Diastereoselective Approaches to *trans*-Hydrindane Derivatives − Total Synthesis of 8-(Phenylsulfonyl)de-A,B-cholestane Precursors to 25-Hydroxyvitamin D_3

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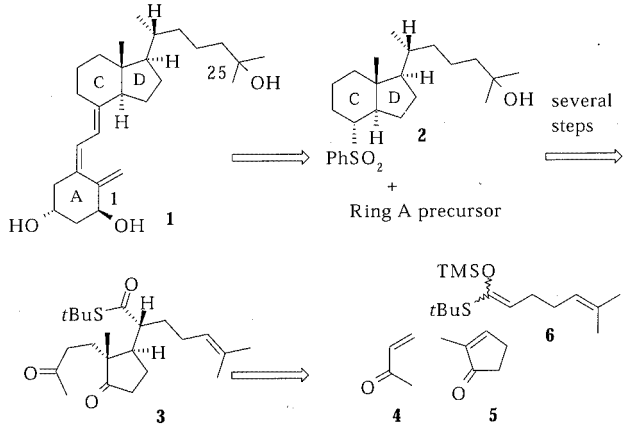
The total diastereoselective synthesis of the C,D rings/side chain building block for the synthesis of 1α,25-dihydroxyvitamin D_3 is described. Two tandem Mukaiyama–Michael additions involving silylated ketene acetals derived from *tert*-butyl 6-methylhept-5-enethioate or *tert*-butyl 6-methylhept-6-enethioate, 2-methylcyclopent-2-en-1-one, and 1-(phenylthio)but-3-en-2-one afforded the corresponding intermediates with the complete carbon framework of the target compound. The further transformation of these key intermediates involved cyclization, oxidation with *m*-CPBA, and reduction of the vinylic sulfone moiety to afford the *trans*-hydrindane ring system. The synthesis comprises five operations and afforded the product in ca. 30% yield. The application of 2-[(phenylthio)methyl]-2-vinyl[1,3]dioxolane and 2-(phenylsulfonylmethyl)-2-vinyl[1,3]dioxolane as Michael acceptors was also examined.

Introduction

The Mukaiyama−Michael conjugate addition reaction[1] with subsequent trapping of the immediate adduct with a carbon electrophile provides an effective method for a simultaneous generation of two carbon−carbon bonds and, if applicable, two or more stereogenic centres. In natural products synthesis, this conjugate addition has been used in tandem with the Tsuji alkylation[2−4] and aldol[5] and imino aldol reactions.[6] In certain systems, intermolecular conjugate addition reactions have triggered sequential transformations giving rise to complex annulation products.[7] We have recently reported on the application of two Mukaiyama−Michael reactions in tandem[8] for a convergent synthesis of the hydrindane derivative **2** (Scheme 1), which served as the key building block for a synthesis of 1α,25-dihydroxyvitamin D_3 (**1**). Treatment of ketene acetals **6** with 2-methylcyclopent-2-en-1-one (**5**) in the presence of trityl hexachloroantimonate as catalyst gave the intermediate adduct, which was treated in situ with methyl vinyl ketone (**4**) as the second Michael acceptor.[9] The obtained intermediate **3**, which included all the requisite carbon atoms and three stereogenic centres of the target compound, was further transformed into compound **2**. This synthetic route was short and efficient in comparison with those previously reported.[10] However, some important methodological questions called for further attention. In particular, it was thought that the replacement of methyl vinyl ketone (**4**) with its sulfur-bearing equivalent, in the form of one of the derivatives **8** or **11**−**13** (Scheme 2), should allow for simple transformation of the respective Michael adduct into **2**. None of the compounds **8** or **11**−**13** had previously been used as a Michael acceptor. We also addressed the question of more efficient incorporation of the tertiary hydroxy group in the side chain of intermediate **2**, which required alterations in the structure of the starting ketene acetal **6**. We now present a full account of our study of diastereoselective approaches to the de-A,B-cholane derivative *rac*-**2**.[11]



Scheme 1

Results and Discussion

Our attention first focused on the application of the easily accessible Michael acceptor **8**, bearing the phenylthio

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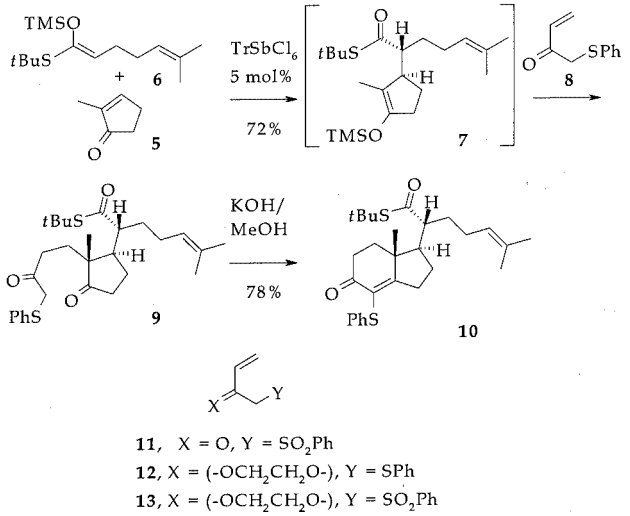


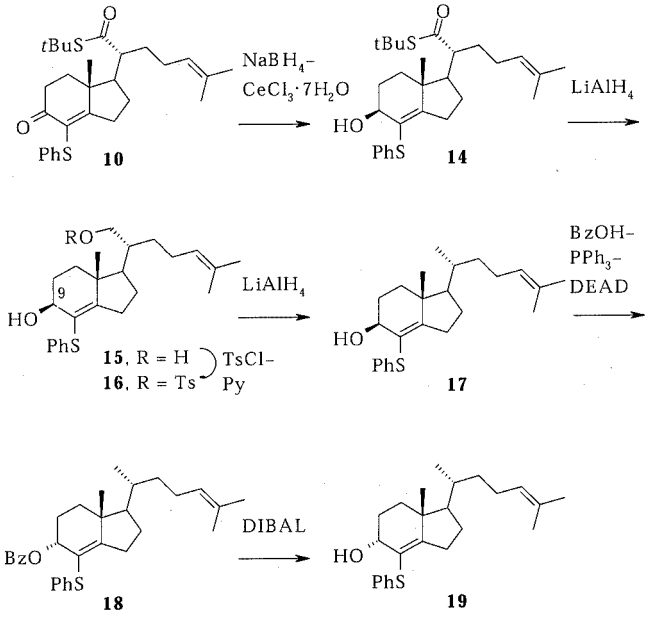
Scheme 2

group,[12,13] in a three-component construction of the dione **9** (Scheme 2). The ketene acetal **6** [a mixture of (*E*) and (*Z*) isomers in a ratio of 95:5] prepared as described earlier[8] was treated with 2-methylcyclopent-2-one (**5**) in the presence of trityl hexachloroantimonate ($TrSbCl_6$, ca. 5 mol%) and the adduct **7** was subsequently treated in situ with the α,β-unsaturated ketone **8**. After the usual isolation, crystalline adduct **9** was obtained in a 72% yield. The relative configurations at the three new asymmetric centres formed during these reactions were ascribed on the grounds of the Mukaiyama stereochemical model,[2] observations on the reaction of silylated cyclopentanone enols with electrophiles,[14] and our own experiences.[3]

Some approaches that would allow utilization of a Michael acceptor bearing the phenylsulfonyl group were examined next. In an attempt to prepare phenylsulfonylmethyl vinyl ketone (**11**) by oxidation of **8**, only polymeric material was obtained. To circumvent these difficulties, **8** was transformed into **12** (67% yield) with ethylene glycol and a catalytic amount of *p*-TsOH in benzene at reflux. Surprisingly, treatment of **8** with the $(TMSOCH_2)_2$/TMSOTf system, viewed as a milder ketalization reagent (the Noyori reagent[15]), was less effective (53% yield). Sulfide **12** was smoothly oxidized into sulfone **13** with Oxone® in the presence of sodium hydrogen carbonate. However, all our attempts to achieve reaction between silyl enol ether **7** and acetal **13** failed. In further investigations along these lines, treatment of acetal **12** with **7** in the presence of an equimolar mixture of $TiCl_4$/Ti(*i*PrO)$_4$ as a catalyst,[16] followed by hydrolysis of the crude product (Amberlyst 15H/acetone), afforded the expected adduct **9** but in low yield (41%).

The experiments described had shown that, of the scrutinized candidates, (phenylthio)methyl vinyl ketone (**8**) was the Michael acceptor of choice. It was important that the adduct **9** was formed as the dominant product, easy to purify by chromatography. No side products arising from addition of two or more molecules of **8** could be detected. In that respect, **8** was found to be superior to methyl vinyl ketone, for which multiple additions present a notorious problem. Cyclization of **9** smoothly afforded the hydrindane derivative **10**.

Our next objectives included the reduction of the thioester functionality and the oxo group, and stereoselective reduction of the double bond at the ring junction. Since it could be anticipated that the ketone **10** should be selectively transformable into each of the epimeric alcohols, we initially focused on the diastereoselective preparation of compounds **17** and **19** (Scheme 3). Reduction of **10** with the $NaBH_4/CeCl_3$ system in MeOH/THF[17] at −78 °C almost quantitatively afforded the hydroxy ester **14**, which was further reduced with $LiAlH_4$ in refluxing THF to give diol **15** in 88% overall yield after chromatography (ca. 3% of epimeric alcohol was also isolated). Kinetically controlled esterification of the diol **15** with tosyl chloride in dichloromethane in the presence of triethylamine and a catalytic amount of DMAP gave monotosylate **16** (86% yield). This was subjected to reduction with $LiAlH_4$ to yield the required alcohol **17**. Finally, alcohol **17** was subjected to Mitsunobu inversion[18] (PPh_3/DEAD, BzOH) followed by DIBALH reduction of benzoate **18** to afford **19** in 85% overall yield.

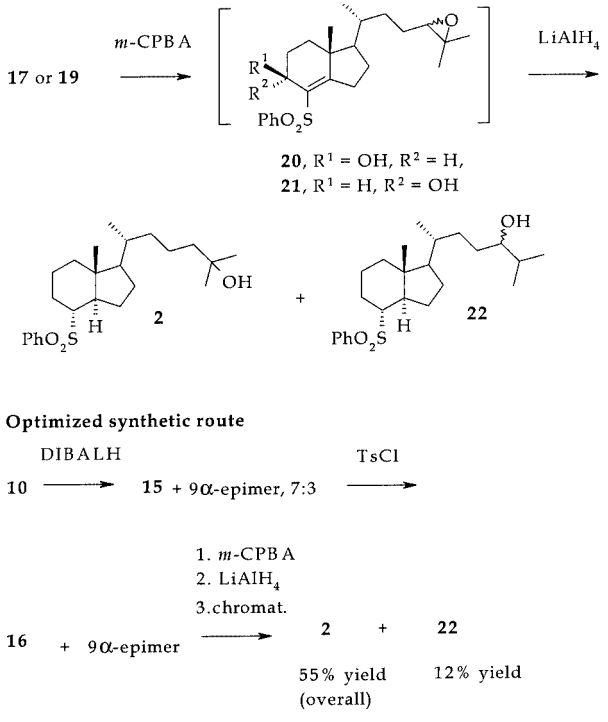


Scheme 3

Our plans for generating the *trans*-hydrindane system from hydrinadane allylic alcohols **17** and/or **19** first required the oxidation of the sulfanyl group to the sulfonyl group, and then conjugate reduction of the respective vinyl sulfones with $LiAlH_4$. Model experiments on the reduction of an analogous vinyl sulfone located in a decalin ring system (a cholestane derivative) were encouraging and showed that (1) the steric course of reduction might depend upon the orientation of the hydroxy group and (2) the hydroxy group (in the 1,2-position to the phenylsulfonyl group) could ultimately be reduced to yield the corresponding sat-

urated sulfone.[19] However, application of this reaction sequence to vinyl sulfides **17** and **19** appeared somewhat more complex, due to the presence of the additional double bond, oxidation of which would produce diastereomers. We therefore decided to proceed with oxidation and reduction steps without isolation of intermediates.

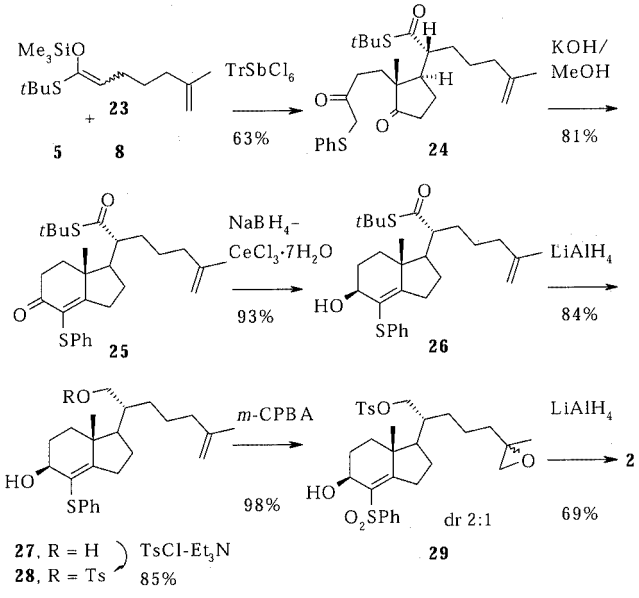
A vinyl sulfide with the hydroxy group in the α orientation (**19**, Scheme 4) was treated with *m*-CPBA (ca. 3.5 molequiv.) in dichloromethane. The crude product was isolated in the usual way and then, without purification, reduced with an excess of $LiAlH_4$. Sulfone **2** was obtained in 73% yield after chromatography. A small amount of a side product was also isolated and identified as the alcohols **22** (mixture of diastereomers), apparently arising from reduction of the epoxide moiety with addition of a hydride ion at the tertiary centre. It should be noted that the use of MeOH to destroy the excess of $LiAlH_4$ (see Exp. Sect.) was important for the generation of only one epimer of **2**, with the sulfonyl group in an equatorial (α) orientation; the axial sulfone group (β) could, if present, be epimerized to **2** under alkaline conditions.[20] With regard to the ring junction, the reduction of **21** was completely selective, affording the *trans*-fused hydrindane system.



Scheme 4

When this reaction sequence was applied to the hydroxy sulfide **17**, the same product, sulfone **2**, was obtained. These experiments showed that, contrary to our initial predictions, the orientation of the hydroxy group had no consequences for the steric course of the double bond reduction. In practice, the 9β-hydroxy isomer **17** (steroid numbering) turned out to be a somewhat more convenient synthetic intermediate, since the corresponding sulfone **20** could be isolated and purified. After accomplishing the stepwise synthesis of sulfone **2**, we were able to improve the whole synthetic approach with regard to the number of steps and the overall yield. The following combination of steps emerged as the optimum: The enone **10** was reduced with DIBALH (CH_2Cl_2/hexane, −78 °C) to afford, after brief chromatography, a mixture of diol **15** and its 9α epimer in a ratio of ca. 7:3 (by ^1H NMR, 94% yield). The diols were then treated with tosyl chloride and, after a brief purification, a mixture of the monotosylates **16** and the 9α epimer was oxidized with *m*-CPBA. The product was treated with an excess of $LiAlH_4$ to give, after chromatography, sulfone **2** along with **22** in 55 and 12% overall yields, respectively, from **10**. In this way the synthesis of the sulfone **2** was achieved in five operations and in 31% overall yield from **6**.

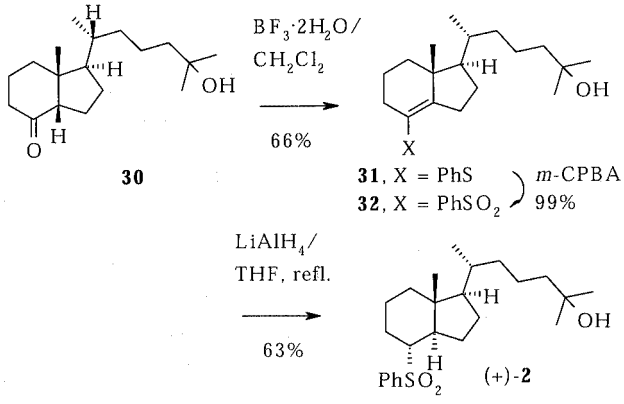
Although sulfone **2** was obtained in a high yield, formation of the side product **22** was a drawback. In the final approach, we chose to alter the side-chain building block in order to secure selectivity for incorporation of the C-25 hydroxy group. Ethyl 6-methylhept-6-enoate[21] was transformed[22] into *S*-*tert*-butyl 6-methylhept-6-enethioate and then into ketene acetal **23** [(*E*)/(*Z*) = 9:1] (Scheme 5). Conjugate addition between **23** and acceptors **5** and **8**, consecutively, afforded the key intermediate **24** in 63% yield, along with a small amount of its cyclization product **25**. Base-catalysed cyclization of **24** gave enone **25**. This was reduced with the Luche reagent to the allylic alcohol **26**, which was in turn further reduced to diol **27**. Selective tosylation followed by *m*-CPBA oxidation provided epoxy sulfone **29** as a mixture of diastereomers in a ratio of ca. 2:1 (by ^1H NMR). Reduction of **29** with an excess of $LiAlH_4$ provided sulfone **2** as the only product.



Scheme 5

Sulfone **2** was crystalline (m.p. 109−110 °C) and easy to purify. However, all our attempts to produce a single crystal

suitable for X-ray analysis failed. The following relay synthesis was therefore performed in order to confirm the structure of **2**. A sample of the known[23] optically active ketone **30** (Scheme 6) was treated with thiophenol and $BF_3{\cdot}2H_2O$ by the procedure developed by Craig and coworkers.[24] The sulfide **31** was oxidized to the sulfone **32** with *m*-CPBA. Reduction of **32** ($LiAlH_4$) gave optically active sulfone (−)-**2** (m.p. 128 °C), which displayed ^1H and ^{13}C NMR spectra identical with those of the racemic product **2**.



Scheme 6

In conclusion, the application of the sulfur-containing acceptors **8**, **12**, and **13** in tandem Mukaiyama−Michael reactions involving ketene acetals **6** or **23** and 2-methylcyclopent-2-en-1-one (**5**) has been scrutinized. Expeditious new approaches to *rac*-hydroxy sulfone **2**, a key building block in the total synthesis of 1α,25-dihydroxyvitamin D_3, have been developed.

Experimental Section

General: Reactions involving silyl enol ethers or organometallic reagents were carried out in flame-dried glassware under argon. THF was dried with Na/K alloy and distilled under argon. NMR spectra were recorded at 200 MHz (^1H) and 50 MHz (^{13}C). Column chromatography was performed on Merck 60 silica gel, 230−400 mesh, and TLC on Merck aluminium sheets, 60 S_{254} silica gel. Organic extracts were dried with anhydrous Na_2SO_4 and the solvents were removed in a rotary evaporator. Optical rotations were measured for $CHCl_3$ solutions.

2-[(Phenylthio)methyl]-2-vinyl[1,3]dioxolane (12). Procedure a: A mixture of ketone **8**[13] (640 mg, 3.60 mmol), ethylene glycol (5 mL), *p*-TsOH (25 mg), and benzene (20 mL) was heated under reflux for 4 h in a flask equipped with a Dean−Stark adapter. After the mixture had cooled, triethylamine (0.25 mL) was added, and the solution was filtered through a pad of SiO_2 (5 g). The solvent was removed, and the residue was chromatographed on SiO_2 (30 g, hexane/EtOAc, 25:1). The main fraction was collected and distilled in a Kugelrohr apparatus (225 °C/0.1 Torr). Ketal **12** (538 mg, 67%) was obtained. ^1H NMR: δ = 7.38−7.12 (m, 2 H, H-*m* aromat.), 7.31−7.11 (m, 3 H, H-*o*, -*p* aromat.), 5.56 (dd, *J* = 17.1, 10.4 Hz, 1 H, C3-H, steroid numbering), 5.49 (dd, *J* = 17.1, 1.75 Hz, 1 H, C4-H*cis*), 5.23 (dd, *J* = 10.4, 1.8 Hz, 1 H, C4-H *trans*), 4.14 (m, 4 H, CH_2CH_2), 3.29 (s, 2 H, C1-H) ppm. ^{13}C NMR: δ = 137.1 (C-*ipso*), 136.5 (C1′), 129.1 (C-*o*), 128.6 (C-*m*), 125.8 (C-*p*), 116.4 (C2′), 107.6 (O−C−O), 65.3 (2C acetal.), 42.3 (*C*SPh) ppm. MS EI (70 eV): *m*/*z* (%) = 222 (8) [M^+], 99 (100), 55 (30). $C_{12}H_{14}O_2S$ (222.30): calcd. C 64.83, H 6.35; found C 64.72, H 6.39. **Procedure b:** $TMSOCH_2CH_2OTMS$ (2.2 mL, 8.99 mmol) was added at −78 °C to a solution of Et_3SiOTf (0.068 mL, 0.3 mmol) in dichloromethane (1 mL), followed by ketone **8** (1.08 g, 6.06 mmol) in dichloromethane (4 mL). The mixture was stirred at −20 °C for 18 h, pyridine (0.1 mL) was added, and the whole mixture was poured into aqueous $NaHCO_3$. The product was extracted with dichloromethane. The extract was dried with Na_2SO_4 containing powdered $NaHCO_3$, and the solvent was evaporated. The residue was chromatographed on SiO_2 (40 g, hexane/EtOAc, 25:1). Ketal **12** (713 mg, 53%) was obtained.

2-[(Phenylsulfonyl)methyl]-2-vinyl[1,3]dioxolane (13): Oxone® (Aldrich, 2.22 g, 3.61 mmol) was added at 0 °C to a stirred mixture of thiol **12** (232 mg, 1.05 mmol), THF (6 mL), methanol (2 mL), water (4 mL), and $NaHCO_3$ (1 g). The mixture was set aside for 14 h and then poured into water. The product was extracted with EtOAc. The solvent was evaporated, and the residue was chromatographed on SiO_2 (18 g, hexane/EtOAc, 5:1). Sulfone **13** (261 mg, 98%) was obtained. ^1H NMR: δ = 7.96−7.87 (m, 2 H, H-*m* aromat.), 7.67−7.47 (m, 3 H, H-*o*, -*p* aromat.), 5.83 (dd, *J* = 17.1, 10.4 Hz, 1 H, C3-H), 5.41 (dd, *J* = 17.1, 1.5 Hz, 1 H, C4-H *cis*), 5.20 (dd, *J* = 10.4, 1.5 Hz, 1 H, C4-H *trans*) ppm. ^{13}C NMR: δ = 140.8 (C-*ipso*), 135.5 (C-*p* or C1′), 133.3 (C1′ or C-*p*), 128.7 (C-*o*), 128.0 (C-*m*), 116.9 (C2′), 105.0 (O−C−O), 64.7 (C acetal.), 62.3 (*C*SO_2Ph) ppm. MS EI (70 eV): *m*/*z* (%) = 227 (21) [$M - C_2H_3$]$^+$, 99 (100), 55 (26); LSIMS (+) (NBA, 6 s, 5 kHz): *m*/*z* (%) = 277 (7) [M + Na]$^+$, 255 (31) [M + H]$^+$. $C_{12}H_{14}O_4S$ (254.30): C 56.68, H 5.55; found C 56.63. H, 5.65.

***S*-*tert*-Butyl 6-Methylhept-5-enethioate:** Trimethylaluminium (2.0 M in hexane, 36 mL, 72.00 mmol) was diluted with dichloromethane (120 mL) and cooled to 0 °C. 2-Methyl-2-propanethiol (6.36 g, 72 mmol) was added dropwise to this solution. The mixture was stirred at 0 °C for 15 min and was then allowed to warm to room temperature (in ca. 10 min), maintained at this temperature for a further 30 min and cooled again to 0 °C. To this thus prepared Weinreb reagent,[22] ethyl 6-methylhept-5-enoate (prepared from the corresponding acid, 7.7 g, 36.0 mmol) was added dropwise, and the mixture was set aside at 0 to 5 °C for 14 h. The reaction was quenched at 0 °C by careful addition of water (100 mL) and then 2% HCl (50 mL). The layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic solutions were washed with water and dried, and the solvent was evaporated. The residue was distilled at 90−91 °C/3 Torr to give the title compound (5.3 g, 70%).[8]

***S*-*tert*-Butyl *rac*-(2*R**)-6-Methyl-2-{(1*R**,2*S**)-2-methyl-3-oxo-2-[3-oxo-4-(phenylthio)butyl]cyclopentyl}hept-5-enethioate (9). Procedure a:** Ketene acetal **6**[8] (3.93 g, 13.6 mmol) in dichloromethane (6 mL) was added at −78 °C, over 20 min, to a stirred solution of enone **5** (1.18 mL, 11 mmol) and $TrSbCl_6$ (350 mg, 0.6 mmol) in dichloromethane (30 mL). After 1.5 h, 1-(phenylthio)but-3-en-2-one (**8**, 1.95 g, 11 mmol) in dichloromethane (6 mL) was added dropwise. The mixture was set aside at −78 °C for 3 h and then allowed to warm to room temp. (in ca. 1 h), and the reaction was then quenched with water (2 mL). After 30 min, the solvent was evaporated. The residue was dried by repeated coevaporation with benzene and then chromatographed on SiO_2 (140 g, hexane/EtOAc, 10:1). Diketone **9** (3.86 g, 72%) was obtained. M.p. 89−90 °C

(methanol). IR (KBr) $\tilde{\nu}$ = 1731, 1708, 1666, 1584 cm^{-1}. ^1H NMR: δ = 7.38−7.12 (m, 5 H, SPh), 5.07 (br. t, *J* = 7.1 Hz, C24-H),3.62 (s, 2 H, S-C8-H), 2.76−0.90 (m, 14 H), overlapping 1.69 (s, 3 H, C27-H *cis*), 1.59 (s, 3 H, C26-H *trans*), 1.41 (s, 9 H, *t*BuS), 0.98 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 221.1 (C14), 204.2 (C9 or 21), 202.9 (C21 or 9), 135.0 (C-*ipso*), 132.2 (C25), 129.8 (C-*o*), 128.9 (C-*m*), 126.6 (C-*p*), 123.5 (C24), 54.1, 51.2, 48.6, 43.9, 43.3, 36.5, 35.7, 31.8, 29.5 (3 C-1, *t*BuS), 29.2, 25.7, 25.2, 22.9, 18.6, 17.7. $C_{28}H_{40}O_3S_2$ (488.76): calcd. C 68.81, H 8.25; found C 68.65, H 8.38. **Procedure b:** Compound **6** (361 mg, 1.26 mmol) was added at −78 °C, over 20 min, to a solution of **5** (0.107 mL, 1.00 mmol) and $TrSbCl_6$ (40 mg) in dichloromethane (3 mL). After 45 min, ketal **12** (220 mg, 1.15 mmol) in dichloromethane (5 mL) was added, followed by a solution of $TiCl_4$ (0.064 mL, 0.58 mmol) and $Ti(iPrO)_4$ (0.171 mL, 0.58 mmol) in dichloromethane (3 mL). The mixture was set aside at −78 °C for 18 h and the reaction was then quenched with saturated aqueous $NaHCO_3$ (3 mL). The mixture was poured into water, and the product was extracted with hexane. The extract was evaporated and the residue was dissolved in acetone (15 mL). Amberlyst 15-H (70 mg) was added. The mixture was stirred for 24 h and filtered, and the solvent was evaporated. The residue was chromatographed on SiO_2 (40 g, hexane/EtOAc, 10:1). Diketone **9** (201 mg, 41%) was obtained, and was identical with the sample described above.

***S*-*tert*-Butyl *rac*-(2*S**)-6-Methyl-2-[(1*R**,7a*R**)-7a-methyl-5-oxo-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]hept-5-enethioate (10):** KOH (30% in methanol, 0.3 mL) was added to a solution of diketone **9** (2.839 g, 5.82 mmol) in methanol (150 mL). The mixture was stirred for 1 h and the solvent was evaporated, and the residue was chromatographed on SiO_2 (100 g, hexane/EtOAc, 20:1). Enone **10** (2.137 g, 78%) was obtained. M.p. 88−89 °C (methanol). ^1H NMR: δ = 7.34−7.03 (m, 5 H, SPh), 5.09 (br. t, *J* = 7.0 Hz, 1 H, C24-H), 2.85−0.80 (m, 13 H), overlapping 1.63 (s, 3 H,C27-H *cis*), 1.54 (s, 3 H, C26-H *trans*), 1.44 (s, 9 H, S*t*Bu), 1.18 (s, 3 H, C-H) ppm. ^{13}C NMR: δ = 202.8 (C21), 193.2 (C9), 184.9 (C14), 135.7 (C-*ipso*), 131.9 (C25), 128.5 (C-*o*), 126.7 (C-*m*), 125.0 (C-*p*), 124.7 (C8), 123.1 (C24), 53.8, 52.0, 48.2, 46.9, 34.3, 33.7, 32.5, 30.2, 29.2, 25.6, 25.4, 24.9, 17.4, 16.3 ppm. $C_{28}H_{38}O_2S_2$ (470.74): calcd. C 71.43, H 8.15; found C 71.25, H 8.25.

***rac*-(1*R**,5*S**,7a*R**)-1-[(1*R**)-1-(Hydroxymethyl)-5-methylhex-4-en-1-yl]-7a-methyl-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (15). Procedure a:** $NaBH_4$ (11.4 mg, 0.300 mmol) was added at −78 °C to a stirred solution of ketone **10** (120 mg, 0.255 mmol) and $CeCl_3{\cdot}7H_2O$ (47 mg, 0.126 mmol) in methanol (3 mL) and THF (2 mL). After 2 h, the mixture was allowed to warm to room temp., stirring was continued for an additional 30 min, and the whole mixture was poured into 10% aqueous tartaric acid. The product **14** was extracted with dichloromethane and the solvent was evaporated. The residue was dissolved in THF (6 mL), and $LiAlH_4$ (0.25 M in THF, 1.5 mL, 0.750 mmol) was added. The mixture was heated at reflux temperature for 40 min. After the mixture had cooled, methanol (0.5 mL) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The solvent was evaporated and the residue was chromatographed on SiO_2 (15 g, hexane/EtOAc, 5:1). Diol **15** (87 mg, 88%) and its 9α epimer (3 mg, 3%) were obtained. **15**: M.p. 97 °C (benzene/hexane, 1:1). ^1H NMR: δ = 7.30−7.08 (m, 5 H, SPh), 5.11 (br. t, *J* = 7.1 Hz, C24-H), 4.15−4.03 (m, 1 H, C9-H), 3.70 (d, *J* = 4.0 Hz, 2 H, C21-H), 2.69−0.85 (m, 14 H), overlapping 1.69 (s, 3 H, C27-H *cis*), 1.61 (s, 3 H, C26-H *trans*), 1.06 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 162.4 (C14), 135.0 (C-*ipso*), 131.8 (C25), 129.0 (C-*o*), 127.7 (C-*m*), 125.7 (C-*p*), 124.4 (C24), 124.2 (C8), 67.9 (C9), 63.0 (C21), 50.9, 46.1 (C13), 40.6, 35.0, 29.1, 28.4, 25.8, 25.7, 25.2, 18.0, 17.7 ppm. $C_{24}H_{34}O_2S$ (386.59): calcd. C 74.56, H 8.86; found C 74.29, H 8.96. *rac*-(1*R**,5*R**,7a*R**)-1-[(1*R**)-1-(Hydroxymethyl)-5-methylhex-4-en-1-yl]-7a-methyl-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol: m.p. 113 °C (benzene/hexane, 1:1). ^1H NMR: δ = 7.30−7.08 (m, 5 H, SPh), 5.11 (br. t, *J* = 7.0 Hz, C24-H), 3.99 (br. d, 1 H, *J* = 1.4 Hz, C9-H), 3.76−3.60 (m, 2 H, *J* = 4.0 Hz, C21-H), 2.75−0.82 (m, 14 H), overlapping 1.69 and 1.61 (2 s, 3H each, C26 and C27), 1.00 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 162.6 (C14), 135.7 (C-*ipso*), 131.5 (C25), 128.9 (C-*o*), 127.6 (C-*m*), 125.5 (C-*p*), 124.4 (C24), 122.5 (C8), 66.2 (C9), 62.9 (C21), 50.6, 45.9 (C13), 40.5, 30.6, 28.9, 27.8, 27.7, 25.6, 25.1, 24.9, 17.6, 17.2 ppm. $C_{24}H_{34}O_2S$ (386.59): calcd. C 74.56, H 8.86; found C 74.50, H 8.95. **Procedure b:** DIBALH (0.7 M in hexane, 4.4 mL, 3.08 mmol) was added at −78 °C to a solution of ketone **10** (205 mg, 0.44 mmol) in dichloromethane (10 mL). The mixture was stirred at −78 °C for 1 h, and then set aside at room temp. for 24 h. Methanol (4 mL) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The solvent was evaporated, and the residue was chromatographed on SiO_2 (18 g). Elution with hexane/EtOAc (5:1) gave **15** (118 mg, 69%) and then its 9α epimer (38 mg, 22%).

***rac*-(2*R**)-2-[(1*R**,5*S**,7a*R**)-5-Hydroxy-7a-methyl-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]-6-methylhept-5-enyl Toluene-4-sulfonate (16):** A solution of diol **15** (110 mg, 0.28 mmol) in dichloromethane (1.5 mL), containing DMAP (8.5 mg, 0.07 mmol), triethylamine (0.5 mL) and pyridine (0.5 mL), was cooled to 0 °C and *p*-TsCl (106 mg, 0.56 mmol) was added. The mixture was set aside at room temp. for 14 h and then poured into 3% sulfuric acid. The product was extracted with dichloromethane. The extract was washed with aqueous $NaHCO_3$ and water, and the solvent was evaporated. The residue was chromatographed on SiO_2 (15 g, hexane/EtOAc, 20:1). Tosylate **16** (130 mg, 86%) was obtained. ^1H NMR: δ = 7.79 (d, *J* = 8.3 Hz, 2 H, H-*o* aromat. Ts), 7.33 (d, *J* = 8.0 Hz, 2 H, H-*m* aromat. Ts), 7.32−7.09 (m, 5 H, SPh), 4.94 (br. t, *J* = 6.9 Hz, C24-H), 4.16−3.87 (m, 3 H, C21-H_2 and C9-H), 2.75−0.89 (m, 14 H), overlapping 2.67 (s, 1 H, C9-OH), 2.43 (s, 3 H, CH_3 Ts), 1.65 (s, 3 H, C27-H (*cis*), 1.49 (s, 3 H, C26-H *trans*), 0.95 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 161.1 (C14), 144.7 (C-*ipso*, Ts), 134.7(C-*ipso*, Ph), 132.6 (C-*p*, Ts), 131.8 (C25), 129.6 (C-*o*,Ts), 128.9 (C-*o*, Ph), 127.8 (C-*m*, Ts or Ph), 127.5 (C-*m*, Ph or Ts),125.6(C-*p*, Ph), 124.5 (C8), 123.5 (C24), 70.2 (C9), 67.4 (C21), 50.3, 45.8 (C13), 37.8, 34.7, 28.7, 28.2, 28.0, 25.7, 25.5, 24.5, 21.5, 17.7, 17.5 ppm. $C_{31}H_{40}O_4S_2$ [M^+]: 540.23685; found 540.23661 (HRMS).

***rac*-(1*R**,5*S**,7a*R**)-7a-Methyl-1-[(1*R**)-6-methylhept-5-en-2-yl]-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (17):** $LiAlH_4$ (0.25 M in THF, 2 mL, 0.500 mmol) was added to a solution of tosylate **16** (101 mg, 0.187 mmol) in THF (1 mL). The mixture was heated at reflux temperature for 1 h. After the mixture had cooled, methanol (0.5 mL) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The extract was concentrated, and the residue was chromatographed on SiO_2 (5 g, hexane/EtOAc, 10:1, 5:1). Alcohol **17** (64 mg, 92%) was obtained. ^1H NMR: δ = 7.31−7.07 (m, 5 H, SPh), 5.09 (br. t, *J* = 7.1, C24-H), 4.14−4.02 (m, 1 H, C9-H), 2.65−0.80 (m, 15 H), overlapping 1.69 (d, *J* = 1.1 Hz, 3 H, C27-H *cis*), 1.61 (s, 3 H, C26-H *trans*), 1.05 (s, 3 H, C18-H), 0.98 (d, $J_{20,21}$ = 6.4 Hz, 3 H, C21-H) ppm. ^{13}C NMR: δ = 163.1 (C14), 135.1 (C-*ipso*), 131.7(C25), 128.9 (C-*o*), 127.4 (C-*m*), 125.5 (C-*p*), 124.7 (C24), 123.7 (C8), 67.8(C9), 56.3, 46.3 (C13), 35.8, 35.5, 34.3,

28.4, 28.3, 26.7, 25.6, 24.6, 18.6, 17.6, 17.5 ppm. $C_{24}H_{34}OS$ [M^+]: 370.23304; found 370.23214; calcd. for $C_{24}H_{32}S$ [$M^+ - H_2O$]: 352.22248; found 352.22218 (HRMS).

***rac*-(1*R**,5*R**,7a*R**)-7a-Methyl-1-[(2*R**)-6-methylhept-5-en-2-yl]-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (19):** DEAD (0.057 mL, 0.360 mmol) in THF (0.2 mL) was added at −78 °C to a stirred solution of alcohol **17** (27 mg, 0.073 mmol), Ph_3P (95 mg, 0.360 mmol) and benzoic acid (40 mg, 0.360 mmol) in THF (1 mL). The mixture was set aside at room temp. for 2 h, and the solvent was evaporated. The residue was chromatographed on SiO_2 (2 g, hexane/EtOAc, 100:1, 50:1, 20:1). Benzoate **18** (31 mg, 90%) was obtained. ^{1}H NMR: δ = 7.94−7.01 (m, 10 H, H aromat. PhS and Bz), 5.51−5.45 (m, C9-H), 5.11 (br. t, *J* = 7.0 Hz, C24-H), 2.85−0.89 (m, 14 H), overlapping 1.70 (s, 3 H, C27-H *cis*), 1.63 (s, 3 H, C26-H *trans*), 1.05 (s, 3 H, C18-H), 1.01 (d, $J_{20,21}$ = 6.0 Hz, C21-H) ppm. ^{13}C NMR: δ = 166.5 (CO Bz), 166.0 (C14), 136.1, 132.5, 131.2, 130.5, 129.5 (C-*o*, Bz), 128.7 (C-*o*, PhS), 128.0 (C-*m*, Bz or PhS), 127.7 (C-*m*, PhS or Bz),127.4, 125.3, 124.7, 118.5, 70.6 (C9), 56.3, 46.1 (C13), 35.5, 34.4, 32.2, 28.2, 26.8, 26.3, 25.6, 24.5, 18.6, 17.6, 16.9. DIBALH (0.7 M in hexane, 0.2 mL, 0.140 mmol) was added at −78 °C to a stirred solution of **18** (31 mg, 0.065 mmol) in dichloromethane (3 mL). After 1 h, the mixture was allowed to warm to room temp. The reaction was quenched with methanol (0.5 mL) and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The solvent was evaporated, and the residue was chromatographed on SiO_2 (1.5 g, hexane/EtOAc, 100:1, 50:1, 20:1). Alcohol **19** (23 mg, 95%) was obtained. ^{1}H NMR: δ = 7.32−7.07 (m, 5 H, SPh), 5.09 (br. t, *J* = 7.0, C24-H), 3.98 (br. s, 1 H, C9-H), 2.76−0.82 (m, 14 H), overlapping 2.19 (br. s, 1 H, C9-OH), 1.69 (d, *J* = 1.1 Hz, 3 H, C27-H *cis*), 1.61 (s, 3 H, C26-H *trans*), 1.01 (s, 3 H, C18-H), 0.99 (d, $J_{20,21}$ = 5.1 Hz, 3 H, C21-H) ppm. ^{13}C NMR: δ = 163.7 (C14), 136.1 (C-*ipso*), 131.3(C25), 129.1 (C-*o*), 127.8 (C-*m*), 125.7 (2 C-*p*), 124.9 (C24), 122.5 (C8), 66.3(C9), 56.3, 46.4 (C13), 35.7, 34.5, 31.73, 28.1, 28.0, 26.4, 25.8, 24.7, 18.8, 17.8, 17.2.

***rac*-(6*R**)-6-[(1*R**,3a*R**,4*R**,7a*R**)-4-(Phenylsulfonyl)-7a-methyloctahydroinden-1-yl]-2-methylheptan-2-ol (2). Procedure a (from Alcohol 17 via Epoxide 20):** *m*-CPBA (60%, 58 mg, 0.202 mmol) was added at 0 °C to a solution of sulfide **17** (21 mg, 0.057 mmol) in dichloromethane (2 mL). The mixture was set aside at room temp. for 2 h and then poured into aqueous $NaHCO_3$. The product was extracted with dichloromethane. The extract was washed with saturated aqueous Na_2SO_3 and water. The solvent was evaporated, and the residue was chromatographed on SiO_2 (2 g, hexane/EtOAc, 10:1, 5:1). Epoxy sulfone **20** (21 mg, 88%) was obtained. ^{1}H NMR: δ = 7.79−7.90 (m, 2 H, H-*m*SO_2Ph), 7.67−7.48 (m, 3 H, H-*o* and -*p* SO_2Ph), 4.76 (br. t, *J* = 7.8 Hz, 1 H, C9-H), 4.04 (br. s, C9-O*H*), 2.96−2.73 (m, 1 H, C15-αH), 2.71−2.62 (m, 1 H, C24-H), 2.40−2.14 (m, 2 H), 2.06−1.81 (m, 3 H), 1.74−0.82 (m, 8 H), overlapping 1.30 (s, 3 H, C27 or 26-H), 1.26 (s, 3 H, C26 or 27-H), 1.01 (s, 3 H, C18-H), 0.95 (d, $J_{20,21}$ = 6.6 Hz, 3 H, C21-H) ppm. ^{13}C NMR: δ = 169.3 (C14), 141.5, 141.5, 133.0 (C-*p*), 128.9 (C-*o*), 126.9 (C-*m*), 65.7 (C9), 64.5, 64.3, 58.3, 58.0, 54.9, 54.7, 47.5, 35.1, 33.7, 33.5, 32.1, 31.9, 27.8, 27.4, 26.7, 25.6, 25.1, 24.7, 18.7, 18.6, 18.5, 17.7 ppm. MS EI (70 eV): *m*/*z* (%) = 416 (1.5) [$M - H_2$]$^+$, 400 (9) [$M - H_2O$]$^+$, 385 (22) [$M - CH_3, - H_2O$]$^+$, 277 (100) [$M - SO_2Ph$]$^+$, 273 (89), 259 (48) [$M - SO_2Ph, - H_2O$]$^+$, 173 (45), [$TsOH_2$]$^+$. LSIMS (+) (NBA, 8 kV): *m*/*z* (%) = 441 (21) [M + Na]$^+$, 417 (11) [$M - H$]$^+$, 401 (29). Epoxy sulfone **20** was dissolved in THF (1 mL), $LiAlH_4$ (0.25 M in THF, 1.5 mL, 0.375 mmol) was added, and the mixture was heated at reflux temp. for 25 min. After the mixture had cooled, methanol (0.5 mL) was added and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The extract was concentrated. TLC analysis of this product indicated the presence of **2** and a small amount of a side product identified as **22**. The crude product was chromatographed on SiO_2 (3 g, hexane/EtOAc, 10:1, 5:1) to give sulfone **2** (17 mg, 73%). M.p. 109 °C (methanol). ^{1}H NMR: δ = 7.91−7.77 (m, 2 H, H-*m* Ph), 7.69−7.48 (m, 3 H, H-*o*, -*p* Ph), 3.03 (br. td, *J* = 11.4, 3.3 Hz, C8-H), 2.12−0.82 (m, 20 H), overlapping 1.20 (s, 6 H, C27-H and C26-H), 0.91 (d, 3 H, $J_{20,21}$ = 6.5 Hz, C21-H), 0.69 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 138.2 (C-*ipso*), 133.2 (C-*p*), 128.8 (C-*o*), 128.6 (C-*m*), 70.9 (C25), 63.7, 54.9, 48.0, 44.5 (C14), 44.2, 38.6, 36.2, 35.4, 29.2, 29.1, 27.8, 27.3, 25.2, 21.0, 20.6, 18.6, 11.7. $C_{24}H_{38}O_3S$ (406.62): calcd. C 70.89, H 9.42; found C 70.87, H 9.45. **Procedure b (from Alcohol 19 via Epoxide 21):** *m*-CPBA (60%, 62 mg, 0.216 mmol) was added to a solution of **19** (23 mg, 0.062 mmol) in dichloromethane (2 mL). After 2 h, the mixture was poured into aqueous $NaHCO_3$, and the product **21** was extracted with dichloromethane. The extract was washed consecutively with aqueous Na_2SO_3 and water. The solvent was evaporated, and the residue was dissolved in THF (1 mL). $LiAlH_4$ (0.25 M in THF, 1.0 mL, 0.25 mmol) was added, and the mixture was heated at reflux temperature for 20 min. After the mixture had cooled, methanol (0.5 mL) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The extract was concentrated, and the residue was chromatographed on SiO_2 (2 g, hexane/EtOAc, 50:1, 10:1, 5:1). Sulfone **2** (16 mg, 64%) was obtained. **Procedure c (from 10 without Isolation of Intermediates):** DIBALH (0.7 M in hexane, 10.32 mL, 7.224 mmol) was added at −78 °C to a solution of **10** (485 mg, 1.032 mmol) in dichloromethane (15 mL). Stirring at −78 °C was continued for 1 h, and the mixture was then set aside at room temp. for 24 h. Methanol (5 mL) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The extract was concentrated and the residue was chromatographed on SiO_2 (40 g, hexane/EtOAc, 10:1, 5:1). A mixture of diol **15** and its 9α epimer (378 mg, 94%, in a ratio of ca. 7:3 by ^{1}H NMR) was obtained. This (374 mg, 0.969 mmol) was dissolved in dichloromethane (35 mL). DMAP (35 mg, 0.287 mmol) and triethylamine (1.5 mL) were added, and the solution was cooled to −20 °C. *p*-TsCl (476 mg, 2.497 mmol) in dichloromethane (1.5 mL) was then added dropwise, and the mixture was set aside at 0 °C for 8 h. The solvent was evaporated and the residue was chromatographed on SiO_2 (40 g, hexane/EtOAc, 20:1, 10:1). A mixture of tosylate **16** and its 9α epimer (485 mg) was obtained. To a solution of this product (485 mg, 0.898 mmol) in dichloromethane (25 mL), *m*-CPBA (50%, 1.146 g, 3.323 mmol) was added at 0 °C. The mixture was set aside at room temp. for 3 h and then poured into aqueous $NaHCO_3$. The product was extracted with dichloromethane. The extract was washed with saturated aqueous $Na_2S_2O_3$ and water, and the solvent was evaporated. The residue was dissolved in THF (11 mL), $LiAlH_4$ (1.0 M in THF, 7 mL, 7.00 mmol) was added, and the mixture was heated at reflux temperature for 30 min. After the mixture had cooled, methanol (2 mL) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The extract was concentrated and the residue was chromatographed on SiO_2 (25 g, hexane/EtOAc, 5:1). (3ξ,6*R**)-6-[(1*R**,3a*R**,4*R**,7a*R**)-4-(Phenylsulfonyl)-7a-methyloctahydroinden-1-yl]-2-methylheptan-3-ol (**22**, 51 mg, 12% yield from **10**) and then sulfone **2** (232 mg, 55% yield from **10**) were obtained. Sulfone **22**: ^{1}H NMR: δ = 7.90−7.77 (m, 2 H, H-*m* Ph), 7.68−7.47 (m, 3 H, H-*o*, -*p* Ph), 3.37−3.21 (m, 1 H, C24-H), 3.02 (br. td, *J* = 11.2, 3.2 Hz, C8-H), 2.12−0.82 (m, 18 H),

overlapping 0.93−0.85 (m, 9 H, C21-H, C26-H, and C27-H), 0.68 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 138.2 (C-*ipso*), 133.2 (C-*p*), 128.8 (C-*o*), 128.6 (C-*m*), 76.8 (C24), 63.6 (C8), 54.9 and 54.8, 48.0, 44.5 (C14), 38.6, 35.5 and 35.3, 33.4 and 33.1, 30.4 (split), 27.7, 25.2, 21.0, 18.9, 18.7 (split), 18.5, 17.1 and 16.6 (C21), 11.7 (C18). LSIMS (+) (NBA, 8 kV): *m*/*z* (%) = 831 (1.2) [2 M + Na]$^+$, 427 (32) [M + Na]$^+$, 405 (1.2) [M + H]$^+$. $C_{24}H_{36}NaO_3S$ [M + Na]$^+$: 427.22829; found 427.22822 (HR LSIMSMS).

***S*-*tert*-Butyl 6-Methylhept-6-enethioate:** This compound was prepared from ethyl 6-methylhept-6-enoate[21] in a way analogous to that described above for the thioester corresponding to **6**. The product was distilled at 100−102 °C/1.0 Torr. ^{1}H NMR: δ = 4.67 (m, 1 H, =CH), 4.64 (m, 1 H, =CH), 2.43 (t, *J* = 7.3 Hz, 2 H, C2-H), 1.99 (t, *J* = 7.1 Hz, 2 H, C5-H), 1.75−1.15 (m, 4 H, C3-H and C4-H), overlapping 1.68 (s, 3 H, =CCH$_3$), 1.43 (s, 9 H, SCCH$_3$) ppm. ^{13}C NMR: δ = 200.3 (C1), 145.3 (C6), 110.1 (C7), 47.7 (S−C), 44.4, 37.3, 29.7, 26.7, 25.2, 22.2 ppm. MS: *m*/*z* (%) = 158 (25), 125 (100), 97 (50), 96 (27), 82 (24), 57 (24), 55 (17). $C_{12}H_{22}OS$ (214.37): calcd. C 67.24, H 10.34; found C 67.00, H 10.26.

(*E*)- and (*Z*)-[1-(*tert*-Butylthio)-6-methylhepta-1,6-dienyloxy]trimethylsilane (23): The thioester described above (1.0 g, 4.7 mmol) was added at −78 °C to a solution of LDA (6.3 mmol) [prepared from *i*Pr$_2$NH (0.713 mg, 7.0 mmol) and BuLi (2.0 M in hexane, 3.15 mL, 6.3 mmol)] in THF, followed after 30 min by TMSCl (1.02 g, 9.4 mmol). The mixture was stirred at −78 °C for 4 h, and was then set aside at room temp. for 12 h. The solvent was evaporated, and the residue was diluted with dry hexane and filtered. The filtrate was concentrated and the residue was distilled in a Kugelrohr apparatus (150 °C/4 Torr). Ketene acetal **23** (1.15 g, 85%) was obtained as a mixture of (*E*)/(*Z*) isomers in a ratio of 9:1 (by ^{1}H NMR, S*t*Bu signals). (*E*) isomer: ^{1}H NMR: δ = 5.21 (t, *J* = 7.4 Hz, 1 H, C2-H), 4.67 (m, 2 H, C7-H$_2$), 2.17 (m, 2 H, C3-H), 2.02 (m, 2 H, C5-H), 1.70 (s, 3 H, C6-CH$_3$), 1.46 (m, 2 H, C4-H), 1.36 (s, 9 H, S*t*Bu), 0.22 (s, 9 H, Si-CH$_3$) ppm. ^{13}C NMR: δ = 145.9 (C1), 145.3 (C6), 120.4 (C2), 109.7 (C7), 46.3 (S-C), 37.4 (C5), 31.8 (SC*C*H$_3$), 28.9 (C3), 28.1 (C4), 22.4 (C6), 0.35 (Si-*C*H$_3$). (*Z*) isomer (diagnostic signals): ^{1}H NMR: δ = 1.33 (s, 9 H, S*t*Bu) ppm. ^{13}C NMR: δ = 125.2 (C2), 109.9 (C7), 37.6 (C5), 31.4 (SC*C*H$_3$), 27.4 (C3), 26.8 (C4), 0.76 (Si-C) ppm. MS EI: *m*/*z* (%) = 286 (0.2), 229 (74), 161 (19), 133 (22), 95 (16), 75 (16), 73 (100), 57 (44), 55 (29), 45 (15), 41 (37). $C_{15}H_{30}OSSi$ (286.56): calcd. C 62.87, H 10.55; found C 62.87, H 10.74.

***S*-*tert*-Butyl *rac*-(2*R**)-6-Methyl-2-{(1*R**,2*R**)-2-methyl-3-oxo-2-[3-oxo-4-(phenylthio)butyl]cyclopentyl}hept-6-enethioate (24) and *S*-*tert*-Butyl *rac*-(2*R**)-6-Methyl-2-[(1*R**,7a*R**)-7a-methyl-5-oxo-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]hept-6-enethioate (25):** Acetal **23** (0.868 g, 3.03 mmol) in dichloromethane (1.5 mL) was added at −78 °C over 15 min to a stirred solution of enone **5** (0.306 g, 3.19 mmol) and TrSbCl$_6$ (101 mg, 0.17 mmol) in dichloromethane (8.5 mL). After 1 h, enone **8** (0.56 g, 3.19 mmol) in dichloromethane (1.5 mL) was added over 15 min. The mixture was set aside at −78 °C for 2 h, and was then allowed to warm to room temp. (ca. 1 h), and the reaction was quenched with water (1.0 mL). The mixture was diluted with hexane and filtered through a pad of Celite. The filtrate was dried with Na$_2$SO$_4$, the solvent was evaporated, and the residue was chromatographed on SiO$_2$ (100 g, hexane/EtOAc, 9:1) to give dione **24** (980 mg, 2.01 mmol, 63%) and enone **25** (60.0 mg, 0.12 mmol, 4.0%). **24:** M.p. 63−64 °C (methanol). IR (KBr): ṽ = 1736, 1712, 1672, 1583 cm^{-1}. ^{1}H NMR: δ = 7.39−7.15 (m, 5 H, SPh), 4.71 (br. s, 1 H, C26-H$_a$), 4.67 (br. s, 1 H, C26-H$_b$), 3.64 (s, 2 H, C8-H), 2.78−0.90 (m, 16 H), overlapping 1.69 (s, 3 H, C27-H), 1.40 (s, 9 H, S-C-C*H*$_3$), 0.99 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 221.5 (C14), 204.4 (C9), 203.2 (C21), 145.1 (C25), 134.9 (C-*ipso*), 129.8 (C-*o*), 128.9 (C-*m*), 126.7 (C-*p*), 110.3 (C26), 54.1, 51.2, 48.7, 43.9, 43.2, 37.6, 36.5, 35.8, 31.0, 29.5 (*t*BuS), 29.1, 24.2, 22.9, 22.1, 18.7. EI MS: *m*/*z* (%) = 488 (68), 398 (31), 309 (21), 275 (86), 196 (43), 179 (22), 167 (21), 147 (22), 135 (23), 123 (66), 57 (100). $C_{28}H_{40}O_3S_2$ (488.76): calcd. C 68.81, H 8.25; found C 68.74, H 8.24. **25:** M.p. 85−86 °C (methanol). IR (KBr): ṽ = 1677, 1601, 1584 cm^{-1}. ^{1}H NMR: δ = 7.30−7.00 (m, 5 H, SPh), 4.70 (br. s, 1 H, C26-H), 4.66 (br. s, 1 H, C26-H), 2.80−1.10 (m, 16 H), overlapping 1.69 (s, 3 H, C27-H), 1.48 (s, 9 H, S*t*Bu), 1.24 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 203.2 (C21), 193.6 (C9), 185.2 (C14), 145.1 (C25), 135.9 (C-*ipso*), 128.8 (C-*o*), 127.1 (C-*m*), 125.4 (C-*p*), 125.1 (C8), 110.3 (C26), 54.2 (C20), 52.4 (C17), 48.7 (S*t*Bu), 47.3 (C13), 37.6, 34.6, 34.1, 32.1, 30.5, 29.6 (S*t*Bu), 26.0, 24.3, 22.2 (C27), 16.7 (C18) ppm. MS EI: *m*/*z* (%) = 470 (100), 414 (11), 353 (22), 305 (27), 271 (13), 256 (20), 255 (25), 243 (22), 149 (26), 147 (45), 95 (25), 91 (30), 57 (77). $C_{28}H_{38}O_2S_2$ (470.74): C 71.44, H 8.14; found 71.42, H 8.17.

***S*-*tert*-Butyl *rac*-(2*R**)-6-Methyl-2-[(1*R**,7a*R**)-7a-methyl-5-oxo-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]hept-6-enethioate (25):** A solution of KOH in methanol (20%, 0.03 mL) was added to a solution of dione **24** (300.0 mg, 0.61 mmol) in methanol (15.0 mL). After 1 h, the solvent was evaporated at room temp. and the residue was chromatographed on SiO$_2$ (15.0 g, hexane/EtOAc, 20:1, 9:1). Enone **25** (233 mg, 0.49 mmol, 81%), identical with the sample described above, was obtained.

***S*-*tert*-Butyl *rac*-(2*R**)-2-[(1*R**,5*S**,7a*R**)-5-Hydroxy-7a-methyl-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]-6-methylhept-6-enethioate (26):** NaBH$_4$ (20.0 mg) was added at −78 °C to a solution of enone **25** (208.0 mg, 0.44 mmol) and CeCl$_3$·7H$_2$O (82.0 mg) in methanol (5.25 mL) and THF (3.5 mL). The mixture was stirred at −78 °C for 2 h, allowed to warm to room temp., and poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The extract was dried with Na$_2$SO$_4$ and the solvent was evaporated. The residue was chromatographed on SiO$_2$ (6.0 g, hexane/EtOAc, 9:1) to give alcohol **26** (192.0 mg, 93%). ^{1}H NMR: δ = 7.31−7.10 (m, 5 H, SPh), 4.69 (br. s, 1 H, C26-H), 4.65 (br. s, 1 H, C26-H), 4.05 (t, *J* = 6.8 Hz, 1 H, C9-H), 2.63−1.20 (m, 16 H), overlapping 1.69 (s, 3 H, C27-H), 1.48 (s, 9 H, S*t*Bu), 1.12 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 203.5 (C21), 161.4 (C14), 145.2 (C25), 134.7 (C-*ipso*), 128.9 (C-*o*), 127.5 (C-*m*), 125.6 (C-*p*), 124.4 (C8), 110.1 (C26), 67.6 (C9), 54.5 (C20), 52.6 (C17), 48.4 (S*t*Bu), 46.1 (C13), 37.6, 34.3, 32.1, 29.6 (S*t*Bu), 28.4, 27.1, 25.8, 24.4, 22.2 (C27), 17.8 (C18) ppm. MS EI: *m*/*z* (%) = 472 (100) [M]$^+$, 395 (31), 227 (21), 181 (27), 149 (23), 147 (21), 131 (34), 95 (30), 57 (44). $C_{28}H_{40}S_2O_2$ [M$^+$]: 472.2469; found 472.2466 (HR MS).

***rac*-(1*R**,5*S**,7a*R**)-1-[(1*R**)-1-Hydroxymethyl-5-methylhex-5-enyl]-7a-methyl-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (27):** LiAlH$_4$ (1.3 mg) was added to a solution of thioester **26** (16.0 mg, 0.034 mmol) in THF (1.5 mL). The mixture was heated at reflux temperature for 30 min. After the mixture had cooled to room temperature, methanol (0.3 mL) was added and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The organic extract was dried with Na$_2$SO$_4$ and the solvent was evaporated. The residue was chromatographed on SiO$_2$ (1.8 g, hexane/EtOAc, 5:1, 4:1) to give diol **27** (11.0 mg, 84%). ^{1}H NMR: δ = 7.45−7.10 (m, 5 H, SPh), 4.75 (br. s, C26-H), 4.03−4.22 (m, 1 H, C9-H), 3.61 (m, 2 H, C21-H), 2.82−0.90 (m, 16 H), overlapping 1.76 (s, 3 H, C27-H), 1.11 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 162.3 (C14), 145.7 (C25), 134.9 (C-*ipso*), 128.9 (C-*o*), 127.5 (C-*m*), 125.6 (C-*p*), 123.9 (C8),

109.8 (C26), 67.8 (C9), 62.8 (C21), 50.8 (C20), 46.1 (C13), 40.9 (C17), 38.1, 34.9, 28.8, 28.4, 25.8, 24.6, 22.4 (C27), 17.9 (C18). MS EI: *m*/*z* (%) = 386 (100), 309 (93), 149 (25), 147 (19), 135 (20), 133 (37), 131 (25), 121 (20), 109 (35), 107 (24), 105 (31), 95 (35), 93 (22), 81 (24), 79 (32), 77 (32), 69 (40), 55 (66). $C_{24}H_{34}O_2S$ [M^+]: 386.2279; found 386.2275 (HRMS).

***rac*-(2*R**)-2-{(5*S**,7a*R**)-[5-Hydroxy-7a-methyl-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]}-6-methylhept-6-enyl Toluene-4-sulfonate (28):** TsCl (24.0 mg, 0.125 mmol) was added at 0 °C to a solution of diol **27** (20.0 mg, 0.05 mmol) in dichloromethane (1.2 mL), containing Et_3N (0.1 mL) and DMAP (1.5 mg). The mixture was stirred at 0−5 °C for 4 h, allowed to warm to room temperature and then poured into 2% sulfuric acid. The product was extracted with dichloromethane. The organic extract was washed successively with aqueous $NaHCO_3$ and water and dried (Na_2SO_4), and the solvents were evaporated. The residue was chromatographed on SiO_2 (2.0 g, hexane/EtOAc, 5:1, 4:1, 2:1). Tosylate **28** was obtained (23.0 mg, 85%). ^{1}H NMR: δ = 7.79 (d, *J* = 8.2 Hz, 2 H, C-*o*-H aromat. Ts), 7.34 (d, *J* = 8.5 Hz, 2 H, C-*m*-H aromat. Ts), 7.60−7.05 (m, 5 H, SPh), 4.67 (br. s, C26-H), 4.57 (br. s, C26-H), 4.20−3.95 (m, 3 H, C21-H_2 and C9-H), 2.78−0.85 (m, 16 H), overlapping 2.44 (s, 3 H, CH_3 Ts), 1.64 (s, 3 H, C27-H), 0.98 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 161.3 (C14), 145 (C25), 144.9 (C-*ipso*, Ts), 134.7 (C-*ipso*, SPh), 132.7 (C-*p*, Ts), 129.8 (C-*o* Ts), 129.1 (C-*o*,Ph), 127.9 (C-*m*, Ts), 127.7 (C-*m*, Ph), 125.8 (C-*p* Ph), 124.7 (C8), 109.9 (C26), 70.3 (C9), 67.5 (C21), 50.3 (C20), 45.9 (C13), 38.5 (C17), 37.7, 34.8, 28.5, 28.2, 28.1, 26.0, 23.9, 22.3, 21.6, 17.8 (C18). MS EI: *m*/*z* (%) = 540 (100), 463 (48), 241 (24), 149 (27), 147 (22), 145 (21), 131 (30), 109 (24), 105 (26), 95 (31), 91 (49), 69 (21), 55 (24). $C_{31}H_{40}O_4S_2$ [M^+]: calcd. 540.2368; found 540.2387 (HR MS).

***rac*-(2*R**)-2-[(5*S**,7a*R**)-5-Hydroxy-7a-methyl-4-(phenylsulfonyl)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]-5-(2-methyloxiranyl)pentyl Toluene-4-sulfonate (29):** *m*-CPBA (70%, 62 mg, 0.25 mmol) was added at 0 °C to a solution of tosylate **28** (30 mg, 0.06 mmol) in dichloromethane (2.3 mL). The mixture was stirred at room temperature for 2 h, and was then poured into aqueous $NaHCO_3$ (4 mL). The product was extracted with dichloromethane. The organic extract was washed successively with aqueous $Na_2S_2O_3$ (10 mL) and water and then dried (Na_2SO_4), and the solvents were evaporated. The residue consisted of epimeric epoxy sulfones **29** (32.0 mg, 98%) in a ratio of 2:1 (by ^{1}H NMR). Major isomer: ^{1}H NMR: δ = 8.05−7.30 (m, 9 H, H-arom.), 4.69 (t, 1 H, C9-H), 3.97 (m, 2 H, C21-H), 2.82−0.85 (m, 16 H), overlapping 2.51 (s, 3 H, CH_3 Ts), 1.21 (s, 3 H, CH_3 Ts), 0.92 (s, 3 H, C18-H) ppm. ^{13}C NMR: 167.8 (C14), 145.0 (C-*ipso* Ts), 141.3 (C-*ipso* Ph), 134.5, 133.3, 132.6, 130.2, 129.9, 129.1, 127.9, 127.1, 70.1 (C21), 65.7 (C9), 56.5 (C25), 53.6 (C26), 49.3 (C20), 47.2 (C13), 37.7, 36.4, 34.2, 28.9, 27.5, 25.8, 21.8, 21.6, 20.8, 18.0 (C18). Diagnostic signals of the minor isomer: ^{1}H NMR: δ = 2.44 (s, 3 H, CH_3 Ts), 1.24 (s, 3 H, C27-H) ppm. ^{13}C NMR: δ = 134.4, 129.7, 53.7, 37.7, 36.6, 29.0, 27.8, 20.8 ppm. $C_{31}H_{40}NaO_7S_2$ [M^+]: calcd. 611.2108; found 611.2124 (HR MS). This mixture was further used without separation.

***rac*-(6*R**)-2-Methyl-6-[(4*R**,7a*R**)-7a-methyl-4-(phenylthio)octahydroinden-1-yl]heptan-2-ol (2):** $LiAlH_4$ (8.2 mg) was added to a solution of epoxysulfone **29** (32.0 mg, 0.054 mmol) in THF (0.5 mL), and the mixture was heated at reflux temperature for 35 min. After the mixture had cooled, methanol (0.5 mL MeOH) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The organic extract was dried (Na_2SO_4) and the solvent was evaporated. The residue was chromatographed on SiO_2 (3.0 g, hexane/EtOAc, 4:1, 3:1, 2:1, 1:1). Sulfone **2** was obtained (15.2 mg, 69%). One crystallization from hexane/benzene gave analytically pure material (12.5 mg), m.p. 109−110 °C identical with a sample described above.

(6*R*)-2-Methyl-6-[(1*R*,7a*R*)-7a-methyl-4-(phenylthio)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]heptan-2-ol (31): $BF_3{\cdot}2H_2O$ (0.07 mL, 1.10 mmol) was added at 0 °C to a solution of **30**[25] (280 mg, 1.00 mmol) and PhSH (1.03 mL, 10 mmol) in dichloromethane (6 mL). The mixture was stirred at 0 °C for 6 h and then poured into 10% aqueous NaOH. The product was extracted with dichloromethane. The extract was washed with water and the solvent was evaporated. The residue was chromatographed on SiO_2 (25 g, hexane/EtOAc, 50:1, 20:1, 5:1). Sulfide **31** (245 mg, 66%) was obtained. $[\alpha]_D^{22}$ = +23.7 (*c* = 1.83). ^{1}H NMR: δ = 7.31−7.06 (m, 5 H, SPh), 2.50−0.89 (m, 19 H), overlapping 1.22 (s, 6 H, C27-H and C26-H), 0.98 (d, 3 H, $J_{20,21}$ = 6.5 Hz, C21-H), 0.98 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 157.1 (C14), 136.1 (C-*ipso*), 128.6 (C-*o*),128.1(C-*m*),125.2 (C-*p*), 119.3 (C8), 70.9 (C25), 56.3, 45.3 (C13),44.2, 36.7, 36.0, 34.6, 30.2, 29.2, 29.1, 27.8, 26.5, 20.6, 20.2, 18.7, 18.1 ppm. MS EI (70 eV): *m*/*z* (%) = 372 (52) [M^+], 375 (11) [$M - CH_3$]$^+$, , 339 (20) [$M - CH_3, - H_2O$]$^+$, 295 (91) [$M - Ph$]$^+$, 277 (25) [$M - Ph, - H_2O$]$^+$, 245 (25) [$M - SPh, - H_2O$)$^+$, 189 (14), 161 (24), 105 (13), 91 (18), 69 (19). $C_{24}H_{36}OS$ [M^+]: calcd. 372.24869; found 372.249 (HRMS).

(6*R*)-6-[(1*R*,7a*R*)-7a-Methyl-4-(phenylsulfonyl)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-yl]-2-methylheptan-2-ol (32): *m*-CPBA (60%, 63 mg, 0.22 mmol) was added at 0 °C to a solution of **31** (37 mg, 0.10 mmol) in dichloromethane (2 mL). The mixture was set aside at room temp. for 2 h and then poured into aqueous $NaHCO_3$. The product was extracted with dichloromethane. The extract was washed with aqueous $Na_2S_2O_3$ and water, and the solvent was evaporated. The residue was chromatographed on SiO_2 (6 g, hexane/EtOAc, 10:1, 5:1, 2:1). Sulfone **32** (40 mg, 99%) was obtained. $[\alpha]_D^{22}$ = +16.3 (*c* = 1.70). ^{1}H NMR: δ = 7.89−7.77 (m, 2 H, H-*m* Ph), 7.63−7.43 (m, 3 H, H-*o*, -*p* Ph), 3.07−2.61 (m, 2 H), 2.43−0.79 (m, 17 H), overlapping 1.20 (s, 6 H, C27-H and C26-H), 0.93 (d, 3 H, $J_{20,21}$ = 6.5 Hz, C21-H), 0.89 (s, 3 H, C18-H) ppm. ^{13}C NMR: δ = 163.2 (C14), 141.2 (C-*ipso*), 132.7 (C-*p*), 128.8 (C-*o*), 128.6 (C8), 127.0 (C-*m*), 70.8 (C25), 54.7, 46.7 (C13), 44.1, 35.9, 35.2, 33.9, 29.2, 29.1, 27.5, 26.8, 24.3, 20.6, 18.8, 18.6, 18.2 ppm. MS EI (70 eV): *m*/*z* (%) = 402 (0.3) [$M - H_2$]$^+$, , 389 (19) [$M - CH_3$]$^+$, 386 (44) [$M - H_2O$]$^+$, 371 (6) [$M - CH_3, - H_2O$]$^+$, 331 (14), 274 (29), 245 (100) [$M - H_2O, - SO_2Ph$]$^+$, 161 (53), 149 (59), 133 (76), 109 (35), 69 (34). LSIMS (+) (NBA, 8 kV): *m*/*z* (%) = 831 (1.2) [2 M + Na]$^+$, 427 (32) [M + Na]$^+$, 405 (1.2) [M + H]$^+$. $C_{24}H_{36}O_3SNa$ [M + Na]$^+$: calcd. 427.22829; found 427.22822 (LSIMS HRMS).

(−)-(6*R*)-6-[(1*R*,3a*R*,4*R*,7a*R*)-7a-Methyl-4-(phenylthio)octahydroinden-1-yl]-2-methylheptan-2-ol [(−)-2]: $LiAlH_4$ (0.25 M in THF, 0.6 mL, 0.150 mmol) was added to a solution of **32** (50 mg, 0.124 mmol) in THF (2 mL), and the mixture was heated at reflux temperature for 20 min. After the mixture had cooled, methanol (0.5 mL) was added, and the whole mixture was poured into 10% aqueous tartaric acid. The product was extracted with dichloromethane. The solvent was evaporated and the residue was chromatographed on SiO_2 (2 g, hexane/EtOAc, 50:1, 10:1, 5:1). Sulfone (+)-**2** (32 mg, 63%) was obtained. M.p. 128 °C (benzene/hexane, 1:5). $[\alpha]_D^{22}$ = −0.35 (*c* = 0.6). ^{1}H and ^{13}C NMR spectra are identical with those of a racemic sample.

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[25] The sample of (1*R*,3a*R*,7a*R*)-1-[(2*R*)-6-hydroxy-6-methylhept-2-yl]-7a-methyloctahydroinden-4-one, which has been stored in a refrigerator for several months, was chromatographed on SiO_2. The major fraction was collected to give the derivative with the *cis*-hydrinadane system: (1*R*,3a*S*,7a*R*)-1-[(2*R*)-6-hydroxy-6-methylhept-2-yl]-7a-methyloctahydroinden-4-one (**30**): ^{1}H NMR: δ = 1.18 (s, 6 H, C26, C27-H), 1.02 (s, 3 H, C18-H), 0.90 (d, *J* = 6.3 Hz, 3 H, C21-H). Ref.[23] ^{1}H NMR: (300 MHz, $CDCl_3$): δ = 1.18 (s, 6 H), 1.02 (s, 3 H), 0.89 (d, *J* = 6.3 Hz, 3 H).

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