132. *Diels-Alder* Approach to Highly Functionalized Tertiary α-Hydroxy Ketones: A Novel Route to the Hexahydrobenzofuran Portion of the Avermectins and Milbemycins

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A highly regio- and stereoselective *Diels-Alder* reaction between dienophiles of type **I** and dienes of type **II** *(Scheme 1)* gives rise to *Diels-Alder* adducts of type **III**. Upon treatment with $BF_3 \cdot Et_2O$, these adducts are smoothly converted into the corresponding enones *(Scheme 6)*. Under mild acidic conditions, enone (±)-**33** gave bicyclic diketone (±)-**34** *via* an intramolecular *Michael*-type addition. Diketone (±)-**34** has the correct relative configuration and a suitable ketone function at C(6) for further conversion into the hexahydrobenzofuran portion of the avermectins and milbemycins.

1. Introduction. – In connection with current synthetic work on chlorotricolide [1] and the hexahydrobenzofuran portion of the avermectins [2] [3], we were faced with the problem of the preparation of highly functionalized tertiary α-hydroxy ketones in bicyclic ring systems. This functional group is present in many natural products with interesting biological activities. An especially interesting molecule in this respect is forskolin [4].

As a general solution to this problem, we describe a highly regio- and stereoselective *Diels-Alder* reaction between the previously unknown dienophiles of type **I** and the now well-known electron-rich *Danishefsky* dienes of type **II** yielding **III** *(Scheme 1)*. In addition, this work has resulted in the development of a general synthetic route to the useful dienophiles **I** and a novel approach to the hexahydrobenzofuran portion of the avermectins and milbemycins.

2. Synthesis of Dienophiles of Type I. – Since dienophiles of type **I** *(Scheme 1)* were not known in the literature, and a wide range of substituents R^1, R^2, and R^3 were necessary to achieve our goal, we devised a general synthesis for such dienophiles starting from L-ascorbic acid. The crucial formation of the acyloxy-enone portion was achieved by elimination of the corresponding threonates **IV** with 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) [5] in THF at −20°. These eliminations proceeded with very high (*Z*)-selectivity (> 10:1) *via* an antiperiplanar mode. The (*Z*)-acyloxy-enones **V** formed were obtained isomerically pure by chromatography.

The required threonates **11**–**13** (see *Scheme 3*) were synthesized from the known 5,6-isopropylidene-L-ascorbic acid (**1**) [8] *(Scheme 2)*. It is noteworthy that the oxidative

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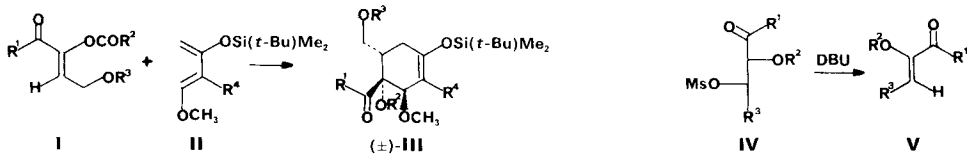
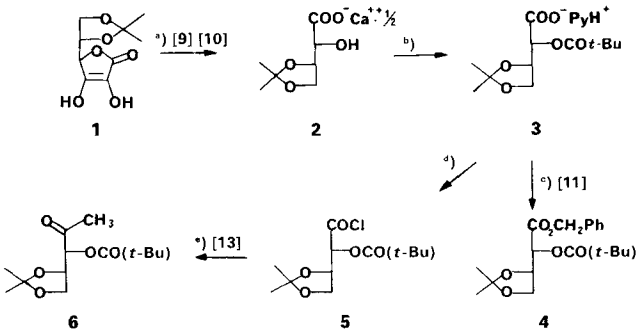
Scheme 1



cleavage of L-ascorbic acid reported by *Isbell* and *Frush* [9] works also with small modifications on **1**. Thus, hemicalcium 3,4-O-isopropylidene-L-threonate (**2**) was obtained on large scale by oxidation of **1** with 30% H_2O_2 solution and $CaCO_3$ in 82% yield[3]). The calcium salt **2** was converted by standard methods *(Scheme 2)* into the pyridinium salt of **3**, which is a very useful C_4 unit. The pyridinium salt **3** was smoothly converted either into the benzyl ester **4**, with *N,N*-dicyclohexylcarbodiimide (DCC), Me_2NPy (4-(*N,N*-dimethylamino)pyridine), and benzyl alcohol in CH_2Cl_2 [11], or the acyl chloride **5**, with oxalyl chloride in THF at −20°. Trapping of the generated HCl by pyridine in the latter process was crucial to avoid partial epimerization at C(2). Menthyl ester **7** (see *Scheme 3*) was obtained from **3** in a similar way as **4**. Among the numerous methods known to convert an acyl chloride into the corresponding methyl ketone [12], we found that the method reported by *Stille* and *Milstein* [13], using Me_4Sn and a Pd(II) catalyst *(Scheme 2)* in HMPA (hexamethylphosphortriamide) was the best. This method gave the methyl ketone **6** in 87% yield with only a trace of the C(3) epimer.

Scheme 2



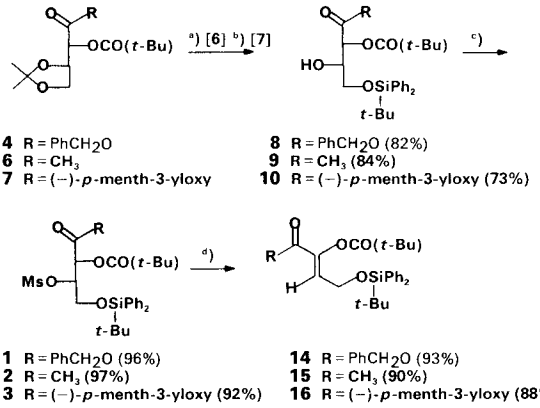
a) H_2O_2, $CaCO_3$. b) $(CH_3)_3CCOCl$, Pyridine, Me_2NPy, CH_2Cl_2 (81.5%). c) DCC, Me_2NPy, $PhCH_2OH$, CH_2Cl_2 (90%). d) Oxalyl chloride, THF, −20° (93%). e) Me_4Sn, $[Pd(Ph_3P)_2(CH_2Ph)Cl]$, HMPA, 45° (87%).

Hydrolysis of the acetonides **4**, **6**, and **7** was achieved with 20% PPTS (pyridinium tosylate) [6] in THF/H_2O 3:1 at 60° for 70 h and selective protection of the primary alcohol group with (*tert*-butyl)diphenylsilyl chloride [7] in pyridine/CH_2Cl_2 with Me_2NPy as catalyst (→**8**, **9**, and **10**, resp.; see *Scheme 3*). Mesylation was then carried out under standard conditions to yield **11**, **12**, and **13**, respectively, and the latter transformed to **14**, **15**, and **16** with DBU in THF at 20°.

To introduce the potential OH group at the CH_3 of the acetyl group of **15**, it was converted *via* **17** into **18** by a modified *Rubottom* procedure [14] *(Scheme 4)*. In this

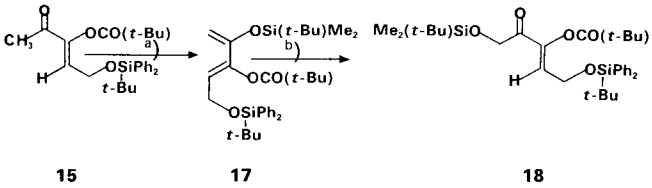
[3]) Acetonide **I** has independently been synthesized by *Wei et al.* [10].

Scheme 3



[a]) Pyridinium tosylate (PPTS), THF/H_2O 3:1, 55–60°. [b]) (t-Bu)Ph_2SiCl, pyridine, CH_2Cl_2. [c]) MsCl, Et_3N, CH_2Cl. [d]) DBU, THF, −20°–RT.

Scheme 4



[a]) [(t-Bu)Me_2Si]OSO_2CF_3, Et_3N (98.5%). [b]) *meta*-Chloroperbenzoic acid, hexane (79%).

manner the desired dienophile **18** was available through a ten-step sequence in an overall yield of 30%.

3. *Diels-Alder* Reactions. – Although there is some precedence for successful *Diels-Alder* reactions between α,-(trimethylsiloxy)-substituted dienophiles and cyclopentadiene [15], there are no examples in which highly substituted dienophiles and dienes are used. *Diels-Alder* reactions are among the few reactions that proceed with high degree of spatial selectivity and, as has been more recently shown, can entail enantioselectivity [16]. To test the stereochemical outcome of our proposed sequence, dienophile **19** [17] and 3-[(*tert*-butyl)dimethylsilyl]-1,3-butadiene **20** [18] were chosen as a model system *(Scheme 5)*. It is noteworthy, that the reaction occurred with exclusive regio- and good stereoselectivity. The major epimer (±)-**21** with the β-MeO group was isolated in 78% yield after chromatography. The observed regiochemistry is in accordance with simple FMO considerations [19] and the β-MeO group at C(3) is the result of the favored *endo* addition.

The β-configuration at C(2) of the adduct (±)-**21** was shown by conversion into ketone (±)-**23** *via* mild hydrolysis (0,1N HCl in THF).

In the 500-MHz ^{1}H-NMR spectrum of (±)-**23**, H–C(3) appears as a *dd* ($J_{ax,eq}$ = 6 Hz and $J_{eq,eq}$ = 4 Hz), which undoubtly indicates an equatorial position. The axial position of the CH_3O group is also clear from the fact that the axial proton at C(1) is considerably shifted downfield (see also *Exper. Part*) and appears as a *dd* ($J_{ax,eq}$ = 5,5 Hz and $J_{ax,ax}$ = 8 Hz).

Scheme 5

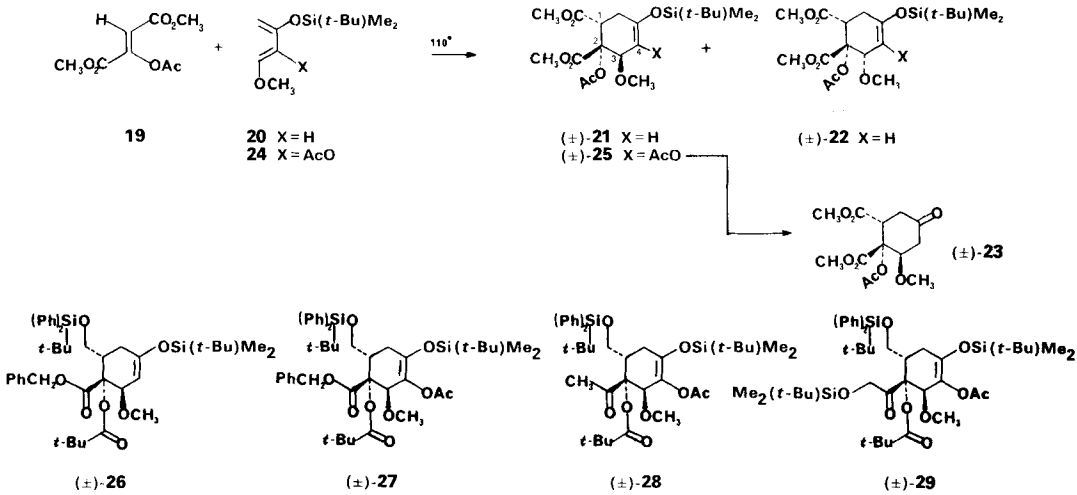


Table. *Results of* Diels-Alder *Reactions*

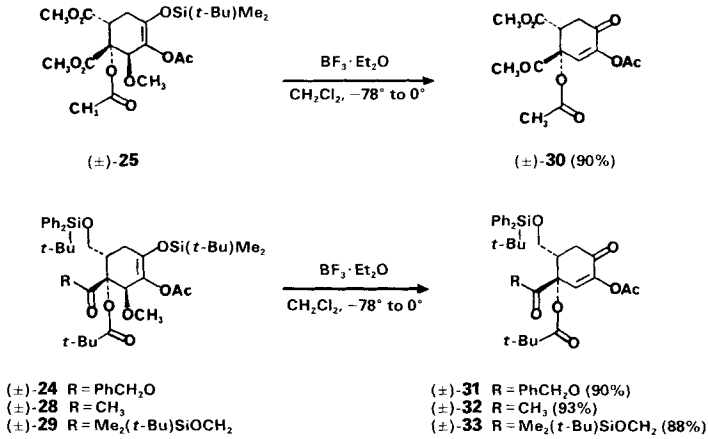
Dienophile	Diene	Reaction conditions	Major β-isomer[a])	Yield [%] of pure β-isomer[a])	β/α Ratio (NMR)
19	**20**	110°, 2 d, benzene	(±)-**21**	78	10:1
19	**24**	140°, 3 d, benzene	(±)-**25**	83	9:1
14	**20**	150°, 4 d, benzene	(±)-**26**	83	9:1
14	**24**	150°, 90 h, benzene	(±)-**27**	75	9:1
15	**24**	145°, 2 d, benzene	(±)-**28**	83	8:1
18	**24**	125°, 2 d, benzene	(±)-**29**	74	6:1

[a]) α and β refer to the position of the MeO group.

All *Diels-Alder* reactions with the dienes **20** and **24** and the dienophiles **14**, **15**, **18**, and **19** showed excellent regio- and good stereoselectivity and gave the corresponding, purifiable isomers **21** and **25–29** with the β-MeO group (see the *Table* and *Scheme 5*). The reactions were all carried out in a seal tube with 5 to 6 equiv. of diene at temperatures ranging from 110 to 150° over a period of 2 to 4 d. The excess diene was removed by distillation under reduced pressure. The *Diels-Alder* adducts were then obtained analytically pure by chromatography on SiO_2.

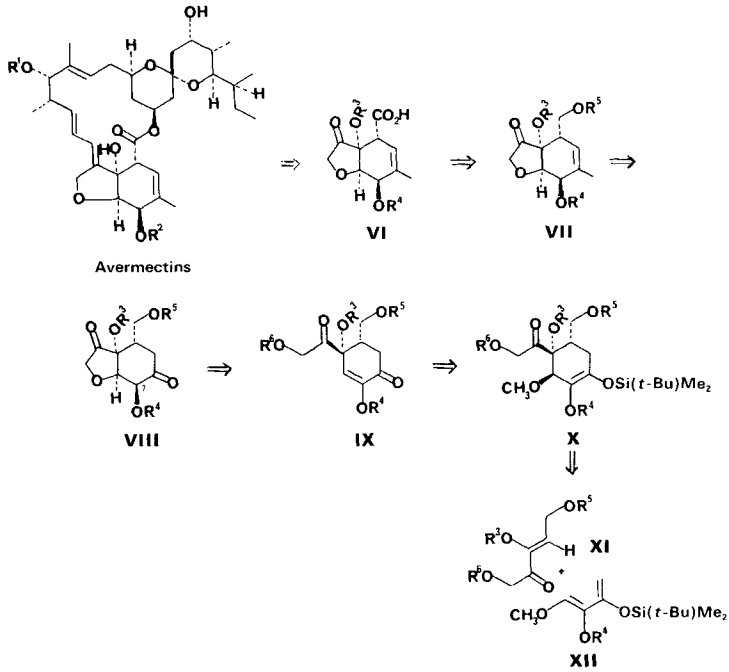
4. Conversion of the *Diels-Alder* Adducts into the Corresponding Enones. – Another key step for the application of the present strategy to the synthesis of the hexahydrobenzofuran portion of the avermectins and milbemycins was the conversion of the *Diels-Alder* adducts (see *Scheme 5* and the *Table*) into the corresponding enones *(Scheme 6)*. We were quite confident, that only a mild method would allow us to isolate the enones (±)-**30**–(±)-**33**. After trying several sets of conditions, we found that $BF_3 \cdot Et_2O$ in CH_2Cl_2 (−78° to 0°) was a very convenient method. It is worth noting that Bu_4NF led to complete aromatization. In the ^{1}H-NMR spectra, the enone protons appear as singulets in the range of 6.8–7.0 ppm and in the IR spectra, the enone CO stretches range from 1690 to 1695 cm^{-1}. The enones were chromatographed on SiO_2 and were reasonably stable at 0°.

Scheme 6



5. A Novel Approach to the Hexahydrobenzofuran Portion of the Avermectins and Milbemycins. – The milbemycins [20] and avermectins [2] [3] (see *Scheme 8*) belong to a recently discovered class of broad spectrum, anthelmintic antiparasitic compounds. Since the first report by *Albers-Schonberg et al.* [2], there has been much interest in the biological properties of the avermectins [21], and these systems have become important synthetic targets.

Scheme 8



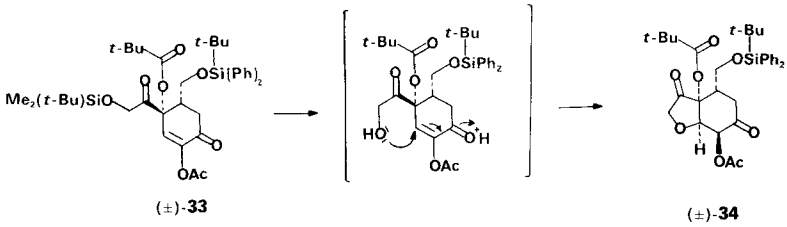
To date, there has been considerable effort on the synthesis of the milbemycins [22] [23] and the spiroacetal portion of the avermectins [24–26], but relatively little work has been published on the hexahydrobenzofuran portion of the avermectins [27–29] [37]. Consequently, we devised a convergent and straight forward approach to the bottom portion of these important molecules through application of the foregoing intermolecular *Diels-Alder* reaction.

In the retrosynthetic analysis (*Scheme 8;* avermectines⇒**VI–XII**), the bicyclic diketone **VIII** was the crucial target molecule inasmuch as it contained the correct relative configuration at all stereogenic centers and the necessary functional group to complete the synthesis. Although *Danishefsky* and coworkers [18] [30] have elegantly demonstrated the scope of electron-rich dienes in organic synthesis, the particular sequence proposed here has not been previously reported. Other important steps in the retrosynthetic analysis involve the conversion of *Diels-Alder* adducts of type **X** into their corresponding enones **IX**, the selective deprotection of the R^6O group and the cyclization to the bicyclic diketone **VIII**.

Although there are some precedents for the intramolecular addition of an alcohol to an enone [31], it was not clear whether enones of type **IX** would be stable to the cyclization conditions, or which configuration would result at the stereogenic center C(7) of **VIII**. Since the required equatorial acyloxy group (R^4O) seemed to be the more stable one, there was also hope for an eventual epimerization at that stage. In a recently published synthesis of (±)-olivacine, *Corey* and *Dittami* [32] found support for such a similar epimerization. Since, under acidic conditions, the whole cyclization should in principle be reversible, one might expect the equatorial acyloxy group (R^4O) to be the favored one.

6. Cyclization of Enone (±)-33 to the Bicyclic Diketone (±)-34. – As mentioned earlier, the use of Bu_4NF to generate the enones from the *Diels-Alder* adducts led to complete aromatization and was, therefore, not the method of choice for the deprotection of R^6O in enone **IX** *(Scheme 8)*. However, THF/1N HCl 5:1 very selectively cleaved only

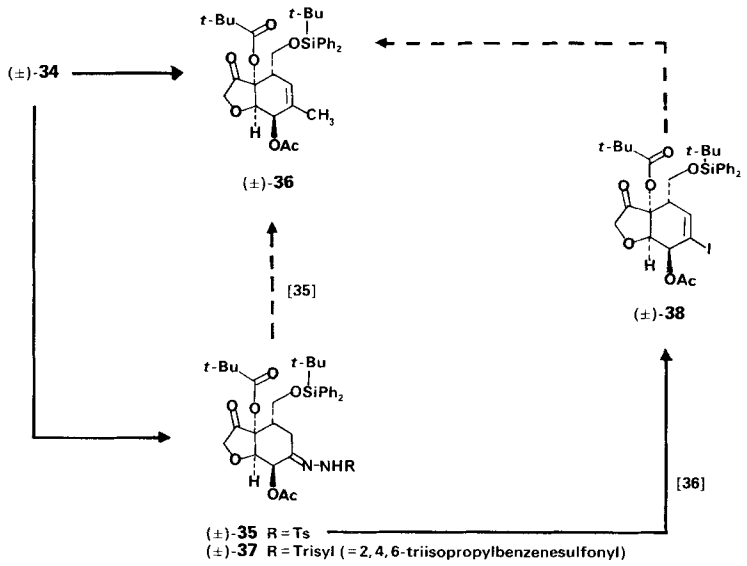
Scheme 9



the (t-Bu)Me_2Si group of (±)-**33**. Under these reaction conditions, the free alcohol group cyclized intramolecularly onto the enone portion and gave the desired bicyclic system as a 6:1 mixture of epimers at C(7) in 88% yield. The major 7β-epimer (±)-**34** could be crystallized and, based on (±)-**33** consumed, was obtained in 76% isolated yield. In contrast to a recently published new spiroacetalization method by *Danishefsky* and *Pearson* [31], where Al_2O_3 was used as catalyst, this cyclization clearly requires an acid catalyst. The reaction proceeds over a period of 16 h at room temperature.

7. Final Transformations. – It was our plan to convert bicyclic diketone (±)-**34** into the monoketone (±)-**36** *(Scheme 10)*. Since it was known from similar compounds that five-membered ring ketones bearing a tertiary pivaloyl group are very hindered, we hoped to use this steric hindrance at C(3) for a selective transformation of the C(6)=O group. Attempts to add C-nucleophiles to the ketone (±)-**34** were either not selective or led to complete decomposition. Selective olefination with the '*Grubbs* reagent' [33] gave only very little (±)-**36** and was, therefore, not of synthetic use. It was found that (±)-**34** was very succeptible to *retro-Michael* reaction. Removal of the pivaloyl and Ac groups was only possible by using NH_3(gas) in dry THF. An important step forward was achieved

Scheme 10



through treatment of diketone (±)-**34** with tosylhydrazine in THF with $MgSO_4$ as H_2O scavenger. This led very selectively to only the C(6) tosylhydrazone (±)-**35** (77%). The IR spectrum clearly indicates that the five-membered ring ketone remained unchanged (1765 cm^{-1}), whereas the six-membered-ring ketone at C(6) formed the tosylhydrazone. Similarly, hydrazone (±)-**37** was obtained in 55% isolated yield.

8. Outlook. – The selective transformation of C(6)=O of diketone (±)-**34** should now allow the final transformation of the tosylhydrazone (±)-**35** into the olefin (±)-**36** under either *Shapiro* conditions [34] [35] or by a procedure of *Barton et al.* [36]. The latter process will give rise to the vinyl iodide (±)-**38**, which can then be transformed by known procedures into (±)-**36** *(Scheme 10)*.

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Experimental Part

General. Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Benzene, pyridine, hexane, oxalyl chloride, $(i\text{-}Pr)_2NEt$ (*Hünig's* base), and CH_2Cl_2 were distilled from powdered CaH_2. DMSO, DMF, and HMPT were vacuum-destilled from powdered CaH_2 and stored over a mixture of 3-Å and 4-Å sieves. Pentane was distilled from Na under Ar. Et_2O, THF, Et_3N, and $(i\text{-}Pr)_2NEt$ were distilled under Ar from Na with sodium benzophenone ketyl as indicator. MeOH was destilled from MeONa and methyl benzoate. MeCN was dried over a mixture of 3-Å and 4-Å sieves. All other reactants were 'reagent grade' unless described otherwise. Et_2O refers to anh. Et_2O (*Malinckrodt* and *Baker*), 'petroleum ether' refers to the 'analyzed reagent' grade hydrocarbon fraction (b.p. 35–60°; *J. T. Baker & Co.*, Philipsburg, NJ). Reported temp. were measured externally. Syringes and reaction flasks were dried at least 12 h in an oven (120–140°) and cooled in a dessicator over anh. $CaSO_4$ prior to use. Anal. TLC: 2.5 × 10 cm precoated TLC plates, SiO_2 *60 F-254*, layer thickness 0.25 mm (*E. Merck & Co.*, Darmstadt, Germany). Columns for chromatography: silica gel *60* (70–230 mesh ASTM). Flash chromatography: *E. Merck* SiO_2 *60* (230–400 mesh ASTM) according to [38]. M.p.: *Hoover* capillary melting point apparatus; uncorrected. $[\alpha]_D$: 1-dm cells of 1-ml capacity, *Jasco* model *DIP-181* polarimeter; $CHCl_3$ was filtered through neutral Al_2O_3 (act. 1) immediately prior to use. IR-Spectra: *Perkin-Elmer 1310* IR spectrometer. ^{1}H-NMR spectra: *Varian EM-390* and *Jeol-GX 400* spectrometer, except where '500 MHz' denotes spectra recorded on a *Bruker WM-500* spectrometer (Southern California Regional NMR facility, Caltech, Pasadena, Ca); chemical shifts in ppm relative to TMS (δ = 0.0 ppm) as an internal standard. ^{13}C-NMR spectra: *Jeol-GX 400* spectrometer. Elemental combustion analysis were performed by *Spang Microanalytical Laboratory*, Eagle Harbor, MI.

*Hemicalcium 3,4-*O*-Isopropylidene-*L*-threonate* (**2**). In a 1.5-l flask was placed 40.0 g of $CaCO_3$, 250 ml of H_2O and 43.2 g (0.2 mol) of *5,6-isopropylidene-*L*-ascorbic acid* (**1**). During the addition of 80 ml of 30% H_2O_2 soln., the temp. was kept below 55°. The mixture was stirred for an additional 3 h at r.t. After filtration, 250 ml of MeCN and 500 ml of acetone were added, and the product was allowed to crystallize in the freezer in two crops affording 31.6 g (81%) of **2** as white crystals; m.p. 257–261° (dec.). $[\alpha]_D$ = +24° (*c* = 1.5, H_2O) (*cf.* [10]). IR (KBr): 3320*s*, 2950*w*, 1570*s*, 1355*m*, 1200*m*, 1050*s*, 835*w*, 780*w*. ^{1}H-NMR ((D$_6$)DMSO, 90 MHz): 4.25–3.55 (*m*, H–C(2), H–C(3), H–C(4)); 3.34 (br. *m*, OH, H_2O); 1.32, 1.25 (2*s*, 2 CH_3).

*Pyridinium 3,4-*O*-Isopropylidene-2-*O*-pivaloyl-*L*-threonate* (**3**). To a stirred soln. of 10.0 g (46.5 mmol) of **2** and 0.5 g of Me_2NPy in 50 ml of pyridine/CH_2Cl_2 1:1 was added 8.41 g (1.5 equiv.) of trimethylacetyl chloride in 20 ml of CH_2Cl_2 within 30 min at 0°. The mixture was stirred for 1 h at 0° and for 24 h at r.t., followed by addition of 20 ml of 10% NaH_2PO_4 soln. The aq. layer was extracted twice with 50 ml of CH_2Cl_2, the combined org. fraction dried ($MgSO_4$) and evaporated. After addition of petroleum ether/Et_2O 4:1, the product crystallized in the freezer within 3 d: 12.9 g (81.4%) of **3**; m.p. 60–61°. $[\alpha]_D$ = 21.6° (*c* = 3.4, $CHCl_3$). IR ($CHCl_3$): 2975*m*, 2925*m*, 1720*s*, 1470*w*, 1365*m*, 1145*s*, 1060*s*, 840*w*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 14.25 (*s*, NH); 8.75–8.55, 7.95–7.65, 7.5–7.2 (3*m*, 5 arom. H); 5.12 (*d*, *J* = 4.5, H–C(2)); 4.75–4.55 (*m*, H–C(3)); 4.2–3.8 (*m*, H–C(4)); 1.47, 1.37 (2*s*, 2 CH_3); 1.30 (*s*, $(CH_3)_3CO_2$).

*Benzyl 3,4-*O*-Isopropylidene-2-*O*-pivaloyl-*L*-threonate* (**4**). To a stirred soln. of 3.0 g (8.8 mmol) of **3**, 1.15 g (1.2 equiv.) of benzyl alcohol, and 30 mg of Me_2NPy in 30 ml of dry CH_2Cl_2 was added 2.0 g (1.1 equiv.) of DCC in 10 ml of CH_2Cl_2 at 0°. The mixture was stirred for 1 h at 0° and for 1 h at r.t. Then, 20 ml of H_2O and 30 ml of CH_2Cl_2 were added. The org. layer was washed twice with sat. $NaHCO_3$ soln., sat. brine, and dried ($MgSO_4$), and evaporated. Chromatography on 100 g of SiO_2 with petroleum ether/Et_2O 5:1 gave, after crystallization, 2.76 g (90%) of **4** as colourless crystals; m.p. 76.5–77.0°. $[\alpha]_D$ = +35.6° (*c* = 2.2, $CHCl_3$). IR ($CHCl_3$): 2950*m*, 2910*w*, 1720*s*, 1465*w*, 1445*w*, 1360*m*, 1135*s*, 1065*s*, 830*w*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.33 (*s*, 5 arom. H); 5.18 (*s*, COOCH_2Ph); 5.10 (*d*, *J* = 4.5, H–C(2)); 4.75–4.45 (*m*, H–C(3)); 4.15–3.75 (*m*, 2 H–C(4)); 1.43, 1.33 (2*s*, 2 CH_3); 1.25 (*s*, $(CH_3)_3CCO_2$). Anal. calc. for $C_{19}H_{26}O_6$: C 65.12, H 7.48; found: C 65.05, H 7.51.

*3,4-*O*-Isopropylidene-2-*O*-pivaloyl-*L*-threonyl Chloride* (**5**). To a stirred soln. of 5.8 ml (66.3 mmol) of oxalyl chloride in 30 ml of dry THF was slowly added 15.0 g (44.2 mmol) of **3** in 30 ml of dry THF at −20°. The mixture was stirred for 1 h at −20° and allowed to warm up to r.t. After filtration and removal of the solvents, addition of 20 ml of Et_2O, stirring at r.t. for 15 min, filtration, and removal of solvents, the remaining oil was dried under reduced pressure, where it crystallized: 11.5 g (93%) of **5** as colourless crystals; m.p. 45–47°. IR ($CHCl_3$): 2960*m*, 1780*s*, 1725*s*, 1700*s*, 1360*m*, 1135*s*, 1065*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 5.20 (*d*, *J* = 6, H–C(2)); 4.9–4.65 (*m*, H–C(3)); 4.25–3.75 (*m*, 2 H–C(4)); 1.47, 1.34 (2*s*, 2 CH_3); 1.30 (*s*, $(CH_3)_3CO_2$).

*1-Deoxy-4,5-*O*-isopropylidene-2-*O*-pivaloyl-*L*-threo-2-pentulose* (**6**). To a stirred soln. of 10.53 g (33.5 mmol) of **5** and 9.0 g (50.3 mmol) of Me_4Sn in 40 ml of dry HMPT was added 60 mg of benzyl(chloro)-bis(triphenylphosphine)palladium(II). The mixture was stirred at r.t. under a CO atmosphere, till blackening

occurred (4 h). After addition of 100 ml of Et_2O/petroleum ether 1:1 and 50 ml of H_2O, drying of the org. phase ($MgSO_4$), and evaporation, the remaining oil was chromatographed on 300 g of SiO_2 with petroleum ether/Et_2O 4:1 affording, after drying under reduced pressure, 7.55 g (87%) of **6** as colourless crystals; m.p. 42–43°. $[\alpha]_D$ = +41.9° (*c* = 1.6, $CHCl_3$). IR ($CHCl_3$): 2965*w*, 2915*w*, 1720*s*, 1710*s*, 1468*w*, 1365*m*, 1140*s*, 1065*m*, 910*w*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 5.00 (*d*, *J* = 3, H–C(3)); 4.65–4.4 (*m*, *J* = 3, H–C(4)); 4.2–3.65 (*m*, 2 H–C(5)); 2.17 (*s*, $COCH_3$); 1.43, 1.33 (2*s*, 2 CH_3)); 1.30 (*s*, $(CH_3)_3CCO_2$). Anal. calc. for $C_{13}H_{22}O_5$: C 60.46, H 8.59; found: C 60.50, H 8.61.

*(1R,2S,5R)-*p*-Menth-3-yl 3,4-Isopropylidene-2-*O*-pivaloyl-*L*-threonate* (**7**). To a stirred soln. of 1.5 g (4.42 mmol) of **3**, 1.04 g (1.5 equiv.) of (–)-*p*-menthol, and 20 mg of Me_2NPy in 15 ml of dry CH_2Cl_2 was added 1.0 g (1.1 equiv.) of DCC in 3 ml of CH_2Cl_2 at 0°. The mixture was stirred for 1 h at 0° and for 12 h at r.t. After addition of 15 ml of Et_2O, filtration, and evaporation 10 ml of H_2O and 30 ml of CH_2Cl_2 were added. The org. layer was washed twice with sat. $NaHCO_3$ soln., dried ($MgSO_4$) and evaporated. Chromatography on SiO_2 gave, after recrystallization from Et_2O/petroleum ether 1.37 g (78%) of **7** as colourless crystals; m.p. 86–88°. $[\alpha]_D$ = –8,8° (*c* = 2.0, $CHCl_3$). IR ($CHCl_3$): 2935*m*, 2900*m*, 2840*w*, 1740*m*, 1710*s*, 1440*w*, 1360*m*, 1280*m*, 1140*s*, 1060*m*, 840*w*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 5.04 (*d*, *J* = 4.5, H–C(2)); 4.9–4.45 (*m*, 2 H); 4.15–3.7 (*m*, 2 H); 2.2–0.55 (*m*, 18 H); 1.43, 1.33 (2*s*, 2 CH_3); 1.27 (*s*, $(CH_3)_3CCO_2$). Anal. calc. for $C_{22}H_{38}O_6$: C 66.30, H 9.61; found: C 66.33, H 9.74.

*Benzyl 4-*O*-[(*tert*-Butyl)diphenylsilyl]-2-*O*-pivaloyl-*L*-threonate* (**8**). To a stirred soln. of 2.2 g (6.28 mmol) of **4** in 30 ml of THF/H_2O 3:1 was added 400 mg of PPTS. After the mixture was stirred for 70 h at 60°, it was quenched by addition of 10 ml of H_2O and 20 ml of CH_2Cl_2, followed by extraction of the aq. layer twice with 20 ml of CH_2Cl_2. The combined org. fractions were dried ($MgSO_4$) and evaporated, and the remaining oil dried under vacuum for 3 h. The crude oil was dissolved in 10 ml of CH_2Cl_2, 1 ml of pyridine and 40 mg of Me_2NPy, to which was added 2.24 g (8.16 mmol) of (*t*-Bu)Ph_2SiCl at 0°. After the mixture was stirred for 2 days at r.t., it was quenched with 5 ml of 1N HCl. The aq. layer was extracted with CH_2Cl_2, the combined org. fractions dried ($MgSO_4$), and evaporated. Chromatography on 100 g of SiO_2 with petroleum ether/Et_2O 5:2 afforded 2.83 g (82%) of **8** as a colourless oil. $[\alpha]_D$ = +7.5° (*c* = 5, $CHCl_3$). IR ($CHCl_3$): 3560*w*, 2935*m*, 2910*m*, 1720*s*, 1450*w*, 1280*m*, 1135*s*, 1100*s*, 900*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.15 (*m*, 15 arom. H); 5.30 (*d*, *J* = 3.0, H–C(2)); 5.17, 5.13 (2*s*, $COOCH_2Ph$); 4.4–4.05 (*m*, H–C(3)); 3.85–3.35 (*m*, 2 H–C(4)); 2.28 (br. *d*, *J* = 6.0, OH); 1.17, 1.05 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{32}H_{40}O_6Si$: C 70.04, H 7.35; found: C 70.06, H 7.38.

*5-*O*-[(*tert*-Butyl)diphenylsilyl-3-*O*-pivaloyl-1-deoxy-*L*-*threo*-2-pentulose* (**9**). To a stirred soln. of 6.95 g (26.9 mmol) of **6** in 100 ml THF/H_2O 3:1 was added 1.39 g of PPTS. The mixture was stirred for 70 h at 60°, followed by addition of 15 ml of H_2O and 50 ml of CH_2Cl_2. The aq. layer was extracted twice with 50 ml of CH_2Cl_2, the combined org. fractions were dried ($MgSO_4$) and evaporated. The remaining colourless oil was dried 3 h under reduced pressure. To a stirred soln. of 5.87 g (26.9 mmol) of crude oil, 3 ml of pyridine and 250 mg of Me_2NPy in 45 ml of dry CH_2Cl_2 was added 10.0 g (35.1 mmol) of (*t*-Bu)Ph_2SiCl at 0°. After the mixture was stirred for 2 d at r.t., it was quenched with 20 ml of 1N HCl. The aq. layer was extracted twice with 30 ml of CH_2Cl_2, the combined org. fractions were dried ($MgSO_4$), and evaporated. Chromatography on 400 g of SiO_2 with petroleum ether/Et_2O afforded 10.32 g (84%) of **9** as a colourless oil. $[\alpha]_D$ = –1.1° (*c* = 6.0, $CHCl_3$). IR ($CHCl_3$): 3580*w*, 2910*m*, 2840*m*, 1710*s*, 1450*m*, 1415*m*, 1350*m*, 1270*m*, 1140*s*, 1100*s*, 900*m*, 820*m*, 690*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.8–7.25 (*m*, 10 arom. H); 5.15 (*d*, *J* = 3.0, H–C(2)); 4.35–4.05 (*m*, *J* = 3.0, H–C(3)); 3.65 (*d*, *J* = 6.0, 2 H–C(4)); 2.35 (br. *d*, *J* = 6.0, OH); 2.17 (*s*, $COCH_3$); 1.20, 1.07 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{26}H_{36}O_5Si$: C 68.38, H 7.95; found: C 68.47, H 7.94.

*(1R,2S,5R)-*p*-Menth-3-yl 2-*O*-Pivaloyl-*L*-threonate* (**10′** ≡ hydrolyzed **7**). To a stirred soln. of 1.1 g (2.76 mmol) of **7** in 12 ml of THF/H_2O 3:1 was added 200 mg of PPTS. The mixture was stirred at 60° for 3 d, followed by addition of 3 ml of H_2O and 10 ml of CH_2Cl_2. The aq. layer was extracted twice with CH_2Cl_2, the combined org. fractions were dried ($MgSO_4$), and evaporated. Crystallization from Et_2O/petroleum ether yielded 890 mg (90%) of **10′** as colourless crystals; m.p. 147–148°. $[\alpha]_D$ = –25.4° (*c* = 2.0, $CHCl_3$). IR ($CHCl_3$): 3560*w*, 3010*w*, 2940*m*, 2905*m*, 2850*m*, 1720*s*, 1440*m*, 1360*m*, 1270*m*, 1140*s*, 975*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 5.10 (*d*, *J* = 3.5, H–C(2)); 4.9–4.55 (*m*, 1 H); 4.25–4.05 (*m*, 1 H); 3.65 (*d*, *J* = 6.0, 2 H–C(4)); 2.65–2.15 (br. *s*, 2 OH); 2.15–0.6 (*m*, 18 H); 1.27 (*s*, $(CH_3)_3C$). Anal. calc. for $C_{19}H_{34}O_6Si$: C 63.66, H 9.56; found: C 63.86, H 9.65.

*Benzyl 4-*O*-[(*tert*-Butyl)diphenylsilyl]-2-*O*-pivaloyl-3-*O*-methanesulfonyl-*L*-threonate* (**11**). To a stirred soln. of 2.30 g (4.19 mmol) of **8** in 30 ml of CH_2Cl_2 and 1 ml of Et_3N was added 624 mg (1.3 equiv.) of MsCl in 5 ml of CH_2Cl_2 at 0° over 30 min. After the mixture was stirred for 30 min at 0° and for 1 h at r.t., it was quenched with 15 ml of 0.5N HCl. The aq. layer was extracted with CH_2Cl_2, the combined org. fractions were dried ($MgSO_4$), and evaporated, and the remaining oil chromatographed on 110 g of SiO_2 with petroleum ether/Et_2O 5:2 affording 2.52 g (96%) of **11** as a colourless oil. $[\alpha]_D$ = +6.2° (*c* = 6.4, $CHCl_3$). IR ($CHCl_3$): 2925*m*, 2840*w*, 1725*s*, 1350*m*, 1175*m*, 1130*m*, 1100*s*, 918*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.1 (*m*, 15 arom, H); 5.50 (*d*, *J* = 3.0, H–C(2)); 5.35–5.0

(*m*, H–C(3)); 5.18 (*s*, COOCH_2Ph); 4.05–3.55 (*m*, 2 H–C(4)); 2.75 (*s*, CH_3SO_2); 1.20, 1.03 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{33}H_{42}O_8SSi$: C 63.23, H 6.75; found: C 63.27, H 6.78.

*5-O-[(*tert*-Butyl)diphenylsilyl]-1-deoxy-4-O-methanesulfonyl-3-O-pivaloyl-*L*-threo-pentulose* (**12**). To a soln. of 2.4 g (5.26 mmol) of **9**, 1.1 g (1.1 equiv.) of Et_3N in 20 ml of CH_2Cl_2 was added 785 mg (1.3 equiv.) of MsCl in 5 ml of CH_2Cl_2 at 0°. After the mixture was stirred for 30 min at 0° and for 30 min at r.t., it was quenched with 10 ml of sat. $NaHCO_3$ soln. The org. layer was washed twice with sat. brine, dried ($MgSO_4$), and evaporated. The remaining oil was chromatographed on 120 g of SiO_2 with petroleum ether/Et_2O 2:1 affording 2.72 g (97%) of **12** as a colourless oil. $[\alpha]_D$ = +6.9° (*c* = 7.0, $CHCl_3$). IR ($CHCl_3$): 2905*w*, 1710*s*, 1350*s*, 1165*m*, 1140*s*, 1100*s*, 900*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.3 (*m*, 10 arom. H); 5.42 (*d*, *J* = 3.0, H–C(2)); 5.25–4.95 (*m*, *J* = 3.0, H–C(3)); 4.05–3.4 (*m*, 2 H–C(4)); 2.92 (*s*, CH_3SO_2); 2.22 (*s*, $COCH_3$); 1.20, 1.07 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{27}H_{38}O_7SSi$: C 60.64, H 7.16; found: C 60.70, H 7.28.

Dimethyl 2-Acetoxyfumarate (**19**) [17]. To a stirred soln. of 1.42 g (10.0 mmol) of dimethyl acetylendicarboxylate in 10 ml of AcOH was added 50 mg of Ag_2CO_3 in small portions at 80°. The mixture was stirred for 4 h at 80°. After evaporation, chromatography on SiO_2 with petroleum ether/Et_2O 2:1 afforded 880 mg (44%) of **19** as a colourless oil. IR ($CHCl_3$): 2920*w*, 1760*m*, 1705*s*, 1640*w*, 1420*m*, 1265*s*, 1150*s*, 1050*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 6.63 (*s*, H–C(3)); 3.82, 3.73 (2*s*, 2 $COOCH_3$); 2.28 (*s*, CH_3CO_2). ^{13}C-NMR ($CDCl_3$, 80 MHz): 167.7, 163.0 (2*s*, 2 $COOCH_3$); 161.5 (*s*, CH_3CO_2); 146.5 (*s*, C(2)); 116.8 (*d*, C(3)); 53.1, 52.0 (2*q*, 2 $COOCH_3$); 20.3 (*q*, CH_3CO_2). Anal. calc. for $C_8H_{10}O_6$: C 47.53, H 4.99; found: C 47.48, H 5.07.

*Benzyl (Z)-4-[(*tert*-Butyl)diphenylsiloxy]-2-pivaloyl-2-butenoate* (**14**). To a stirred soln. of 416 mg (0.66 mmol) of **11** in 10 ml of dry THF was added 120 mg (1.2 equiv.) DBU in 5 ml of THF at 0°. After the reaction was stirred for 1 h at 0° and for 30 min at r.t., it was quenched with 15 ml of 0.1N HCl and 15 ml of Et_2O. The combined org. fractions were dried ($MgSO_4$), the solvents removed, and the remaining oil was chromatographed on 40 g of SiO_2 with petroleum ether/Et_2O 7:1 affording 325 mg (93%) of **14** as a colourless oil. IR ($CHCl_3$): 2940*m*, 2910*m*, 2840*m*, 1735*s*, 1710*s*, 1450*w*, 1270*m*, 1100*s*, 900*w*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.1 (*m*, 15 arom. H); 6.67 (*t*, *J* = 6.0, H–C(3)); 5.15 (*s*, COOCH_2Ph); 4.23 (*d*, *J* = 6.0, 2 H–C(4)); 1.07, 1.02 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{32}H_{38}O_5Si$: C 72.42, H 7.22; found: C 72.31, H 7.14.

*1-Acetyl-(Z)-3-[(*tert*-butyl)diphenylsiloxy]prop-1-enyl Pivalate* (**15**). To a stirred soln. of 6.0 g (11.2 mmol) of **12** in 50 ml of dry THF was added, within 1 h, 2.05 g (1.2 equiv.) of DBU in 10 ml of THF at –20°. After the mixture was stirred for 1 h at –20°, it was allowed to gradually warm up to r.t., where it was stirred for an additional 30 min, followed by addition of 25 ml of 0.1N HCl and 30 ml of Et_2O. The aq. layer was extracted twice with 30 ml of Et_2O, the combined org. fractions were dried ($MgSO_4$), and evaporated, and the remaining oil was chromatographed on 200 g of SiO_2 with petroleum ether/Et_2O 8:1 affording 4.43 g (90%) of **15** as a colourless oil, which crystallized upon drying under reduced pressure; m.p. 32–34°. IR ($CHCl_3$): 2910*m*, 2840*w*, 1735*s*, 1675*s*, 1410*w*, 1350*m*, 1100*s*, 900*w*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.1 (*m*, 10 arom. H); 6.48 (*t*, *J* = 6.0, H–C(2)); 4.30 (*d*, *J* = 6.0, 2 H–C(3)); 2.23 (*s*, CH_3CO); 1.13, 1.07 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{26}H_{34}O_4Si$: C 71.19, H 7.81; found: C 71.00, H 7.78.

*(1*R*,2*S*,5*R*)-*p*-Menth-3-yl 4-[(*tert*-Butyl)diphenylsiloxy]-2-pivaloyl-2-butenoate* (**16**). To a stirred soln. of 700 mg (1.95 mmol) of **10'**, 400 mg of pyridine, 30 mg of Me_2NPy in 6 ml of CH_2Cl_2 was added 832 mg (1.5 equiv.) of (*t*-Bu)Ph_2SiCl. The mixture was stirred for 30 min at 0° and for 36 h at r.t., followed by addition of 5 ml of 1N HCl. The aq. layer was extracted twice with 10 ml of CH_2Cl_2, the combined org. fractions were dried ($MgSO_4$), and evaporated, and the remaining oil chromatographed on SiO_2 affording 722 mg (81%) of **10**, which was immediately dissolved in 6 ml of CH_2Cl_2. After addition of 0.5 ml of Et_3N and 272 mg (1.5 equiv.) of MsCl at 0°, the mixture was stirred for 1 h at 0°, followed by addition of 5 ml of 1N HCl. The aq. layer was extracted twice with 10 ml of CH_2Cl_2, the combined org. fractions were dried ($MgSO_4$) and evaporated. The remaining oil was dried under vacuum for 2 h affording 786 mg (93%) of **13**, which was dissolved in 6 ml of THF. After addition of 362 mg (1.5 equiv.) of DBU at 0°, the mixture was stirred for 2 h at 0° and for 1 h at r.t., followed by addition of 5 ml of 1N HCl and 10 ml of Et_2O. The aq. layer was extracted twice with 10 ml of Et_2O, the combined org. layers were dried ($MgSO_4$) and evaporated. The remaining oil was chromatographed on SiO_2 with petroleum ether/Et_2O 6:1 affording 568 mg (88%) of **16** as a colourless oil. $[\alpha]_D$ = –33.0° (*c* = 8.0, $CHCl_3$). IR ($CHCl_3$): 3040*w*, 2940*s*, 2840*s*, 1740*s*, 1710*s*, 1660*w*, 1450*w*, 1355*w*, 1300*m*, 1275*m*, 1235*m*, 1105*s*, 1020*m*, 905*m*, 820*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.8–7.15 (*m*, 10 arom. H); 6.60 (*t*, *J* = 6.0, H–C(3)); 4.85–4.55 (*m*, 1 H); 4.22 (*d*, *J* = 6.0, 2 H–C(4)); 2.15–0.55 (*m*, 18 H); 1.13, 1.04 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{35}H_{50}O_5Si$: C 72.62, H 8.71; found: C 72.76, H 8.68.

*(Z)-1-{1'-[(*tert*-Butyl)dimethylsiloxy]vinyl}-3-[(*tert*-butyl)diphenylsiloxy]prop-1-enyl Pivalate* (**17**). To a stirred soln. of 1.97 g (4.48 mmol) of **15** and 1 ml of Et_3N in 15 ml of THF was added 1.38 ml (1.3 equiv.) of [(*t*-Bu)Me_2Si]OSO_2CF_3 at 0°. After the mixture was stirred for 30 min at 0° and for 2 h at r.t., it was quenched with

15 ml of sat. $NaHCO_3$ soln. and 30 ml of Et_2O. The aq. layer was extracted twice with 30 ml of Et_2O, the combined org. fractions were dried ($MgSO_4$) and evaporated, and the remaining oil was chromatographed on 120 g of SiO_2 with petroleum ether/Et_2O 20:1 affording 2.44 g (98.5%) of **17** as a colourless oil. IR ($CHCl_3$): 2930*s*, 2905*s*, 2840*s*, 1730*s*, 1590*m*, 1450*w*, 1320*w*, 1240*m*, 1100*s*, 1000*s*, 820*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.8–7.15 (*m*, 10 arom. H); 5.98 (*t*, *J* = 6.0, H–C(2)); 4.35, 4.27 (2 br. *s*, 2 H–C(2)); 4.13 (*d*, *J* = 6.0, 2 H–C(3)); 1.10, 1.00, 0.98 (3*s*, 3 $(CH_3)_3C$); 0.18 (s, (*t*-Bu)Me_2Si). Anal. calc. for $C_{32}H_{48}O_4Si_2$: C 69.51, H 8.75; found: C 69.31, H 8.61.

*(Z)-1-{2'-[(*tert*-Butyl)dimethylsiloxy]acetyl}-3-[(*tert*-butyl)diphenylsiloxy]prop-1-enyl Pivalate* (**18**). To a stirred soln. of 1.36 g (2.46 mmol) of **17** in 25 ml of hexane was added over a period of 2 h 765 mg (1.8 equiv.) of *meta*-chloroperbenzoic acid at 0° in 4 portions. After the mixture was stirred for an additional 3 h at 0°, the solid was filtered off, the solvent removed, and the remaining oil chromatographed on 50 g of SiO_2 with petroleum ether/Et_2O 15:1 affording 1.1 g (79%) of **18** as a colourless oil. IR ($CHCl_3$): 2935*s*, 2905*s*, 2840*m*, 1735*s*, 1697*m*, 1450*m*, 1355*w*, 1245*m*, 1100*s*, 830*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.1 (*m*, 10 arom. H); 6.58 (*t*, *J* = 6.0, H–C(2)); 4.45 (*s*, 2 H–C(2')); 4.28 (*d*, *J* = 6.0, 2 H–C(3)); 1.13, 1.05, 0.92 (3*s*, 3 $(CH_3)_3C$); 0.10 (*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{32}H_{48}O_5Si_2$: C 67.56, H 8.51; found: C 67.49, H 8.59.

*(Z)-2-[(*tert*-Butyl)dimethylsiloxy]-1-(methoxymethylidene)prop-2-enyl Acetate* (**24**). To a stirred soln. of 6.0 g (37.9 mmol) of (*Z*)-1-(methoxymethylidene)-2-oxopropyl acetate, 13.3 ml of Et_3N in 60 ml of THF was added 10.45 ml (1.2 equiv.) of [(*t*-Bu)Me_2Si]$OSOCF_3$ at 0°. The mixture was stirred for 1 h at 0° and quenched with 50 ml of sat. $NaHCO_3$ soln. and 50 ml of Et_2O. The org. layer was dried ($MgSO_4$) and evaporated, and the remaining oil was chromatographed on SiO_2 with petroleum ether/Et_2O 4:1 affording 10.1 g (98%) of crude product, which gave, after careful distillation at 140°/10^{-2} Torr, 8.88 g (86%) of **24** as a colourless liquid. IR ($CHCl_3$): 2910*m*, 2840*w*, 1745*s*, 1660*w*, 1585*w*, 1450*w*, 1360*m*, 1290*m*, 1230*s*, 1130*s*, 1110*s*, 890*m*, 820*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 6.43 (*s*, CH_3OCH); 4.23, 4.10 (2*d*, *J* = 2.0, 2 H–C(3)); 3.67 (*s*, CH_3O); 2.18 (*s*, CH_3CO_2); 0.97 (*s*, $(CH_3)_3C$); 0.20 (*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{13}H_{24}O_4Si$: C 57.31, H 8.88; found: C 57.40, H 8.91.

*Dimethyl (±)-(1*RS*,2*SR*,3*SR*)-2-Acetoxy-5-[(*tert*-butyl)dimethylsiloxy]-3-methoxycyclohex-4-en-1,2-dicarboxylate* ((±)-**21**). A soln. of 150 mg (0.74 mmol) of **19**, 500 mg (2.33 mmol) of *3-[(*tert*-butyl)dimethylsiloxy]-1-methoxy-1,3-butadiene* (**20**) and 1 crystal of pyrogallol in 3 ml of dry benzene was sealed under reduced pressure and heated for 2 d at 110°. Solvents and excess diene were distilled off, and the residue was chromatographed on 20 g of SiO_2 with petroleum ether/Et_2O 3:1 affording 240 mg (78%) of pure (±)-**21** as a colourless oil. IR ($CHCl_3$): 2940*m*, 2840*w*, 1720*s*, 1655*w*, 1420*w*, 1360*m*, 1245*s*, 1180*s*, 1080*s*, 890*m*, 830*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 4.97 (*d*, *J* = 4.5, H–C(4)); 4.08 (*d*, *J* = 4.5, H–C(3)); 3.73, 3.67 (2*s*, 2 $COOCH_3$); 3.65–3.45 (*m*, H–C(1)); 3.33 (*s*, CH_3O); 2.24 (*d*, *J* = 7.5, 2 H–C(6)); 2.05 (*s*, CH_3CO_2); 0.93 (*s*, $(CH_3)_3C$); 0.20 (*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{19}H_{32}O_8Si$: C 54.79, H 7.74; found: C 54.89, H 7.52.

*Dimethyl (±)-(1*RS*,2*SR*,3*SR*)-2-Acetoxy-3-methoxy-5-oxocyclohexane-1,2-dicarboxylate* ((±)-**23**). To a stirred soln. of 150 mg (0.36 mmol) of (±)-**21** in 1.5 ml of THF was added 0.3 ml of 1N HCl. The mixture was stirred for 3 h at r.t., followed by addition of 2 ml sat. of $NaHCO_3$ soln. and 5 ml of Et_2O. The org. layer was dried ($MgSO_4$) and evaporated, and the remaining oil dried under reduced pressure, where it crystallized. Recrystallization from petroleum ether/Et_2O 3:1 yielded 90 mg (83%) of (±)-**23**; m.p. 97–98°. IR ($CHCl_3$): 2940*w*, 1720*s*, 1425*m*, 1355*m*, 1200*s*, 1090*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 4.25–4.05 (*m*, H_{ax}–C(3)); 4.0–3.8 (*m*, H_{ax}–C(1)); 3.73, 3.63 (2*s*, 2 $COOCH_3$); 3.35 (*s*, CH_3O); 2.95–2.35 (*m*, 2 H–C(4), 2 H–C(6)); 2.10 (*s*, CH_3CO_2). Anal. calc. for $C_{13}H_{18}O_8$: C 51.66, H 6.00; found: C 51.62, H 5.94.

*Dimethyl (±)-(1*RS*,2*SR*,3*SR*)-2,4-Diacetoxy-5-[(*tert*-butyl)dimethylsiloxy]-3-methoxycyclohex-4-en-1,6-dicarboxylate* ((±)-**25**). A soln. of 100 mg (0.49 mmol) of **19**, 674 mg (5.0 equiv.) of **24**, and 1 crystal of pyrogallol in 0.5 ml of benzene was heated for 2 d in a sealed tube under reduced pressure. The solvent and excess diene were distilled off. The remaining oil was chromatographed on 15 g of SiO_2 with petroleum ether/Et_2O 2:1 affording 196 mg (83%) of (±)-**25** as a colourless oil. IR ($CHCl_3$): 2940*m*, 2910*w*, 2840*w*, 1740*s*, 1700*m*, 1430*w*, 1360*m*, 1190*s*, 1115*m*, 1080*m*, 900*m*, 840*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 4.23 (*s*, H–C(3)); 3.73, 3.68 (2*s*, 2 $COOCH_3$); 3.7–3.45 (*m*, hidden *AB*, H–C(1)); 2.52 (*t*, *J* = 8.0, 2 H–C(6)); 2.13, 2.08 (2*s*, 2 CH_3CO_2); 0.93 (*s*, $(CH_3)_3C$); 0.17 (*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{21}H_{34}O_{10}Si$: C 53.15, H 7.22; found: C 53.07, H 7.15.

*(±)-(1*RS*,2*RS*,6*SR*)-4-[(*tert*-Butyl)dimethylsiloxy]-6-{[(*tert*-butyl)diphenylsiloxy]methyl}-2-methoxy-1-pivaloyloxycyclohex-3-en-1-carboxylate* ((±)-**26**). A soln. of 202 mg (0.38 mmol) of **14**, 408 mg (5 equiv.) of **20** and 1 crystal of pyrogallol in 1 ml of benzene were heated for 4 days at 150° in a sealed tube under vacuum. The solvent and excess diene were distilled off under vacuum, and the remaining oil was chromatographed twice on SiO_2 with petroleum ether/Et_2O 10:1 affording 235 mg (83%) of (±)-**26** as a colourless oil. IR ($CHCl_3$): 2910*m*, 2840*m*, 1735*s*, 1720*s*, 1655*m*, 1440*m*, 1360*m*, 1245*m*, 1145*s*, 1100*s*, 1080*s*, 900*m*, 830*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.2 (*m*, 15 arom. H); 5.11, 5.05 (2*d*, *J* = 1.3, $COOCH_2Ph$); 4.98 (*d*, *J* = 5.0, H–C(3)); 4.44, 4.43 (*dd*, *J* = 10, 4, H–C(6)); 3.90

(*d*, *J* = 5.0, H–C(2)); 3.2 (*s*, CH_3O); 3.2–3.1, 3.05–2.95 (2*m*, 2 H); 2.71, 2.70 (*dd*, *J* = 18, 5, H_{eq}–C(5)); 1.76, 1.73 (*dd*, *J* = 18, 10, H_{ax}–C(5)); 1.04, 0.96, 0.93 (3*s*, 3 $(CH_3)_3C$); 0.18, 0.16 (2*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{43}H_{60}O_7Si_2$: C 69.31, H 8.12; found: C 69.31, H 8.16.

*Benzyl (±)-(1*RS*,2*RS*,6*SR*)-3-Acetoxy-4-[(*tert*-butyl)dimethylsiloxy]-6-{[(*tert*-butyl)diphenylsiloxy]-methyl}-2-methoxy-1-pivaloyloxy-cyclohex-3-en-1-carboxylate* ((±)-**27**). A soln. of 241 mg (0.45 mmol) of **14**, 618 mg (5 equiv.) of **24** and 1 crystal of pyrogallol in 1 ml of benzene were heated for 90 h at 150° in a sealed tube under vacuum. The solvent and excess diene were distilled off under vacuum, and the remaining oil was chromatographed on 50 g of SiO_2 with petroleum ether/Et_2O 4:1 affording 275 mg (75%) of (±)-**27** as a colourless oil. IR ($CHCl_3$): 2915*m*, 2840*w*, 1730*s*, 1700*m*, 1450*w*, 1355*m*, 1145*m*, 1075*s*, 900*m*, 835*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.15 (*m*, 15 arom. H); 5.05 (*s*, COOCH_2Ph); 4.43 (br. *d*, *J* = 6.0, H–C(6)); 3.93 (*s*, H–C(2)); 3.23 (*s*, CH_3O); 3.2–2.65 (*m*, 3 H); 2.10 (*s*, CH_3CO_2); 1.95–1.75 (*m*, H_{eq}–C(5)); 1.03, 1.00, 0.93 (3*s*, 3 $(CH_3)_3C$); 0.17, 0.13 (2*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{45}H_{62}O_9Si_2$: C 67.30, H 7.78; found: C 67.33, H 7.71.

*(±)-(1*RS*,2*RS*,6*SR*)-3-Acetoxy-4-[(*tert*-butyl)dimethylsiloxy]-6-{[(*tert*-butyl)diphenylsiloxy]methyl}-2-methoxycyclohex-3-en-1-yl Pivalate* ((±)-**28**). A mixture of 300 mg (0.68 mmol) of **15**, 1.10 g (6 equiv.) of **24** and 1 crystal of pyrogallol in 1 ml of benzene was heated for 2 d at 145° in a sealed tube under vacuum. The solvent and excess diene were distilled off under vacuum and the remaining oil was chromatographed on 30 g of SiO_2 with petroleum ether/Et_2O 5:1 affording 400 mg (83%) of (±)-**28** as a colourless oil. IR ($CHCl_3$): 2940*m*, 2840*m*, 1740*m*, 1715*s*, 1700*m*, 1450*w*, 1155*s*, 1075*s*, 900*m*, 830*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.15 (*m*, 10 arom. H); 4.2–4.05 (*m*, H–C(6)); 4.06 (*s*, H–C(2)); 3.5–2.6 (*m*, 3 H); 3.33 (*s*, CH_3O); 2.12 (*s*, CH_3CO); 1.98 (*s*, CH_3CO_2); 1.95–1.6 (*m*, H–C(5)); 1.08, 1.03, 0.92 (3*s*, 3 $(CH_3)_3C$); 0.17, 0.13 (2*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{39}H_{58}O_8Si_2$: C 65.88, H 8.22; found: 65.71, H 8.20.

*(±)-(1*RS*,2*RS*,6*SR*)-3-Acetoxy-4-[(*tert*-butyl)dimethylsiloxy]-1-{[(*tert*-butyl)dimethylsiloxy]acetyl}-6-{[(*tert*-butyl)diphenylsiloxy]methyl}-2-methoxycyclohex-3-en-1-yl Pivalate* ((±)-**29**). A soln. of 938 mg (1.65 mmol) of **18**, 2.70 g (6 equiv.) of **24** and 1 crystal of pyrogallol in 3 ml of benzene was heated for 2 d at 120° in a sealed tube under vacuum. The solvent and excess diene were distilled off under vacuum and the remaining oil was chromatographed on 100 g of SiO_2 with petroleum ether/Et_2O 10:1 affording 154.5 mg (16.5%) of recovered **18** and 860 mg (74%) of (±)-**28** as a colourless oil. IR ($CHCl_3$): 2949*s*, 2920*s*, 1740*s*, 1715*s*, 1700*m*, 1360*m*, 1250*m*, 1145*s*, 1105*s*, 1080*s*, 905*m*, 835*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.7–7.3 (*m*, 10 arom. H); 4.45–4.25 (*AB*, 2 H); 4.33 (*s*, H–C(2)); 4.05–3.95 (*m*, H–C(6)); 3.38 (*s*, CH_3O); 3.25–3.1, 3.0–2.9 (2*m*, 2 H); 2.05–1.95 (*m*, H–C(5)); 1.07, 1.03, 0.91, 0.88 (4*s*, 4 $(CH_3)_3C$); 0.17, 0.12, 0.04 (3*s*, 2 (*t*-Bu)Me_2Si). Anal. calc. for $C_{45}H_{72}O_9Si_2$: C 64.24, H 8.63; found: C 63.92, H 8.60.

*Dimethyl (±)-(1*RS*,2*SR*)-2,4-Diacetoxy-5-oxocyclohex-3-en-1,2-dicarboxylate* ((±)-**30**). To a stirred soln. of 100 mg (0.21 mmol) of (±)-**25** in 1 ml of dry CH_2Cl_2 was added 39 µl (1.5 equiv.) of $BF_3 \cdot Et_2O$ at −78°. The mixture was stirred for 2 h at −78° and allowed to warm up to 0°, where it was quenched with 2 ml of 10% NH_4Cl soln. and 5 ml of Et_2O. The aq. layer was extracted twice with 5 ml of Et_2O, the combined org. fractions were dried ($MgSO_4$) and evaporated. Crystallization from petroleum ether/Et_2O 1:1 afforded 62 mg (90%) of (±)-**30**; m.p. 140–144° (dec.). IR ($CHCl_3$): 2940*w*, 1735*s*, 1695*s*, 1425*w*, 1360*m*, 1180*m*, 1110*m*, 1020*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 6.78 (*s*, H–C(3)); 3.80, 3.68 (2*s*, 2 $COOCH_3$); 3.55–3.35 (*m*, H–C(1)); 3.1–2.9 (*dd*, 2 H–C(6)); 2.22, 2.10 (2*s*, 2 CH_3CO_2).

*Benzyl (±)-(1*RS*,6*SR*)-3-Acetoxy-6-{[(*tert*-butyl)diphenylsiloxy]methyl}-4-oxo-1-pivaloyloxycyclohex-2-en-1-carboxylate* ((±)-**31**). To a stirred soln. of 150 mg (0.19 mmol) of (±)-**27** in 1 ml of dry CH_2Cl_2 was added 34 µl (1.5 equiv.) $BF_3 \cdot Et_2O$ at −78°. The mixture was stirred for 2 h at −78° and allowed to warm up to 0°, where it was quenched with 2 ml of 10% NH_4Cl soln. and 5 ml of Et_2O. The aq. layer was extracted twice with 5 ml of Et_2O, the combined org. fractions were dried ($MgSO_4$) and the remaining oil chromatographed on 15 g of SiO_2 with petroleum ether/Et_2O 2:1 affording 118 mg (90%) of (±)-**31** as a colourless oil. IR ($CHCl_3$): 3020*w*, 2930*m*, 1750*s*, 1725*s*, 1690*s*, 1450*m*, 1360*m*, 1270*w*, 1135*s*, 1100*s*, 1055*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.05 (*m*, 15 arom. H); 7.00 (*s*, H–C(2)); 5.1–5.0 (*AB*, COOCH_2Ph); 4.0–3.45 (*m*, 2 H); 3.15–2.35 (*m*, 3 H); 2.22 (*s*, CH_3CO_2); 1.05, 1.02 (2*s*, 2 $(CH_3)_3C$).

*(±)-(1*RS*,6*SR*)-3-Acetoxy-1-acetyl-6-{[(*tert*-butyl)diphenylsiloxy]methyl}-4-oxocyclohex-2-en-1-yl Pivalate* ((±)-**32**). To a stirred soln. of 64 mg (0.09 mmol) of (±)-**28** in 1 ml of dry CH_2Cl_2 was added 17 µl (1.5 equiv.) $BF_3 \cdot Et_2O$ at −78°. The mixture was stirred for 2 h at −78° and allowed to gradually warm up to 0°, where it was quenched with 2 ml of 10% NH_4Cl soln. and 5 ml of Et_2O. The aq. layer was extracted twice with 5 ml of Et_2O, the combined org. fractions were dried ($MgSO_4$) and evaporated, and the remaining oil chromatographed on 7 g of SiO_2 with petroleum ether/Et_2O 2:1 affording, after crystallization, from Et_2O/hexane 47 mg (93%) of (±)-**32** as colourless crystals, m.p. 106–110°. IR ($CHCl_3$): 2940*m*, 2915*m*, 2840*w*, 1755*s*, 1690*s*, 1460*w*, 1415*w*, 1360*m*, 1135*s*,

1100*s*, 1090*s*, 900*m*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.75–7.25 (*m*, arom. H); 6.90 (*s*, H–C(3)); 3.95–3.45 (*m*, 2 H–C(6)); 2.23, 2.15 (2*s*, CH_3CO, CH_3CO_2); 1.12, 1.02 (2*s*, 2 $(CH_3)_3C$). Anal. calc. for $C_{32}H_{40}O_7Si$: C 68.06, H 7.14; found: C 67.88, H 7.13.

*(±)-(1*RS*,6*SR*)-3-Acetoxy-1-{[(*tert*-butyl)dimethylsiloxy]acetyl}-6-{[(*tert*-butyl)diphenylsiloxy]methyl}-4-oxocyclohex-2-en-1-yl Pivalate* ((±)-**33**). To a stirred soln. of 378 mg (0.45 mmol) of (±)-**29** in 3 ml of dry CH_2Cl_2 was added 85 µl (1.5 equiv.) $BF_3 \cdot Et_2O$ at −78°. The mixture was stirred for 2 h at −78° and allowed to gradually warm up to 0°, where it was quenched with 4 ml of 10% NH_4Cl soln. and 10 ml of Et_2O. The combined org. fractions were dried ($MgSO_4$) and evaporated, and the remaining oil was chromatographed on 30 g of SiO_2 with petroleum ether/Et_2O 6:1 affording 278 mg (88%) of (±)-**33** as a colourless oil. IR ($CHCl_3$): 2940*s*, 2910*s*, 2840*m*, 1750*m*, 1715*s*, 1690*s*, 1455*m*, 1355*m*, 1245*m*, 1135*s*, 1100*s*, 830*s*. ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.7–7.15 (*m*, 10 arom. H); 6.90 (*s*, H–C(2)); 4.45 (*s*, 2 H); 3.95–3.4, 3.15–2.8, 2.75–1.9 (3*m*, 4 H); 2.20 (2, CH_3CO_2); 1.10, 1.03, 0.90 (3*s*, 3 $(CH_3)_3C$); 0.07 (*s*, (*t*-Bu)Me_2Si). Anal. calc. for $C_{38}H_{54}O_8Si_2$: C 65.67, H 7.83; found: C 65.76, H 7.90.

*(±)-(3a*RS*,4*SR*,7*SR*,7a*RS*)-7-Acetyl-4-{[(*tert*-butyl)diphenylsiloxy]methyl}-2,3,3a,4,5,6,7,7a-octahydro-3,6-dioxobenzo[*b*]furan-3a-yl Pivalate* ((±)-**34**). A soln. of 230 mg (0.33 mmol) of (±)-**33** in THF/1N HCl 3:1 was stirred for 17 h at r.t., followed by addition of 2 ml of H_2O and 10 ml of Et_2O. The org. layer was dried ($MgSO_4$) and evaporated, and the remaining oil was chromatographed on 20 g of SiO_2 with petroleum ether/Et_2O 1:1 affording 165 mg (86%) of a 6:1 mixture of epimers at C(7). Crystallization from petroleum ether/Et_2O 3:1 gave 145 mg (76%) of pure (±)-**34** as white needles; m.p. 134–136°. IR ($CHCl_3$): 2960*m*, 2930*m*, 1775*m*, 1755*s*, 1735*s*, 1430*w*, 1370*w*, 1210*m*, 1150*m*, 1110*s*, 1090*s*, 915*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 7.7–7.35 (*m*, 10 arom. H); 5.39 (*d*, J = 6.0, H–C(7)); 4.49 (*d*, J = 6.0, H–C(8)); 4.31, 4.09 (*AB*, J_{AB} = 17.0, 2 H–C(2)); 4.05–4.0 (*dd*, J = 11.5, 5.0, H_{ax}–C(4)); 3.6–3.55 (*t*, J = 10.0, 1 H); 3.05–2.95 (*dd*, J = 18.5, 7.0, H_{eq}–C(5)); 2.85–2.75 (*m*, 1 H); 2.4–2.3 (*dd*, J = 18.5, 11.5, H_{ax}–C(5)); 2.18 (*s*, CH_3CO_2); 1.03, 1.01 (2*s*, 2 $(CH_3)_3C$). ^{13}C-NMR ($CDCl_3$, 400 MHz): 205.3, 200.1, 176.4, 169.1, 135.0, 132.0, 130.4, 128.5, 81.6, 80.1, 79.0, 70.2, 61.3, 38.9, 38.0, 36.8, 27.8, 27.4, 21.4, 20.1. Anal. calc. for $C_{32}H_{40}O_8Si$: C 66.18, H 6.94; found: C 66.27, H 7.08.

*(±)-(3a*RS*,4*SR*,7*SR*,7a*RS*)-7-Acetyl-4-{[(*tert*-butyl)diphenylsiloxy]methyl}-2,3,3a,4,5,6,7,7a-octahydro-3-oxo-6-(tosylhydrazono)benzo[*b*]furan-3a-yl Pivalate* ((±)-**35**). To a stirred soln. of 48 mg (0.083 mmol) of (±)-**34** in 1 ml of dry THF with 100 mg of $MgSO_4$ was added 46 mg (3 equiv.) of tosylhydrazine. After 24 h at r.t. and evaporation, the residue was chromatographed on 6 g of SiO_2 affording 48 mg (77%) of (±)-**35** as a colourless oil, which crystallized from Et_2O; m.p. 123–125°. IR ($CHCl_3$): 3260*w*, 3020*w*, 2940*w*, 2920*m*, 2840*w*, 1765*s*, 1720*s*, 1590*w*, 1420*w*, 1360*m*, 1255*m*, 1160*s*, 1110*s*, 1080*s*, 900*w*, 690*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 7.8–7.2 (*m*, 14 arom. H); 7.02 (*s*, 1 H); 5.32 (*d*, J = 6.0, H–C(7)); 4.36 (*d*, J = 6.0, H–C(8)); 4.28, 4.02 (*AB*, J_{AB} = 11.5, 2 H–C(2)); 4.15–4.05 (*m*, H–C(4)); 3.65–3.55, 3.5–3.4 (2*m*, 2 H); 2.55–2.4 (*m*, H_{eq}–C(5)); 2.41 (*s*, CH_3); 2.10 (*s*, CH_3CO_2); 1.9–1.75 (*m*, H_{ax}–C(5)); 1.06, 1.02 (2*s*, 2 $(CH_3)_3C$).

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