Stereospecific Synthesis of (−)-β-Turmerone and (−)-Bisacurol

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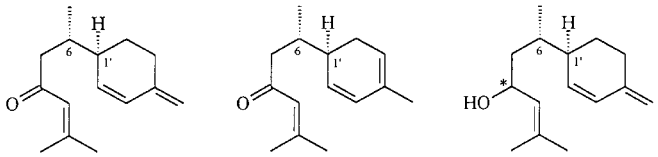
The structure of (+)-β-turmerone ((+)-**1a**), a constituent of the rhizomes of *Curcuma longa* LINN., and *Curcuma xanthorriza*, is established as (1′*R*,6*S*)-2-methyl-6-(4′-methylenecyclohex-2′-en-1′-yl)hept-2-en-4-one by synthesis of its enantiomer (−)-**1a**, and of the corresponding (1′*S*,6*S*)-diastereoisomer (+)-**1b** as well. In a stereospecific seventeen-step procedure, the monoterpene diols **2a** and **2b** of well-established configuration are converted into the target compounds (−)-**1a** and (+)-**1b**, respectively. Moreover, (−)-bisacurol (−)-**3a**(II), the enantiomer of another bisabolane sesquiterpene derived from *Curcuma xanthorriza*, is obtained as a single stereoisomer and shown to be (1′*S*,6*R*)-2-methyl-6-(4′-methylenecyclohex-2′-en-1′-yl)hept-2-en-4-ol, the relative configuration at the remaining OH-substituted chiral center C(4) still being unknown.

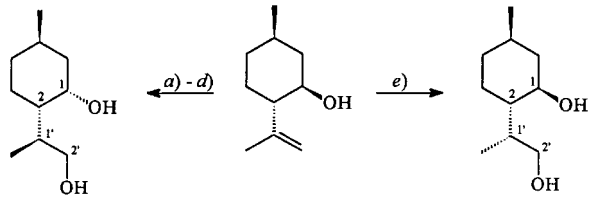
1. Introduction. – In 1982, *Golding* and coworkers [1] first reported the isolation and the constitutional determination of two isomeric turmerones **1a** and **4** from the dried ground rhizomes (also called turmeric) of *Curcuma longa* LINN.; referring to their monoterpene-counterparts β- and α-phellandrene, (+)-**1a** and **4** have been named β- and α-turmerone. In the same year, *Hikino* and coworkers [2] claimed to have discovered a novel sesquiterpene called curlone as an ingredient of the same plant. After comparison of the spectral data and the proposed structures, it became obvious that β-turmerone and curlone are identical. As an additional feature, *Hikino* and coworkers [2] determined the configuration at C(6) as (*S*) by dehydrogenation of (+)-**1a** to the known (*S*)-*ar*-turmerone (*Honwad* and *Rao* [3]). Based on the assumption of a thermodynamically most stable arrangement, the interpretation of ^{1}H-NMR data led to conclusion that C(1′) had (*S*)-configuration, too. In a paper published in 1989 by *Itokawa* and coworkers [4], the proposed (1′*S*,6*S*)-configuration was adopted concerning (+)-β-turmerone and the corresponding allylic alcohol **3a** (bisacurol), isolated from *Curcuma xanthorriza*. Finally, in 1992 *Golding* and *Pombo* [5] thoroughly reinvestigated their preliminary results by means of high-resolution NMR techniques and chiroptical methods, came to the conclusion that the configuration of (+)-β-turmerone was (1′*R*,6*S*). Even though *Golding*'s latest observations appeared to be the most convincing to us (see also [6]), we decided to establish the absolute configuration of compound (+)-**1a** by a stereospecific synthesis. Since there are methods described in the literature, both diols **2a** and **2b** are readily accessible, and they were chosen as starting materials for a reaction sequence leading to the desired turmerones of both diastereoisomeric series. Provided that the chiral centers at C(2) and C(1′) of **2a** and **2b** remain untouched until the final stage, they represent the conclusive spatial arrangement in the corresponding turmerones.



(+)-**1a** **4** **3a**

2. Results. – 2.1. *Establishing the Stereogenic Centers.* – Diol **2b** was prepared by diastereoselective hydroboration of (−)-isopulegol (**5**) according to *Schulte-Elte* and *Ohloff* (*Scheme 1*) [7]. It is worth mentioning that we obtained pure **2b** starting from technical-grade **5**, which in fact contains up to 25% of *neo*-isopulegol. Repeated crystallization of the crude mixture of the isomeric hydroboration products from Et_2O at $-20°$ gave **2b** in good yields[1]). On the other hand, the diastereoisomeric diol **2a** was obtained in 44% overall yield from the same starting material **5**, *via* a reaction sequence first introduced by *Friedrich* and *Bohlmann* [9] and *Kocienski* and coworkers [10][2]).

Scheme 1



2a **5** **2b**

a) ($COCl_2$), DMSO, Et_3N, CH_2Cl_2, $-78°$. *b*) Li(sec-Bu)$_3$BH, THF, $-78°$. *c*) *t*-BuOOH, [VO(acac)$_2$], C_6H_6, 0° [9]. *d*) $NaBH_3CN$, $BF_3 \cdot Et_2O$ [10]. *e*) B_2H_6, THF, 0°; H_2O_2, NaOH [7].

Separately[3]) both **2a** and **2b** were selectively monoprotected as thexyldimethylsilyl ethers **6a**,**b** utilizing TDSCl (chlorodimethyl(1,1,2-trimethylpropyl)silane; 1 equiv.) and 1*H*-imidazol in DMF (*Scheme 2*[4])). *Swern* oxidation [11] of the remaining secondary alcohol function (and, therefore, extinction of one stereogenic center) gave the configurationally stable monoterpene ketones **7a** and **7b**, whose diastereoisomeric relationship was determined by comparison of NMR data. Considering that the configuration at C(2) and C(5) was derived from the same starting material **5**, compounds **7a** and **7b** must display opposite configuration at C(1′). The formation of the *transoid* diene system present in (−)-*β*-turmerone ((−)-**1a**) was initiated by successful kinetically controlled formation of the trimethylsilyl enol ethers **8a**,**b** with lithium diisopropyl-

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[1]) The relative and absolute configuration of the diol (m.p. 104.5°, $[\alpha]_D^{22} = -19.6$ ($c = 2.67$, $CHCl_3$)) is undoubtedly the one depicted in *Scheme 1* as was established by an X-ray diffraction analysis of **2b** [8].

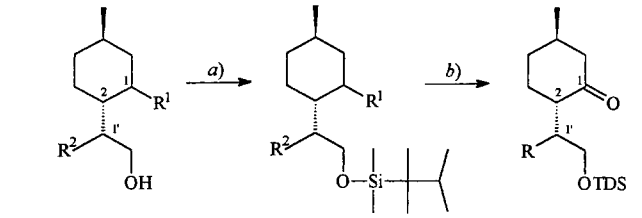
[2]) As an additional experimental feature, it is notable that pure (−)-isopulegon was provided in at least 90% isolated yield by application of *Swern* oxidation on **5** as described in the case of compounds **7a**/**7b** (see below, *Scheme 2*). Furthermore, we found that crystallization of the intermediate epoxy alcohol (m.p. 45°, $[\alpha]_D^{22} = +36.5$ ($c = 2.61$, $CHCl_3$)) from pentane at $-20°$ is suitable to achieve maximum stereoisomeric purity of **2a**.

[3]) The further reaction sequences were continued separately in both diastereoisomeric series. For simplicity, they are shown in joint schemes, where possible.

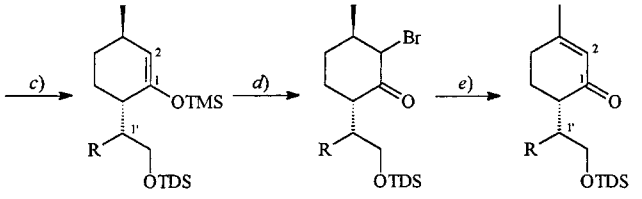
[4]) The descriptors *α*/*β* are attributed to the substituents below/above the plane of the paper, respectively.

amide (LDA)/Me_3SiCl in THF at $-78°$, leaving the vicinal center of chirality at C(2) of **7a**,**b** untouched. Subsequent bromination could be performed by treatment with *N*-bromosuccinimide (NBS) in THF at 0° [12]. Evaluation of the NMR data of the crude bromo ketones demonstrates that in both cases, one diastereoisomer was formed predominantly (probably the axial bromo compounds). Heating **9a**,**b** to 140–150° in collidine (2,4,6-trimethylpyridine) according to [13] led to the formation of the desired enones **10a**,**b** in an isolated overall yield of 60–65% starting from the corresponding ketones **7a**,**b**, whereas complete decomposition was observed during standard elimination procedures employing LiCl according to [14], or LiBr/Li_2CO_3 according to [15], both in DMF.

Scheme 2



2a R^1 = α–OH, R^2 = β–Me **6a** R^1 = α–OH, R^2 = β–Me **7a** R = β–Me
b R^1 = β–OH, R^2 = α–Me **b** R^1 = β–OH, R^2 = α–Me **b** R = α–Me



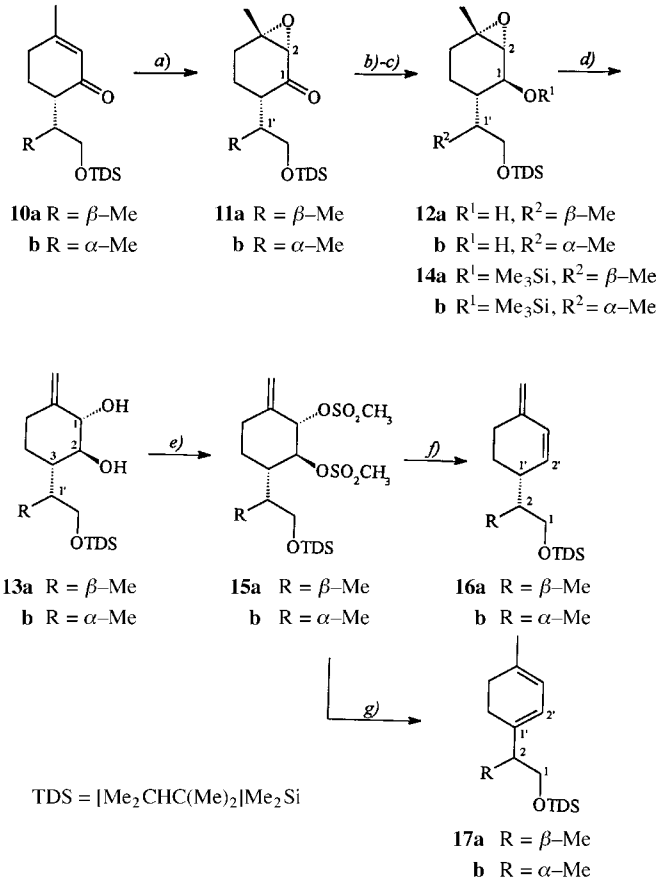
8a R = β–Me **9a** R = β–Me **10a** R = β–Me
b R = α–Me **b** R = α–Me **b** R = α–Me

TDS = $[Me_2CHC(Me)_2]Me_2Si$, TMS = Me_3Si

a) TDSCl, 1*H*-imidazole, DMF, 0°. *b*) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, $-78°$. *c*) LDA, Me_3SiCl, THF, $-78°$. *d*) NBS, THF, 0°. *e*) Collidine, 145°.

Treatment of **10a**,**b** with alkaline hydrogen-peroxide solution resulted in the formation of a complex mixture of diastereoisomeric epoxy ketones containing *ca.* 60% of an epoxy ketone **11a**,**b** (*Scheme 3*[4])), predominantly formed along with some by-products whose exact configuration remained unknown at that time. Nevertheless, each epoxy-ketone mixture was converted to the corresponding epoxy alcohols **12a**,**b** with $NaBH_4$ in the presence of $CeCl_3$, a method first applied to epoxy ketones by *Rücker* and coworkers [16] to synthesize *trans*-epoxy alcohols exclusively. At this stage, we originally intended to achieve a one-step rearrangement to give the ene-diols **13a**,**b** with lithium dialkylamides. Surprisingly, no reaction was observed in the case of the unprotected alcohols **12a**,**b**, which might be explained by the less favorable formation of an intermediate 1,2-diolate dianion. Thus, the mixed epoxy alcohols first had to be

Scheme 3



a) H_2O_2, NaOH, MeOH, 0°. *b*) $NaBH_4$, $CeCl_3$, MeOH, 0°. *c*) Me_3SiCl, Et_3N, THF. *d*) $LiNEt_2$, THF, reflux. *e*) MsCl, Et_3N, CH_2Cl_2, 0°. *f*) NaI, cat. pyridine, acetone, reflux. *g*) NaI, cat. TsOH, acetone, reflux.

protected as Me_3Si ethers **14a**,**b** to give the ene-diols **13a**,**b** upon treatment with $LiNEt_2$ in refluxing THF, followed by aqueous workup. Fortunately, in the case of the diols derived from enone **10b**, the less polar main fraction, separated by column chromatography, was found to contain only totally pure **13b**; analysis of the constituents of the minor, more polar fraction gave evidence that partial epimerization at C(6) had occurred during the preceding alkaline epoxidation. In contrast, the major more polar chromatographic diol fraction obtained from enone **10a** contained mainly **13a**, along with further isomers; however, we managed to remove the bulk of the undesired C(3) epimer (less polar fraction). The *all-trans* structures of **13a**,**b** were elucidated by analysis of ^{1}H-NMR coupling constants of the protons at C(1), C(2), and C(3)[5]).

[5]) Additionally, their acetonide derivatives were prepared ($Me_2C(OMe)_2$/Py·TsOH, DMF, 80°), and no significant conformational change for the six-membered ring was detected by ^{1}H-NMR spectroscopy, implying a *trans*-diequatorial arrangement for the vicinal OH groups.

Both the diastereoisomerically pure **13b** and the slightly impure **13a** cleanly reacted with methanesulfonyl chloride MsCl and Et_3N in CH_2Cl_2 to form the dimesylates **15b** and **15a**, respectively (*Scheme 3*[4])); the latter could now be easily purified by simple crystallization from pentane, since **15a** was the only solid among all the isomeric dimesylates. Therefore, both **15a** and **15b** were accessible in a diastereoisomerically pure form. In a most simple procedure, the *transoid* dienes **16a**,**b** were then prepared by refluxing the dimesylates in acetone in the presence of excess NaI and small amounts of pyridine, without any detectable isomerization of the C=C bonds[6]).

Thereby, we were able to get hold of the diastereoisomerically pure diene building blocks of well-defined configurations. However, the route described above was hampered by the drawback that partial epimerization at C(6) had taken place during the epoxidation of the configurationally pure intermediates **10a**,**b** to **11a**,**b**. Accordingly, the configuration of **16a**,**b** at C(1′) was not totally undisputed. In order to preserve the complete stereospecifity at this stage of our synthetic approach to β-turmerone, we developed an alternative procedure which prevented loss of configurational homogeneity. Thus, reduction of enone **10b** with $NaBH_4/CeCl_3$ in MeOH according to [17] led to the allylic *cis*-alcohol **18** (65% yield, after chromatographic removal of traces of the *trans*-alcohol)[7])(*Scheme 4*). The C=C bond of **18** could be epoxidized in a highly stereoselective manner to give **12c**, once again employing the $[VO(acac)_2]$/*t*-BuOOH reagent [20]. Formation of the Me_3Si ether **14c** (a longer reaction time was required than for **14a**,**b**) and subsequent treatment with $LiNEt_2$ as described before, provided the unsaturated *cis*-diol **13c**. Discouraged by the observation that the dimesylate of **13c**, which was much more difficult to prepare than dimesylates **15a**,**b**, underwent no visible reductive elimination with NaI in acetone, we decided to prepare the carbonothioate **19**. The latter was obtained after reaction with thiophosgene and pyridine in C_6H_6. Subsequent refluxing of **19** in $P(OMe)_3$ for 24 h gave **16b** which was identical with the one isolated before[8]).

2.2. *Side-Chain Modification.* Side-chain modification was initiated by cleavage of the silyl ether **16a**,**b** under standard conditions with Bu_4NF in THF and subsequent reaction of **20a**,**b**[9])[10]) with 4-nitrobenzenesulfonyl chloride (*Scheme 5*). The 4-nitrobenzenesulfonates **21a**,**b**, in contrast to their tosylate counterparts, were isolated as solid substances, allowing crystallization from Et_2O/pentane as a welcome additional purification procedure. Nucleophilic displacement of the sulfonate moiety in **21a**,**b** by

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[6]) If catalytic amounts of TsOH were used instead of pyridine, the endocyclic dienes **17a** and **17b** were the only products. In an additional experiment, **16b** was converted to **17b** by refluxing it in acetone in the presence of 1% TsOH, NaI, and I_2.

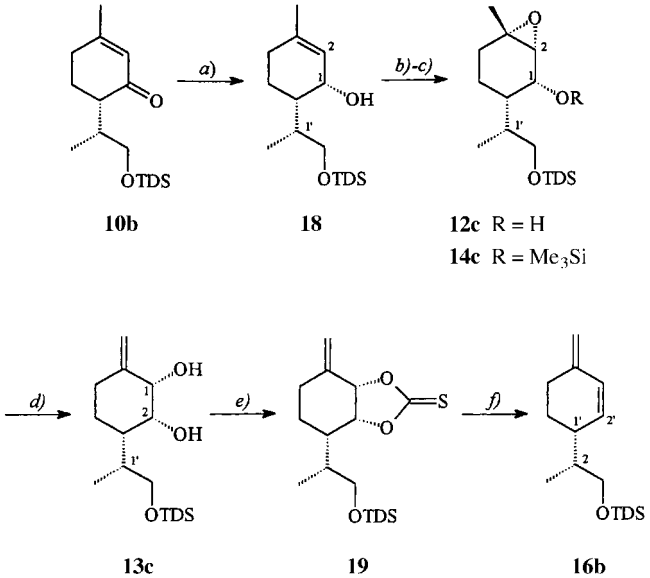
[7]) Assignment of the relative configuration was performed by comparison of ^{1}H- and ^{13}C-NMR data with those of the well-known monoterpenes *cis*- and *trans*-piperitol [18] [19].

[8]) Traces of concomitantly formed **17b** were removed by selective formation of its *Diels-Alder* adduct with maleic anhydride, followed by alkaline workup and column chromatography.

[9]) At this stage, we also carried out esterifications of **20a**,**b** with both (−)-(1*S*,4*R*) and (+)-(1*R*,4*S*)-camphanic acid according to *Gerlach* and coworkers [21] to determine the enantiomer purity of these compounds. Thus, **20a** was found to be a 80:20 mixture of enantiomers (60% ee), while **20b** was found to be totally enantiomerically pure with respect to ^{1}H and ^{13}C-NMR analysis of the camphanoates.

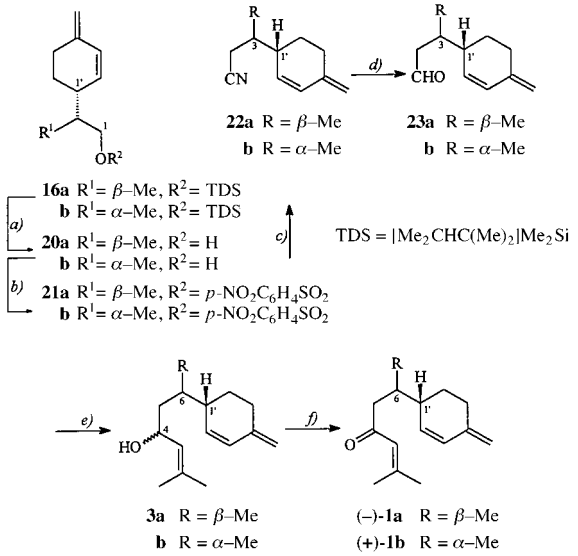
[10]) An X-ray diffraction analysis of the (+)-(1*R*,4*S*)-camphanic acid ester of **20b** was performed [22], establishing unambiguously not only the relative configuration of the ester, but also the absolute configuration of **20b** (and indirectly that of **20a**).

Scheme 4



a) $NaBH_4$, $CeCl_3$, MeOH, 0°. *b*) *t*-BuOOH, [VO(acac)$_2$], C_6H_6, 0°. *c*) Me_3SiCl, Et_3N, THF. *d*) $LiNEt_2$, THF, reflux. *e*) $CSCl_2$, pyridine, C_6H_6, 0°. *f*) $P(OMe)_3$, reflux; maleic anhydride, C_6H_6, reflux.

Scheme 5[4])



a) $Bu_4NF \cdot 3H_2O$, THF. *b*) 4-$NO_2C_6H_4SO_2Cl$, 4-(dimethylamino)pyridine (DMAP), pyridine, 0°. *c*) KCN, DMSO, r.t. *d*) DIBAH, Et_2O, 78° → r.t. *e*) $Me_2C{=}CHMgBr$, THF. *f*) PDC, CH_2Cl_2.

cyanide ion in DMSO at room temperature resulted in clean formation of the unsaturated nitriles **22a**,**b**. Reduction was accomplished, thereafter, at $-78°$ with an excess of diisobutylaluminium hydride (DIBAH) in Et_2O, followed by reaction of **23a**,**b** with 2-methylprop-1-enylmagnesium bromide in THF. The resulting allylic alcohols **3a**,**b** were each obtained as a diastereoisomer mixture with respect to C(4). Chromatographic separation of the two diastereoisomeric alcohols **3a** yielded pure samples of (+)-**3a**(I) and (−)-**3a**(II) (see *Exper. Part*). The final step of our synthesis was performed by pyridinium-dichromate oxidation of the allylic-alcohol mixtures **3a** and **3b** and chromatographic purification of the resulting (−)-*β*-turmerone ((−)-**1a**) and the diastereoisomer (+)-**1b**, respectively.

3. Discussion. – In *Table 1*, ^{13}C-NMR data (100.62 MHz, $CDCl_3$ and C_6D_6) of synthetic *β*-turmerone (−)-**1a** and the diastereoisomer (+)-**1b** (see also *Fig. 1*) and the data published by *Hikino* and coworkers [2] (25 MHz, $CDCl_3$), *Itokawa* and coworkers [4] (67.2 MHz, $CDCl_3$), and *Golding* and *Pombo* [5] (75 MHz, C_6D_6) are compared. (^{1}H-NMR Chemical shifts and coupling constants of (−)-**1a** (*Fig. 2*) and (+)-**1b** are very similar, apart from minor differences recorded for the *d* of Me−C(6) (0.87 and 0.90 ppm in $CDCl_3$, resp.). Obviously, (−)-**1a** fits very well the data of natural (+)-*β*-turmerone[11]) (indicating an identical relative configuration), whereas (+)-**1b** differs significantly in the chemical shifts assigned to C(5), *Me*−C(6), C(1′), C(2′), C(3′), and C(6′).

Table 1. *Comparison of ^{13}C-NMR Data of β-Turmerones*

	(−)-**1a** ($CDCl_3$)	(+)-**1b** ($CDCl_3$)	Natural compound [2] ($CDCl_3$)	Natural compound [4] ($CDCl_3$)	(−)-**1a** (C_6D_6)	(+)-**1b** (C_6D_6)	Natural compound [5] (C_6D_6)
Me−C(6)	16.44 (*q*)	17.02 (*q*)	16.5 (*q*)	16.6 (*q*)	16.71 (*q*)	17.21 (*q*)	17.42 (*q*)
C(1)	20.63 (*q*)	20.68 (*q*)	20.7 (*q*)	20.7 (*q*)	20.53 (*q*)	20.54 (*q*)	21.21 (*q*)
C(6′)	24.85 (*t*)	25.81 (*t*)	25.0 (*t*)	25.0 (*t*)	25.28 (*t*)	26.05 (*t*)	25.99 (*t*)
Me−C(2)	27.60 (*q*)	27.65 (*q*)	27.7 (*q*)	27.7 (*q*)	27.24 (*q*)	27.21 (*q*)	27.88 (*q*)
C(5′)	30.06 (*t*)	30.28 (*t*)	30.1 (*t*)	30.1 (*t*)	30.55 (*t*)	30.68 (*t*)	31.23 (*t*)
C(6)	33.29 (*d*)	33.25 (*d*)	33.3 (*d*)	33.4 (*d*)	33.36 (*d*)	33.24 (*d*)	34.07 (*d*)
C(1′)	40.42 (*d*)	40.84 (*d*)	40.5 (*d*)	40.5 (*d*)	40.81 (*d*)	41.14 (*d*)	41.51 (*d*)
C(5)	48.56 (*t*)	48.21 (*t*)	48.6 (*t*)	48.7 (*t*)	48.69 (*t*)	48.28 (*t*)	49.38 (*t*)
CH_2=C(4′)	110.29 (*t*)	110.44 (*t*)	110.3 (*t*)	110.3 (*t*)	110.60 (*t*)	110.67 (*t*)	111.28 (*t*)
C(3)	124.01 (*d*)	124.19 (*d*)	124.1 (*d*)	124.1 (*d*)	124.39 (*d*)	124.51 (*d*)	125.09 (*d*)
C(3′)	129.99 (*d*)	130.43 (*d*)	130.0 (*d*)	130.1 (*d*)	130.48 (*d*)	130.79 (*d*)	131.18 (*d*)
C(2′)	133.71 (*d*)	133.28 (*d*)	133.7 (*d*)	133.8 (*d*)	133.99 (*d*)	133.65 (*d*)	134.67 (*d*)
C(4′)	143.28 (*s*)	143.39 (*s*)	143.3 (*s*)	143.4 (*s*)	143.60 (*s*)	143.71 (*s*)	144.32 (*s*)
C(2)	155.00 (*s*)	154.92 (*s*)	154.9 (*s*)	155.0 (*s*)	153.75 (*s*)	153.65 (*s*)	154.36 (*s*)
C(4)	200.77 (*s*)	200.83 (*s*)	200.7 (*s*)	200.8 (*s*)	199.06 (*s*)	199.11 (*s*)	199.69 (*s*)

Moreover, optical rotations of (−)-**1a** ($[\alpha]_D^{22} = -2.25$ ($c = 1.38$, $CHCl_3$)) and (+)-**1b** ($[\alpha]_D^{22} = +84.3$ ($c = 0.50$, $CHCl_3$)) were recorded, but the data published by *Hikino* and coworkers [2] ($[\alpha]_D^{22} = -0.03$ ($c = 2.16$, $CHCl_3$)), and *Itokawa* and coworkers [4] ($[\alpha]_D^{22} = -13.8$ ($c = 0.77$, MeOH)) appeared to be less reliable than a comparison with the CD investigations of *Golding* and *Pombo* [5]. Thus, our CD spectra of

[11]) The ^{13}C-NMR data of (−)-**1a** in C_6D_6 fit well those of [5], apart from a regular shift of all signals of *ca.* 0.7 ppm which, in our view, is most likely due to different calibrations, *i.e.*, in our case $SiMe_4$ (= 0.00 ppm) and C_6D_6 (= 128.01 ppm).

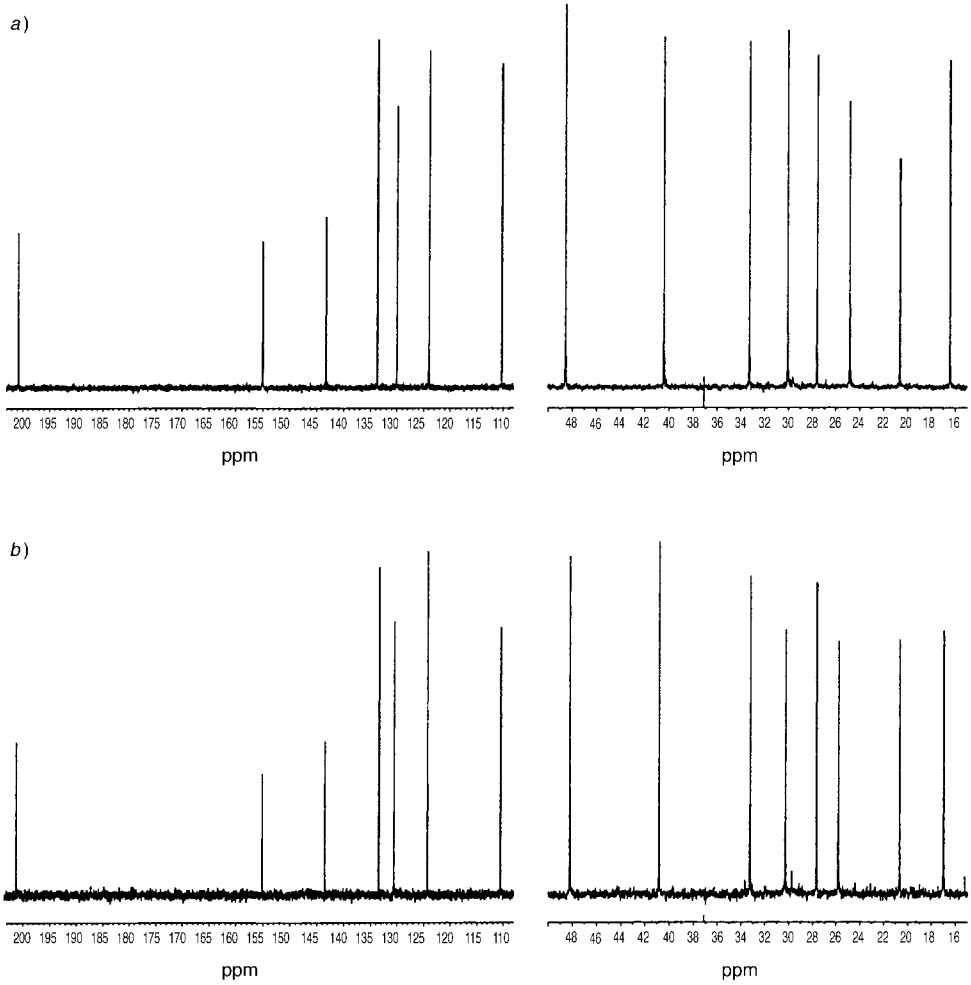


Fig. 1. *Detail of the* ^{13}*C-NMR spectra* (100.62 MHz, $CDCl_3$) a) *of (−)-***1a** *and* b) (+)-**1b**

(−)-**1a** in EtOH (*Fig. 3*) showed a strong, negative maximum at 243 nm ($\Delta\varepsilon = -3.72$ dm^3 mol^{-1} cm^{-1}), while *Golding* and *Pombo* observed a positive maximum in MeOH, cyclohexane, $CHCl_3$ [5], and EtOH ($\Delta\varepsilon_{max} = +6.81$ dm^3 mol^{-1} cm^{-1} at 240 nm, unpublished results submitted to us in 1986). The CD spectra (+)-**1b** in EtOH, on the other hand, exhibited a positive maximum at 245 nm ($\Delta\varepsilon_{max} = 6.13$ dm^3 mol^{-1} cm^{-1}), $\Delta\varepsilon = 0$ at 236 nm, and a negative maximum at 226 nm ($\Delta\varepsilon_{min} = -7.67$ dm^3 mol^{-1} cm^{-1}). Combining both NMR and CD data, we have no doubt that the (1′*S*,6*R*)-isomer (−)-**1a** is the synthetic enantiomer of natural (1′*R*,6*S*)-configured (+)-*β*-turmerone.

Comparison of the ^{13}C-NMR data (100.62 MHz, $CDCl_3$) of (+)-**3a**(I), (−)-**3a**(II), and **3b** with natural bisacurol [4] (67.2 MHz in $CDCl_3$) is presented in *Table 2*. Isomer (−)-**3a**(II) fits best for the natural product, while (+)-**3a**(I) and **3b** show significant deviations. Thus, (−)-**3a**(II) and the sample isolated from *Curcuma xanthorriza* are of

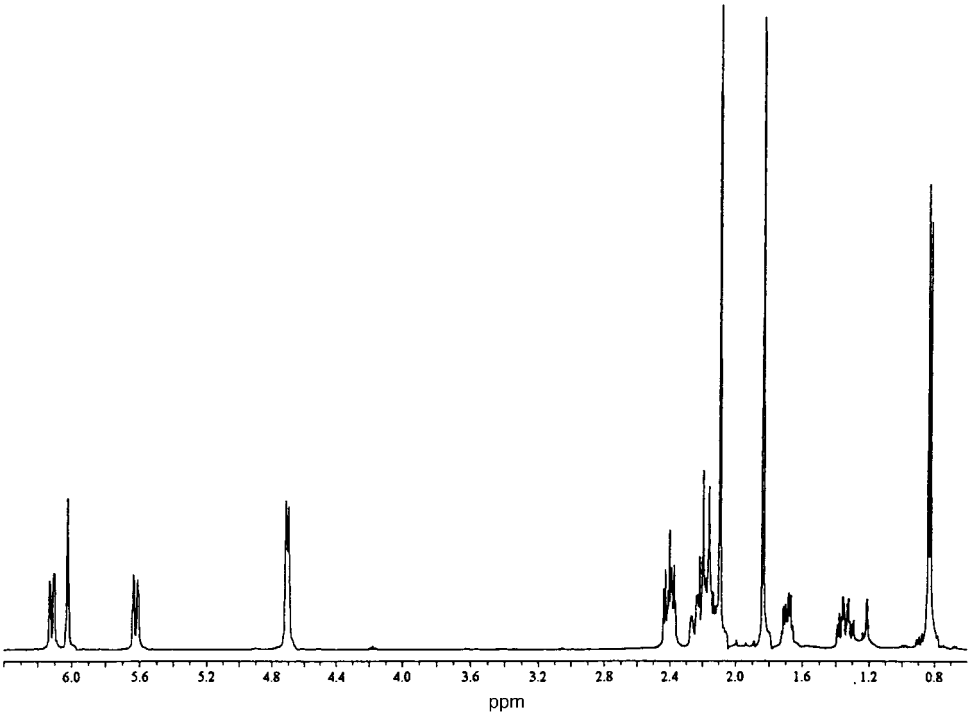


Fig. 2. *^{1}H-NMR Spectrum* (400 MHz, $CDCl_3$) *of (−)-***1a**

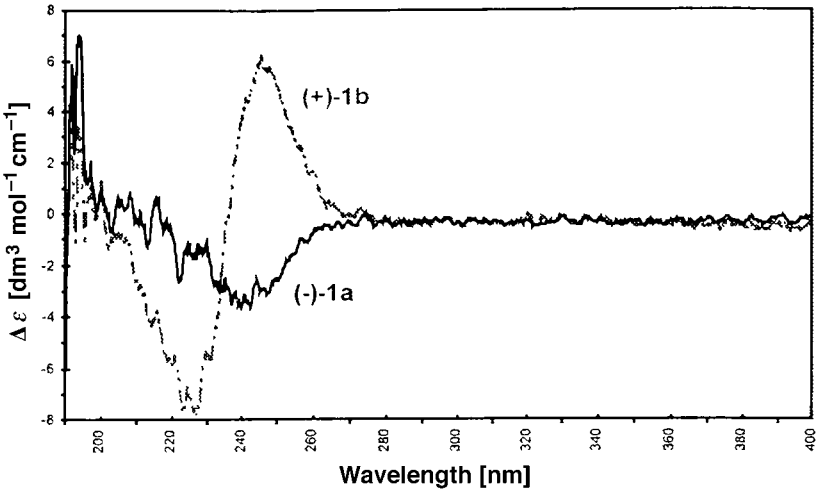


Fig. 3. *CD Spectra (EtOH) of (−)-***1a** *and (+)-***1b** ($c = 4.5 \cdot 10^{-4}$ mol/l). Average of 5 measurements.

the same relative configuration. Taking into account that oxidation of (−)-**3a**(II) gives (1′*S*,6*R*)-configured (−)-**1a**, while oxidation of natural bisacurol gives (1′*R*,6*S*)-*β*-turmerone (see [4]), (−)-**3a**(II) is the synthetic enantiomer of natural (1′*R*,6*S*)-bisacurol[12]). Surprisingly, *Itokawa* and coworkers [4] reported a negative optical rotation of the natural compound in MeOH, while we found a negative rotation, too (in $CHCl_3$; values recorded in MeOH were not significantly different from 0°) (see *Exper. Part*).

Table 2. *Comparison of ^{13}C-NMR Data of Bisacurols*

	(+)-**3a**(I)	(−)-**3a**(II)	**3b**	Bisacurol [4]
Me−C(6)	15.69 (*q*)	16.10 (*q*)	16.40, 17.06 (2*q*)	16.4 (*q*)
C(1)	18.01 (*q*)	18.04 (*q*)	18.12, 18.24 (2*q*)	18.3 (*q*)
C(6′)	24.30 (*t*)	24.17 (*t*)	25.83, 25.85 (2*t*)	24.5 (*t*)
Me−C(2)	25.62 (*q*)	25.62 (*q*)	25.71, 25.80 (2*q*)	25.8 (*q*)
C(5′)	30.21 (*t*)	30.16 (*t*)	30.36, 30.43 (2*t*)	30.4 (*t*)
C(6)	32.93 (*d*)	33.30 (*d*)	32.88, 33.41 (2*d*)	33.6 (*d*)
C(1′)	40.87 (*d*)	40.51 (*d*)	41.04, 41.29 (2*d*)	40.8 (*d*)
C(5)	41.91 (*t*)	41.83 (*t*)	41.53, 41.61 (2*t*)	42.1 (*t*)
C(4)	66.44 (*d*)	66.81 (*d*)	66.60, 67.19 (2*d*)	67.3 (*d*)
CH_2=C(4′)	109.92 (*t*)	109.85 (*t*)	110.10, 110.17 (2*t*)	110.1 (*t*)
C(3)	128.68 (*d*)	128.18 (*d*)	128.20, 128.71 (2*d*)	128.3 (*d*)
C(3′)	129.61 (*d*)	129.56 (*d*)	130.02, 130.09 (2*d*)	129.8 (*d*)
C(2)	134.05 (*s*)	134.83 (*s*)	134.35, 135.61 (2*s*)	135.6 (*s*)
C(2′)	134.63 (*d*)	134.53 (*d*)	133.62, 133.74 (2*d*)	134.7 (*d*)
C(4′)	143.42 (*s*)	143.30 (*s*)	143.56, 143.60 (2*s*)	143.6 (*s*)

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Experimental Part

General. All reagents and solvents were commercially available and used without further purification. Abs. THF was distilled twice from KOH and once from CaH_2. Solns. were dried with Na_2SO_4. TLC: *Merck* silica gel *60* F_{254} plates (Art. No. 5554); detection with UV, phosphomolybdic acid, $KMnO_4$, I_2, or anisaldehyde. Column chromatography (CC): *Merck* silica gel *60* (230–400 mesh). M.p.: *Büchi-571* instrument; not corrected. Optical rotations: *Perkin-Elmer 141* automatic polarimeter; $CHCl_3$ solns. at 22°, 10-cm path, 1-ml or 5-ml cell. UV Spectra: *Hitachi-U-2000* spectrophotometer; λ_{max} in nm, ε in $dm^3\,mol^{-1}\,cm^{-1}$. CD Spectra: *Jasco-J-710* spectropolarimeter; λ in nm, $\Delta\varepsilon$ in $dm^3\,mol^{-1}\,cm^{-1}$. IR Spectra: *Shimadzu-470* spectrometer; films or KBr discs; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker-DRX-400* spectrometer (^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz); in $CDCl_3$; δ in ppm rel. to internal Me_4Si (= 0.00 ppm, ^{1}H) and $CDCl_3$ (= 77.02 ppm, ^{13}C), *J* in Hz. MS: *Finnigan Mat-8230* spectrometer (70 eV); *m*/*z* (rel. %).

(1′S,6R)-2-Methyl-6-(4′-methylidenecyclohex-2′-en-1′-yl)hept-2-en-4-one (*(−)*-**1a**). A soln. of **3a** (400 mg, 1.82 mmol) and pyridine (0.5 ml) in CH_2Cl_2 (150 ml) was cooled to 0°, and PDC (4.10 g, 10.9 mmol) was added. Stirring was continued for 1 h at 0° and 24 h at r.t. CH_2Cl_2 (250 ml) and Et_3N (20 ml) were added at 0°, the mixture was filtered through a plug of silica gel (5 cm), washed with further CH_2Cl_2 (250 ml), and dried. Evaporation gave a slightly yellow oil (450 mg). Purification by CC (cyclohexane/Et_2O 40:1; R_f 0.15) yielded (−)-**1a** (115 mg, 29%). $[\alpha]_D = -2.25$ ($c = 1.38$). UV (MeOH): 234.4 (27200). CD (EtOH): min. 239.2 (−3.58). IR: 3077 (C=*CH*$_2$), 3020 (C=*C*−*H*), 2957, 2932, 2874 (C−H), 1687 (*α*,*β*-unsat. C=O), 1620 (C=C), 877 (C=*CH*$_2$). ^{1}H-NMR: 0.87 (*d*, $^3J = 6.5$, Me−C(6)); 1.37 (*m*, 1 H−C(6′)); 1.72 (*m*, 1 H−C(6′)); 1.90 (*s*, Me−C(2)); 2.14 (*s*, Me(1)); 2.19–2.32 (*m*, 1 H−C(5), H−C(6), H−C(1′), 1 H−C(5′)); 2.41–2.49

[12]) The configuration at C(4) remains unknown.

(*m*, 1 H–C(5), 1 H–C(5′)); 4.75 (*m*, CH_2=C(4′)); 5.66 (*d*, ^3J = 10.0, 1 H–C(2′)); 6.06 (*s*, H–C(3)); 6.17 (*dd*, ^3J = 10.0, ^4J = 2.0, H–C(3′)). ^{13}C-NMR: *Table 1*; assignment by H,H-COSY, CH correlation (HMQC), and C,H long-range correlation (HMBC). MS: 218 (7, M^+), 120 (100), 105 (15), 91 (12), 83 (31), 55 (20), 39 (5).

(1′S,6S)-2-Methyl-6-(4′-methylenecyclohex-2′-en-1′-yl)hept-2-en-4-one ((+)-**1b**). As described for (−)-**1a**, with **3b** (280 mg, 1.27 mmol): pure (+)-**1b** (72 mg, 26%), after CC (cyclohexane/Et_2O 40 : 1; R_f 0.15). $[\alpha]_D$ = +84.30 (*c* = 0.50; $CHCl_3$). UV (MeOH): 233.4 (31600). CD (EtOH): max. 245.0 (+ 6.13), 235.8 (0), min. 226 (− 7.67). IR: 3077 (C=*C*H_2), 3022 (C=*C*−*H*), 2931, 2873 (C–H), 1687 (*α*,*β*-unsat. C=O), 1621 (C=C), 878 (C=*C*H_2). ^{1}H-NMR: 0.90 (*d*, ^3J = 6.5, Me–C(6)); 1.36 (*m*, H–C(6′)); 1.78 (*m*, 1 H–C(6′)); 1.87 (*d*, ^4J = 1.0, Me–C(2)); 2.13 (*d*, ^4J = 1.0, Me(1)); 2.16–2.33 (*m*, 1 H–C(5), H–C(6), H–C(1′), 1 H–C(5′)); 2.40–2.48 (*m*, 1 H–C(5), 1 H–C(5′)); 4.75 (*m*, CH_2=C(4′)); 5.66 (*d*, ^3J = 10.0, H–C(2′)); 6.05 (*s*, H–C(3)); 6.18 (*dd*, ^3J = 10.0, ^4J = 2.2, H–C(3′)). ^{13}C-NMR: *Table 1*; assignment by H,H-COSY, C,H correlation (HMQC), and C,H long-range correlation (HMBC). MS: 218 (12, M^+), 120 (100), 105 (12), 91 (10), 83 (23), 55 (8), 39 (4).

*(1*R*,1′*R*,2*S*,5*R*)-2-(2-Hydroxy-1-methylethyl)-5-methylcyclohexanol* (**2b**). Diborane was produced by addition of $BF_3 \cdot Et_2O$ (664 mmol) to a slurry of $NaBH_4$ (22.8 g, 600 mmol) in diglyme (200 ml) at r.t. and subsequent heating to 90°. The gas was bubbled through an ice-cooled soln. of (−)-isopulegol (tech. grade; 46.2 g, 300 mmol) in THF (500 ml) *via* a continous Ar stream. The THF soln. was stirred at 0° and at r.t. for 1 h each. At 0° 3N NaOH (150 ml, 450 mmol) was added slowly, followed by 30% aq. H_2O_2 soln. (180 ml, 1.76 mol) and heating under reflux for 30 min. The cold mixture was extracted with AcOEt and the combined org. layer washed with brine, dried, and evaporated. The oily crude materials of five such reactions were combined, dissolved in dry Et_2O, and allowed to precipitate at −20°. The precipitate was crystallized three more times (dissolution in the required amount of dry Et_2O under reflux and crystallization at −20°) until the melting point and optical rotation reached maximum values. Yield 96.5 g. M.p. 104.5° (Et_2O). $[\alpha]_D$ = −19.60 (*c* = 2.67, $CHCl_3$). IR: 3300–3500 (O–H), 2963, 2947, 2915, 2875 (C–H), 1104, 1066 (C–OH). ^{1}H-NMR: 0.92 (*d*, ^3J = 6.5, Me–C(1′)); 0.96 (*d*, ^3J = 7.3, Me–C(5)); 0.86–1.02 (*m*, 2 H), 1.18–1.29 (*m*, 1 H), 1.31–1.47 (*m*, 2 H), 1.53–1.59 (*m*, 1 H), 1.61–1.68 (*m*, 1 H), 1.80–1.87 (*m*, 1 H), 1.93–1.98 (*m*, 1 H), H–C(2) to H–C(6), H–C(1′), 3.28 (*ddd*, ^3J = 10.3, 10.3, 4.1, H–C(1)); 3.56 (*dd*, ^2J = 10.5, ^3J = 3.1, 1 H–C(2′)); 3.63 (*dd*, ^2J = 10.5, ^3J = 5.3, 1 H–C(2′)). ^{13}C-NMR: 11.91 (*q*, *Me*–C(1′)); 22.10 (*q*, *Me*–C(5)); 29.72 (*t*, C(3)); 31.46 (*d*, C(5)); 34.64 (*t*, C(4)); 38.71 (*d*, C(1′)); 44.40 (*t*, C(6)); 48.64 (*d*, C(2)); 66.86 (*t*, C(2′)); 69.81 (*d*, C(1)). MS: 172 (19, M^+), 154 (40), 136 (34), 124 (57), 112 (54), 97 (61), 71 (65), 69 (72), 57 (73), 43 (100).

*(1′S,4*R*,6*R*)/(1′S,4S,6*R*)-2-Methyl-6-(4′-methylenecyclohex-2′-en-1′-yl)hept-2-en-4-ol* (**3a**). To Mg (1.35 g, 56.3 mmol; powdered, not stabilized), a soln. of 1-bromo-2-methylprop-1-ene (3.79 g, 2.80 mmol) in THF (25 ml) and 1,2-dibromoethane (3 drops) were added. The mixture was kept under reflux for 15 min and stirred at r.t. for another 15 min. A soln. of **23a** (920 mg, 5.61 mmol) in THF (10 ml) was added dropwise. Then the mixture was stirred at r.t. for 1 h, quenched with sat. aq. NH_4Cl soln. (120 ml), and extracted with Et_2O. The combined org. phase was washed with H_2O and brine, and dried. Evaporation gave crude **3a** (1.25 g). CC (cyclohexane/AcOEt 10 : 1) provided pure (+)-**3a**(I) (130 mg, 11%; R_f 0.20), pure (−)-**3a**(II) (150 mg, 12%; R_f 0.16), and a mixture of both diastereoisomers (120 mg, 10%).

*Data of (+)-***3a**(I). $[\alpha]_D$ = +41.85 (*c* = 1.74, $CHCl_3$), $[\alpha]_D$ = +37.21 (*c* = 0.48, MeOH). IR: 3300–3400 (O–H), 3076 (C=*C*H_2), 3020 (C=*C*−*H*), 2957, 2931, 2872 (C–H), 1674 (C=C), 1635, 1596 (conj. C=C), 1130 (C–OH), 876 (C=*C*H_2). ^{1}H-NMR: 0.84 (*d*, ^3J = 6.8, Me–C(6)); 1.16–1.70 (*m*, 2 H–C(5), H–C(6), 2 H–C(6′)); 1.63, 1.66 (2*s*, Me(1), Me–C(2)); 2.14–2.41 (*m*, H–C(1′), 2 H–C(5′)); 4.36 (*m*, H–C(4)); 4.69 (*m*, CH_2=C(4′)); 5.13 (*d*, ^3J = 8.8, H–C(3)); 5.61 (*d*, ^3J = 9.9, H–C(2′)); 6.09 (*dd*, ^3J = 9.9, ^4J = 1.9, H–C(3′)). ^{13}C-NMR: *Table 2*. MS: 220 (4, M^+), 202 (5), 149 (70), 120 (100), 105 (23), 85 (29), 57 (39), 41 (54).

Data of (−)-**3a**(II). $[\alpha]_D$ = −15.71 (*c* = 2.83, $CHCl_3$); $[\alpha]_D \approx 0$ (*c* = 1.45, MeOH) ([4]: $[\alpha]_D$ = −8.6 (MeOH) for natural bisacurol). IR: 3300–3400 (O–H), 3076 (C=*C*H_2), 3020 (C=*C*−*H*), 2959, 2930, 2873 (C–H), 1674 (C=C), 1635, 1597 (conj. C=C), 1130 (C–OH), 876 (C=*C*H_2). ^{1}H-NMR: 0.78 (*d*, ^3J = 6.8, Me–C(6)); 1.20–1.65 (*m*, 2 H–C(5), H–C(6), 2 H–C(6′)); 1.62, 1.65 (2*s*, Me(1), Me–C(2)); 2.15–2.40 (*m*, H–C(1′), 2 H–C(5′)); 4.34 (*m*, H–C(4)); 4.66 (*m*, CH_2=C(4′)); 5.05 (*d*, ^3J = 9.0, H–C(3)); 5.58 (*d*, ^3J = 9.8, H–C(2′)); 6.07 (*dd*, ^3J = 9.8, ^4J = 2.2, H–C(3′)). ^{13}C-NMR: *Table 2*. MS: 220 (2, M^+), 202 (9), 125 (35), 120 (100), 105 (37), 85 (36), 57 (29), 41 (59).

*(1′S,4*R*,6S/(1′S,4S,6S)-2-Methyl-6-(4′-methylenecyclohex-2′-en-1′-yl)hept-2-en-4-ol* (**3b**). As described for **3a** with **23b** (246 mg, 1.50 mmol): **3b** (300 mg, 91%), diastereomer mixture. IR: 3300–3400 (O–H), 3076 (C=*C*H_2), 3022 (C=*C*−*H*), 2957, 2931, 2873 (C–H), 1674 (C=C), 1635, 1596 (conj. C=C), 1049 (C–OH), 876 (C=*C*H_2). ^{1}H-NMR: 0.86, 0.89 (2*d*, ^3J = 6.5, 6.8, Me–C(6)); 1.15–1.60 (*m*, 2 H–C(5), H–C(6), 2 H–C(6′));

1.65, 1.67, 1.68, 1.70 (4*s*, Me(1), Me–C(2)); 2.15–2.40 (*m*, H–C(1′), 2 H–C(5′)); 4.40 (*m*, H–C(4)); 4.71 (*m*, CH_2=C(4′)); 5.08, 5.15 (2*d*, ^3J = 8.8, 9.0, H–C(3)); 5.63, 5.66 (2*m*, H–C(2′)); 6.13 (*m*, H–C(3′)). ^{13}C-NMR: *Table 2*. MS: 220 (2, M^+), 202 (10), 125 (22), 120 (100), 109 (15), 105 (12), 85 (30), 41 (35).

*(1*S*,1′*S*,2*S*,5*R*)-2-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-5-methylcyclohexanol* (**6a**). Diol **2a** (20.0 g, 116 mmol) and 1*H*-imidazole (20.0 g, 294 mmol) were dissolved in DMF (200 ml) at 0°. A soln. of TDSCl ([(Me$_2$CHCMe$_2$]Me$_2$SiCl; 21.6 g, 121 mmol) in DMF (20 ml) was added within 1 h. The mixture was stirred at 0° for 3 h and at r.t. for 12 h. Cyclohexane (400 ml) was added and the mixture washed with H_2O and brine, dried, and evaporated: **6a** (31.2 g, 85%). Colorless oil. A pure sample was obtained by CC (cyclohexane/AcOEt 10:1; R_f 0.50). $[\alpha]_D$ = +5.44 (*c* = 5.79). IR: 3300–3500 (O–H), 2956, 2925, 2869 (C–H), 1161 (C–OH), 1072 (C–OSi). ^{1}H-NMR: 0.00 (*s*, Me$_2$Si); 0.73 (*d*, Me–C(1′)); 0.74 (*s*, Me$_2$CHC*Me*$_2$); 0.76 (*d*, ^3J = 7.0, *Me*$_2$CHCMe$_2$); 0.82 (*d*, ^3J = 7.0, Me–C(5)); 0.93 (*m*, 1 H); 1.05 (*m*, 1 H); 1.25–1.80 (*m*, 8 H, H–C(2) to H–C(6), H–C(1′), Me$_2$C*H*CMe$_2$); 3.38 (*dd*, ^2J = 10.2, ^3J = 6.0, 1 H–C(2′)); 3.53 (*dd*, ^2J = 10.2, ^3J = 2.6, 1 H–C(2′)); 3.94 (*m*, H–C(1)). ^{13}C-NMR: –3.83 (*q*, Me$_2$Si); 15.99 (*q*, *Me*–C(1′)); 18.24, 18.27 (2*q*, Me$_2$CHC*Me*$_2$); 20.06, 20.16 (2*q*, *Me*$_2$CHCMe$_2$); 22.27 (*q*, *Me*–C(5)); 25.01 (*s*, Me$_2$CHCMe$_2$); 25.19 (*t*, C(3)); 25.91 (*d*, C(5)); 33.91 (*d*, Me$_2$*C*HCMe$_2$); 35.32 (*t*, C(4)); 37.90 (*d*, C(1′)); 41.76 (*t*, C(6)); 46.06 (*d*, C(2)); 65.83 (*t*, C(2′)); 65.97 (*d*, C(1)). MS: 255 (18), 211 (51), 137 (85), 105 (37), 95 (90), 75 (100).

*(1*R*,1′*R*,2*S*,5*R*)-2-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-5-methylcyclohexanol* (**6b**). As described for **6a**, with **2b** (20.0 g, 116 mmol): **6b** (33.2 g, 91%). Pure samples were obtained by CC (cyclohexane/AcOEt 10:1; R_f 0.55). $[\alpha]_D$ = –12.07 (*c* = 5.52). IR: 3300–3500 (O–H), 2955, 2919, 2868 (C–H), 1150 (C–OH), 1089 (C–OSi). ^{1}H-NMR: 0.00 (*s*, Me$_2$Si); 0.73, 0.74 (2*s*, Me$_2$CHC*Me*$_2$); 0.76 (*d*, ^3J = 7.0, *Me*$_2$CHCMe$_2$); 0.79 (*d*, ^3J = 6.3, Me–C(1′)); 0.80 (*d*, ^3J = 7.5, Me–C(5)); 0.90–1.40 (*m*, 5 H), 1.44–1.50 (*m*, 1 H), 1.52–1.59 (*m*, 2 H), 1.75–1.83 (*m*, 1 H), 1.87–1.95 (*m*, 1 H, H–C(2) to H–C(6), H–C(1′), Me$_2$C*H*CMe$_2$); 3.28 (*ddd*, ^3J = 10.3, 10.3, 4.2, H–C(1′)); 3.46 (*dd*, ^2J = 10.0, ^3J = 3.0, H–C(2′)); 3.52 (*dd*, ^2J = 10.0, ^3J = 5.5, H–C(2′)). ^{13}C-NMR: –3.66, –3.63 (2*q*, Me$_2$Si); 12.61 (*q*, *Me*–C(1′)); 18.39 (*q*, Me$_2$CHC*Me*$_2$); 20.16, 20.18 (2*q*, *Me*$_2$CHCMe$_2$); 22.11 (*q*, *Me*–C(5)); 25.20 (*s*, Me$_2$CHCMe$_2$); 28.92 (*t*, C(3)); 31.35 (*d*, *C*(5)); 33.98 (*d*, Me$_2$*C*HCMe$_2$); 34.75 (*t*, C(4)); 38.10 (*d*, C(1′)); 43.90 (*t*, C(6)); 49.08 (*d*, C(2)); 67.50 (*t*, C(2′)); 69.77 (*d*, C(1)). MS: 314 (1, M^+), 229 (38), 211 (25), 137 (96), 104 (81), 95 (94), 81 (100), 75 (93).

*(1′*S*,2*S*,5*R*)-2-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-5-methylcyclohexanone* (**7a**). To a soln. of (COCl)$_2$ (19.2 g, 151 mmol) in CH_2Cl_2 (400 ml) at –78°, DMSO (23.4 g, 300 mmol) in CH_2Cl_2 (50 ml) was added dropwise within 30 min, followed by **6a** (30.0 g, 95.4 mmol) in CH_2Cl_2 (50 ml). The soln. was stirred for 1 h, Et_3N (45.0 g, 445 mmol) was added at –78° and the mixture was allowed to reach r.t. within 3 h. After addition of CH_2Cl_2 (400 ml), the mixture was washed with H_2O, 5% aq. HCl soln., and brine, dried, and evaporated. CC (cyclohexane/AcOEt 20:1; R_f 0.45) furnished **7a** (19.4 g, 65%). $[\alpha]_D$ = –11.33 (*c* = 7.29). IR: 2956, 2928, 2868 (C–H), 1711 (C=O), 1086 (C–OSi). ^{1}H-NMR: –0.01, 0.00 (2*s*, Me$_2$Si); 0.73 (*d*, ^3J = 7.0, Me–C(1′)); 0.76 (*s*, Me$_2$CHC*Me*$_2$); 0.81 (*d*, ^3J = 7.0, *Me*$_2$CHCMe$_2$); 0.95 (*d*, ^3J = 6.3, Me–C(5)); 1.25–1.35 (*m*, 2 H), 1.50–1.59 (*m*, 1 H), 1.72–1.96 (*m*, 4 H, H–C(3) to H–C(5), H–C(1′), Me$_2$C*H*CMe$_2$); 2.15–2.24 (*m*, 1 H–C(6)); 2.31 (*ddd*, H–C(2)); 2.36–2.44 (*dd*, 1 H–C(6)); 3.31 (*dd*, ^2J = 9.8, ^3J = 7.5, 1 H–C(2′)); 3.41 (*dd*, ^2J = 9.8, ^3J = 5.5, 1 H–C(2′)). ^{13}C-NMR: –3.60 (*q*, Me$_2$Si); 12.84 (*q*, *Me*–C(1′)); 18.49 (*q*, Me$_2$CHC-*Me*$_2$); 20.34 (*q*, *Me*$_2$CHCMe$_2$); 22.36 (*q*, *Me*–C(5)); 25.05 (*s*, Me$_2$CHCMe$_2$); 26.89 (*t*, C(3)); 33.07 (*d*, C(5)); 34.05 (*t*, C(4)); 34.30 (*d*, Me$_2$*C*HCMe$_2$); 35.31 (*d*, C(1′)); 49.76 (*d*, C(2)); 50.83 (*t*, C(6)); 65.64 (*t*, C(2′)); 212.23 (*s*, C(1)). MS: 227 (95), 209 (77), 135 (47), 107 (41), 93 (73), 75 (100).

*(1′*R*,2*S*,5*R*)-2-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-5-methylcyclohexanone* (**7b**). As described for **7a** with **6b** (30.0 g, 95.4 mmol). CC (cyclohexane/AcOEt 20:1; R_f 0.45) furnished **7b** (18.5 g, 62%). $[\alpha]_D$ = –1.54 (*c* = 4.82). IR: 2958, 2928, 2869 (C–H), 1712 (C=O), 1084 (C–OSi). ^{1}H-NMR: 0.01 (*s*, Me$_2$Si); 0.77 (*s*, Me$_2$CHC*Me*$_2$); 0.83 (*d*, ^3J = 6.8, *Me*$_2$CHCMe$_2$); 0.89 (*d*, ^3J = 6.8, Me–C(1′)); 0.95 (*d*, ^3J = 6.0, Me–C(5)); 1.18–1.41 (*m*, 2 H), 1.51–1.57 (*m*, 1 H), 1.75–1.96 (*m*, 4 H, H–C(3) to H–C(5), H–C(1′), MeC*H*CMe$_2$); 2.05 (*ddd*, H–C(2)); 2.20–2.33 (*m*, 2 H–C(6)); 3.47 (*m*, 2 H–C(2′)). ^{13}C-NMR: –3.71 (*q*, Me$_2$Si); 15.42 (*q*, *Me*–C(1′)); 18.45, 18.47 (2*q*, Me$_2$CHC*Me*$_2$); 20.28 (*q*, *Me*$_2$CHCMe$_2$); 22.27 (*q*, *Me*–C(5)); 24.97 (*s*, Me$_2$CHCMe$_2$); 29.79 (*t*, C(3)); 34.10 (*t*, C(4)); 34.20 (*d*, Me$_2$*C*HCMe$_2$); 34.48 (*d*, C(5)); 35.74 (*d*, C(1′)); 51.08 (*t*, C(6)); 52.12 (*d*, C(2)); 64.93 (*t*, C(2′)); 212.29 (*s*, C(1)). MS: 312 (2, M^+), 227 (92), 209 (44), 153 (37), 152 (34), 137 (85), 135 (27), 119 (22), 113 (52), 84 (60), 81 (40), 75 (100).

*(1′*S*,3*R*,6*S*)-{{6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-3-methylcyclohex-1-en-1-yl}-oxy}trimethylsilane* (**8a**). LDA was prepared from (i-Pr)$_2$NH (15.2 g, 150 mmol) and 2.5M BuLi in hexanes (60 ml, 150 mmol) in THF (250 ml) at 0°. The LDA soln. was cooled to –78°, **6a** (15.0 g, 48.0 mmol) in THF (60 ml) was added within 30 min, and stirring was continued for another 30 min, followed by addition of Me_3SiCl (32.6 g, 300 mmol) in THF (60 ml) within 30 min. The mixture was warmed to r.t. overnight. Cyclohexane (400 ml) was

added and the mixture washed with sat. aq. $NaHCO_3$ soln., dried, and evaporated: **8a** (18.5 g, quant.). A pure sample was obtained by CC (cyclohexane/AcOEt 25:1; R_f 0.85). $[\alpha]_D = +2.37$ ($c = 3.00$). IR: 2959, 2868 (C–H), 1657 (C=C), 1145, 1089 (C–OSi). ^{1}H-NMR: 0.05 (*s*, Me_2Si); 0.15 (*s*, Me_3Si); 0.67 (*d*, $^3J = 6.8$, Me–C(1′)); 0.78 (*s*, Me_2CHCMe_2); 0.86 (*d*, $^3J = 6.8$, Me_2CHCMe_2); 0.90 (*d*, $^3J = 7.0$, Me–C(3)); 1.05–2.40 (*m*, 8 H, H–C(3) to H–C(6), H–C(1′), Me_2CHCMe_2); 3.40 (*m*, 2 H–C(2′)); 4.71 (*m*, H–C(2)). ^{13}C-NMR: −3.53, −3.41 (2*q*, Me_2Si); 0.48 (*q*, Me_3Si); 11.15 (*q*, *Me*–C(1′)); 18.53, 18.55 (2*q*, Me_2CHCMe_2); 20.36, 20.38 (2*q*, Me_2CHCMe_2); 22.04 (*t*, C(5)); 22.90 (*q*, *Me*–C(3)); 25.07 (*s*, Me_2CHCMe_2); 30.09 (*d*, C(3)); 31.61 (*t*, C(4)); 34.27 (*d*, Me_2CHCMe_2); 34.73 (*d*, C(1′)); 39.38 (*d*, C(6)); 65.97 (*t*, C(2′)); 112.72 (*d*, C(2)); 151.78 (*s*, C(1)). MS: 369 (2), 299 (12), 257 (19), 224 (23), 209 (33), 184 (41), 147 (70), 73 (69), 40 (100).

*(1′*R*,3*R*,6*S*)-{[6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-3-methylcyclohex-1-en-1-yl]oxy}trimethylsilane* (**8b**). As described for **8a**, with **6b** (15.0 g, 48.0 mmol): **8b** (18.5 g, quant.). Pure samples were obtained by CC (cyclohexane/AcOEt 25:1; R_f 0.85). $[\alpha]_D = +8.62$ ($c = 3.34$). IR: 2957, 2927, 2868 (C–H), 1653 (C=C), 1148, 1091 (C–OSi). ^{1}H-NMR: 0.05 (*s*, Me_2Si); 0.17 (*s*, Me_3Si); 0.82 (*s*, Me_2CHCMe_2); 0.87 (*d*, $^3J = 6.8$, Me_2CHCMe_2); 0.90 (*d*, Me–C(1′), Me–C(3)); 1.25–1.38 (*m*, 1 H), 1.55–1.75 (*m*, 4 H), 1.85–1.93 (*m*, 1 H); 2.10–2.19 (*m*, 2 H, H–C(3) to H–C(6), H–C(1′), Me_2CHCMe_2); 3.41 (*dd*, $^2J = {}^3J = 9.2$, 1 H–C(2′)); 3.56 (*dd*, $^2J = 9.2$, $^3J = 4.8$, 1 H–C(2′)); 4.65 (*m*, H–C(2)). ^{13}C-NMR: −3.38, −3.29 (2*q*, Me_2Si); 0.27 (*q*, Me_3Si); 13.88 (*q*, *Me*–C(1′)); 18.56 (*q*, Me_2CHCMe_2); 20.41 (*q*, Me_2CHCMe_2); 22.87 (*q*, *Me*–C(3)); 25.09 (*s*, Me_2CHCMe_2); 26.29 (*t*, C(5)); 30.15 (*d*, C(3)); 31.83 (*t*, C(4)); 34.30 (*d*, Me_2CHCMe_2); 37.70 (*d*, C(1′)); 41.53 (*d*, C(6)); 66.47 (*t*, C(2′)); 111.95 (*d*, C(2)); 151.80 (*s*, C(1)). MS: 385/384 (4/11, M^+), 299 (84), 257 (83), 224 (35), 211 (70), 184 (78), 147 (100), 73 (61).

*(1′*S*,6*S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-3-methylcyclohex-2-en-1-one* (**10a**). To a soln. of **8a** (18.5 g, 48.0 mmol) in THF (500 ml) at 0°, *N*-bromosuccinimide (9.20 g, 51.7 mmol) was added in one portion, and the mixture was stirred at 0° for 2 h. Sat. aq. $NaHCO_3$ soln. (200 ml) was added and the mixture extracted with Et_2O, washed with sat. aq. Na_2CO_3 soln., H_2O, and brine, dried, and evaporated carefully at r.t. The crude bromo ketone (cyclohexane/AcOEt 20:1; R_f 0.55) and collidine (150 ml) were heated to 145–150° for 1 h. The cold mixture was filtered and washed with Et_2O. The solvent and the bulk of the collidine were distilled off (0.1 mbar). The residue was once again dissolved in Et_2O (1000 ml), washed with 5% aq. HCl soln., sat. aq. $NaHCO_3$ soln., H_2O, and brine, dried, and evaporated. CC (cyclohexane/AcOEt 8:1; R_f 0.45) gave **10a** (10.5 g, 70% overall from **6a**). $[\alpha]_D = +6.25$ ($c = 3.52$). UV (MeOH): 233.4 (13100). IR: 2957, 2867 (CH), 1670 (α,β-unsat. C=O), 1639 (C=C), 1082 (C–OSi). ^{1}H-NMR: 0.07 (*s*, Me_2Si); 0.70 (*d*, $^3J = 6.8$, Me–C(1′)); 0.78 (*s*, Me_2CHCMe_2); 0.82 (*d*, $^3J = 6.8$, 6 H, Me_2CHCMe_2); 1.50–1.71 (*m*, 1 H–C(5), H–C(1′), Me_2CHCMe_2); 1.88 (*s*, Me–C(3)); 2.22–2.55 (*m*, 2 H–C(4), 1 H–C(5), H–C(6)); 3.36 (*dd*, $^2J = 10.0$, $^3J = 8.5$, 1 H–C(2′)); 3.44 (*dd*, $^2J = 10.0$, $^3J = 6.0$, 1 H–C(2′)); 5.81 (*s*, H–C(2)). ^{13}C-NMR: −3.68, −3.53 (2*q*, Me_2Si); 12.14 (*q*, *Me*–C(1′)); 18.45 (*q*, Me_2CHCMe_2); 20.27 (*q*, Me_2CHCMe_2); 22.34 (*t*, C(5)); 24.06 (*q*, *Me*–C(3)); 24.98 (*s*, Me_2CHCMe_2); 30.87 (*t*, C(4)); 33.02 (*d*, C(1′)); 34.14 (*d*, Me_2CHCMe_2); 46.15 (*d*, C(6)); 65.38 (*t*, C(2′)); 127.08 (*d*, C(2)); 161.04 (*s*, C(3)); 201.23 (*s*, C(1)). MS: 295 (5), 225 (100), 133 (27), 105 (58), 75 (92).

*(1′*R*,6*S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-3-methylcyclohex-2-en-1-one* (**10b**). As described for **10a**, with **8b** (18.5 g, 48.0 mmol). CC (cyclohexane/AcOEt 8:1; R_f 0.45) gave **10b** (11.0 g, 74% overall from **6b**). $[\alpha]_D = +11.45$ ($c = 4.42$). UV (MeOH): 233.2 (11800). IR: 3030 (C=*CH*), 2957, 2867 (C–H), 1672 (α,β-unsat. C=O), 1638 (C=C), 1095 (C–OSi). ^{1}H-NMR: −0.01, 0.00 (2*s*, Me_2Si); 0.75 (*s*, Me_2CHCMe_2); 0.80 (*d*, $^3J = 6.8$, Me_2CHCMe_2); 0.87 (*d*, $^3J = 6.8$, Me–C(1′)); 1.53 (*m*, Me_2CHCMe_2); 1.78–1.90 (*m*, 1 H–C(5), H–C(1′)); 1.85 (*s*, Me–C(3)); 2.09–2.26 (*m*, 2 H–C(4), 1 H–C(5), H–C(6)); 3.45 (*dd*, $^2J = 9.8$, $^3J = 5.8$, 1 H–C(2′)); 3.50 (*dd*, $^2J = 9.8$, $^3J = 5.4$, 1 H–C(2′)); 5.74 (*s*, H–C(2)). ^{13}C-NMR: −3.67, −3.65 (2*q*, Me_2Si); 14.75 (*q*, *Me*–C(1′)); 18.41 (*q*, Me_2CHCMe_2); 20.20 (*q*, Me_2CHCMe_2); 23.95 (*q*, *Me*–C(3)); 24.79 (*t*, C(5)); 24.95 (*s*, Me_2CHCMe_2); 30.54 (*t*, C(4)); 34.07 (*d*, Me_2CHCMe_2); 34.62 (*d*, C(1′)); 48.05 (*d*, C(6)); 65.54 (*t*, C(2′)); 126.83 (*d*, C(2)); 160.54 (*s*, C(3)); 200.89 (*s*, C(1)). MS: 225 (16), 219 (100), 203 (22), 131 (5), 129 (5), 73 (10).

*(1′*S*,2*S*,3*S*,6*S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-2,3-epoxy-3-methylcyclohexanone* (*=(1′*S*,1a*S*,3*S*,5a*S*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-one*; **11a**). A soln. of **10a** (20.0 g, 64.4 mmol) in MeOH (400 ml) was cooled to −10°. Then, 30% aq. H_2O_2 soln. (40 ml, 392 mmol) was added, followed by 6M NaOH (10.5 ml, 63 mmol), while the internal temp. was kept below 0°. The mixture was stirred at 0° until completion of the reaction (TLC monitoring). Brine (400 ml) was added, and the mixture was extracted with Et_2O. The combined org. layers were washed with sat. aq. $NaHCO_3$ soln., H_2O, and brine, dried, and evaporated: 19.6 g (93%) of **11a**. Colorless oil. A purified sample was obtained by CC (cyclohexane/AcOEt 8:1; R_f 0.50), as a diastereoisomer mixture. IR: 2959, 2868 (C–H), 1705 (C=O), 1252 (epoxide), 1089 (C–OSi). ^{1}H-NMR (major diastereoisomer): −0.06 (*s*, Me_2Si); 0.58

(*d*, ^3J = 7.2, Me–C(1′)); 0.69 (*s*, Me_2CHCMe_2); 0.73 (*d*, ^3J = 6.8, Me_2CHCMe_2); 1.32 (*s*, Me–C(3)); 2.94 (*s*, H–C(2)); 3.30–3.40 (*m*, 2 H–C(2′)). ^{13}C-NMR (major diastereoisomer): – 3.79, – 3.73 (2*q*, Me_2Si); 11.66 (*q*, Me–C(1′)); 15.22 (*t*, C(5)); 18.27, 18.38 (2*q*, Me_2CHCMe_2); 20.07 (*q*, Me_2CHCMe_2); 21.56 (*q*, *Me*–C(3)); 25.00 (*s*, Me_2CHCMe_2); 28.33 (*t*, C(4)); 33.98 (*d*, Me_2CHCMe_2); 35.26 (*d*, C(1′)); 46.91 (*d*, C(6)); 61.94 (*d*, C(2)); 62.60 (*s*, C(3)); 64.51 (*t*, C(2′)); 207.03 (*s*, C(1)). MS: 241 (100), 225 (22), 213 (23), 211 (25), 199 (37), 121 (40), 105 (29), 75 (80), 73 (30).

*(1′*R,*2*S,*3*S,*6*S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-2,3-epoxy-3-methylcyclohexanone* (= *(1′*R,*1a*S,*3*S,*5a*S*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-one*; **11b**). As described for **11a**, with **10b** (20.0 g, 64.4 mmol): 20.1 g (96%) of **11b**. Colorless oil. Purified samples were obtained by CC (cyclohexane/AcOEt 8:1; R_f 0.50), as a diastereoisomer mixture. IR: 2959, 2867 (C–H), 1703 (C=O), 1252 (epoxide), 1088 (C–OSi). ^{1}H-NMR (major diastereoisomer): – 0.04 (*s*, Me_2Si); 0.72 (*s*, Me_2CHCMe_2); 0.74–0.78 (*d*, Me–C(1′), Me_2CHCMe_2); 1.33 (*s*, Me–C(3)); 2.94 (*s*, H–C(2)); 3.34–3.42 (*m*, 2 H–C(2′)). ^{13}C-NMR (major diastereoisomer): – 3.77, – 3.72 (2*q*, Me_2Si); 13.74 (*q*, *Me*–C(1′)); 18.30, 18.36 (2*q*, Me_2CHCMe_2); 18.44 (*t*, C(5)); 20.01 (*q*, Me_2CHCMe_2); 21.70 (*q*, *Me*–C(3)); 24.93 (*s*, Me_2CHCMe_2); 28.67 (*t*, C(4)); 34.04 (*d*, Me_2CHCMe_2); 37.63 (*d*, C(1′)); 48.20 (*d*, C(6)); 61.22 (*s*, C(3)); 62.64 (*d*, C(2)); 65.03 (*t*, C(2′)); 207.76 (*s*, C(1)). MS: 241 (100), 225 (24), 213 (27), 211 (24), 199 (39), 121 (43), 105 (19), 75 (70), 73 (27).

*(1*S,*1′*S,*2*R,*3*S,*6*S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-2,3-epoxy-3-methylcyclohexanol* (= *(1′*S,*1a*R,*2*S,*3*S,*5a*S*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-ol*; **12a**). To a soln. of **11a** (19.6 g, 60.0 mmol) and $CeCl_3 \cdot 7H_2O$ (23.5 g, 63.1 mmol) in MeOH (390 ml) at 0°, $NaBH_4$ (2.35 g, 62.1 mmol) was added within 10 min. After stirring at 0° (30 min) and r.t. (30 min), $CHCl_3$ (1000 ml) was added and the mixture washed with sat. aq. NH_4Cl soln., H_2O, and brine, dried, and evaporated: 17.6 g (89%) of **12a**. Colorless oil. A purified sample was obtained by CC (cyclohexane/AcOEt 5:1; R_f 0.30, 0.35), as a diastereoisomer mixture. IR: 3300–3400 (O–H), 2958, 2868 (C–H), 1252 (epoxide), 1145 (C–OH), 1090 (C–OSi). ^{1}H-NMR (major diastereoisomer): 0.02 (*s*, Me_2Si); 0.76 (*d*, Me–C(1′)); 0.77 (*s*, Me_2CHCMe_2); 0.80 (*d*, Me_2CHCMe_2); 1.26 (*s*, Me–C(3)); 2.88 (*d*, H–C(2)); 3.35–3.42 (*m*, H–C(1)); 3.55–3.65 (*m*, 2 H–C(2′)). ^{13}C-NMR (major diastereoisomer): – 3.55 (*q*, Me_2Si); 14.05 (*q*, Me–C(1′)); 18.35, 18.43 (2*q*, Me_2CHCMe_2); 18.66 (*t*, C(5)); 20.15 (*q*, Me_2CHCMe_2); 22.42 (*q*, *Me*–C(3)); 25.02 (*s*, Me_2CHCMe_2); 30.21 (*t*, C(4)); 33.93 (*d*, Me_2CHCMe_2); 37.41 (*d*, C(1′)); 43.69 (*d*, C(6)); 58.61 (*s*, C(3)); 63.78 (*d*, C(2)); 66.62 (*t*, C(2′)); 68.83 (*d*, C(1)). MS: 225 (14), 213 (11), 151 (44), 133 (23), 123 (29), 121 (34), 105 (54), 93 (31), 75 (100).

*(1*S,*1′*R,*2*R,*3*S,*6*S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-2,3-epoxy-3-methylcyclohexanol* (= *(1′*R,*1a*R,*2*S,*3*S,*5a*S*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-ol*; **12b**). As described for **12a**, with **11b** (20.1 g, 61.5 mmol): 19.2 g (95%) of **12b**. Colorless oil. Purified samples were obtained by CC (cyclohexane/AcOEt 5:1; R_f 0.30, 0.35), as a diastereoisomer mixture. IR: 3300–3400 (O–H), 2959, 2870 (C–H), 1252 (epoxide), 1131 (C–OH), 1088 (C–OSi). ^{1}H-NMR (major diastereoisomer): 0.06, 0.07 (2*s*, Me_2Si); 0.78–0.83 (*m*, 15 H, Me–C(1′), Me_2CHCMe_2, Me_2CHCMe_2); 1.26 (*s*, *Me*–C(3)); 2.90 (*m*, H–C(2)); 3.40–3.58 (*m*, H–C(1), 2 H–C(2′)). ^{13}C-NMR (major diastereoisomer): – 3.74 (*q*, Me_2Si); 11.23 (*q*, *Me*–C(1′)); 18.28 (*q*, Me_2CHCMe_2); 20.02 (*q*, Me_2CHCMe_2); 22.38 (*q*, *Me*–C(3)); 22.46 (*t*, C(5)); 25.10 (*s*, Me_2CHCMe_2); 30.54 (*t*, C(4)); 33.86 (*d*, Me_2CHCMe_2); 37.56 (*d*, C(1′)); 45.45 (*d*, C(6)); 58.71 (*s*, C(3)); 63.61 (*d*, C(2)); 65.32 (*d*, C(1)); 67.94 (*t*, C(2′)). MS: 225 (14), 151 (37), 133 (23), 123 (26), 121 (33), 107 (22), 105 (51), 93 (30), 81 (39), 75 (100).

*(1*R,*1′*R,*2*R,*3*S,*6*S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-2,3-epoxy-3-methylcyclohexanol* (= *(1′*R,*1a*R,*2*R,*3*S,*5a*S*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-ol*; **12c**). To **18** (2.40 g, 7.68 mmol) and [VO(acac)$_2$] (100 mg, 0.38 mmol) in benzene (100 ml), 6.0M *t*-BuOOH in CH_2Cl_2 (5.00 ml, 30.0 mmol) in benzene (40 ml) was added at 0–5° within 15 min. After stirring for 2 h at 0–5°, Et_2O (250 ml) was added. The mixture was washed with 10% aq. $Na_2S_2O_3$ soln., H_2O, and brine; dried, and evaporated: **12c** (2.55 g, 99%). A pure sample was obtained by CC (cyclohexane/AcOEt 5:1; R_f 0.40). $[\alpha]_D$ = + 58.69 (*c* = 3.41). IR: 3300–3400 (O–CH), 2954, 2871 (C–H), 1249 (epoxide), 1119 (C–OH), 1083 (C–OSi). ^{1}H-NMR: – 0.02, – 0.03 (2*s*, Me_2Si); 0.75 (*s*, Me_2CHCMe_2); 0.79 (*d*, ^3J = 7.0, Me_2CHCMe_2); 0.93 (*d*, ^3J = 6.8, Me–C(1′)); 1.26 (*s*, *Me*–C(3)); 1.05–1.20 (*m*, 2 H), 1.54–1.63 (*m*, 3 H), 1.92–1.98 (*m*, 1 H); 2.22–2.27 (*m*, 1 H, 2 H–C(4), 2 H–C(5), H–C(6), H–C(1′), Me_2CHCMe_2); 3.15 (*d*, ^3J = 5.5, H–C(2)); 3.42 (*dd*, ^2J = 9.9, ^3J = 3.6, 1 H–C(2′)); 3.49 (*dd*, ^2J = 9.9, ^3J = 4.5, 1 H–C(2′)); 4.03 (*m*, H–C(1)). ^{13}C-NMR: – 3.86, – 3.80 (2*q*, Me_2Si); 15.62 (*q*, *Me*–C(1′)); 16.96 (*t*, C(5)); 18.40 (*q*, Me_2CHC(*Me*)$_2$); 20.20 (*q*, Me_2CHCMe_2); 22.71 (*q*, *Me*–C(3)); 24.92 (*s*, Me_2CHCMe_2); 30.88 (*t*, C(4));

34.14 (*d*, Me_2CHCMe$_2$); 34.94 (*d*, C(1′)); 41.44 (*d*, C(6)); 60.87 (*s*, C(3)); 62.02 (*d*, C(2)); 64.39 (*d*, C(1)); 65.45 (*t*, C(2′)). MS: 225 (17), 151 (37), 133 (20), 123 (28), 121 (32), 105 (54), 93 (33), 81 (42), 75 (100).

(1S,1′S,2S,3S)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-6-methylenecyclohexane-1,2-diol (**13a**). $LiNEt_2$ was prepared from Et_2NH (21.9 g, 300 mmol) in THF (400 ml) and 2.5M BuLi in hexanes (120 ml, 300 mmol) at 0°. A soln. of **14a** (21.4 g, 53.4 mmol) in THF (80 ml) was added within 15 min, and the mixture was heated under reflux for 2 h. Sat. aq. Na_2CO_3 soln. (300 ml) was added at r.t., the mixture stirred for 30 min and extracted with $CHCl_3$, the combined org. layer washed with sat. aq. NH_4Cl soln., H_2O, and brine, dried, and evaporated. CC (cyclohexane/AcOEt 5:1) gave fractions of 2.40 g (R_f 0.25) and 5.15 g (R_f 0.20). The more polar, main fraction (R_f 0.20) was found to be 90% pure **13a** mixed with a further diastereoisomer (10%). IR: 3300–3400 (O–H), 3092 (C=*CH*$_2$), 2957, 2866 (C–H), 1656 (C=CH$_2$), 1156, 1130 (C–OH), 1087 (C–OSi), 875 (C=*CH*$_2$). ^{1}H-NMR (major diastereoisomer): 0.04 (*s*, Me_2Si); 0.75 (*d*, ^3J = 7.0, Me–C(1′)); 0.79 (*s*, 6 H, Me_2CHC*Me*$_2$); 0.83 (*d*, ^3J = 7.0, *Me*$_2$CHCMe$_2$); 1.05 (*m*, 1 H), 1.50–1.70 (*m*, 3 H), 1.90–2.05 (*m*, 2 H), 2.23–2.31 (*m*, 1 H, H–C(3), 2 H–C(4), 2 H–C(5), H–C(1′), Me_2C*H*CMe$_2$); 3.11 (*dd*, ^3J = 8.9, 8.9, H–C(2)); 3.40–3.50 (*m*, 2 H–C(2′)); 3.83 (*d*, ^3J = 8.9, 1 H–C(1)); 4.75 (*m*, 1 H, CH_2=C(6)); 4.98 (*m*, 1 H, CH_2=C(6)). ^{13}C-NMR (major diastereoisomer): −3.65, −3.50 (2*q*, Me_2Si); 11.97 (*q*, *Me*–C(1′)); 18.43, 18.46 (2*q*, Me_2CHC*Me*$_2$); 20.24, 20.28 (2*q*, *Me*$_2$CHCMe$_2$); 25.04 (*t*, C(4)); 25.43 (*s*, Me_2SCH*C*Me$_2$); 32.93 (*t*, C(5)); 34.10 (*d*, Me_2*C*HCMe$_2$); 34.71 (*d*, C(1′)); 43.56 (*d*, C(3)); 66.61 (*t*, C(2′)); 77.30 (*d*, C(2)); 77.37 (*d*, C(1)); 105.62 (*t*, *C*H$_2$=C(6)); 147.51 (*s*, C(6)). MS: 225 (75), 151 (72), 150 (40), 133 (57), 109 (39), 107 (46), 105 (47), 93 (39), 75 (100).

(1S,1′R,2S,3S)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-6-methylenecyclohexane-1,2-diol (**13b**). As described for **13a**, with **14b** (23.4 g, 58.4 mmol). CC (cyclohexane/AcOEt 5:1) gave pure **13b** (4.82 g, 23% overall from **10b**; R_f 0.25) and 2.35 g of two diastereoisomers (R_f 0.20; 70:30 ratio by NMR). **13b**: $[\alpha]_D$ = +21.80 (*c* = 1.47). IR: 3300–3400 (O–H), 3093 (*C*=*CH*$_2$); 2957, 2869 (C–H), 1657 (C=CH$_2$), 1129, 1050 (C–OH), 1088 (C–OSi), 875 (C=*CH*$_2$). ^{1}H-NMR: 0.08 (*s*, Me_2Si); 0.81, 0.82 (2*s*, Me_2CHC*Me*$_2$); 0.84 (*d*, ^3J = 6.8, *Me*$_2$CHCMe$_2$); 0.87 (*d*, ^3J = 7.2, Me–C(1′)); 1.15–1.25 (*m*, 1 H), 1.52–1.64 (*m*, 3 H), 1.86–1.92 (*m*, 1 H), 1.95–2.05 (*m*, 1 H), 2.27–2.32 (*m*, 1 H, H–C(3), 2 H–C(4), 2 H–C(5), H–C(1′), Me_2C*H*CMe$_2$); 3.15 (*dd*, ^3J = 9.0, 9.0, H–C(2)); 3.54 (*dd*, ^2J = 10.0, ^3J = 3.6, 1 H–C(2′)); 3.60 (*dd*, ^2J = 10.0, ^3J = 5.8, 1 H–C(2′)); 3.85 (*d*, ^3J = 9.0, H–C(1)); 4.77 (*m*, 1 H, CH_2=C(6)); 5.03 (*m*, 1 H, CH_2=C(6)). ^{13}C-NMR: −3.59 (*q*, Me_2Si); 12.86 (*q*, *Me*–C(1′)); 18.42 (*q*, Me_2CHC*Me*$_2$); 20.18, 20.20 (2*q*, Me_2CHC*Me*$_2$); 25.20 (*s*, Me_2CH*C*Me$_2$); 28.73 (*t*, C(4)); 33.20 (*t*, C(5)); 33.97 (*d*, Me_2*C*HCMe$_2$); 37.29 (*d*, C(1′)); 46.55 (*d*, C(3)); 67.04 (*t*, C(2′)); 76.10 (*d*, C(2)); 76.92 (*d*, C(1)); 105.68 (*t*, *C*H$_2$=C(6)); 147.00 (*s*, C(6)). MS: 328 (1, M^+), 225 (100), 151 (77), 150 (38), 133 (50), 109 (28), 107 (32), 105 (29), 93 (24), 75 (67).

(1S,1′R,2R,3S)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-6-methylenecyclohexane-1,2-diol (**13c**). As described for **13a** with **14c** (2.25 g, 5.61 mmol): **14c** (1.75 g, 95%). A pure sample was prepared by CC (cyclohexane/AcOEt 5:1; R_f 0.21). $[\alpha]_D$ = +2.69 (*c* = 2.90). IR: 3300–3400 (O–H), 3088 (C=*CH*$_2$), 2958, 2899, 2866 (C–H), 1657 (C=CH$_2$), 1146, 1130 (C–OH), 1096 (C–OSi), 874 (C=*CH*$_2$). ^{1}H-NMR: 0.03 (*s*, 3 H, Me_2Si); 0.04 (*s*, 3 H, Me_2Si); 0.78 (*s*, Me_2CHC*Me*$_2$); 0.82 (*d*, ^3J = 6.8, *Me*$_2$CHCMe$_2$); 0.91 (*d*, ^3J = 7.0, Me–C(1)); 1.25–1.80 (*m*, 5 H), 1.85–1.93 (*m*, 1 H), 2.32–2.39 (*m*, 1 H, H–C(3), 2 H–C(4), 2 H–C(5), H–C(1′), Me_2C*H*CMe$_2$); 3.46 (*m*, 2 H–C(2′)); 3.90 (*m*, H–C(2)); 3.95 (*m*, H–C(1)); 4.87 (*m*, 1 H, CH_2=C(6)); 5.01 (*m*, 1 H, CH_2=C(6)). ^{13}C-NMR: −3.67, −3.61 (2*q*, Me_2Si); 16.40 (*q*, *Me*–C(1′)); 18.38 (*q*, Me_2CHC*Me*$_2$); 20.15, 20.18 (2*q*, *Me*$_2$CHCMe$_2$); 22.70 (*t*, C(4)); 25.05 (*s*, Me_2CHC*Me*$_2$); 33.15 (*t*, C(5)); 34.03 (*d*, Me_2*C*HCMe$_2$); 37.53 (*d*, C(1′)); 44.36 (*d*, C(3)); 65.14 (*t*, C(2′)); 73.26 (*d*, C(2)); 74.32 (*d*, C(1)); 107.43 (*t*, *C*H$_2$=C(6)); 147.40 (*s*, C(6)). MS: 329 (2, M^+), 225 (91), 151 (44), 133 (55), 105 (44), 75 (100).

(1S,1′S,2R,3S,6S)-{6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-2,3-epoxy-3-methylcyclohexyl}oxy}trimethylsilane (= *(1′S,1aR,2S,3S,5aS)-{{3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-yl}oxy}trimethylsilane*; **14a**). A soln. of **12a** (17.6 g, 53.6 mmol) and Et_3N (43.4 g, 429 mmol) in THF (400 ml) was cooled to 0°, and Me_3SiCl (23.3 g, 214 mmol) in THF (50 ml) was added within 30 min. The mixture was stirred at 0° for 2 h and at r.t. for 12 h. Et_2O (1000 ml) was added and the resulting mixture washed with sat. aq. $NaHCO_3$ soln. and brine, dried, and evaporated: **14a** (21.4 g, quant.). A purified sample was obtained by CC (cyclohexane/AcOEt 10:1; R_f 0.80), as a diastereomer mixture. IR: 2957, 2867 (C–H), 1252 (epoxide), 1091, 1042 (C–OSi). ^{1}H-NMR (major diastereoisomer): 0.02 (*s*, Me_2Si); 0.13 (*s*, Me_3Si); 0.65 (*d*, ^3J = 7.0, Me–C(1′)); 0.78 (*s*, Me_2CHC*Me*$_2$); 0.83 (*d*, ^3J = 6.8, *Me*$_2$CHCMe$_2$); 1.27 (*s*, Me–C(3)); 2.80 (*d*, H–C(2)); 3.30–3.48 (*m*, H–C(1), 2 H–C(2′)). ^{13}C-NMR (major diastereoisomer): −3.54, −3.44 (2*q*, Me_2Si); 0.19 (*q*, Me_3Si); 10.66 (*q*, *Me*–C(1′)); 15.77 (*t*, C(5)); 18.50 (*q*, Me_2CHC*Me*$_2$); 20.32 (*q*, *Me*$_2$CHCMe$_2$); 22.67 (*q*, *Me*–C(3)); 25.04 (*s*, Me_2CH*C*Me$_2$); 30.31 (*t*, C(4)); 34.12 (*d*, Me_2*C*HCMe$_2$); 34.21

(*d*, C(1′)); 41.88 (*d*, C(6)); 58.83 (*s*, C(3)); 64.91 (*d*, C(2)); 66.50 (*t*, C(2′)); 68.93 (*d*, C(1)). MS: 315 (25), 225 (25), 147 (52), 133 (59), 93 (20), 81 (26), 75 (36), 73 (100).

*(1*S*,1′*R*,2*R*,3*S*,6*S*)-{[6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl]-2,3-epoxy-3-methylcyclohexyl}oxy}trimethylsilane* (= *(1′*R*,1a*R*,2*S*,3*S*,5a*S*)-{[3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-yl]oxy}trimethylsilane*; **14b**). As described for **14a** with **12b** (19.2 g, 58.4 mmol): **14b** (23.4 g, quant.). A purified sample was obtained by CC (cyclohexane/AcOEt 10:1; R_f 0.80), as a diastereomer mixture. IR: 2957, 2867 (C–H), 1251 (epoxide), 1092, 1042 (C–OSi). ^{1}H-NMR (major diastereoisomer): −0.01 (*s*, Me_2Si); 0.11 (*s*, Me_3Si); 0.76 (*s*, Me_2CHCMe_2); 0.80 (*d*, Me_2CHCMe_2); 0.83 (*d*, Me–C(1′)); 1.23 (*s*, Me–C(3)); 2.73 (*d*, H–C(2)); 3.20 (*m*, H–C(1)); 3.34–3.46 (*m*, 2 H–C(2′)). ^{13}C-NMR (major diastereoisomer): −3.65 (*q*, Me_2Si); 0.51 (*q*, Me_3Si); 15.79 (*q*, *Me*–C(1′)); 17.19 (*t*, C(5)); 18.45 (*q*, Me_2CHCMe_2); 20.30 (*q*, Me_2CHCMe_2); 22.63 (*q*, *Me*–C(3)); 24.96 (*s*, Me_2CHCMe_2); 30.68 (*t*, C(4)); 34.07 (*d*, Me_2CHCMe_2); 35.02 (*d*, C(1′)); 45.69 (*d*, C(6)); 58.72 (*s*, C(3)); 64.72 (*d*, C(2)); 64.88 (*t*, C(2′)); 69.50 (*d*, C(1)). MS: 315 (23), 225 (100), 223 (48), 151 (43), 147 (94), 133 (89), 105 (30), 75 (37), 73 (100).

*(1*R*,1′*R*,2*R*,3*S*,6*S*)-{[6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-2,3-epoxy-3-methylcyclohexyl}oxy}trimethylsilane* (= *(1′*R*,1a*R*,2*R*,3*S*,5a*S*)-{[3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}hexahydro-5a-methyl-1-benzoxiren-2-yl]oxy}trimethylsilane*; **14c**). As described for **14a**, with **12c** (2.25 g, 6.85 mmol), Et_3N (11.1 g, 110 mmol), THF (100 ml), Me_3SiCl (5.95 g, 54.8 mmol), and THF (10 ml) (at 0° for 1 h and at r.t. for 24 h). Workup with Et_2O (400 ml): **14c** (2.75 g, quant.). A pure sample was obtained by CC (cyclohexane/AcOEt 10:1; R_f 0.80). $[\alpha]_D = +69.71$ ($c = 3.64$). IR: 2958, 2905, 2867 (C–H), 1250 (epoxide), 1079, 1050 (C–OSi). ^{1}H-NMR: −0.02, −0.01 (2*s*, Me_2Si); 0.11 (*s*, Me_3Si); 0.77 (*s*, Me_2CHCMe_2); 0.82 (*d*, $^3J = 7.0$, Me_2CHCMe_2); 0.88 (*d*, Me–C(1′)); 1.24 (*s*, Me–C(3)); 1.00–1.35 (*m*, 3 H), 1.45–1.60 (*m*, 3 H), 1.92–1.98 (*m*, 1 H, 2 H–C(4), 2 H–C(5), H–C(6), H–C(1′), Me_2CHCMe_2); 2.94 (*d*, $^3J = 5.0$, H–C(2)); 3.48 (*m*, 2 H–C(2′)); 4.13 (*m*, H–C(1)). ^{13}C-NMR: −3.77, −3.73 (2*q*, Me_2Si); 0.27 (*q*, Me_3Si); 15.64 (*q*, *Me*–C(1′)); 17.29 (*t*, C(5)); 18.47 (*q*, Me_2CHCMe_2); 20.28 (*q*, Me_2CHCMe_2); 22.82 (*q*, *Me*–C(3)); 24.97 (*s*, Me_2CHCMe_2); 31.48 (*t*, C(4)); 34.25 (*d*, Me_2CHCMe_2); 34.65 (*d*, C(1′)); 42.23 (*d*, C(6)); 58.81 (*s*, C(3)); 61.73 (*d*, C(2)); 65.51 (*t*, C(2′)); 66.31 (*d*, C(1)). MS: 315 (30), 225 (83), 223 (38), 151 (34), 147 (73), 133 (68), 75 (59), 73 (100).

*(1*S*,1′*S*,2*S*,3*S*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-6-methylenecyclohexane-1,2-diyl Bis(methanesulfonate)* (**15a**). To a soln. of **13a** (5.15 g, 15.7 mmol; including 10% of unknown diastereoisomer) and Et_3N (15.1 g, 149 mmol) in CH_2Cl_2 (250 ml) at 0°, a soln. of MsCl (7.12 g, 62.2 mmol) in CH_2Cl_2 (50 ml) was added within 10 min, and the mixture was stirred at 0° for 2 h. Sat. aq. $NaHCO_3$ soln. (400 ml) was added, the mixture extracted with CH_2Cl_2, washed with H_2O, sat. aq. NH_4Cl, and brine, dried, and evaporated. Purification of the crude product by CC (cyclohexane/AcOEt 5:1; R_f 0.22) gave **15a** (5.60 g; only a single diastereoisomer detectable by NMR) that was dissolved in the required amount of pentane under reflux and allowed to crystallize (3 h at r.t., 3 h at 0°, overnight at −20°): highly pure **15a** (4.89 g, 16% overall from **10a**). M.p. 79° (pentane). Colorless crystals. $[\alpha]_D = +26.21$ ($c = 0.74$). IR (KBr): 3024 (C=CH_2), 2961, 2888, 2865 (C–H), 1664 (C=CH_2), 1342/1356, 1169/1177 (SO_2), 1105 (C–OSO_2), 1095 (C–OSi), 875 (C=CH_2). ^{1}H-NMR: 0.03, 0.04 (2*s*, Me_2Si); 0.73 (*d*, $^3J = 6.8$, Me–C(1′)); 0.79 (*s*, Me_2CHCMe_2); 0.84 (*d*, $^3J = 6.8$, Me_2CHCMe_2); 0.99–1.11 (*m*, 1 H), 1.52–1.62 (*m*, 1 H), 1.70–1.80 (*m*, 1 H), 1.92–2.00 (*m*, 1 H), 2.05–2.16 (*m*, 2 H), 2.37–2.43 (*m*, 1 H, H–C(3), 2 H–C(4), 2 H–C(5), H–C(1′), Me_2CHCMe_2); 3.09 (*s*, 1 $MeSO_2$); 3.10 (*s*, 1 $MeSO_2$); 3.34 (*dd*, $^2J = 10.0$, 10.0, 1 H–C(2′)); 3.47 (*dd*, $^2J = 10.0$, $^3J = 5.5$, 1 H–C(2′)); 4.48 (*dd*, $^3J = 9.0$; 10.0, H–C(2)); 4.96 (*d*, $^3J = 9.0$, H–C(1)); 5.01 (*m*, 1 H, CH_2=C(6)); 5.17 (*m*, 1 H, CH_2=C(6)). ^{13}C-NMR: −3.78, −3.58 (2*q*, Me_2Si); 10.00 (*q*, *Me*–C(1′)); 18.40 (*q*, Me_2CHCMe_2); 20.24 (*q*, Me_2CHCMe_2); 23.36 (*t*, C(4)); 24.94 (*s*, Me_2CHCMe_2); 32.42 (*t*, C(5)); 33.50 (*d*, C(1′)); 34.12 (*d*, Me_2CHCMe_2); 38.90, 39.07 (2*q*, $MeSO_2$); 41.74 (*d*, C(3)); 65.41 (*t*, C(2′)); 82.23, 82.36 (2*d*, C(1), C(2)); 110.41 (*t*, CH_2=C(6)); 141.91 (*s*, C(6)). MS: 303 (25), 207 (16), 153 (46), 133 (100), 105 (21), 93 (18), 91 (17), 75 (30).

*(1*S*,1′*R*,2*S*,3*R*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-6-methylenecyclohexane-1,2-diyl Bis(methanesulfonate)* (**15b**). As described for **15a**, with **13b** (4.82 g, 14.7 mmol). Purification of the crude product by CC (cyclohexane/AcOEt 5:1; R_f 0.20) gave **15b** (4.65 g, 65%). Colorless oil. $[\alpha]_D = +11.55$ ($c = 2.86$). IR: 2958, 2869 (C–H), 1661 (C=CH_2), 1360, 1177 (SO_2), 1149, 1130 (C–OSO_2), 1088 (C–OSi), 866 (C=CH_2). ^{1}H-NMR: 0.02 (*s*, Me_2Si); 0.77 (*s*, Me_2CHCMe_2); 0.80 (*d*, $^3J = 6.8$, Me_2CHCMe_2); 0.92 (*d*, $^3J = 7.0$, Me–C(1′)); 1.15–1.25 (*m*, 1 H), 1.52–1.58 (*m*, 1 H), 1.72–1.76 (*m*, 1 H), 1.80–1.84 (*m*, 1 H), 1.93–1.98 (*m*, 1 H), 2.10–2.14 (*m*, 1 H), 2.38–2.43 (*m*, 1 H, H–C(3), 2 H–C(4), 2 H–C(5), H–C(1′), Me_2CHCMe_2); 3.09 (*s*, 1 $MeSO_2$); 3.10 (*s*, 1 $MeSO_2$); 3.41 (*dd*, $^2J = 10.0$, $^3J = 6.3$, 1 H–C(2′)); 3.50 (*dd*, $^2J = 10.0$, $^3J = 6.0$, 1 H–C(2′)); 4.69 (*dd*, $^3J = 9.1$, 10.0, H–C(2)); 4.89 (*d*, $^3J = 9.1$, H–C(1)); 5.00 (*m*, 1 H, CH_2=C(6)); 5.18 (*m*, 1 H, CH_2=C(6)). ^{13}C-NMR: −3.81, −3.76 (2*q*, Me_2Si); 14.03 (*q*, *Me*–C(1′)); 18.36 (*q*, Me_2CHCMe_2);

20.10, 20.11 (2*q*, Me_2CCHMe_2); 24.45 (*t*, C(4)); 24.96 (*s*, Me_2CHCMe_2); 32.52 (*t*, C(5)); 32.92 (*d*, C(1′)); 33.92 (*d*, Me_2CHCMe_2); 38.86, 39.08 (2*q*, $MeSO_2$); 46.21 (*d*, C(3)); 63.77 (*t*, C(2′)); 82.30, 83.39 (2*d*, C(1), C(2)); 110.64 (*t*, CH_2=C(6)); 141.84 (*s*, C(6)). MS: 303 (25), 225 (14), 223 (11), 207 (24), 153 (33), 149 (11), 133 (100), 105 (21), 75 (31).

*(1′*R,2S*)-Dimethyl{[2-(4′-methylenecyclohex-2′-en-1′-yl)propyl]oxy}(1,1,2-trimethylpropyl)silane* (**16a**). A soln. of **15a** (8.25 g, 17.0 mmol), NaI (20.6 g, 137 mmol), and pyridine (1.0 ml) in acetone (210 ml) was stirred under reflux for 1 h. Cyclohexane (800 ml) was added at r.t. and the mixture washed with 10% aq. $Na_2S_2O_3$ soln., H_2O, and brine, dried, and evaporated. CC (cyclohexane/AcOEt 5:1) yielded **16a** (3.15 g, 63%; R_f 0.95) and **15a** (1.95 g, 24%, R_f 0.22). **16a**: $[\alpha]_D = -1.70$ (*c* = 1.41). IR: 3077 (C=CH_2), 3022 (C=$C-H$), 2957, 2867 (C−H), 1636, 1597 (conj. C=C), 1094 (C−OSi), 876 (C=CH_2). ^{1}H-NMR: 0.07 (*s*, Me_2Si); 0.83 (*d*, Me(3)); 0.84 (*s*, Me_2CHCMe_2); 0.88 (*d*, ^3J = 6.8, Me_2CHCMe_2); 1.39 (*m*, 1 H−C(6′)); 1.62 (*m*, H−C(2)); 1.66–1.76 (*m*, 1 H−C(6′), Me_2CHCMe_2); 2.22–2.45 (*m*, H−C(1′), 2 H−C(5′)); 3.48 (*m*, 2 H−C(1)); 4.72 (*m*, CH_2=C(4′)); 5.68 (*d*, ^3J = 9.9, H−C(2′)); 6.12 (*dd*, ^3J = 9.9, ^4J = 2.3, H−C(3′)). ^{13}C-NMR: −3.48, −3.42 (2*q*, Me_2Si); 13.32 (*q*, Me(3)); 18.61 (*q*, Me_2CHCMe_2); 20.44 (*q*, Me_2CHCMe_2); 24.27 (*t*, C(6′)); 25.16 (*s*, Me_2CHCMe_2); 30.10 (*t*, C(5′)); 34.33 (*d*, Me_2CHCMe_2); 37.08 (*d*, C(2)); 39.75 (*d*, C(1′)); 65.80 (*t*, C(1)); 110.11 (*t*, CH_2=C(4′)); 129.64 (*d*, C(3′)); 134.88 (*d*, C(2′)); 143.47 (*s*, C(4′)). MS: 294 (1, M^+), 209 (45), 134 (100), 119 (20), 115 (20), 105 (13), 93 (13), 91 (23), 89 (18), 75 (43), 73 (19), 59 (12).

*(1′*R,2R*)-Dimethyl{[2-(4′-methylenecyclohex-2′-en-1′-yl)propyl]oxy}(1,1,2-trimethylpropyl)silane* (**16b**). *From* **15b**: As described for **15a**, with **15b** (5.30 g, 10.9 mmol). CC (cyclohexane/AcOEt 5:1) yielded **16b** (2.00 g, 62%; R_f 0.95) and **15b** (1.20 g, 23%; R_f 0.20).

From **19**: A soln. of **19** (1.75 g, 4.72 mmol) in $P(OMe)_3$ (20 ml) was heated under reflux for 24 h. Cyclohexane (400 ml) was added at r.t. and the mixture washed with 10% aq. NaOH soln., H_2O, and brine, dried, and evaporated to give 1.65 g of a yellow oil. The crude product and maleic anhydride (500 mg, 5.10 mmol) were heated under reflux for 30 min in benzene (30 ml). Then, 10% aq. NaOH soln. (20 ml) was added at r.t. and the mixture stirred for 15 min. Cyclohexane (300 ml) was added, the mixture washed with 10% aq. NaOH soln., H_2O, and brine, dried, and evaporated. CC (cyclohexane/AcOEt 25:1; R_f 0.80) yielded **16b** (550 mg, 40%). $[\alpha]_D = +18.28$ (*c* = 2.05). IR: 3078 (C=CH_2), 3025 (C=$C-H$), 2958, 2933, 2867 (C−H), 1636, 1596 (conj. C=C), 1095 (C−OSi), 876 (C=CH_2). ^{1}H-NMR: 0.09 (*s*, Me_2Si); 0.86 (*s*, Me_2CHCMe_2); 0.90 (*d*, Me(3), Me_2CHCMe_2); 1.48 (*m*, 1 H−C(6′)); 1.64 (*m*, H−C(2), Me_2CHCMe_2); 1.76 (*m*, 1 H−C(6′)); 2.30–2.46 (*m*, H−C(1′), 2 H−C(5′)); 3.49 (*dd*, ^2J = 10.0, ^3J = 6.3, 1 H−C(1)); 3.55 (*dd*, ^2J = 10.0, ^3J = 5.9, 1 H−C(1)); 4.75 (*m*, CH_2=C(4′)); 5.76 (*d*, ^3J = 10.0, H−C(2′)); 6.15 (*d*, ^3J = 10.0, H−C(3′)). ^{13}C-NMR: −3.52 (*q*, Me_2Si); 13.83 (*q*, Me(3)); 18.54 (*q*, Me_2CHCMe_2); 20.37 (*q*, Me_2CHCMe_2); 25.11 (*s*, Me_2CHCMe_2); 27.04 (*t*, C(6′)); 30.42 (*t*, C(5′)); 34.29 (*d*, Me_2CHCMe_2); 37.50 (*d*, C(2)); 39.59 (*d*, C(1′)); 65.74 (*t*, C(1)); 110.09 (*t*, CH_2=C(4)); 129.74 (*d*, C(3′)); 133.07 (*d*, C(2′)); 143.48 (*s*, C(4′)). MS: 294 (2, M^+), 209 (50), 134 (100), 119 (16), 115 (17), 105 (11), 91 (18), 89 (13), 75 (28), 73 (12).

*(1*R,1′R,6S*)-6-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-3-methylcyclohex-2-en-1-ol* (**18**). To a soln. of **10b** (5.00 g, 16.1 mmol) and $CeCl_3 \cdot 7H_2O$ (6.60 g, 17.7 mmol) in MeOH (200 ml) at 0°, $NaBH_4$ (910 mg, 24.1 mmol) was added within 10 min. After stirring at 0° (30 min) and r.t. (30 min), $CHCl_3$ (500 ml) was added and the mixture washed with sat. aq. NH_4Cl soln., H_2O, and brine, dried and evaporated: 5.00 g of a colorless oil. CC (cyclohexane/AcOEt 15:1) gave 550 mg of a first fraction (R_f 0.35) and **18** (2.77 g, 55%; R_f 0.30). $[\alpha]_D = +92.67$ (*c* = 4.01). IR: 3300–3400 (O−H), 2958, 2930, 2911, 2829 (C−H), 1674 (C=C), 1108 (C−OH), 1074 (C−OSi). ^{1}H-NMR: 0.01 (*s*, Me_2Si); 0.77 (*s*, Me_2CHCMe_2); 0.80 (*d*, ^3J = 6.8, Me_2CHCMe_2); 0.94 (*d*, ^3J = 7.0, Me−C(1′)); 1.30–1.42, 1.50–1.70 (2*m*, 2 H−C(5), H−C(1′), Me_2CHCMe_2); 1.60 (*s*, Me−C(3)); 1.79–1.95, 2.26 (2*m*, 2 and 1 H, resp., 2 H−C(4), H−C(6)); 3.51 (*m*, 2 H−C(2′)); 3.99 (*m*, H−C(1)); 5.56 (*d*, ^3J = 5.3, H−C(2)). ^{13}C-NMR: −3.83, −3.77 (2*q*, Me_2Si); 15.96 (*q*, *Me*−C(1′)); 18.36 (*q*, Me_2CHCMe_2); 19.47 (*t*, C(5)); 20.17 (*q*, Me_2CHCMe_2); 23.29 (*q*, *Me*−C(3)); 24.96 (*s*, Me_2CHCMe_2); 31.33 (*t*, C(4)); 34.09 (*d*, Me_2CHCMe_2); 36.32 (*d*, C(1′)); 41.76 (*d*, C(6)); 65.24 (*d*, C(1)); 65.50 (*t*, C(2′)); 123.86 (*d*, C(2)); 138.64 (*s*, C(3)). MS: 312 (2, M^+), 275 (31), 225 (26), 219 (86), 203 (26), 147 (27), 135 (100), 93 (49), 73 (50).

*(1*S,1′R,2R,3S*)-3-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylpropyl}-6-methylenecyclohexane-1,2-diyl Carbonothioate = (1′*R,3a*R,4*S,7a*S*)-4-{2′-{[Dimethyl(1,1,2-trimethylpropyl)silyl]oxy}-1′-methylethyl}-hexahydro-7-methylene-1,3-benzodioxol-2-thione*; (**9**). To **13c** (1.64 g, 5.00 mmol) and pyridine (2.0 ml) in C_6H_6 (30 ml) at 0–5°, thiophosgene (1.15 g, 10 mmol) in C_6H_6 (15 ml) was added dropwise. The soln. was stirred at 0° for 15 min and at r.t. for 2 h. Et_2O (200 ml) was added and the mixture filtered, washed with H_2O and sat. aq. NH_4Cl soln., dried, and evaporated: **19** (1.82 g, 98%). A pure sample was prepared by CC (cyclohexane/AcOEt 5:1; R_f 0.55). $[\alpha]_D = +5.36$ (*c* = 1.12). IR: 3084 (C=CH_2), 2958, 2867 (C−H), 1656 (C=CH_2), 1158 (C=S),

1129 (C–O), 1100 (C–OSi), 874 (C=*CH*$_2$). ^{1}H-NMR: 0.00 (*s*, Me_2Si); 0.75 (*s*, Me_2CHC*Me*$_2$); 0.80 (*d*, ^3J = 6.8, *Me*$_2$CHCMe_2); 0.98 (*d*, ^3J = 6.4, Me–C(1′)); 1.31–1.81 (*m*, 5 H), 2.06–2.14 (*m*, 1 H), 2.43–2.49 (*m*, 1 H, H–C(3), 2 H–C(4), 2 H–C(5), H–C(1′), Me_2C*H*CMe_2); 3.47 (*m*, 1 H–C(2′)); 3.59 (*m*, 1 H–C(2′)); 5.05 (*m*, H–C(2)); 5.09 (*m*, 1 H, CH_2=C(6)); 5.18 (*d*, ^3J = 7.6, H–C(1)); 5.21 (*m*, 1 H, CH_2=C(6)). ^{13}C-NMR: −3.78, −3.74 (2*q*, Me_2Si); 15.21 (*q*, *Me*–C(1′)); 18.49 (*q*, Me_2CHC*Me*$_2$); 20.28 (*q*, *Me*$_2$CHCMe_2); 21.82 (*t*, C(4)); 25.03 (*s*, Me_2CHCMe_2); 28.25 (*t*, C(5)); 34.25 (*d*, Me_2*C*HCMe_2); 36.02 (*d*, C(1′)); 37.94 (*d*, C(3)); 64.80 (*t*, C(2′)); 83.21, 83.42 (2*d*, C(1), C(2)); 116.98 (*t*, *C*H_2=C(6)); 138.96 (*s*, C(6)); 192.12 (*s*, C=S). MS: 371 (1, M^+), 285 (4), 225 (100), 195 (26), 133 (51), 105 (32), 91 (27), 75 (72), 73 (27), 43 (24).

*(1′*R*,2*S*)-2-(4′-Methylenecyclohex-2′-en-1′-yl)propan-1-ol* (**20a**). To **16a** (2.24 g, 7.60 mol) in THF (40 ml), a soln. of $Bu_4NF \cdot 3H_2O$ (4.80 g, 15.2 mmol) in THF (20 ml) was added at 0° within 10 min. The mixture was stirred for 2 h at 0° and for 12 h at r.t. AcOEt (500 ml) was added and the org. layer washed with H_2O, sat. aq. $NaHCO_3$ soln. and brine, dried, and evaporated: 2.20 g of a colorless oil. CC (cyclohexane/AcOEt 5:1; R_f 0.25) yielded **20a** (1.04 g, 90%). $[\alpha]_D$ = −0.64 (*c* = 0.79). IR: 3300–3400 (O–H), 3077 (C=*CH*$_2$), 3021 (C=*C*–*H*), 2957, 2934, 2876 (C–H), 1635, 1596 (conj. C=C), 1035 (C–OH), 878 (C=*CH*$_2$). ^{1}H-NMR: 0.83 (*d*, ^3J = 7.0, Me(3)); 1.40 (*m*, 1 H–C(6′)); 1.67 (*m*, 1 H–C(6′)); 1.73 (*m*, H–C(2)); 2.18–2.42 (*m*, H–C(1′), 2 H–C(5′)); 3.45 (*dd*, ^2J = 10.8, ^3J = 6.6, 1 H–C(1)); 3.55 (*dd*, ^2J = 10.8, ^3J = 6.5, 1 H–C(1)); 4.71 (*m*, CH_2=C(4′)); 5.64 (*d*, ^3J = 10.0, H–C(2′)); 6.11 (*d*, ^3J = 10.0, H–C(3′)). ^{13}C-NMR: 13.07 (*q*, Me(3)); 24.20 (*t*, C(6′)); 29.86 (*t*, C(5′)); 37.10 (*d*, C(2)); 39.66 (*d*, C(1′)); 65.75 (*t*, C(1)); 110.25 (*t*, *C*H_2=C(4′)); 129.80 (*d*, C(3′)); 134.12 (*d*, C(2′)); 143.20 (*s*, C(4′)); assignment by H,H COSY, C,H correlation (HMQC), and C,H long-range correlation (HMBC). MS: 152 (27, M^+), 137 (37), 134 (41), 119 (100), 93 (93), 91 (74), 79 (47), 77 (46), 69 (22), 43 (23).

*(1′*R*,2*R*)-2-(4′-Methylenecyclohex-2′-en-1′-yl)propan-1-ol* (=*(β*R*,1*R*)-β-Methyl-4-methylenecyclohex-2-ene-1-ethanol*; **20b**). As described for **20a**, with **16b** (1.30 g, 4.41 mmol): 1.25 g of a colorless oil. CC (cyclohexane/AcOEt 5:1; R_f 0.25) yielded **20b** (595 mg, 89%). $[\alpha]_D$ = +19.62 (*c* = 2.61). IR: 3300–3400 (O–H), 3077 (C=*CH*$_2$), 3023 (C=*C*–*H*), 2956, 2932, 2877 (C–H), 1635, 1595 (conj. C=C), 1036 (C–OH), 878 (C=*CH*$_2$). ^{1}H-NMR: 0.85 (*d*, ^3J = 7.0, Me(3)); 1.39 (*m*, 1 H–C(6′)); 1.64 (*m*, H–C(2)); 1.72 (*m*, 1 H–C(6′)); 2.18–2.40 (*m*, H–C(1′), 2 H–C(5′)); 3.40 (*dd*, ^2J = 10.7, ^3J = 7.0, H–C(1)); 3.54 (*dd*, ^2J = 10.7, ^3J = 6.2, 1 H–C(1)); 4.70 (*m*, CH_2=C(4′)); 5.66 (*d*, ^3J = 9.8, H–C(2′)); 6.10 (*d*, ^3J = 9.8, H–C(3′)). ^{13}C-NMR: 13.46 (*q*, Me(3)); 26.56 (*t*, C(6′)); 30.16 (*t*, C(5′)); 37.36 (*d*, C(2)); 39.40 (*d*, C(1′)); 65.41 (*t*, C(1)); 110.27 (*t*, *C*H_2=C(4′)); 129.89 (*d*, C(3′)); 132.44 (*d*, C(2′)); 143.12 (*s*, C(4′)); assignment by H,H COSY, C,H correlation (HMQC), and C,H long-range correlation (HMBC). MS: 152 (22, M^+), 137 (26), 134 (38), 121 (10), 119 (43), 93 (100), 93 (88), 79 (59), 77 (61), 41 (38), 39 (29).

*(1′*R*,2*S*)-2-(4′-Methylenecyclohex-2′-en-1′-yl)propyl 4-Nitrobenzenesulfonate* (**21a**). To a soln. of **20a** (1.11 g, 7.30 mmol) and DMAP (10 mg) in pyridine (70 ml), 4-nitrobenzenesulfonyl chloride (4.85 g, 21.9 mmol) was added at 0° in 3 portions, and the mixture was stirred at 0° for 3 h. Sat. aq. $NaHCO_3$ soln. (100 ml) was added and the mixture extracted with $CHCl_3$, washed with H_2O and brine, dried, and evaporated without heating (0.05 mbar). The crude product (2.40 g) was dissolved in Et_2O, the soln. filtered through a plug of silica gel (15 cm), the filtrate evaporated, and the residue allowed to precipitate overnight at −20° from Et_2O (10 ml): **21a** (1.85 g, 75%). Yellowish crystals. R_f 0.30 (cyclohexane/AcOEt 10:1). M.p. 44–45° (Et_2O). $[\alpha]_D$ = +6.51 (*c* = 0.80). IR (KBr): 3110 (arom. C–H), 3074 (C=*CH*$_2$), 3015 (C=*C*–*H*), 2972, 2936, 2895, 2869 (C–H), 1637, 1599 (conj. C=C), 1609 (arom. C=C), 1540, 1314 (NO_2), 1367, 1184 (SO_2), 1094 (C–O), 880 (C=*CH*$_2$). ^{1}H-NMR: 0.84 (*d*, ^3J = 7.0, Me(3)); 1.31 (*m*, 1 H–C(6′)); 1.57 (*m*, H–C(2)); 1.93 (*m*, 1 H–C(6′)); 2.15–2.38 (*m*, H–C(1′), 2 H–C(5′)); 3.97 (*dd*, ^2J = 9.6, ^3J = 6.5, 1 H–C(1)); 4.05 (*dd*, ^2J = 9.6, ^3J = 6.3, 1 H–C(1)); 4.71 (*m*, CH_2=C(4′)); 5.48 (*d*, ^3J = 9.9, H–C(2′)); 6.08 (*d*, ^3J = 9.9, H–C(3′)); 8.06 (*d*, ^3J = 8.9, 2 H_o); 8.36 (*d*, ^3J = 8.9, 2 H_m). ^{13}C-NMR: 13.03 (*q*, Me(3)); 24.21 (*t*, C(6′)); 29.36 (*t*, C(5′)); 36.61 (*d*, C(1′)); 36.83 (*d*, C(2)); 74.25 (*t*, C(1)); 111.17 (*t*, *C*H_2=C(4′)); 124.39 (*d*, C_m); 129.12 (*d*, C_o); 130.64 (*d*, C(3′)); 131.65 (*d*, C(2′)); 141.62 (*s*, C_{ipso}); 142.33 (*s*, C(4′)); 150.59 (*s*, C_p). MS: 337 (12, M^+), 134 (100), 119 (54), 105 (21), 93 (54), 91 (50), 79 (12), 77 (27), 41 (11).

*(1′*R*,2*R*)-2-(4′-Methylenecyclohex-2′-en-1′-yl)propyl 4-Nitrobenzenesulfonate* (**21b**). As described for **21a**, with **20b** (650 mg, 4.30 mmol): **21b** (1.01 g, 70%). Yellowish crystals. R_f 0.30 (cyclohexane/AcOEt 10:1). M.p. 43–44° (Et_2O). $[\alpha]_D$ = +9.48 (*c* = 1.11). IR (KBr): 3113 (arom C–H), 3076 (C=*CH*$_2$), 3027 (C=*C*–*H*), 2977, 2957, 2929, 2915, 2872, 2858 (C–H), 1636, 1597 (conj. C=C), 1610 (arom. C=C), 1541, 1313 (NO_2), 1366, 1182 (SO_2), 1095 (C–O), 878 (C=*CH*$_2$). ^{1}H-NMR: 0.88 (*d*, ^3J = 7.0, Me(3)); 1.25 (*m*, 1 H–C(6′)); 1.66 (*m*, H–C(2)); 1.87 (*m*, 1 H–C(6′)); 2.15–2.36 (*m*, H–C(1′), 2 H–C(5′)); 3.96 (*dd*, ^2J = 9.6, ^3J = 6.8, 1 H–C(1)); 4.04 (*dd*, ^2J = 9.6, ^3J = 5.9, 1 H–C(1)); 4.70 (*m*, CH_2=C(4′)); 5.51 (*d*, ^3J = 9.8, H–C(2′)); 6.07 (*d*, ^3J = 9.8, H–C(3′)); 8.06 (*d*, ^3J = 8.9, 2 H_o); 8.36 (*d*, ^3J = 8.9, 2 H_m). ^{13}C-NMR: 13.52 (*q*, Me(3)); 25.90

(*t*, C(6′)); 29.72 (*t*, C(5′)); 36.56 (*d*, C(2)); 37.25 (*d*, C(1′)); 74.18 (*t*, C(1)); 111.16 (*t*, *C*H$_2$=C(4′)); 124.36 (*d*, C$_m$); 129.09 (*d*, C$_o$); 130.65 (*d*, C(3′)); 130.77 (*d*, C(2′)); 141.52 (*s*, C$_{ipso}$); 142.35 (*s*, C(4′)); 150.57 (*s*, C$_p$). MS: 37 (29, M^+), 134 (100), 119 (60), 105 (23), 93 (67), 91 (50), 79 (14), 77 (31), 41 (12).

(1′S,3R)-3-(4′-Methylenecyclohex-2′-en-1′-yl)butanenitrile (=*β*R,*1*S*)-β-Methyl-4-methylenecyclohex-2-ene-1-propanenitrile*; **22a**). KCN (990 mg, 15.2 mmol) was added to a soln. of **21a** (1.70 g, 5.10 mmol) in DMSO (47 ml) and stirred at r.t. for 2 h. The mixture was diluted with Et$_2$O (500 ml) and washed with sat. aq. NaHCO$_3$ soln., H$_2$O, and brine, dried, and evaporated: **22a** (780 mg, 95%). Pure samples were obtained by CC (cyclohexane/AcOEt 10 : 1; R_f 0.40). $[\alpha]_D = +4.21$ ($c = 0.43$). IR: 3077 (C=*C*H$_2$), 3021 (C=*C*−*H*), 2958, 2855 (C−H), 2246 (C≡N), 1637, 1598 (conj. C=C), 879 (C=*C*H$_2$). ^{1}H-NMR: 1.05 (*d*, $^3J = 6.8$, Me(4)); 1.30 (*m*, 1 H−C(6′)); 1.73 (*m*, H−C(3)); 1.94 (*m*, 1 H−C(6′)); 2.25 (*m*, 1 H−C(2)); 2.36 (*m*, 1 H−C(2)); 2.25–2.45 (*m*, H−C(1′), 2 H−C(5′)); 4.79 (*m*, CH$_2$=C(4′)); 5.60 (*d*, $^3J = 10.0$, H−C(2′)); 6.18 (*d*, $^3J = 10.0$, H−C(3′)). ^{13}C-NMR: 16.41 (*q*, Me(4)); 21.95 (*t*, C(2)); 24.69 (*t*, C(6′)); 29.44 (*t*, C(5′)); 34.95 (*d*, C(3)); 39.47 (*d*, C(1′)); 111.50 (*t*, *C*H$_2$=C(4′)); 119.13 (*s*, C(1)); 131.10 (*d*, C(3′)); 131.23 (*d*, C(2′)); 142.45 (*s*, C(4′)). MS: 161 (10, M^+), 120 (11), 93 (100), 91 (37), 77 (31). 41 (14).

(1′S,3S)-3-(4′-Methylenecyclohex-2′-en-1′-yl)butanenitrile (=*β*S,*1*S*)-β-Methyl-4-methylenecyclohex-2-ene-1-propanenitrile*; **22b**). As described for **22a**, with **21b** (1.12 g, 3.30 mmol): **22b** (550 mg, 96%). A pure sample was obtained by CC (cyclohexane/AcOEt 10 : 1; R_f 0.40). $[\alpha]_D = +11.91$ ($c = 0.76$). IR: 3078 (C=*C*H$_2$), 3025 (C=*C*−*H*), 2963, 2935 (C−H), 2245 (C≡N), 1636, 1597 (conj. C=C), 882 (C=*C*H$_2$). ^{1}H-NMR: 1.09 (*d*, $^3J =$ 6.8, Me(4)); 1.32 (*m*, 1 H−C(6′)); 1.79 (*m*, H−C(3)); 1.92 (*m*, H−C(6′)); 2.22 (*dd*, $^2J = 16.8$, $^3J = 8.1$, 1 H−C(2)); 2.35 (*dd*, $^2J = 16.8$, $^3J = 5.0$, 1 H−C(2)); 2.25–2.46 (*m*, H−C(1′), 2 H−C(5′)); 4.77 (*m*, CH$_2$=C(4′)); 5.60 (*d*, $^3J = 9.8$, H−C(2′)); 6.18 (*d*, $^3J = 9.8$, H−C(3′)). ^{13}C-NMR: 16.79 (*q*, Me(4)); 21.55 (*t*, C(2)); 25.49 (*t*, C(6′)); 29.57 (*t*, C(5′)); 34.70 (*d*, C(3)); 39.70 (*d*, C(1′)); 111.41 (*t*, CH$_2$=C(4′)); 119.11 (*s*, C(1)); 130.86 (*d*, C(3′)); 131.11 (*d*, C(2′)); 142.36 (*s*, C(4′)). MS: 161 (12, M^+), 120 (12), 105 (6), 93 (100), 91 (36), 79 (10), 77 (33), 41 (13).

(1′S,3R)-3-(4′-Methylenecyclohex-2′-en-1′-yl)butanal (=*(β*R,*1*S*)-β-Methyl-4-methylenecyclohex-2-ene-1-propanal*; **23a**). To a soln. of **22a** (920 mg, 5.71 mmol) in abs. Et$_2$O (115 ml) at −65°, 20% DIBAH in hexane (17.3 ml, 18.6 mmol) was added within 15 min. The mixture was allowed to reach r.t. within 2 h and stirred for another 1 h. Sat. aq. NH$_4$Cl soln. (160 ml) was added at 0° and the aq. layer extracted with Et$_2$O. The combined organic phase was washed with H$_2$O and brine, dried, and evaporated: **23a** (900 mg, 96%). Pure samples were obtained by CC (cyclohexane/AcOEt/Et$_3$N 100 : 10 : 1; R_f 0.45). $[\alpha]_D = -2.37$ ($c = 4.02$). IR: 3077 (C=*C*H$_2$), 3023 (C=*C*−*H*), 2957, 2932, 2874 (C−H), 1725 (C=O), 1635, 1597 (conj. C=C), 878 (C=*C*H$_2$). ^{1}H-NMR: 0.92 (*d*, $^3J = 6.3$, Me(4)); 1.35 (*m*, 1 H−C(6′)); 1.70 (*m*, 1 H−C(6′)); 2.15–2.48 (*m*, 2 H−C(2), H−C(3), H−C(1′), 2 H−C(5′)); 4.75 (*m*, CH$_2$=C(4′)); 5.63 (*d*, $^3J = 9.9$, H−C(2′)); 6.16 (*d*, $^3J = 9.9$, H−C(3′)); 9.74 (*m*, CHO). ^{13}C-NMR: 16.72 (*q*, Me(4)); 24.95 (*t*, C(6′)); 29.87 (*t*, C(5′)); 31.73 (*d*, C(3)); 40.41 (*d*, C(1′)); 48.21 (*t*, C(2)); 110.86 (*t*, *C*H$_2$=C(4′)); 130.54 (*d*, C(3′)); 132.76 (*d*, C(2′)); 142.96 (*s*, C(4′)); 202.69 (*d*, C(1)). MS: 164 (3, M^+), 120 (100), 105 (21), 93 (47), 91 (39), 77 (28), 41 (10).

(1′S,3S)-3-(4′-Methylenecyclohex-2′-en-1′-yl)butanal (=*(β*S,*1*S*)-β-Methyl-4-methylenecyclohex-2-ene-1-propanal*; **23b**). As described for **23a**, with **22b** (520 mg, 3.22 mmol): **23b** (470 mg, 89%). Pure samples were obtained by CC (cyclohexane/AcOEt/Et$_3$N 100 : 10 : 1; R_f 0.45). $[\alpha]_D = +54.00$ ($c = 0.70$). IR: 3078 (*C*=*C*H$_2$), 3023 (C=*C*−*H*), 2959, 2935, 2876, 2832 (C−H), 2718 (O=*C*−*H*), 1725 (C=O), 1635, 1596 (conj. C=C), 879 (C=*C*H$_2$). ^{1}H-NMR: 0.91 (*d*, $^3J = 6.5$, Me(4)); 1.29 (*m*, 1 H−C(6′)); 1.74 (*m*, 1 H−C(6′)); 2.12–2.43 (*m*, 2 H−C(2), H−C(3), H−C(1′), 2 H−C(5′)); 4.70 (*m*, CH$_2$=C(4′)); 5.57 (*d*, $^3J = 10.0$, H−C(2′)); 6.12 (*d*, $^3J =$ 10.0, H−C(3′)); 9.69 (*m*, CHO). ^{13}C-NMR: 17.15 (*q*, Me(4)); 25.40 (*t*, C(6′)); 29.91 (*t*, C(5′)); 31.57 (*d*, C(3)); 40.55 (*d*, C(1′)); 47.63 (*t*, C(2)); 110.74 (*t*, *C*H$_2$=C(4′)); 130.64 (*d*, C(3′)); 132.41 (*d*, C(2′)); 142.83 (*s*, C(4′)); 202.37 (*d*, C(1)). MS: 164 (3, M^+), 120 (100), 105 (21), 93 (45), 91 (40), 77 (31), 41 (11).

REFERENCES

[1] B. T. Golding, E. Pombo, C. J. Samuel, *J. Chem. Soc., Chem. Commun.* **1982**, 363.
[2] Y. Kiso, Y. Suzuki, Y. Oshima, H. Hikino, *Phytochemistry* **1983**, *22*, 596.
[3] V. K. Honwad, A. S. Rao, *Tetrahedron* **1964**, *20*, 2921.
[4] S. Uehara, I. Yasuda, K. Takeya, H. Itokawa, *Chem. Pharm. Bull.* **1989**, *37*, 237.
[5] B. T. Golding, E. Pombo, *J. Chem. Soc., Perkin Trans. 1* **1992**, 1519.
[6] H. Preut, W. Kreiser, W. Dummer, *Acta Crystallogr., Sect. C* **1986**, *42*, 743.
[7] K. H. Schulte-Elte, G. Ohloff, *Helv. Chim. Acta* **1967**, *50*, 153.

[8] F. Körner, M. Schürmann, H. Preut, W. Kreiser, *Acta Crystallogr., Sect. C* **1999**, *55*, in press.
[9] D. Friedrich, F. Bohlmann, *Tetrahedron* **1988**, *44*, 1369.
[10] S. Gill, P. Kocienski, A. Kohler, A. Pontiroli, L. Qun, *Chem. Commun*. **1996**, 1743.
[11] A. J. Mancuso, S.-L. Huang, D. Swern, *J. Org. Chem*. **1978**, *43*, 2480.
[12] R. H. Reuss, A. Hassner, *J. Org. Chem.* **1974**, *39*, 1785.
[13] P. L. Julian, W. J. Karpel, *J. Am. Chem. Soc*. **1950**, *72*, 362.
[14] R. Joly, J. Warnant, *Bull. Soc. Chim. Fr.* **1958**, 366.
[15] M. B. Floyd, M. J. Weiss, *J. Org. Chem*. **1979**, *44*, 71.
[16] G. Rücker, H. Hörster, W. Gajewski, *Synth. Commun*. **1980**, *10*, 623.
[17] D. R. Borcherding, S. A. Scholtz, R. T. Borchardt, *J. Org. Chem.* **1987**, *52*, 5457.
[18] P. G. Forster, E. L. Ghisalberti, P. R. Jefferies, *Tetrahedron* **1987**, 3007 and lit. cit. therein.
[19] Azizur-Rahman, H. Klein, J. Dressel, H. Mayr, *Tetrahedron* **1988**, *44*, 6041.
[20] J. P. Marino, J. C. Jaen, *J. Am. Chem. Soc*. **1982**, *104*, 3165.
[21] H. Gerlach, D. Kappes, R. K. Boeckman Jr., G. N. Maw, *Org. Synth*. **1993**, *71*, 48; Ed. L. E. Overman, J. Wiley & Sons, New York, 1993, and lit. cit. therein.
[22] F. Körner, M. Schürmann, H. Preut, W. Kreiser, *Acta Crystallogr., Sect. C* **1999**, *55*, in press.

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