α-Thioalkylation of Zinc Dienolates as an Entry to 4-Substituted 1-*tert*-Butoxy-7a-methylhexahydroindenes[1,2]

Thomas Köhler[a], Thomas Huhn[a*] and Ulrich Groth[a]

[a] *Fachbereich Chemie und Konstanz Research School Chemical Biology der Universität Konstanz, Universitätsstrasse 10, Fach 720, D-78457 Konstanz, Germany.*

contacting e-mail Thomas.Huhn@uni-konstanz.de

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Hexahydroindenes **10** are readily available in 3 steps with an overall yield of 41 – 45 % starting from the Hajos Wiechert ketone **1**. Alkylation of the α,β-unsaturated ketone **1** at C-4 has been achieved by thioalkylation of the corresponding zinc dienolate 2 with α-chlorosulfides of type **3**. Subsequent in situ reduction and desulfurization of the β-(phenylthio) ketones **4** leads directly to the 4-substituted hexahydroindene-5-ols **6** which can be deoxygenated via their mesylates to the hexahydroindenes **10**.

Introduction

4-Substituted hexahydro-inden-5-ols and the corresponding hexahydroindene derivatives are important intermediates in the stereoselective synthesis of 19-norsteroids.[3] Moreover, they can serve as intermediates for the synthesis of 5,6,7,7a-tetrahydro-4H-indenes, which have been successfully employed as chiral templates in the asymmetric synthesis of allylic alcohols *via* a Diels-Alder reaction, diastereoselective adduct transformation and retro Diels-Alder reaction sequence.[4]

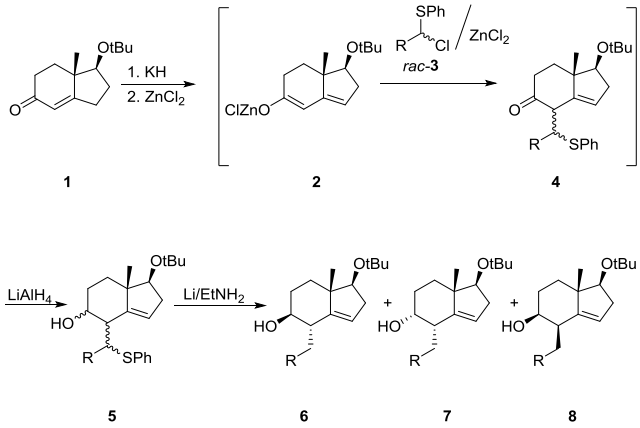
Base-induced alkylation of the α,β-unsaturated ketone **1**[5] usually affords the 4-substituted hexahydroindene-5-ones in only moderate yields[6] due to the high basicity of the corresponding alkali dienolates.[6b] Moreover, an undesirable *O*-alkylation cannot be avoided and mixtures of the *C*- and *O*-alkylated products are formed.[6a,c,e] Only the use of highly S_N2 reactive[7] electrophiles like α-bromoacetophenone affords the 4-substituted hexahydroinden-5-ones in reasonable yields.[8]

In an extension of our previously reported method for the synthesis of 4-substituted hexahydroindene-5-ones **4** by thioalkylation of zinc dienolate **2**,[9] we report here the synthesis of 4-substituted hexahydroinden-5-ols **6** and their corresponding hexahydroindene derivatives **10** by *in situ* reduction of the initially formed 4-substituted hexahydroindene-5-ones **4**.

Results and discussion

Deprotonation of the α,β-unsaturated ketone **1** was performed with potassium hydride in THF. It turned out, that this reaction had to be carried out at r.t. over a period of 3 h in order to achieve complete formation of the potassium dienolate. At lower temperatures the deprotonation was incomplete, whereas at higher reaction temperatures considerable decomposition took place. The transmetalation to the corresponding zinc dienolate **2** was performed with 1.3 equiv. of zinc chloride at -30 °C. The transmetalation was completed within 1 h. The excess of zinc chloride promotes the subsequent Lewis acid catalyzed thioalkylation. 1.1 equiv. of the α-chlorosulfides *rac*-**3** were added at -70 °C and the reaction

mixture was allowed to warm up slowly to r.t. According to TLC analysis the thioalkylation takes places at -30 °C to -20 °C. Exclusively, α-thioalkylation at C-4 took place. There was no evidence for the formation of any *O*-alkylated product. ^{1}H NMR spectroscopical analysis of the crude alkylation product indicates that β,γ-unsaturated ketones **4** were formed initially (**Scheme 1**). Under the reaction condition no isomerization of the double bond into the more favorable α,β-unsaturated position was observed. Considerable isomerization was observed only at temperatures above 0 °C. However, upon aqueous acidic work-up the double bond of these β,γ-unsaturated ketones **4** isomerized back into conjugation with the carbonyl group to afford the more stable α,β-unsaturated ketones (not shown).



Scheme 1: Thioalkylation of Hajos Wiechert ketone (**1**) with subsequent *in situ* reduction to afford 4-substituted hexahydro-inden-5-ols **6-8**.

This isomerization can be avoided by *in situ* reduction of the carbonyl group. This was achieved the best by using $LiAlH_4$ for the reduction (**Scheme 1**). After aqueous work-up the diastereomeric phenylthio alcohols **5** were reductively desulfurized by using lithium in liquid ethyl amine affording the homoallylic alcohols **6** as mixtures of diastereomers. The diastereoselectivity of the thioalkylation in favor of the 4α-isomer was only moderate (49 - 54 % d.e.). The diastereoselectivity of the reduction at C-5 highly depends on the reducing agent (**Table 1**).

Table 1: Chemical yields and ratio of diastereomers (d.r.)

3 - 8	R	Reducing agent	d.r.[a] **6 :**	**7 :**	**8**	yield (%) of **6 – 8**[b]
a	Me	$LiAlH_4$	70	7	23	73
b	Et	$LiAlH_4$	68	8	24	76
c	*n*-Pr	$LiAlH_4$	72	5	23	78
d	*n*-Bu	$LiAlH_4$	68	7	25	74
e	*n*-Pent	$LiAlH_4$	71	7	22	75
e	*n*-Pent	DIBAH	37	34	29	73
e	*n*-Pent	L-Selectride	7	62	31	73
e	*n*-Pent	K-Selectride	37	34	29	68

[a] separated by flash column chromatography; [b] isolated yields.

Lithium aluminium hydride yields in general predominately the 5*S*-configurated reduction products **6** whereas the reduction with L-selectride affords mainly the 5*R*-configurated reduction products **7**. In any case, the three homoallylic alcohols **6** - **8** can be separated easily by simple flash chromatography on silica gel (**Table 1**). The (4*R*, 5*R*)-diastereomer was not detectable.

The configuration at C-5 was determined by a ^{1}H NMR spectroscopical analysis of the corresponding (+)-(*R*)- and (-)-(*S*)-MTPA ester[10] for **6e** and **7e**. According to this analysis C-5 possesses the *S* configuration for **6e** whereas **7e** has *R* configuration at C-5. The relative configuration between C-4 and C-5 could be determined via their coupling constant (**Figure 1**). For diastereoisomers **6** the 6-membered ring adopts a chair conformation in which both the 5-OH and the 4-substituent are equatorial while the angular 7a-Me is axial. Hence the $J_{H\text{-}4,H\text{-}5}$ of 10-11 Hz found for compounds **6** corresponds to a trans-diaxial coupling of protons H-4, H-5. Therefore, C-4 must possess the *S* configuration. Likewise, a conformational model of diastereoisomers **7** indicates an axial 5-OH and an equatorial 4-substituent, in

agreement with the axial-equatorial coupling constant values of 2.4-2.6 Hz observed for protons H-4, H-5. Therefore, C-4 must possess the *S* configuration in homoallylic alcohols **7**.

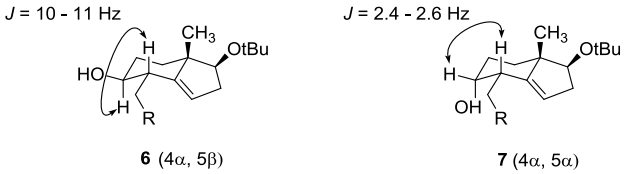


Figure 1: Assignment of relative stereochemistry between C4 and C5.

Reduction of Hajos-Wiechert ketone **1** affords in general 5β–configured alcohols due to a hydride attack from the less shielded α–side.[11] Therefore it can be assumed that the minor diastereomer formed during thioalkylation, which has the thioalkyl group on the β-side, is being reduced to the *cis*-disposed homoallylic alcohol **8** with *S* configuration at C-5.

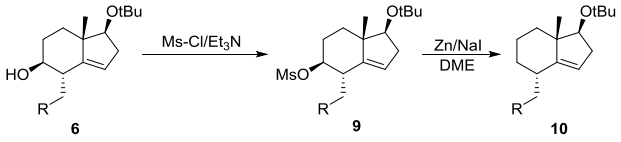
The equatorial homoallylic alcohols **6** and **8** undergo smooth mesylation, whereas the axial alcohol **7** is unreactive (**Tables 2 & 3**). Under more drastic conditions using DMAP, mesylation of the axial alcohol **7** results in elimination (presumably E2): this is consistent with the trans-diaxial position of H-4 and the leaving group.

Table 2: Chemical yields of the two step deoxygenation process to yield hexahydroindenes **10**.

6, 9, 10	R	Yield (%)[a] of **9**	Yield (%)[a] of **10**
a	Me	98	92
b	Et	98	89
c	*n*-Pr	98	85
d	*n*-Bu	97	85
e	*n*-Pent	98	87

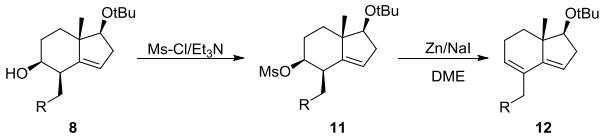
[a] isolated yields.

Mesylates **9** and **11** were deoxygenated according to Fujimotos protocol by using sodium iodide and zinc in dimethoxyethane.[12] Reductive deoxygenation proceeds smoothly to afford hexahydroindenes **10** in 85 - 92 % yield for the conformationally stable, diequatorial diastereoisomer **9**, in which the *cis*-relationship between H-4 and the leaving group precludes E2-elimination (**Scheme 2**).



Scheme 2: Mesylation and deoxygenation of hexahydroinden-5-ols **6** to afford hexahydroindenes **10**.

In contrast, a *trans*-relationship exists between H-4 and 5-OMs for diastereoisomer **11**, again resulting in elimination (**Scheme 3**).



Scheme 3: Mesylation and elimination of hexahydroinden-5-ols **8** to afford tetrahydroindenes **12**.

Possibly this elimination might proceed via an alternative conformer in which the large 4-substituent is equatorial while H-4 and 5-OMs have a trans-diaxial orientation.

Table 3: Chemical yields of two step elimination process to yield tetrahydroindenes **12**.

8	**11, 12**	R	Yield (%)[a] of **11**	Yield (%)[a] of **12**
a	**a**	Me	98	83
c	**b**	*n*-Pr	99	77
e	**c**	*n*-Pent	98	81

[a] isolated yields.

Conclusions

In summary, 4α-substituted hexahydroindenes **10** which are valuable intermediates in natural product synthesis can be prepared starting from the Hajos-Wiechert ketone **1** in three steps with an overall yield of 41 - 45 %.

Acknowledgements

We thank Dr. E. Ottow, *Bayer-Schering pharmaceutical research*, for providing substantial amounts of Hajos-Wiechert ketone (**1**) and the *BASF AG* and the *Wacker AG* for providing other valuable starting materials.

Experimental part

Infrared (IR) spectra were recorded on a Perkin-Elmer FT IR 1600 spectrometer. NMR spectra: Varian XL 200 , Varian VXR 200, Bruker AC 250 spectrometer for ^{1}H and ^{13}C NMR. Chemical shifts are given in parts per million (δ) by using tetramethylsilane as an internal standard. Mass spectra were recorded on a Varian MAT 312 spectrometer. Optical rotations were measured on a Perkin Elmer Mod. 241 MC polarimeter. The melting points were measured in open capillary tubes on a Gallenkamp Melting Point Apparatus and are not corrected. TLC analyses were performed on Polygram Sil G/UV_{254} silica gel plates (Macherey & Nagel). Merck silica gel 60 (0.040-0.063 mm) was used for flash chromatography. Combustion analyses were carried out by the microanalytical laboratory of the University of Konstanz. All reactions were carried out under inert gas atmosphere, except those involving hydrolysis. All reagents were purified and dried if necessary before use by standard laboratory procedures.[13] THF was freshly distilled from Na/K alloy prior to use. CCl_4 was distilled from P_4O_{10}. The ethereal $ZnCl_2$ solution was purchased from Aldrich. The phenyl sulfides were prepared from the corresponding halides or mesylates with thiophenol and K_2CO_3 in acetone.[14]

α-Chlorosulfides rac*-3.**[15] ***General Procedure: *N*-Chlorosuccinimide (0.82 g, 6.1 mmol) was added in a single portion to a stirred solution of the corresponding alkylphenyl sulfide (5.5 mmol) in CCl_4 (12 ml) at 2 °C and stirring was continued at this temperature till the succinimide was drifting on the surface of the solution. The mixture was cooled to -20 °C, the succinimide was filtered off under an argon atmosphere and the filtrate was concentrated *in vacuo* to afford the moisture-sensitive α-chlorosulfides in almost quantitative yield. These chlorosulfides *rac*-**3** were used immediately after drying *in vacuo* (0 °C, 0.01 Torr) without further purification.

***(1S,4S,5S,7aS) 1-tert-Butoxy-4-alkyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ols* 6**. *General Procedure:* Potassium hydride (0.45 g of a 35% suspension in mineral oil, 11.2 mmol) was washed three times with pentane and then three times with THF (10 ml each) and suspended in THF (30 ml). A solution of the α,β-unsaturated ketone **1** (1.55 g, 7.0 mmol) in THF (15 ml) was added at r.t. and stirring was continued for 1 h at r.t. and for 3 h at 45 °C. The solution was cooled down to -30 °C and a solution of zinc chloride in diethyl ether (1.0 *M*, 12.6 ml, 12.6 mmol) was added at -30 °C and stirring was continued for 1 h. The reaction mixture was cooled down to -70 °C, a solution of the α-chlorosulfide **3** (11.9 mmol) in THF (10 ml) was added under stirring, the solution was allowed to warm up to -15 °C within 12 h and stirring was continued for 6 h. $LiAlH_4$ (0.53 g, 14.0 mmol) was added at -70 °C and the reaction mixture was allowed to warm up to r.t. within 8 h. H_2O (3 ml) was added carefully to destroy an excess of $LiAlH_4$ and the solvent was removed *in vacuo* (25 °C / 18 Torr). Diethyl ether (50 ml) and 1 *N* HCl (20 ml) were added under stirring. The organic layer was extracted with H_2O, a saturated aqueous $NaHCO_3$ solution and again with H_2O (20 ml each), dried with $MgSO_4$ and the solvent was

removed *in vacuo* (20 °C / 18 Torr). The residue - the crude product **5** - was dissolved in diethyl ether (5 ml) and used directly for the desulfurization to the homoallylic alcohol **6**. In a 100 ml two-necked flask equipped with a dropping funnel containing a built-in sintered glass disk (porosity P 1) at the bottom and a dry ice condenser at the top, 100 mg (14.3 mmol) of lithium was deposited on the sintered glass disk in an inert atmosphere. At -30 °C ethylamine was placed into the flask via a gas inlet tube. After 25 ml of ethylamine had condensed in the flask insertion was stopped and a solution of the crude β-(phenylthio)-ketone **5** in 5 ml of diethyl ether was added. The solution was kept under reflux at ~ 20 °C. The lithium was slowly dissolved by the condensing ethylamine and a blue solution of lithium in ethylamine dropped continuously into the reaction mixture. The addition of the lithium solution was stopped when the reaction mixture retained its dark blue color for more than 10 sec. Then diethyl ether (20 ml) and 1.08 g (20 mmol) of NH_4Cl were added and the ethylamine was removed at 20-25 °C within 20-30 min. Subsequently, diethyl ether (50 ml) and 1 *N* HCl (30 ml) were added. The layers were separated and the aqueous layer was extracted twice with diethyl ether (10 ml each). The combined organic layers were extracted with H_2O, twice with a saturated aqueous $NaHCO_3$ solution, twice with H_2O (20 ml each) and then dried with $MgSO_4$. The solvent was removed *in vacuo* (20 °C/12 Torr) and the crude homoallylic alcohol **6** purified by flash chromatography.

1-tert-Butoxy-4-ethyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ols (**6a**, **7a** and **8a**): According to the general procedure potassium hydride (0.45 g, 11.2 mmol), the α,β-unsaturated ketone **1** (1.55 g, 7.0 mmol), a zinc chloride solution (1.0 *N* in diethyl ether, 12.6 ml, 12.6 mmol), α-chloroethyl phenyl sulfide (**3a**) (2.06 g, 11.9 mmol) and $LiAlH_4$ (0.53 g, 14.0 mmol) were used to afford 0.90 g (51 %) of (4α,5β)-**6a**, 97 mg (5.5 %) of (4α,5α)-**7a** and 0.30 g (17 %) of (4β,5β)-**8a** as colorless solids after chromatography with diethyl ether/petroleum ether (1:2) on silica gel (110 g).

(1S,4S,5S,7aS)-1-tert-Butoxy-4-ethyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**6a**): R_f = 0.37. M.p.: 66 - 71 °C. $[\alpha]^{20}_D$ = + 27.2° (c = 1.0, $CHCl_3$). IR (nujol): ν = 3600-3100 (OH), 3040 (C=C), 1635 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 8 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.99 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, C(CH_3)$_3$], 0.90 - 2.50 (m; 10 H, CH_2, C-4-H and OH), 3.26 (ddd, J_{ae} = 4.3 Hz, J_{aa} = 11 Hz; 1 H, C-5-H), 3.74 (dd, *J* = 7.5 and 8 Hz; 1 H, C-1-H), 5.21 (dd, *J* = 2 and 5 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.17 (C-2'), 16.78 (C-7a-CH_3), 28.73 [C(<u>C</u>H$_3$)$_3$], 19.90, 32.06, 37.00 and 39.43 (C-1', C-2, C-6 and C-7), 45.85 (C-4), 47.07 (C-7a), 72.57 [<u>C</u>(CH_3)$_3$], 73.73 (C-5), 82.03 (C-1), 117.84 (C-3), 148.60 (C-3a). MS (70 eV): *(m/z)* (%) = 252 (10) [M^+], 195 (12) [M^+ - C_4H_9], 179 (60) [M^+ - OC_4H_9], 149 (58) [M^+ - C_4H_9OH - C_2H_5], 57 (100) [$C_4H_9^+$]. $C_{16}H_{28}O_2$ (252.4): calcd. C 76.14, H 11.18; found C 76.01, H 11.22.

(1S,4S,5R,7aS)-1-tert-Butoxy-4-ethyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**7a**): R_f = 0.43. M.p.: 44 - 53 °C. $[\alpha]^{20}_D$ = - 5.0° (c = 1.0, $CHCl_3$). IR (nujol): ν = 3550 - 3150 (OH), 3040 (C=C), 1635 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 7.5 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.97 (s; 3 H, C-7a-CH_3), 1.17 [s; 9 H, OC(CH_3)$_3$], 0.90 - 2.49 (m; 10 H, C-4-H , CH_2 and OH), 3.83 (t,

^3J = 8.1 Hz; 1 H, C-1-H), 3.99 (ddd, J = 2.6 Hz; 1 H, C-5-H), 5.29 (dd, ^3J = 4.5 Hz, ^3J = 2.1 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.58 (C-2'), 16.56 (C-7a-CH_3), 28.77 [OC($\underline{C}H_3)_3$], 20.65, 29.68, 33.48 and 38.84 (C-1', C-2, C-6 and C-7), 43.08 (C-4), 46.94 (C-7a), 67.84 (C-5), 72.63 [O$\underline{C}$($CH_3)_3$], 82.44 (C-1), 119.78 (C-3), 147.92 (C-3a). MS (70 eV): *(m/z)* (%) = 252 (16) [M^+], 196 (30) [M^+ - C_4H_8], 178 (100) [M^+ - C_4H_9OH], 149 (90) [M^+ - C_4H_9OH - C_2H_5], 57 (75) [$C_4H_9^+$]. $C_{16}H_{28}O_2$ (252.4): calcd. C 76.14, H 11.18; found C 76.10, H 11.16.

(1S,4R,5S,7aS)-1-tert-Butoxy-4-ethyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**8a**): R_f = 0.32. M.p.: 96 °C. $[\alpha]^{20}_D$ = - 45.3° (c = 1.5, $CHCl_3$). IR (nujol): ν = 3400 - 3050 (OH), 3025 (C=C), 1635 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 7.3 Hz; 3 H, CH_2-C$\underline{H}_3$), 1.02 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC($CH_3)_3$], 0.80 - 2.40 (m; 10 H, C-4-H , CH_2 and OH), 3.70 (dd, ^3J = 8.5 Hz, J = 7.7 Hz; 1 H, C-1-H), 3.72 - 3.82 (m; 1 H, C-5-H), 5.27 (t, J = 1.2 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.17 (C-2'), 17.80 (C-7a-CH_3), 28.76 [OC($\underline{C}H_3)_3$], 18.54, 27.34, 37.61 and 38.33 (C-1', C-2, C-6 and C-7), 45.61 (C-7a), 47.37 (C-4), 72.59 [O$\underline{C}$($CH_3)_3$], 73.63 (C-5), 82.88 (C-1), 122.70 (C-3), 148.00 (C-3a). MS (70 eV): *(m/z)* (%) = 252 (7) [M^+], 178 (40) [M^+ - C_4H_9OH], 57 (100) [$C_4H_9^+$]. $C_{16}H_{28}O_2$ (252.4): calcd. C 76.14, H 11.18; found C 76.08, H 11.19.

***1-tert-Butoxy-4-propyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol*s** (**6b**, **7b** and **8b**): According to the general procedure potassium hydride (0.45 g, 11.2 mmol), the α,β-unsaturated ketone **1** (1.55 g, 7.0 mmol), a zinc chloride solution (1.0 *N* in diethyl ether, 12.6 ml, 12.6 mmol), α-chloropropyl phenyl sulfide (**3b**) (2.38 g, 11.9 mmol) and $LiAlH_4$ (0.53 g, 14.0 mmol) were used to afford 0.97 g (52 %) of (4α,5β)-**6b**, 0.11 g (6 %) of (4α,5α)-**7b** and 0.34 g (18 %) of (4β,5β)-**8b** as colorless solids after chromatography with diethyl ether/petroleum ether (1: 4) on silica gel (100 g).

(1S,4S,5S,7aS)-1-tert-Butoxy-4-propyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**6b**): R_f = 0.20. M.p.: 86 °C. $[\alpha]^{20}_D$ = + 35.7° (c = 1.1, $CHCl_3$). IR (nujol): ν = 3400 - 3100 (OH), 1630 cm^{-1} (C=C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 7.0 Hz; 3 H, CH_2-C$\underline{H}_3$), 1.00 (s; 3 H, C-7a-CH_3), 1.18 [s; 9 H, OC($CH_3)_3$], 1.19 (ddd, ^2J = 13.0 Hz, $^3J_{aa}$ = 13.5 Hz, $^3J_{ae}$ = 4.0 Hz; 1 H, C-7_{ax}-H), 1.29 - 1.58 (m; 4 H, C-1'-H, C-2'-H_2 and OH), 1.63 (dddd, ^2J = 12.7 Hz, $^3J_{aa}$ = 13.5 Hz, $^3J_{aa}$ = 10.3 Hz, $^3J_{ae}$ = 3.5 Hz; 1 H, C-6_{ax}-H), 1.65 - 1.71 (m; 1 H, C-1'-H), 1.74 (dt, ^2J = 13.0 Hz, $^3J_{ea}$ and $^3J_{ee}$ = 3.5 Hz; 1 H, C-7_{eq}-H), 1.84 (dddd, ^2J = 12.7 Hz, $^3J_{ea}$ = 4.2 Hz, $^3J_{ea}$ = 4.0 Hz, $^3J_{ee}$ = 3.5 Hz; 1 H, C-6_{eq}-H), 1.93 - 1.99 (m; 1 H, C-4-H), 2.19 (dddd, ^2J = 15.5 Hz, ^3J = 8.0 and 4.4 Hz, ^5J = 1.9 Hz; 1 H, C-2-H), 2.38 (dddd, ^2J = 15.5 Hz, ^3J = 7.8 and 1.8 Hz, ^5J = 2.9 Hz; 1 H, C-2-H), 3.20 (ddd, ^3J = 10.3, 10.3 and 4.2 Hz; 1 H, C-5-H), 3.71 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 5.17 (dd, ^3J = 4.4 und 1.8 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.71 (C-3'), 16.78 (C-7a-CH_3), 28.74 [OC($\underline{C}H_3)_3$], 20.30, 29.84, 32.14, 37.08 and 39.45 (C-1', C-2, C-2', C-6 and C-7), 44.75 (C-4), 47.15 (C-7a), 72.58 [O$\underline{C}$($CH_3)_3$], 74.35 (C-5), 82.01 (C-1), 117.80 (C-3), 149.17 (C-3a). MS (70 eV): *(m/z)* (%) = 266 (7) [M^+], 210 (14) [M^+ - C_4H_8], 192 (97) [M^+ - C_4H_9OH], 163 (42) [M^+ - C_4H_9OH - C_2H_5], 57 (100) [$C_4H_9^+$], 43 (25) [$C_3H_7^+$], 41 (44) [$C_3H_5^+$]. $C_{17}H_{30}O_2$ (266.4): calcd. C 76.64, H 11.35; found C 76.60, H 11.33.

(1S,4S,5R,7aS)-1-tert-Butoxy-4-propyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**7b**): R_f = 0.44. M.p.: 40-49 °C. $[\alpha]^{20}_D$ = - 7.1° (c = 1.1, $CHCl_3$). IR (film): ν = 3600 - 3100 (OH), 3040 (C=C), 1635 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 6.6 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.97 (s; 3 H, C-7a-CH_3), 1.14 [s; 9 H, OC$(CH_3)_3$], 0.80 - 2.50 (m; 12 H, C-4-H, CH_2 and OH), 3.84 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 3.97 (ddd, ^3J = 2.6 Hz; 1 H, C-5-H), 5.31 (d, ^3J = 2.4 Hz; 1 H, C-3-H). **^{13}C** NMR (50.3 MHz, $CDCl_3$): δ = 14.11 (C-4'), 16.59 (C-7a-CH_3), 28.79 [OC(<u>C</u>H$_3$)$_3$], 23.12, 27.67, 29.29, 33.52 and 38.89 (C-1', C-2, C-2', C-6 and C-7), 41.42 (C-4), 46.99 (C-7a), 68.57 (C-5), 72.76 [O<u>C</u>$(CH_3)_3$], 82.48 (C-1), 119.97 (C-3), 147.87 (C-3a). MS (70 eV): *(m/z)* (%) = 266 (8) [M^+], 210 (12) [M^+ - C_4H_8], 192 (82) [M^+ - C_4H_8 - H_2O], 163 (42) [M^+ - C_4H_8 - H_2O - C_2H_5], 57 (100) [$C_4H_9^+$], 43 (32) [$C_3H_7^+$], 41 (42) [$C_3H_5^+$]. $C_{17}H_{30}O_2$ (266.4): calcd. C 76.64, H 11.35; found C 76.58, H 11.29.

(1S,4R,5S,7aS)-1-tert-Butoxy-4-propyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**8b**): R_f = 0.19. M.p.: 93 °C. $[\alpha]^{20}_D$ = - 44.9° (c = 1.2, $CHCl_3$). IR (nujol): ν = 3400 - 3100 cm^{-1} (OH). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 6.8 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.97 (s; 3 H, C-7a-CH_3), 1.188 [s; 9 H, OC$(CH_3)_3$], 1.10 - 2.50 (m; 12 H, C-4-H, CH_2 and OH), 3.54 - 3.79 (m; 1 H, C-5-H), 3.72 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 5.28 (dd, ^3J = 2.2 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.17 (C-4'), 17.92 (C-7a-CH_3), 28.88 [OC(<u>C</u>H$_3$)$_3$], 22.83, 25.49, 29.87, 37.72 and 38.46 (C-1', C-2, C-2', C-6 and C-7), 45.51 (C-4), 45.63 (C-7a), 72.64 [O<u>C</u>$(CH_3)_3$], 73.63 (C-5), 82.94 (C-1), 122.83 (C-3), 148.96 (C-3a). MS (70 eV): *(m/z)* (%) = 266 (4) [M^+], 210 (16) [M^+ - C_4H_8], 192 (76) [M^+ - C_4H_8 – H_2O], 163 (57) [M^+ - C_4H_8 – H_2O - C_2H_5], 57 (100) [$C_4H_9^+$], 43 (28) [$C_3H_7^+$], 41 (51) [$C_3H_5^+$]. $C_{17}H_{30}O_2$ (266.4): calcd. C 76.64, H 11.35; found C 76.54, H 11.21.

1-tert-Butoxy-4-butyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ols (**6c**, **7c** and **8c**): According to the general procedure potassium hydride (0.27 g, 6.7 mmol), the α,β-unsaturated ketone **1** (0.93 g, 4.2 mmol), a zinc chloride solution (1.0 *N* in diethyl ether, 7.6 ml, 7.6 mmol), α-chlorobutyl phenyl sulfide (**3c**) (1.44 g, 7.2 mmol) and $LiAlH_4$ (0.38 g, 10.0 mmol) were used to afford 0.66 g (56 %) of (4α,5β)-**6c**, 47 mg (4 %) of (4α,5α)-**7c** and 0.21 g (18 %) of (4β,5β)-**8c** as colorless solids after chromatography with diethyl ether/petroleum ether (1: 4) on silica gel (65 g).

(1S,4S,5S,7aS)-1-tert-Butoxy-4-butyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**6c**): R_f = 0.24. M.p.: 77 - 79 °C. $[\alpha]^{20}_D$ = + 34.0° (c = 1.0, $CHCl_3$). IR (nujol): ν = 3600 - 3100 (OH), 3040 (C=C), 1635 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.2 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.96 (s; 3 H, C-7a-CH_3), 1.13 [s; 9 H, OC$(CH_3)_3$], 0.75 - 2.48 (m; 14 H, C-4-H, CH_2 and OH), 3.20 (dt, $^3J_{ae}$ = 4.0 Hz, $^3J_{aa}$ = 10.4 Hz; 1 H, C-5-H), 3.70 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 5.17 (dd, ^3J = 4.6 and 2.2 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.11 (C-4'), 16.78 (C-7a-CH_3), 28.74 [OC(<u>C</u>H$_3$)$_3$], 23.31, 27.11, 28.31, 32.05, 37.01 and 39.35 (C-1', C-2, C-2', C-3', C-6 and C-7), 44.89 (C-4), 47.17 (C-7a), 72.57 [O<u>C</u>$(CH_3)_3$], 74.34 (C-5), 82.02 (C-1), 117.85 (C-3), 149.18 (C-3a). MS (70 eV): *(m/z)* (%) = 280 (6) [M^+], 262 (2) [M^+ - H_2O], 223 (31) [M^+ - C_4H_9], 206 (100) [M^+ - C_4H_8 - H_2O], 57 (30) [$C_4H_9^+$]. $C_{18}H_{32}O_2$ (280.5): calcd. C 77.09, H 11.50; found C 76.91, H 11.39.

(1S,4S,5R,7aS)-1-tert-Butoxy-4-butyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**7c**): R_f = 0.33. $[\alpha]^{20}_D$ = - 8.9° (c = 1.2, $CHCl_3$). IR (film): ν = 3600 - 3200 (OH), 3040 (C=C), 1635 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.6 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.95 (s; 3 H, C-7a-CH_3), 1.15 [s; 9 H, OC(CH_3)$_3$], 0.80 - 2.55 (m; 14 H, C-4-H, CH_2 and OH), 3.81 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 3.93 (ddd, ^3J = 2.6 Hz; 1 H, C-5-H), 5.28 (d, ^3J = 2.4 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.12 (C-4'), 16.56 (C-7a-CH_3), 28.77 [OC(<u>C</u>H$_3$)$_3$], 23.05, 27.62, 29.31, 29.72, 33.49 and 38.82 (C-1', C-2, C-2', C-3', C-6 and C-7), 41.39 (C-4), 46.96 (C-7a), 68.53 (C-5), 72.60 [O<u>C</u>(CH$_3$)$_3$], 82.44 (C-1), 119.73 (C-3), 148.01 (C-3a). MS (70 eV): *(m/z)* (%) = 280 (7) [M^+], 262 (4) [M^+ - H_2O], 224 (19) [M^+ - C_4H_8], 206 (72) [M^+ - C_4H_8 - H_2O], 149 (57) [M^+ - C_4H_9 - C_4H_8 - H_2O], 57 (100) [$C_4H_9^+$], 43 (25) [$C_3H_7^+$], 41 (39) [$C_3H_5^+$]. $C_{18}H_{32}O_2$ (280.5): calcd. C 77.09, H 11.50; found C 77.01, H 11.42.

(1S,4R,5S,7aS)-1-tert-Butoxy-4-butyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**8c**): R_f = 0.18. M.p.: 92 °C. $[\alpha]^{20}_D$ = - 45.6° (c = 1.1, $CHCl_3$). IR (nujol): ν = 3300 - 3100 cm^{-1} (OH). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.8 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.99 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 1.10 - 2.52 (m; 14 H, C-4-H, CH_2 and OH), 3.56 - 3.82 (m; 1 H, C-5-H), 3.69 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 5.25 (dd, ^3J = 2.4 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.13 (C-4'), 17.89 (C-7a-CH_3), 28.76 [OC(<u>C</u>H$_3$)$_3$], 22.75, 25.43, 27.27, 29.94, 37.65 and 38.37 (C-1', C-2, C-2', C-3', C-6 and C-7), 45.46 (C-4), 45.58 (C-7a), 72.59 [O<u>C</u>(CH$_3$)$_3$], 73.59 (C-5), 82.87 (C-1), 122.42 (C-3), 148.53 (C-3a). MS (70 eV): *(m/z)* (%) = 280 (5) [M^+], 224 (10) [M^+ - C_4H_8], 206 (55) [M^+ - C_4H_8 - H_2O], 57 (100) [$C_4H_9^+$].$C_{18}H_{32}O_2$ (280.5): calcd. C 77.09, H 11.50; found C 76.70, H 11.44.

1-tert-Butoxy-4-pentyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ols (**6d**, **7d** and **8d**): According to the general procedure potassium hydride (0.28 g, 6.9 mmol), the α,β-unsaturated ketone **1** (0.93 g, 4.2 mmol), a zinc chloride solution (1.0 *N* in diethyl ether, 7.5 ml, 7.5 mmol), α-chloropentyl phenyl sulfide (**3d**) (1.53 g, 7.1 mmol) and $LiAlH_4$ (0.30 g, 7.9 mmol) were used to afford 0.62 g (50 %) of (4α,5β)-**6d**, 64 mg (5 %) of (4α,5α)-**7d** and 0.23 g (19 %) of (4β,5β)-**8d** as colorless solids after chromatography with diethyl ether/petroleum ether (1: 3) on silica gel (180 g).

(1S,4S,5S,7aS)-1-tert-Butoxy-4-pentyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**6d**): R_f = 0.32. M.p.: 73 °C. $[\alpha]^{20}_D$ = + 31.5° (c = 1.0, $CHCl_3$). IR (nujol): ν = 3350 - 3050 (OH), 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.8 Hz ; 3 H, CH_2-C<u>H</u>$_3$), 0.99 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.80 - 2.12 (m; 14 H, C-4-H, CH_2 and OH), 2.21 (dddd, ^2J = 15.6 Hz, ^3J = 8.2 and 4.4 Hz, ^5J = 1.8 Hz; 1 H, C-2-H), 2.41 (dddd, ^2J = 15.6 Hz, ^3J = 7.8 and 1.8 Hz, ^5J = 2.9 Hz; 1 H, C-2-H), 3.23 (ddd, ^3J = 10.4, 10.4 and 4.2 Hz; 1 H, C-5-H), 3.73 (dd, ^3J = 8.2 and 7.8 Hz; 1 H, C-1-H), 5.19 (dd, ^3J = 4.4 and 1.8 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.16 (C-5'), 16.77 (C-7a-CH_3), 28.72 [OC(<u>C</u>H$_3$)$_3$], 22.68, 26.75, 27.49, 32.12, 32.64, 37.05 and 39.44 (C-1', C-2, C-2', C-3', C-4', C-6 and C-7), 44.89 (C-4), 47.13 (C-7a), 72.54 [O<u>C</u>(CH$_3$)$_3$], 74.27 (C-5), 81.97 (C-1), 117.77 (C-3), 149.11 (C-3a). MS (70 eV): *(m/z)* (%) = 294 (2) [M^+], 238 (5) [M^+ - C_4H_8], 220 (45) [M^+ - C_4H_8 - H_2O], 57 (100) [$C_4H_9^+$], 41 (56) [$C_3H_5^+$]. $C_{19}H_{34}O_2$ (294.5): calcd. C

77.50, H 11.64; found C 77.57, H 11.75.

(1S,4S,5R,7aS)-1-tert-Butoxy-4-pentyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**7d**): R_f = 0.39. $[\alpha]^{20}_D$ = - 8.5° (c = 1.0, $CHCl_3$). IR (film): ν = 3550 - 3150 (OH), 1635 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.6 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.97 (s; 3 H, C-7a-CH_3), 1.17 [s; 9 H, OC(CH_3)$_3$], 0.81 - 2.51 (m; 16 H, C-4-H, CH_2 and OH), 3.83 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 3.95 (ddd, ^3J = 2.4 Hz; 1 H, C-5-H), 5.29 (dd, ^3J = 4.2 and 1.6 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.10 (C-5'), 16.56 (C-7a-CH_3), 28.76 [OC(<u>C</u>H$_3$)$_3$], 22.68, 26.73, 27.86, 29.69, 32.21, 33.48 and 38.81 (C-1', C-2, C-2', C-3', C-4', C-6 and C-7), 41.38 (C-4), 46.93 (C-7a), 68.49 (C-5), 72.60 [O<u>C</u>(CH$_3$)$_3$], 82.41 (C-1), 119.73 (C-3), 147.95 (C-3a). MS (70 eV): *(m/z)* (%) = 294 (12) [M^+], 238 (25) [M^+ - C_4H_8], 220 (60) [M^+ - C_4H_8 - H_2O], 57 (80) [$C_4H_9^+$], 43 (100) [$C_3H_7^+$], 41 (71) [$C_3H_5^+$]. $C_{19}H_{34}O_2$ (294.5): calcd. C 77.50, H 11.64; found C 77.62, H 11.69.

(1S,4R,5S,7aS)-1-tert-Butoxy-4-pentyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**8d**): R_f = 0.25. M.p.: 101 °C. $[\alpha]^{20}_D$ = - 47.1° (c = 1.0, $CHCl_3$). IR (nujol): ν = 3350 - 3050 (OH), 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.4 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.01 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.81 - 1.92 (m; 13 H, CH_2 and OH), 2.10 - 2.35 (m; 2 H, C-2-H_2), 2.40 - 2.52 (m; 1 H, C-4-H), 3.69 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 3.68 - 3.82 (m; 1 H, C-5-H), 5.25 (dd, ^3J = 2.6 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.10 (C-5'), 17.90 (C-7a-CH_3), 28.74 [OC(<u>C</u>H$_3$)$_3$], 22.60, 25.66, 27.27, 27.30, 31.91, 37.64 and 38.35 (C-1', C-2, C-2', C-3', C-4', C-6 and C-7), 45.47 (C-4), 45.56 (C-7a), 72.57 [O<u>C</u>(CH$_3$)$_3$], 73.55 (C-5), 82.85 (C-1), 122.40 (C-3), 148.51 (C-3a). MS (70 eV): *(m/z)* (%) = 294 (3) [M^+], 238 (5) [M^+ - C_4H_8], 220 (40) [M^+ - C_4H_8 - H_2O], 57 (100) [$C_4H_9^+$], 41 (65) [$C_3H_5^+$]. $C_{19}H_{34}O_2$ (294.5): calcd. C 77.50, H 11.64; found C 77.80, H 11.92.

***1-tert-Butoxy-4-hexyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol*s** (**6e**, **7e** and **8e**): According to the general procedure potassium hydride (0.22 g, 5.5 mmol), the α,β-unsaturated ketone **1** (0.74 g, 3.3 mmol), a zinc chloride solution (1.0 *N* in diethyl ether, 6.5 ml, 6.5 mmol), α-chlorohexyl phenyl sulfide (**3e**) (1.29 g, 5.6 mmol) and $LiAlH_4$ (0.30 g, 8.0 mmol) were used to afford 0.54 g (53 %) of (4α,5β)-**6e**, 52 mg (5 %) of (4α,5α)-**7e** and 0.17 g (17 %) of (4β,5β)-**8e** as colorless solids after chromatography with diethyl ether/petroleum ether (1: 4) on silica gel (70 g).

(1S,4S,5S,7aS)-1-tert-Butoxy-4-hexyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**6e**): R_f = 0.30. M.p.: 77 - 79 °C. $[\alpha]^{20}_D$ = + 30.2° (c = 1.0, $CHCl_3$). IR (nujol): ν = 3350 - 3050 (OH), 3040 (C=CH), 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.8 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.95 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.80 - 2.62 (m; 18 H, CH, CH_2 and OH), 3.23 (ddd, ^3J = 10.3, 10.3 und 4.4 Hz; 1 H, C-5-H), 3.73 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 5.19 (dd, ^3J = 4.6 and 2.2 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.11 (C-6'), 16.77 (C-7a-CH_3), 28.72 [OC(<u>C</u>H$_3$)$_3$], 22.72, 27.03, 27.54, 30.07, 31.88, 32.11, 37.05 and 39.45 (C-1', C-2, C-2', C-3', C-4', C-5', C-6 and C-7), 44.89 (C-4), 47.13 (C-7a), 72.54 [O<u>C</u>(CH$_3$)$_3$], 74.27 (C-5), 81.97 (C-1), 117.77 (C-3), 149.12 (C-3a). MS (70 eV): *(m/z)* (%) = 308 (5) [M^+], 250 (25) [M^+ - C_4H_{10}]), 234 (90) [M^+ - C_4H_8 - H_2O], 206 (100) [M^+ -C_4H_8 - C_2H_4 - H_2O], 57 (98) [$C_4H_9^+$].

$C_{20}H_{36}O_2$ (308.5): calcd. C 77.87, H 11.76; found C 77.93, H 11.63.

(1S,4S,5R,7aS)-1-tert-Butoxy-4-hexyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**7e**): R_f = 0.37. $[\alpha]^{20}_D$ = - 8.0° (c = 1.0, $CHCl_3$). IR (film): ν = 3500 - 3200 (OH), 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.5 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.97 (s; 3 H, C-7a-CH_3), 1.17 [s; 9 H, OC(CH_3)$_3$], 0.80 - 2.49 (m; 18 H, C-4-H, CH_2 and OH), 3.83 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 3.95 (ddd, ^3J = 2.6 Hz; 1 H, C-5-H), 5.30 (dd, ^3J = 4.2 and 1.4 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.12 (C-6'), 16.57 (C-7a-CH_3), 28.76 [OC(<u>C</u>H$_3$)$_3$], 22.68, 27.03, 27.92, 29.68, 29.29, 31.89, 33.47 and 38.81 (C-1', C-2, C-2', C-3', C-4', C-5', C-6 and C-7), 41.39 (C-4), 46.93 (C-7a), 68.48 (C-5), 72.54 [O<u>C</u>(CH_3)$_3$], 82.41 (C-1), 119.69 (C-3), 147.98 (C-3a). MS (70 eV): *(m/z)* (%) = 308 (10) [M^+], 234 (15) [M^+ - C_4H_8 - H_2O], 166 (100) [M^+ - C_6H_{13} - C_4H_9], 57 (60) [$C_4H_9^+$]. $C_{20}H_{36}O_2$ (308.5): calcd. C 77.87, H 11.76; found C 77.98, H 11.67.

(1S,4R,5S,7aS)-1-tert-Butoxy-4-hexyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene-5-ol (**8e**): R_f = 0.24. M.p.: 98 °C. $[\alpha]^{20}_D$ = - 52.1° (c = 1.0, $CHCl_3$). IR (nujol): ν = 3350 - 3050 (OH), 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.4 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.02 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.80 - 1.94 (m; 15 H, CH_2 and OH), 2.15 - 2.37 (m; 2 H, C-2-H_2), 2.40 - 2.58 (m; 1 H, C-4-H), 3.69 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 3.68 - 3.81 (m; 1 H, C-5-H), 5.25 (dd, ^3J = 2.8 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.10 (C-6'), 17.92 (C-7a-CH_3), 28.76 [OC(<u>C</u>H$_3$)$_3$], 22.66, 25.73, 27.29, 27.61, 29.77, 31.83, 37.67 and 38.37 (C-1', C-2, C-2', C-3', C-4', C-5', C-6 and C-7), 45.49 (C-4), 45.59 (C-7a), 72.57 [O<u>C</u>(CH_3)$_3$], 73.56 (C-5), 82.86 (C-1), 122.39 (C-3), 148.56 (C-3a). MS (70 eV): *(m/z)* (%) = 308 (8) [M^+], 234 (10) [M^+ - C_4H_8 - H_2O], 206 (100) [M^+ - C_4H_8 - C_2H_4 - H_2O), 57 (38) [$C_4H_9^+$]. $C_{20}H_{36}O_2$ (308.5): calcd. C 77.87, H 11.76; found C 77.92, H 11.78.

Mesylation of homoallylic alcohols* 6 *and* 8. - *General Procedure: To a solution of homoallylic alcohol **6** or **8** (0.5 mmol) in dichloromethane (5 ml) methanesulfonyl chloride (0.05 ml, 0.58 mmol) and triethylamine (0.09 ml, 0.64 mmol) were added at 0 °C via syringe under stirring and stirring was continued for 1 h at 0 °C and for an additional 1 at r.t.. The solvent was removed *in vacuo* (25 °C / 18 Torr) and diethyl ether (50 ml) and 1 *N* HCl (20 ml) were added under stirring. The organic layer was extracted with H_2O, a saturated aqueous $NaHCO_3$ solution and again with H_2O (20 ml each), dried with $MgSO_4$ and the solvent was removed *in vacuo* (20 °C / 18 Torr). The residue - the crude mesylate **9** or **11** - was used directly for the deoxygenation without any further purification.

(1S,4S,5S,7aS) 1-tert-Butoxy-4-ethyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydro-indene (**9a**): According to the general procedure alcohol (4α,5β)-**6a** (0.16 g, 0.63 mmol), methanesulfonyl chloride (85 mg, 0.06 ml, 0.74 mmol) and triethylamine (75 mg, 0.10 ml, 0.74 mmol) were used to afford 0.21 g (98 %) of mesylate **9a** as a colorless liquid. R_f = 0.39 (diethyl ether/petroleum ether, 1: 2). IR (film): ν = 1640 (C=C), 1360 and 1160 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.5 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.00 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.84 - 2.52 (m; 9 H, C-4-H and CH_2), 3.03 (s; 3 H, OSO_2CH_3), 3.73 (t, ^3J = 7.5 Hz; 1 H, C-1-H), 4.36 (dt, ^3J = 10.0 and 4.0

Hz; 1 H, C-5-H), 5.26 - 5.36 [br. s; 1 H, C-3-H]. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 10.94 (C-2'), 16.60 (C-7a-CH_3), 28.67 [OC($\underline{C}H_3)_3$], 20.00, 29.55, 36.43 and 38.92 (C-1', C-2, C-6 and C-7), 39.40 and 43.24 (OSO_2CH_3 and C-4), 46.84 (C-7a), 72.66 [O$\underline{C}$($CH_3)_3$], 81.52 (C-1), 84.54 (C-5), 120.04 (C-3), 146.40 (C-3a). MS (70 eV): *(m/z)* (%) = 330 (8) [M^+], 178 (80) [M^+ - CH_3SO_3 - C_4H_9], 79 (20) [$CH_3SO_2^+$], 57 (100) [$C_4H_9^+$]. $C_{17}H_{30}O_4S$ (330.5): calcd. (330.1865); found (330.1865) (MS).

(1S,4S,5S,7aS) 1-tert-Butoxy-4-propyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydroindene (**9b**): According to the general procedure alcohol (4α,5β)-**6b** (0.13 g, 0.50 mmol), methanesulfonyl chloride (68 mg, 0.05 ml, 0.59 mmol) and triethylamine (75 mg, 0.10 ml, 0.74 mmol) were used to afford 0.17 g (98 %) of mesylate **9b** as a colorless liquid. R_f = 0.45 (diethyl ether/petroleum ether, 1: 2). IR (film): ν = 1630 (C=C), 1350 and 1160 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.0 Hz; 3 H, CH_2-C$\underline{H}_3$), 1.00 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC($CH_3)_3$], 1.05 - 2.50 (m; 11 H, C-4-H and CH_2), 3.03 (s; 3 H, OSO_2CH_3), 3.74 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 4.29 (ddd, ^3J = 10.8, 10.6 and 4.8 Hz; 1 H, C-5-H), 5.29 (dd, ^3J = 2.8 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.47 (C-3'), 16.60 (C-7a-CH_3), 28.67 [OC($\underline{C}H_3)_3$], 19.96, 29.70, 31.55, 36.52 and 39.42 (C-1', C-2, C-2', C-6 and C-7), 38.30 and 41.95 (OSO_2CH_3 and C-4), 46.93 (C-7a), 72.74 [O$\underline{C}$($CH_3)_3$], 81.50 (C-1), 85.23 (C-5), 120.03 (C-3), 146.95 (C-3a). MS (70 eV): *(m/z)* (%) = 344 (3) [M^+], 288 (5) [M^+ - C_4H_8], 249 (3) [M^+ - CH_3SO_3], 192 (70) [M^+ - CH_3SO_3 - C_4H_9], 79 (34) [$CH_3SO_2^+$], 57 (100) [$C_4H_9^+$], 41 (48) [$C_3H_5^+$]. $C_{18}H_{32}O_4S$ (344.5): calcd. (344.2021); found (344.2021) (MS).

(1S,4S,5S,7aS) 1-tert-Butoxy-4-butyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydroindene (**9c**): According to the general procedure alcohol (4α,5β)-**6c** (0.17 g, 0.60 mmol), methanesulfonyl chloride (79 mg, 0.05 ml, 0.69 mmol) and triethylamine (70 mg, 0.10 ml, 0.69 mmol) were used to afford 0.21 g (98 %) of mesylate **9c** as a colorless liquid. R_f = 0.31 (diethyl ether/petroleum ether, 1: 4). IR (film): ν = 1630 (C=C), 1350 and 1160 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.7 Hz; 3 H, CH_2-C$\underline{H}_3$), 1.00 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC($CH_3)_3$], 1.10 - 2.53 (m; 13 H, CH and CH_2), 3.02 (s; 3 H, OSO_2CH_3), 3.74 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 4.29 (ddd, ^3J = 10.8, 10.4 and 4.8 Hz; 1 H, C-5-H), 5.29 (d, ^3J = 2.4 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.12 (C-4'), 16.59 (C-7a-CH_3), 28.66 [OC($\underline{C}H_3)_3$], 23.08, 27.07, 28.86, 29.66, 36.49 and 39.40 (C-1', C-2, C-2', C-3', C-6 and C-7), 38.91 and 42.07 (OSO_2CH_3 and C-4), 46.92 (C-7a), 72.71 [O$\underline{C}$($CH_3)_3$], 81.49 (C-1), 85.13 (C-5), 120.01 (C-3), 146.96 (C-3a). MS (70 eV): *(m/z)* (%) = 358 (10) [M^+], 302 (30) [M^+ - C_4H_8], 262 (20) [M^+ - CH_3SO_3H], 206 (60) [M^+ - CH_3SO_3 - C_4H_9], 57 (100) [$C_4H_9^+$]. $C_{19}H_{34}O_4S$ (358.5): calcd. (358.2178); found (358.2178) (MS).

(1S,4S,5S,7aS) 1-tert-Butoxy-4-pentyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydroindene (**9d**): According to the general procedure alcohol (4α,5β)-**6d** (0.15 g, 0.50 mmol), methanesulfonyl chloride (79 mg, 0.05 ml, 0.69 mmol) and triethylamine (75 mg, 0.10 ml, 0.74 mmol) were used to afford 0.18 g (97 %) of mesylate **9d** as a colorless liquid. R_f = 0.39 (diethyl ether/petroleum ether, 1: 3). IR (film): ν = 3040 (C=CH), 1350 and 1170 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ =

0.89 (t, ^3J = 6.4 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.00 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.80 - 2.53 (m; 15 H, C-4-H and CH_2), 3.02 (s; 3 H, OSO_2CH_3), 3.74 (t, ^3J = 7.8 Hz; 1 H, C-1-H), 4.28 (ddd, ^3J = 10.6, 10.6 and 4.5 Hz; 1 H, C-5-H), 5.29 (d, ^3J = 2.8 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.13 (C-5'), 16.61 (C-7a-CH_3), 28.67 [OC(<u>C</u>H$_3$)$_3$], 22.58, 26.42, 27.40, 29.68, 32.32, 36.51 and 39.42 (C-1', C-2, C-2', C-3', C-4', C-6 and C-7), 38.92 and 42.13 (OSO_2CH_3 and C-4), 46.92 (C-7a), 72.72 [O<u>C</u>(CH_3)$_3$], 81.49 (C-1), 85.15 (C-5), 120.01 (C-3), 146.98 (C-3a). MS (70 eV): *(m/z)* (%) = 372 (3) [M^+], 276 (35) [M^+ - CH_3SO_3H], 220 (50) [M^+ - CH_3SO_3 - C_4H_9], 191 (90) [M^+ - CH_3SO_3 - C_4H_9 - C_2H_5], 79 (30) [$CH_3SO_2^+$], 57 (100) [$C_4H_9^+$], 41 (40) [$C_3H_5^+$].

(1S,4S,5S,7aS) 1-tert-Butoxy-4-hexyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydroindene (**9e**): According to the general procedure alcohol (4α,5β)-**6e** (0.22 g, 0.70 mmol), methanesulfonyl chloride (115 mg, 0.08 ml, 1.00 mmol) and triethylamine (100 mg, 0.14 ml, 1.00 mmol) were used to afford 0.27 g (98 %) of mesylate **9e** as a colorless liquid. R_f = 0.31 (diethyl ether/petroleum ether, 1: 4). IR (film): ν = 3040 (C=CH), 1635 (C=C), 1350 and 1165 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.4 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.00 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 1.01 - 2.52 (m; 17 H, CH and CH_2), 3.02 (s; 3 H, OSO_2CH_3), 3.74 (t, ^3J = 7.8 Hz; 1 H, C-1-H), 4.29 (ddd, ^3J = 10.8, 10.4 and 4.6 Hz; 1 H, C-5-H), 5.29 (d, ^3J = 2.4 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.09 (C-6'), 16.60 (C-7a-CH_3), 28.67 [OC(<u>C</u>H$_3$)$_3$], 22.67, 26.71, 27.46, 29.70, 29.78, 31.76, 36.52 and 39.43 (C-1', C-2, C-2', C-3', C-4', C-5', C-6 and C-7), 38.92 and 42.14 (OSO_2CH_3 and C-4), 46.93 (C-7a), 72.72 [O<u>C</u>(CH_3)$_3$], 81.50 (C-1), 85.19 (C-5), 120.03 (C-3), 146.98 (C-3a). MS (70 eV): *(m/z)* (%) = 386 (2) [M^+], 330 (4) [M^+ - C_4H_8], 234 (100) [M^+ - CH_3SO_3 - C_4H_9], 57 (60) [$C_4H_9^+$], 41 (15) [$C_3H_5^+$]. $C_{21}H_{38}O_4S$ (386.6): calcd. (386.2490); found (386.2490) (MS).

(1S,4R,5S,7aS) 1-tert-Butoxy-4-ethyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydroindene (**11a**): According to the general procedure alcohol (4β,5β)-**8a** (0.11 g, 0.44 mmol), methanesulfonyl chloride (85 mg, 0.06 ml, 0.74 mmol) and triethylamine (75 mg, 0.10 ml, 0.74 mmol) were used to afford 0.14 g (98 %) of mesylate **11a** as a colorless liquid. R_f = 0.40 (diethyl ether/petroleum ether, 1: 2). IR (film): ν = 1635 (C=C), 1350 and 1170 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 7.4 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.04 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 1.02 - 2.41 (m; 8 H, CH_2), 2.64 (dt, J = 12.0 Hz, J = 6.0 Hz; 1 H, C-4-H), 3.01 (s; 3 H, OSO_2CH_3), 3.71 (t, ^3J = 8.1 Hz; 1 H, C-1-H), 4.74 (ddd, J = 12.0 Hz, J = 5.1 and 3.9 Hz; 1 H, C-5-H), 5.34 (t, J = 2.2 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.87 (C-2'), 17.70 (C-7a-CH_3), 28.68 [OC(<u>C</u>H$_3$)$_3$], 19.35, 24.98, 37.20 and 38.30 (C-1', C-2, C-6 and C-7), 38.51 and 45.88 (OSO_2CH_3 and C-4), 45.34 (C-7a), 72.65 [O<u>C</u>(CH_3)$_3$], 82.49 and 83.83 (C-1 and C-5), 124.52 (C-3), 145.72 (C-3a). MS (70 eV): *(m/z)* (%) = 330 (8) [M^+], 274 (10) [M^+ - C_4H_8], 178 (95) [M^+ - CH_3SO_3 - C_4H_9], 149 (100) [M^+ - CH_3SO_3 - C_4H_9 - C_2H_5], 57 (90) [$C_4H_9^+$]. $C_{17}H_{30}O_4S$ (358.5): calcd. (358.2178); found (358.2178) (MS).

(1S,4R,5S,7aS) 1-tert-Butoxy-4-butyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydroindene (**11b**): According to the general procedure alcohol (4β,5β)-**8c** (0.16 g, 0.57 mmol), methanesul-

fonyl chloride (79 mg, 0.05 ml, 0.69 mmol) and triethylamine (67 mg, 0.09 ml, 0.66 mmol) were used to afford 0.20 g (99 %) of mesylate **11b** as a colorless liquid. R_f = 0.27 (diethyl ether/petroleum ether, 1: 4). IR (film): ν = 1635 (C=C), 1350 and 1160 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.7 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.04 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 1.02 - 2.42 (m; 12 H, CH_2), 2.51 - 2.65 (m; 1 H, C-4-H), 3.01 (s; 3 H, OSO_2CH_3), 3.70 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 4.65 - 4.79 (m; 1 H, C-5-H), 5.32 (dd, ^3J = 2.6 and 2.4 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.03 (C-4'), 17.85 (C-7a-CH_3), 28.71 [OC(<u>C</u>H$_3$)$_3$], 22.52, 25.00, 26.10, 29.66, 37.33 and 38.40 (C-1', C-2, C-2', C-3', C-6 and C-7), 38.55 and 44.10 (OSO_2CH_3 and C-4), 45.39 (C-7a), 72.65 [O<u>C</u>(CH$_3$)$_3$], 82.55 and 83.80 (C-1 and C-5), 124.30 (C-3), 146.32 (C-3a). MS (70 eV): *(m/z)* (%) = 358 (3) [M^+], 302 (6) [M^+ - C_4H_8], 262 (5) [M^+ - CH_3SO_3H], 206 (100) [M^+ - CH_3SO_3 - C_4H_9], 57 (95) [$C_4H_9^+$]. $C_{19}H_{34}O_4S$ (358.5): calcd. (358.2178); found (358.2178) (MS).

(1S,4R,5S,7aS) 1-tert-Butoxy-4-hexyl-7a-methyl-5-methylsulfonyloxy-1,4,5,6,7,7a-2H-hexahydroindene (**11c**): According to the general procedure alcohol (4β,5β)-**8e** (0.15 g, 0.50 mmol), methanesulfonyl chloride (79 mg, 0.05 ml, 0.69 mmol) and triethylamine (67 mg, 0.09 ml, 0.66 mmol) were used to afford 0.19 g (98 %) of mesylate **11c** as a colorless liquid. R_f = 0.26 (diethyl ether/petroleum ether, 1: 4). IR (film): ν = 1640 (C=C), 1350 and 1165 cm^{-1} (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.7 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.03 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.80 - 2.44 (m; 16 H, CH_2), 2.65 - 2.81 (m; 1 H, C-4-H), 3.01 (s; 3 H, OSO_2CH_3), 3.70 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 4.65 - 4.79 (m; 1 H, C-5-H), 5.32 (dd, ^3J = 3.0 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.06 (C-6'), 17.85 (C-7a-CH_3), 28.69 [OC(<u>C</u>H$_3$)$_3$], 22.60, 24.97, 26.40, 27.24, 29.14, 31.74, 37.29 and 38.37 (C-1', C-2, C-2', C-3', C-4', C-5', C-6 and C-7), 38.52 and 44.11 (OSO_2CH_3 and C-4), 45.34 (C-7a), 72.66 [O<u>C</u>(CH$_3$)$_3$], 82.52 and 83.78 (C-1 and C-5), 124.28 (C-3), 146.26 (C-3a). MS (70 eV): *(m/z)* (%) = 386 (2) [M^+], 330 (2) [M^+ - C_4H_8], 290 (7) [M^+ - CH_3SO_3H], 234 (55) [M^+ - CH_3SO_3 - C_4H_9], 57 (100) [$C_4H_9^+$]. $C_{21}H_{38}O_4S$ (386.6): calcd. (386.2490); found (386.2490) (MS).

(1S,4S,7aS) 1-tert-Butoxy-4-alkyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindenes **10 and** ***(1S,7aS) 1-tert-Butoxy-4-alkyl-7a-methyl-1,6,7,7a-2H-tetrahydroindenes*** **12**. - *General Procedure:* To a solution of mesylate **9** or **11** (0.5 mmol) in dimethoxyethane (10 ml) sodium iodide (0.38 g, 2.5 mmol) and zinc dust (1.64 g, 25.0 mmol) were added at r.t. with stirring. The flask was completely covered with aluminium foil and stirring was continued for 3 h at 80 °C. The reaction mixture was filtered through celite (10 g) and the celite was rinsed three times with petroleum ether (25 ml each). The combined organic layers were extracted with H_2O and a saturated aqueous NaCl solution (15 ml each) and dried with $MgSO_4$. The solvent was removed *in vacuo* (20 °C/12 Torr) and the crude product **10** or **12** purified by chromatography on silica gel.

(1S,4R,7aS) 1-tert-Butoxy-4-ethyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene (**10a**): According to the general procedure mesylate **9a** (0.21 g, 0.63 mmol), sodium iodide (0.48 g, 3.2 mmol) and zinc dust (2.07 g, 31.7 mmol) were used to afford 0.19 g (92 %) of hexahydroindene **10a** as a colorless liquid

after chromatography with diethyl ether/petroleum ether (1: 100) on silica gel (35 g). R_f = 0.38. $[\alpha]^{20}_D$ = - 33.8° (c = 1.1, $CHCl_3$). IR (film): ν = 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.5 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.95 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.60 - 2.44 (m; 11 H, C-4-H and CH_2), 3.75 (dd, ^3J = 8.2 and 8.0 Hz; 1 H, C-1-H), 5.11 (dd, ^3J = 4.6 and 2.3 Hz; 1 H, C-3-H). **^{13}C** NMR (50.3 MHz, $CDCl_3$): δ = 11.61 (C-2'), 16.86 (C-7a-CH_3), 28.77 [OC(<u>C</u>H$_3$)$_3$], 38.04 (C-4), 22.45, 25.01, 32.20, 38.39 and 40.20 (C-1', C-2, C-5, C-6 and C-7), 47.20 (C-7a), 72.40 [O<u>C</u>(CH_3)$_3$], 82.72 (C-1), 114.74 (C-3), 152.14 (C-3a). MS (70 eV): *(m/z)* (%) = 236 (40) [M^+], 180 (45) [M^+ - C_4H_8], 151 (100) [M^+ - C_4H_8 - $C_2H_5^+$], 57 (42) [$C_4H_9^+$]. $C_{16}H_{28}O$ (236.4): calcd. C 81.29, H 11.94; found C 81.23, H 11.86.

(1S,4R,7aS) 1-tert-Butoxy-4-propyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene (**10b**): According to the general procedure mesylate **9b** (0.23 g, 0.67 mmol), sodium iodide (0.50 g, 3.3 mmol) and zinc dust (2.2 g, 33.4 mmol) were used to afford 0.15 g (89 %) of hexahydroindene **10b** as a colorless liquid after chromatography with diethyl ether/petroleum ether (1: 50) on silica gel (35 g). R_f = 0.53. $[\alpha]^{20}_D$ = - 0.4° (c = 1.0, $CHCl_3$). IR (film): ν = 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.0 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.93 (s; 3 H, C-7a-CH_3), 1.14 [s; 9 H, OC(CH_3)$_3$], 0.64 - 2.03 (m; 11 H, C-4-H and CH_2), 2.11 (dddd, ^2J = 15.3 Hz, ^3J = 8.4 and 4.0 Hz, ^5J = 3.0 Hz; 1 H, C-2-H), 2.33 (dddd, ^2J = 15.3 Hz, ^3J = 8.0 and 1.6 Hz, ^5J = 3.0 Hz; 1 H, C-2-H), 3.74 (dd, ^3J = 8.4 and 8.0 Hz; 1 H, C-1-H), 5.10 (dd, ^3J = 4.0 and 1.6 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.46 (C-3'), 16.88 (C-7a-CH_3), 28.77 [OC(<u>C</u>H$_3$)$_3$], 36.14 (C-4), 20.17, 22.49, 32.74, 34.65, 38.38 and 40.21 (C-1', C-2, C-2', C-5, C-6 and C-7), 47.21 (C-7a), 72.45 [O<u>C</u>(CH_3)$_3$], 82.73 (C-1), 114.71 (C-3), 152.39 (C-3a). MS (70 eV): *(m/z)* (%) = 250 (4) [M^+], 194 (21) [M^+ - C_4H_8], 151 (97) [M^+ - C_4H_8 - $C_3H_7^+$], 57 (100) [$C_4H_9^+$], 41 (95) [$C_3H_5^+$]. $C_{17}H_{30}O$ (250.4): calcd. C 81.54, H 12.08; found C 81.47, H 11.96.

(1S,4R,7aS) 1-tert-Butoxy-4-butyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene (**10c**): According to the general procedure mesylate **9c** (0.21 g, 0.55 mmol), sodium iodide (0.41 g, 2.7 mmol) and zinc dust (1.54 g, 27.4 mmol) were used to afford 0.13 g (85 %) of hexahydroindene **10c** as a colorless liquid after chromatography with diethyl ether/petroleum ether (1: 60) on silica gel (17 g). R_f = 0.38. $[\alpha]^{20}_D$ = - 8.9° (c = 1.0, $CHCl_3$). IR (film): ν = 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.6 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.94 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.70 - 2.43 (m; 15 H, C-4-H and CH_2), 3.75 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 5.12 (dd, ^3J = 4.2 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.17 (C-4'), 16.88 (C-7a-CH_3), 28.78 [OC(<u>C</u>H$_3$)$_3$], 36.41 (C-4), 22.52, 23.13, 29.35, 32.10, 32.83, 38.39 and 40.22 (C-1', C-2, C-2', C-3', C-5, C-6 and C-7), 47.23 (C-7a), 72.43 [O<u>C</u>(CH_3)$_3$], 82.74 (C-1), 114.74 (C-3), 152.40 (C-3a). MS (70 eV): *(m/z)* (%) = 264 (5) [M^+], 208 (15) [M^+ - C_4H_8], 151 (100 %) [M^+ - C_4H_8 - $C_4H_9^+$], 57 (65) [$C_4H_9^+$], 41 (97) [$C_3H_5^+$]. $C_{18}H_{32}O$ (264.5): calcd. C 81.75, H 12.20; found C 81.54, H 12.01.

(1S,4R,7aS) 1-tert-Butoxy-4-pentyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene (**10d**): According to the general procedure mesylate **9d** (0.16 g, 0.44 mmol), sodium iodide (0.34 g, 2.3 mmol) and zinc dust (1.48 g, 22.5 mmol) were used to afford 0.11 g (85 %) of hexahydroindene **10d** as a colorless liquid

after chromatography with diethyl ether/petroleum ether (1: 3) on silica gel (15 g). R_f = 0.83. $[\alpha]^{20}_D$ = - 16.6° (c = 1.1, $CHCl_3$). IR (film): ν = 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.8 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.95 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.62 - 2.43 (m; 17 H, C-4-H and CH_2), 3.75 (dd, ^3J = 8.2 and 8.0 Hz; 1 H, C-1-H), 5.11 (dd, ^3J = 4.6 and 2.2 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.15 (C-5'), 16.89 (C-7a-CH_3), 28.79 [OC(<u>C</u>H$_3$)$_3$], 36.45 (C-4), 22.53, 22.74, 26.81, 28.89, 32.38, 32.82, 38.41 and 40.23 (C-1', C-2, C-2', C-3', C-4', C-5, C-6 and C-7), 47.23 (C-7a), 72.42 [O<u>C</u>(CH$_3$)$_3$], 82.75 (C-1), 114.75 (C-3), 152.39 (C-3a). MS (70 eV): *(m/z)* (%) = 278 (20) [M^+], 222 (40) [M^+ - C_4H_8], 151 (100) [M^+ - C_4H_8 - C_5H_{11}+], 57 (21) [$C_4H_9^+$]. $C_{19}H_{34}O$ (278.5): calcd. C 81.95, H 12.31; found C 81.84, H 12.30.

(1S,4R,7aS) 1-tert-Butoxy-4-hexyl-7a-methyl-1,4,5,6,7,7a-2H-hexahydroindene (**10e**): According to the general procedure mesylate **9e** (0.26 g, 0.68 mmol), sodium iodide (0.49 g, 3.3 mmol) and zinc dust (2.13 g, 32.6 mmol) were used to afford 0.17 g (87 %) of hexahydroindene **10e** as a colorless liquid after chromatography with diethyl ether/petroleum ether (1: 100) on silica gel (40 g). R_f = 0.27. $[\alpha]^{20}_D$ = - 24.3° (c = 1.0, $CHCl_3$). IR (film): ν = 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.4 Hz; 3 H, CH_2-C<u>H</u>$_3$), 0.96 (s; 3 H, C-7a-CH_3), 1.16 [s; 9 H, OC(CH_3)$_3$], 0.65 - 2.43 (m; 19 H, C-4-H and CH_2), 3.75 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 5.11 (dd, ^3J = 4.4 and 2.0 Hz; 1 H, C-3-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.13 (C-6'), 16.89 (C-7a-CH_3), 28.78 [OC(<u>C</u>H$_3$)$_3$], 36.44 (C-4), 22.52, 22.71, 27.08, 28.89, 31.95, 32.43, 32.83, 38.40 and 40.23 (C-1', C-2, C-2', C-3', C-4', C-5, C-5', C-6 and C-7), 47.23 (C-7a), 72.40 [O<u>C</u>(CH$_3$)$_3$], 82.73 (C-1), 114.71 (C-3), 152.36 (C-3a). MS (70 eV): *(m/z)* (%) = 292 (20) [M^+], 236 (45) [M^+ - C_4H_8], 151 (100 %, M^+ - C_4H_8 - $C_6H_{13}^+$], 57 (60) [$C_4H_9^+$]. $C_{20}H_{36}O$ (292.5): calcd. C 82.13, H 12.41; found C 81.89, H 12.23.

(1S,7aS) 1-tert-Butoxy-4-ethyl-7a-methyl-1,6,7,7a-2H-tetrahydroindene (**12a**): According to the general procedure mesylate **11a** (0.15 g, 0.43 mmol), sodium iodide (0.32 g, 2.2 mmol) and zinc dust (1.41 g, 21.5 mmol) were used to afford 84 mg (83 %) of tetrahydroindene **12a** as a colorless liquid after chromatography with diethyl ether/petroleum ether (1: 2) on silica gel (35 g). R_f = 0.78. $[\alpha]^{20}_D$ = - 47.8° (c = 0.2, $CHCl_3$). IR (film): ν = 1630 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (s; 3 H, C-7a-CH_3), 1.04 (t, ^3J = 7.5 Hz; 3 H, CH_2-C<u>H</u>$_3$), 1.17 [s; 9 H, OC(CH_3)$_3$], 0.70 - 2.48 (m; 6 H, CH_2), 2.15 (q, ^3J = 7.5 Hz; 2 H, C<u>H</u>$_2$-CH_3), 3.76 (t, ^3J = 8.0 Hz; 1 H, C-1-H), 5.38 (br. s; 1 H, C-3-H), 5.42 - 5.56 (m; 1 H, C-5-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.06 (C-2'), 15.45 (C-7a-CH_3), 28.76 [OC(<u>C</u>H$_3$)$_3$], 23.52, 24.99, 34.10 and 38.09 (C-1', C-2, C-6 and C-7), 45.09 (C-7a), 72.47 [O<u>C</u>(CH$_3$)$_3$], 81.53 (C-1), 116.60 (C-3), 123.36 (C-5), 134.99 (C-4), 146.11 (C-3a). MS (70 eV): *(m/z)* (%) = 234 (30) [M^+], 178 (50) [M^+ - C_4H_8], 149 (90) [M^+ - C_4H_8 - $C_2H_5^+$], 57 (100) [$C_4H_9^+$]. $C_{16}H_{26}O$ (234.4): calcd. C 81.99, H 11.18; found C 82.05, H 11.25.

(1S,7aS) 1-tert-Butoxy-4-butyl-7a-methyl-1,6,7,7a-2H-tetrahydroindene (**12b**): According to the general procedure mesylate **11b** (0.19 g, 0.52 mmol), sodium iodide (0.39 g, 2.6 mmol) and zinc dust (1.70 g, 26.0 mmol) were used to afford 0.11 g (77 %) of tetrahydroindene **12b** as a colorless liquid after chromatography with diethyl ether/petroleum ether (1: 4) on silica gel (17 g). R_f = 0.75. $[\alpha]^{20}_D$ = -

65.9° (c = 1.0, $CHCl_3$). IR (film): ν = 1630 cm^{-1} (C=C). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (s; 3 H, C-7a-CH_3), 0.90 (t, ^3J = 7.0 Hz; 3 H, CH_2-C$\underline{H}_3$), 1.18 [s; 9 H, OC$(CH_3)_3$], 0.65 - 2.40 (m; 12 H, CH_2), 3.76 (dd, ^3J = 8.0 and 7.8 Hz; 1 H, C-1-H), 5.38 (t, ^3J = 2.3 Hz; 1 H, C-3-H), 5.45 - 5.52 (m; 1 H, C-5-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.03 (C-4'), 15.45 (C-7a-CH_3), 28.76 [OC($\underline{C}H_3)_3$], 22.65, 23.54, 30.98, 32.14, 34.09 and 38.08 (C-1', C-2, C-2', C-3', C-6 and C-7), 45.11 (C-7a), 72.46 [O$\underline{C}(CH_3)_3$], 81.51 (C-1), 116.67 (C-3), 124.46 (C-5), 133.63 (C-4), 146.12 (C-3a). MS (70 eV): *(m/z)* (%) = 262 (15) [M^+], 205 (20) [M^+ - $C_4H_9^+$], 57 (100) [$C_4H_9^+$], 41 (60) [$C_3H_5^+$]. $C_{18}H_{30}O$ (262.4): calcd. C 82.38, H 11.52; found C 82.29, H 11.46.

(1S,7aS) 1-tert-Butoxy-4-hexyl-7a-methyl-1,6,7,7a-2H-tetrahydroindene (**12c**): According to the general procedure mesylate **11c** (0.18 g, 0.45 mmol), sodium iodide (0.34 g, 2.3 mmol) and zinc dust (1.48 g, 22.6 mmol) were used to afford 0.11 g (81 %) of tetrahydroindene **12c** as a colorless liquid after chromatography with diethyl ether/petroleum ether (1: 4) on silica gel (16 g). R_f = 0.72. $[\alpha]^{20}_D$ = - 56.3° (c = 0.5, $CHCl_3$). IR (film): ν = 1640 cm^{-1} (C=C). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.4 Hz; 3 H, CH_2-C$\underline{H}_3$), 0.89 (s; 3 H, C-7a-CH_3), 1.18 [s; 9 H, OC$(CH_3)_3$], 0.62 - 2.41 (m; 16 H, CH_2), 3.76 (dd, ^3J = 8.6 and 7.8 Hz; 1 H, C-1-H), 5.37 (t, ^3J = 2.4 Hz; 1 H, C-3-H), 5.45 - 5.53 (m; 1 H, C-5-H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.12 (C-6'), 15.49 (C-7a-CH_3), 28.79 [OC($\underline{C}H_3)_3$], 22.65, 23.57, 29.27, 29.74, 31.80, 32.48, 34.14 and 38.13 (C-1', C-2, C-2', C-3', C-4', C-5', C-6 and C-7), 45.17 (C-7a), 72.48 [O$\underline{C}(CH_3)_3$], 81.55 (C-1), 116.70 (C-3), 124.48 (C-5), 133.74 (C-4), 146.18 (C-3a). MS (70 eV): *(m/z)* (%) = 290 (45) [M^+], 233 (65) [M^+ - $C_4H_9^+$], 205 (100) [M^+ - $C_6H_{13}^+$], 57 (60) [$C_4H_9^+$]. $C_{20}H_{34}O$ (290.5): calcd. C 82.69, H 11.80; found C 82.61, H 11.72.

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