52.7, 50.0, 46.7, 42.5, 42.4, 39.8, 39.7, 39.5, 38.1, 37.3, 36.5, 32.0, 30.9, 29.5, 28.3, 27.1, 21.1, 19.5, 19.2, 14.4 (*anti*), 14.1 (*syn*), 13.8 (*anti*), 13.1 (*syn*) and 11.7; m/z 773 (M$^+$ − C$_4$H$_9$, 7), 291 (20) and 199 (100). m/z 773.4963 (M$^+$ − C$_4$H$_9$). C$_{51}$H$_{69}$O$_4$Si requires 773.4965.

Compounds 20. ν_{max} (film)/cm^{-1} 3072, 3031, 1733, 1560, 1170, 1150, 1106, 1090, 1037, 822, 799 and 738; δ_H (270 MHz) 7.69–7.32 (10H, m, 2 × Ph), 5.11 (1H, d, J 4.6, 6-H), 4.61 (2H, s, O-CH$_2$-O), 4.12 (2H, q, J 7.0, CH_2CH$_3$), 3.51 (1H, m, 3-H), 3.46 (1H, m, 22-H), 3.37 (*syn*) and 3.35 (*anti*) (3H, s each, OMe), 2.48 (1H, m, 24-H), 1.25 (3H, t, J 7.0, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.87 (3H, t, J 7.3, Me), 0.71 (3H, d, J 7.3, 20-Me) and 0.64 (3H, s, 13-Me); δ_C (100.4 MHz) 176.1, 141.1, 135.7, 134.8, 129.4, 127.4, 121.1, 96.8 (*syn*), 96.0 (*anti*), 80.0 (*syn*), 78.2 (*anti*), 73.2, 60.1, 56.7, 55.7, 52.3, 50.0, 42.4, 42.3, 40.1, 39.8, 37.2, 36.4, 35.9, 35.3, 34.8, 31.8, 27.9, 27.0, 24.4, 21.0, 20.4, 19.4, 19.1, 14.3 (*anti*), 14.2 (*syn*), 12.7 and 11.6; m/z 669 (M$^+$ − C$_4$H$_9$, 33), 217 (22) and 199 (100). m/z 699.4415 (M$^+$ − C$_4$H$_9$). C$_{44}$H$_{63}$O$_5$Si requires 699.4445.

Compounds 21. ν_{max} (film)/cm^{-1} 3072, 3051, 1727, 1590, 1266, 1153, 1106, 1090, 1037, 822, 799 and 736; δ_H (400 MHz) 7.68–7.36 (10H, m, 2 × Ph), 5.12 (1H, br s, 6-H), 4.65–4.53 (2H, m, OCH$_2$O), 4.10 (2H, m, CH_2CH$_3$), 3.53 (1H, m, 3-H), 3.42 (1H, m, 22-H), 3.37 (*syn*) and 3.35 (*anti*) (3H, s each, OMe), 2.49 (1H, m, 24-H), 1.25 (3H, t, J 7.2, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.91 (3H, d, J 6.8, 20-Me), 0.88 (9H, s, CMe$_3$) and 0.64 (3H, s, 13-Me); δ_C (67.8 MHz) 177.3 (*anti*), 177.0 (*syn*), 141.2, 135.7, 134.8, 129.4, 127.4, 121.0,

96.8 (*anti*), 96.1 (*syn*), 78.4, 73.2, 60.2, 56.7 (*syn*), 56.6 (*anti*), 55.6, 52.2, 47.0, 42.4, 42.3, 39.9, 39.8, 38.9, 37.6, 37.2, 36.4, 31.8, 30.8, 29.4, 27.8, 27.0, 24.3, 22.6, 21.0, 20.4, 19.4, 19.1, 14.1, 12.6 and 11.7; m/z 727 ($M^+ - C_4H_9$, 19), 666 (9) and 199 (100). m/z 727.4723 ($M^+ - C_4H_9$). $C_{46}H_{67}O_5Si$ requires 727.4758.

Compounds 22. ν_{max} (film)/cm^{-1} 3447, 3065, 3034, 1733, 1590, 1240, 1190, 1111, 1080, 1024, 1005, 960, 822, 799 and 737; δ_H (270 MHz) 7.69–7.33 (10H, m, 2 × Ph), 5.11 (1H, br s, 6-H), 4.12 (2H, m, C*H*$_2$CH$_3$), 3.57 (1H, m, 22-H), 3.53 (1H, m, 3-H), 2.55 (*syn*) and 2.46 (*anti*) (1H, m each, 24-H), 1.26 (3H, t, J 7.3, CH$_2$C*H*$_3$), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.92 (3H, d, J 7.0, 20-Me), 0.89 (3H, t, J 5.7, Me) and 0.68 (*anti*) and 0.65 (*syn*) (3H, s each, 13-Me); δ_C (67.8 MHz) 179.5 (*anti*), 176.3 (*syn*), 141.2, 135.6, 134.7, 129.3, 127.4, 120.8, 73.2, 71.0, 61.1 (*anti*), 60.3 (*syn*), 56.3, 53.0, 50.1, 42.7, 42.4, 41.7 (*syn*), 41.6 (*anti*), 39.7, 38.5, 37.2, 36.5, 33.7, 31.9, 27.4, 27.1, 26.7 (*anti*), 26.4 (*syn*), 24.8, 24.4, 21.1, 19.5, 19.2, 14.5 (*syn*), 14.1 (*anti*), 12.0 (*anti*), 11.9 (*syn*) and 11.8; m/z 641 ($M^+ - C_4H_9$, 4), 595 ($M^+ - C_4H_9 - C_2H_6O$, 28), 499 (17) and 199 (100). m/z 641.4023 ($M^+ - C_4H_9$). $C_{41}H_{57}O_4Si$ requires 641.4026.

Compounds 23. ν_{max} (film)/cm^{-1} 3684, 3066, 3048, 1737, 1590, 1242, 1180, 1111, 1082, 1024, 1005, 957, 819, 796 and 736; δ_H (400 MHz) 7.69–7.34 (10H, m, 2 × Ph), 5.12 (1H, br s, 6-H), 4.13 (2H, m, C*H*$_2$CH$_3$), 3.57 (1H, m, 22-H), 3.53 (1H, m, 3-H), 2.65 (*syn*) and 2.46 (*anti*) (1H, m each, 24-H), 1.26 (3H, t, J 7.3, CH$_2$C*H*$_3$), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.90 (3H, d, J 6.4, 20-Me), 0.88 (3H, t, J 6.8, Me) and 0.69 (*anti*) and 0.65 (*syn*) (3H, s each, 13-Me); δ_C (67.8 MHz) 176.5, 141.2, 135.6, 134.7, 129.3, 127.3, 121.0, 73.2, 71.0, 60.3, 56.3, 53.0, 50.1, 42.6, 42.4, 42.2, 40.1, 39.8, 38.5, 37.2, 36.5, 35.4, 33.7, 32.9, 31.9, 27.1, 24.4, 21.1, 20.8, 20.7, 19.5, 19.2, 14.1 (*syn*), 13.9 (*anti*), 12.2 (*anti*), 12.0 (*syn*) and 11.9; m/z 655 ($M^+ - C_4H_9$, 1), 609 ($M^+ - C_4H_9 - C_2H_6O$, 19), 499 (36) and 199 (100). m/z 609.3765 ($M^+ - C_4H_9 - C_2H_6O$). $C_{40}H_{53}O_3Si$ requires 609.3764.

Compound *syn*-24. An oil; ν_{max} (film)/cm^{-1} 3700, 3068, 3048, 1726, 1604, 1251, 1182, 1108, 1082, 1025, 1016, 955, 819, 795 and 731; δ_H (270 MHz) 7.68–7.33 (10H, m, 2 × Ph), 5.11 (1H, d, J 4.9, 6-H), 4.14 (2H, m, C*H*$_2$CH$_3$), 3.55 (1H, m, 22-H), 3.49 (1H, m, 3-H), 2.70 (1H, m, 24-H), 1.26 (3H, t, J 7.3, CH$_2$C*H*$_3$), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.91 (3H, d, J 6.5, 20-Me), 0.88 (6H, d, J 6.5, CH(C*H*$_3$)$_2$) and 0.65 (3H, s, 13-Me); δ_C (67.8 MHz) 176.7, 141.2, 135.6, 134.7, 129.3, 127.3, 121.0, 73.2, 70.9, 60.3, 56.3, 53.0, 50.1, 42.6, 42.5, 42.4, 42.3, 40.5, 39.8, 37.2, 36.5, 33.4, 31.9, 27.2, 27.1, 26.3, 24.4, 23.1, 22.2, 21.1, 19.5, 19.2, 14.5, 12.2 and 11.9; m/z 669 ($M^+ - C_4H_9$, 5), 623 ($M^+ - C_4H_9 - C_2H_6O$, 19), 499 (28) and 199 (100). m/z 623.3956 ($M^+ - C_4H_9 - C_2H_6O$). $C_{41}H_{55}O_3Si$ requires 623.3920.

Compound *anti*-24. An oil; ν_{max} (film)/cm^{-1} 3740, 3064, 3028, 1732, 1612, 1241, 1174, 1107, 1089, 1018, 1005, 960, 821, 790 and 732; δ_H (270 MHz) 7.68–7.35 (10H, m, 2 × Ph), 5.11 (1H, br s, 6-H), 4.13 (2H, m, C*H*$_2$CH$_3$), 3.69 (1H, m, 22-H), 3.53 (1H, m, 3-H), 2.51 (1H, m, 24-H), 1.25 (3H, t, J 6.8, CH$_2$C*H*$_3$), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.90 (3H, d, J 6.8, 20-Me), 0.88 (6H, d, J 4.9, CH(C*H*$_3$)$_2$) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 177.5, 141.2, 135.6, 134.7, 129.3, 127.3, 120.9, 73.2, 72.5, 60.3, 56.4, 53.1, 50.1, 42.7, 42.5, 42.4, 41.9, 41.8, 39.8, 37.2, 36.5, 33.3, 31.9, 27.5, 27.1, 26.2, 24.4, 23.2, 22.1, 21.1, 19.5, 19.2, 14.3, 12.3 and 11.9; m/z 669 ($M^+ - C_4H_9$, 2), 623 ($M^+ - C_4H_9 - C_2H_6O$, 11), 499 (8) and 199 (100). m/z 623.3956 ($M^+ - C_4H_9 - C_2H_6O$). $C_{41}H_{55}O_3Si$ requires 623.3920.

Compounds 25. ν_{max} (film)/cm^{-1} 3528, 3070, 3034, 1734, 1590,

1255, 1189, 1111, 1081, 1024, 1010, 958, 821, 798 and 736; δ_H (270 MHz) 7.68–7.32 (10H, m, 2 × Ph), 5.11 (1H, br s, 6-H), 4.10 (2H, m, C*H*$_2$CH$_3$), 3.68 (1H, m, 22-H), 3.52 (1H, m, 3-H), 2.64 (*syn*) and 2.49 (*anti*) (1H, m each, 24-H), 1.25 (3H, t, J 6.8, CH$_2$C*H*$_3$), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.88 (9H, s, CMe$_3$) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 178.1, 141.2, 135.7, 134.7, 129.3, 127.3, 120.9, 73.2, 71.9, 60.4, 56.3, 53.0, 50.0, 45.9, 42.3, 39.8, 39.5, 37.2, 36.5, 35.3, 31.9, 30.8, 29.5, 27.5, 27.1, 24.5, 21.1, 19.5, 19.2, 14.5 (*syn*), 14.2 (*anti*), 12.3 and 11.9; m/z 683 ($M^+ - C_4H_9$, 2), 637 ($M^+ - C_4H_9 - C_2H_6O$, 11), 499 (10) and 199 (100). m/z 637.4130 ($M^+ - C_4H_9 - C_2H_6O$). $C_{42}H_{57}O_3Si$ requires 637.4077.

Compounds 26. ν_{max} (film)/cm^{-1} 3070, 3031, 1726, 1591, 1293, 1179, 1180, 1109, 1089, 1027, 821, 797 and 737; δ_H (400 MHz) 7.69–7.33 (15H, m, 3 × Ph), 5.11 (1H, br s, 6-H), 4.53 (1H, d, J 11.2, C*H*H), 4.29 (1H, d, J 11.2, CH*H*), 4.10 (2H, m, C*H*$_2$CH$_3$), 3.51 (1H, m, 3-H), 3.28 (1H, m, 22-H), 2.73 (*syn*) and 2.65 (*anti*) (1H, m each, 24-H), 1.21 (3H, t, J 7.0, CH$_2$C*H*$_3$), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.88 (3H, t, J 6.4, Me) and 0.66 (3H, s, 13-Me); δ_H (400 MHz; C_6D_6) 7.85–7.22 (15H, m, 3 × Ph), 5.25 (1H, br s, 6-H), 4.59 (1H, d, J 12.0, *syn* and *anti* C*H*H), 4.39 (*syn*) and 4.38 (*anti*) (1H, d each, J 12.0, CH*H*), 4.01 (2H, m, C*H*$_2$CH$_3$), 3.81 (1H, m, 3-H), 3.52 (1H, m, 22-H), 3.00 (*syn*) and 2.91 (*anti*) (1H, m each, 24-H), 1.25 (9H, s, CMe$_3$) and 0.67 (3H, s, 13-Me); δ_C (100.4 MHz) 176.8, 141.3, 138.9, 135.8, 134.8, 132.0, 129.4, 128.3, 128.1, 127.4, 121.1, 79.2, 73.2, 72.1, 71.1, 60.0, 56.2, 52.6, 50.0, 43.7, 42.7, 42.4, 42.0, 39.6, 37.2, 36.6, 36.5, 35.7, 31.9, 31.6, 27.2, 27.0, 24.4, 22.6, 21.0, 19.4, 19.1, 14.4, 12.3 and 11.8; m/z 731 ($M^+ - C_4H_9$, 10), 668 (8), 277 (15) and 199 (100). m/z 731.4435 ($M^+ - C_4H_9$). $C_{48}H_{63}O_4Si$ requires 731.4496.

Compound *syn*-27. An oil; ν_{max} (film)/cm^{-1} 3072, 3032, 1733, 1590, 1263, 1179, 1111, 1110, 1028, 822, 799 and 740; δ_H (270 MHz) 7.69–7.26 (15H, m, 3 × Ph), 5.11 (1H, d, J 4.6, 6-H), 4.53 (1H, d, J 10.8, C*H*H), 4.30 (1H, d, J 10.8, CH*H*), 4.08 (2H, q, J 7.3, C*H*$_2$CH$_3$), 3.53 (1H, m, 3-H), 3.26 (1H, m, 22-H), 2.69 (1H, m, 24-H), 1.23 (3H, t, J 7.3, CH$_2$C*H*$_3$), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.90 (3H, d, J 6.5, 20-Me), 0.88 (3H, t, J 6.8, Me) and 0.66 (3H, s, 13-Me); δ_H (270 MHz; C_6D_6) 7.83–7.42 (15H, m, 3 × Ph), 5.23 (1H, br s, 6-H), 4.59 (1H, d, J 10.8, C*H*H), 4.37 (1H, d, J 10.8, CH*H*), 4.03 (2H, m, CH$_2$CH$_3$), 3.80 (1H, m, 22-H), 3.54 (1H, m, 3-H), 2.97 (1H, m, 24-H), 1.25 (9H, s, CMe$_3$) and 0.67 (3H, s, 13-H); δ_C (67.8 MHz) 176.5, 141.0, 138.7, 135.5, 134.5, 129.2, 128.0, 127.8, 127.2, 120.9, 79.1, 73.1, 70.9, 59.9, 56.2, 52.5, 49.9, 42.6, 42.4, 41.9, 39.6, 37.1, 36.5, 36.4, 35.7, 31.8, 31.7, 31.5, 27.2, 27.0, 24.3, 22.6, 21.0, 20.6, 19.4, 19.1, 14.4, 12.3 and 11.8. m/z 745.4579 ($M^+ - C_4H_9$). $C_{49}H_{65}O_4Si$ requires 745.4652.

Compounds 28. ν_{max} (film)/cm^{-1} 3071, 3020, 1733, 1590, 1266, 1181, 1111, 1087, 1029, 822, 800 and 736; δ_H (270 MHz) 7.68–7.33 (15H, m, 3 × Ph), 5.11 (1H, d, J 5.2, 6-H), 4.53 (*syn* and *anti*) (1H, d, J 12.0, C*H*H), 4.31 (*syn*) and 4.30 (*anti*) (1H, d each, J 12.0, CH*H*), 4.08 (2H, q, J 7.3, C*H*$_2$CH$_3$), 3.52 (1H, m, 3-H), 3.26 (1H, m, 22-H), 2.79 (*syn*) and 2.71 (*anti*) (1H, m each, 24-H), 1.23 (3H, t, J 7.3, CH$_2$C*H*$_3$), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.89 (3H, d, J 6.5, 20-Me), 0.85 (6H, d, J 6.2, CH(C*H*$_3$)$_2$) and 0.66 (3H, s, 13-Me); δ_H (400 MHz; C_6D_6) 7.85–7.21 (15H, m, 3 × Ph), 5.24 (1H, d, J 5.2, 6-H), 4.60 (1H, d, J 12.0, *syn* and *anti* C*H*H), 4.39 (*syn*) and 4.38 (*anti*) (1H, d each, J 12.0, CH*H*), 4.01 (2H, m, C*H*$_2$CH$_3$), 3.81 (1H, m, 3-H), 3.52 (1H, m, 22-H), 3.10 (*syn*) and 3.00 (*anti*) (1H, m each, 24-H), 1.25 (9H, s) and 0.67 (3H, s, 13-Me); δ_C (67.8 MHz) 177.0, 141.3, 139.0, 135.7, 134.8, 133.4, 129.4, 128.3, 128.0, 127.4, 121.1, 79.3, 73.2 (*syn*), 72.1 (*anti*), 71.1, 60.0, 56.3, 52.6, 50.0, 42.7, 42.5, 40.3, 39.6, 37.2, 36.6, 36.5, 32.3, 31.9, 27.2, 27.0, 26.2, 24.4, 23.0, 22.1, 21.0, 19.4, 19.1, 14.4 (*anti*), 14.0 (*syn*), 12.3 and 11.8; m/z 759 ($M^+ - C_4H_9$, 15), 277 (15)

and 199 (100). m/z 759.4841 (M$^+$ − C$_4$H$_9$). C$_{50}$H$_{67}$O$_4$Si requires 759.4809.

Compounds 29. ν_{max} (film)/cm^{-1} 1728, 1112, 1091, 1029, 820, 794 and 736; δ_H (400 MHz) 7.69–7.32 (15H, m, 3 × Ph), 5.13 (1H, br s, 6-H), 4.54 (1H, d, J 12.0, CHH), 4.34 (1H, d, J 12.0, CHH), 4.09 (2H, m, CH_2CH$_3$), 3.53 (1H, m, 3-H), 3.24 (1H, m, 22-H), 2.81 (*syn*) and 2.71 (*anti*) (1H, m each, 24-H), 1.24 (3H, t, J 7.6, CH$_2$CH_3), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.91 (3H, d, J 4.8, 20-Me), 0.87 (9H, s, CMe$_3$) and 0.66 (3H, s, 13-Me); δ_H (400 MHz; C$_6$D$_6$) 7.83–7.21 (15H, m, 3 × Ph), 5.24 (1H, br s, 6-H), 4.59 (*syn*) and 4.58 (*anti*) (1H, d each, J 12.0, CHH), 4.42 (*syn*) and 4.37 (*anti*) (1H, d each, J 12.0, CHH), 4.02 (2H, m, CH_2CH$_3$), 3.79 (1H, m, 3-H), 3.45 (1H, m, 22-H), 3.10 (*syn*) and 2.97 (*anti*) (1H, m each, 24-H), 1.26 (9H, s, CMe$_3$), 0.92 (9H, s, CMe$_3$) and 0.66 (*anti*) and 0.62 (*syn*) (3H, s each, 13-Me); δ_C (100.4 MHz) 177.9, 141.3, 139.1, 135.7, 134.8, 129.4, 129.3, 128.2, 127.4, 121.0, 79.4, 73.2, 71.1 (*anti*), 71.0 (*syn*), 60.0 (*anti*), 59.9 (*syn*), 56.2, 52.6, 50.0, 47.6, 42.7, 42.4, 39.6, 38.7, 38.1, 37.2, 36.6, 31.8, 30.9, 29.7, 29.5, 27.0, 21.0, 19.4, 19.1, 14.2, 12.3 and 11.8; m/z 774 (M$^+$ − C$_4$H$_9$, 6), 497 (18), 291 (8) and 199 (100). m/z 773.4968 (M$^+$ − C$_4$H$_9$). C$_{51}$H$_{69}$O$_4$Si requires 773.4965.

Compounds 30. ν_{max} (film)/cm^{-1} 3072, 3030, 1733, 1590, 1257, 1179, 1106, 1090, 1040, 822, 800 and 736; δ_H (270 MHz) 7.69–7.32 (10H, m, 2 × Ph), 5.11 (1H, d, J 5.1, 6-H), 4.67 (1H, d, J 7.0, OCHHO), 4.55 (1H, d, J 7.0, OCHHO), 4.13 (2H, m, CH_2CH$_3$), 3.53 (1H, m, 3-H), 3.43 (1H, m, 22-H), 3.37 (*syn*) and 3.36 (*anti*) (3H, s each, OMe), 2.62 (*syn*) and 2.46 (*anti*) (1H, m each, 24-H), 1.25 (3H, t, J 7.3, CH$_2$CH_3), 1.06 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.91 (3H, d, J 7.0, 20-Me), 0.88 (3H, t, J 5.4, Me) and 0.65 (3H, s, 13-Me); δ_C (67.8 MHz) 176.4, 141.1, 135.6, 134.7, 129.3, 127.3, 121.0, 95.7, 77.9, 73.2, 60.1, 56.3, 55.8, 52.8, 50.1, 42.7, 42.5, 42.0, 39.8, 38.5, 37.3, 36.5, 35.9, 31.9, 31.7, 27.2, 27.1, 24.4, 22.7, 21.1, 20.7, 19.5, 19.2, 14.5, 12.5 and 11.9; m/z 699 (M$^+$ − C$_4$H$_9$, 59), 217 (33) and 199 (100). m/z 699.4453 (M$^+$ − C$_4$H$_9$). C$_{44}$H$_{63}$O$_5$Si requires 699.4445.

Preparation of authentic compound 35

To a solution of β-sitosterol (31 mg, 0.75 mmol), prepared from stigmasterol following the reported procedures,[16] in dry CH$_2$Cl$_2$ (1 cm^3) was added 55 mg (0.81 mmol, 11 equiv.) of imidazole. After stirring at 0 °C for 10 min, 0.05 cm^3 (0.19 mmol, 2.6 equiv.) of TBDPSCl was added and the mixture was stirred at 0 °C for 1 h. The solution was diluted with CH$_2$Cl$_2$, and washed with water and saturated brine and then dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel [eluent: hexane–ethyl acetate (40 : 1)] to give **35** (29.5 mg, 60%) as an oil; ν_{max} (film)/cm^{-1} 3072, 3030, 1590, 1262, 1077, 1030, 821, 799 and 743; δ_H (270 MHz) 7.68–7.35 (10H, m, 2 × Ph), 5.11 (1H, d, J 5.1, 6-H), 3.53 (1H, m, 3-H), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me), 0.90 (3H, d, J 7.0, 20-Me) and 0.65 (3H, s, 13-Me); δ_C (100.4 MHz) 141.3, 135.8, 134.8, 129.4, 127.4, 121.1, 73.3, 56.8, 56.0, 50.0, 45.8, 42.5, 42.3, 39.8, 37.2, 36.5, 36.1, 33.9, 31.9, 31.6, 29.1, 28.2, 27.0, 26.0, 24.3, 23.1, 21.0, 19.8, 19.1, 19.0, 18.8, 14.1, 12.0 and 11.8; m/z 595 (M$^+$ − C$_4$H$_9$, 54), 503 (24), 429 (49), 355 (66), 281 (53), 221 (68) and 199 (100). m/z 595.4324 (M$^+$ − C$_4$H$_9$). C$_{41}$H$_{59}$OSi requires 595.4335.

Preparation of imidazol-1-ylthiocarbonyloxy compound 31

To a solution of **14** (116 mg, 0.165 mmol) in CH$_2$Cl$_2$ (4 cm^3) was added 1,1′-thiocarbonyldiimidazole (455 mg, 2.55 mmol) and the solution was stirred at room temperature for 15 h. Chromatography on silica gel [eluent: hexane–ethyl acetate (30 : 1)] gave imidazol-1-ylthiocarbonyloxy compound **31** (118 mg, 89%) as an oil; δ_H (270 MHz) 8.30 (1H, s), 7.60 (1H, s), 7.68–7.32 (10H, m, 2 × Ph), 7.03 (1H, s), 5.65 (1H, m, 22-H),

5.09 (1H, br s, 6-H), 4.14 (2H, m, CH_2CH$_3$), 3.52 (1H, m, 3-H), 1.25 (3H, m, CH$_2$CH_3), 1.10 (3H, d, J 7.2, 20-Me), 1.05 (9H, s, CMe$_3$), 0.97 (3H, s, 10-Me) and 0.66 (3H, s, 13-Me); δ_C (67.8 MHz) 184.0, 175.2, 141.2, 136.7, 135.7, 134.7, 130.7, 129.4, 127.4, 121.0, 117.9, 86.3, 73.1, 60.6, 56.3, 52.3, 49.8, 43.4, 42.4, 41.9, 39.6, 38.6, 37.1, 36.4, 35.0, 31.8, 31.6, 28.7, 27.0, 24.3, 22.6, 20.9, 19.4, 19.1, 14.1, 11.7 and 11.6.

Radical mediated reduction of imidazol-1-ylthiocarbonyloxy compound 31

To a solution of **31** (118 mg, 0.146 mmol) in toluene (5 cm^3) was added Bu$^n_3$SnH (0.628 cm^3, 2.33 mmol) and a catalytic amount of AIBN. The solution was stirred at room temperature for 1 h and then chromatographed on silica gel [eluent: hexane–ethyl acetate (40 : 1)] to give **32** (66 mg, 66%) as an oil; δ_H (270 MHz) 7.68–7.33 (10H, m, 2 × Ph), 5.11 (1H, br s, 6-H), 4.14 (2H, m, CH_2CH$_3$), 3.50 (1H, m, 3-H), 1.26 (3H, m, CH$_2$CH_3), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me) and 0.63 (3H, s, 13-Me); δ_C (67.8 MHz) 176.3, 141.1, 135.6, 134.7, 129.3, 127.3, 121.0, 73.2, 59.9, 56.7, 55.7, 50.1, 47.8, 42.5, 42.3, 39.8, 37.3, 36.5, 35.8, 33.5, 31.9, 28.5, 28.2, 27.1, 25.3, 24.3, 21.1, 19.5, 19.2, 18.8, 15.4, 14.5, 12.0 and 11.9.

Methylation of ester 32

To a solution of the ester **32** (48 mg, 0.07 mmol) in diethyl ether (1.5 cm^3) was added a solution of methyllithium in hexane (1.03 mol dm^{-3}; 0.69 cm^3, 0.71 mmol) at 0 °C and the solution was stirred at this temperature for 2 h. The reaction was quenched by addition of water. The product was extracted with ethyl acetate and the extract was washed with water and brine, and then dried over anhydrous sodium sulfate. The crude product was chromatographed on silica gel [eluent: hexane–ethyl acetate (30 : 1)] to give **33** (37 mg, 79%) as an oil; δ_H (270 MHz) 7.69–7.32 (10H, m, 2 × Ph), 5.11 (1H, br s, 6-H), 3.53 (1H, m, 3-H), 1.16 (6H, s, 25-Me), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me) and 0.65 (3H, s, 13-Me); δ_C (67.8 MHz) 141.2, 135.6, 134.7, 129.3, 127.3, 121.0, 74.2, 73.3, 56.8, 55.9, 51.8, 50.1, 42.5, 42.4, 39.8, 37.3, 36.6, 36.3, 35.8, 31.9, 31.7, 28.3, 27.6, 27.1, 26.9, 24.4, 23.6, 22.7, 21.1, 19.5, 19.2, 19.0, 18.8, 12.3 and 11.9.

Dehydration of 33

To a solution of the alcohol **33** (10 mg, 0.015 mmol) in pyridine (1 cm^3) cooled to 0 °C was added MsCl (0.10 cm^3, 1.3 mmol) and the resulting solution was stirred at 0 °C for 15 h. Water was added and the product was extracted with diethyl ether. The ethereal solution was washed successively with water, aqueous HCl (0.5 mol dm^{-3}) and brine, and then dried over anhydrous sodium sulfate. The crude product was chromatographed on silica gel [eluent: hexane–ethyl acetate (30 : 1)] to give diene **34** (5.2 mg, 54%) as an oil; δ_H (270 MHz) 7.69–7.35 (10H, m, 2 × Ph), 5.11 (1H, br s, 6-H), 4.71 (1H, s, =CHH), 4.63 (1H, s, CHH), 3.53 (1H, m, 3-H), 1.05 (9H, s, CMe$_3$), 0.98 (3H, s, 10-Me) and 0.64 (3H, s, 13-Me); δ_C (67.8 MHz) 147.8, 141.2, 135.6, 134.7, 129.3, 127.3, 121.0, 111.0, 73.3, 56.8, 55.9, 50.1, 49.8, 48.9, 42.5, 42.3, 39.8, 37.3, 36.6, 36.0, 33.8, 32.0, 31.7, 29.7, 28.2, 27.1, 26.1, 24.3, 21.1, 19.5, 19.0, 18.2, 14.3, 12.1 and 11.9.

Hydrogenation of 34

A solution of the diene **34** (15 mg) in ethanol–ethyl acetate (1 : 2; 1.5 cm^3) was stirred at room temperature in the presence of a catalytic amount of 10% Pd–C under a hydrogen atmosphere for 5.5 h to give **35** (11 mg, 72%), whose spectral data were identical with those of the authentic samples prepared as above.

Compound 6′

An oil; δ_H (270 MHz) 6.22 (1H, s, C*H*H), 5.64 (1H, s, CH*H*), 4.22 (2H, m, C*H*$_2$CH$_3$), 3.80 (1H, m, 22-H), 3.32 (3H, s, OMe), 2.76 (1H, t, *J* 3.0, 6-H), 1.31 (3H, t, *J* 6.9, CH$_2$C*H*$_3$), 1.02 (3H, s, 10-Me), 0.95 (3H, d, *J* 6.3, 20-Me) and 0.64 (3H, s, 13-Me).

Compound 16′

An oil; δ_H (270 MHz) 5.35 (1H, d, *J* 5.3, 6-H), 4.14 (2H, q, *J* 7.2, C*H*$_2$CH$_3$), 3.92 (1H, m, 3-H), 3.61 (1H, m, 22-H), 1.26 (3H, t, *J* 7.2, CH$_2$C*H*$_3$), 1.06 (3H, s, 10-Me), 0.91 (3H, d, *J* 6.3, 20-Me), 0.88 (6H, d, *J* 6.6, CH(C*H*$_3$)$_2$) and 0.67 (3H, s, 13-Me); δ_C (67.8 MHz) 176.5, 141.3, 122.0, 77.1, 60.1, 56.4, 52.5, 50.0, 44.2, 42.1, 41.9, 41.2, 40.8, 40.2, 39.6, 38.7, 36.3, 34.3, 31.7, 27.6, 26.1, 24.2, 22.9, 22.6, 22.1, 20.9, 19.2, 14.4, 11.8 and 11.7.

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