25. Stereoselective Synthesis of 2,4,6-Trimethylcyclohex-4-ene-1,3-diol Derivatives and of Polypropionate Fragments with Four Contiguous Stereogenic Centers[1])

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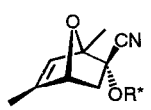
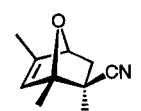
The *Diels-Alder* adduct (±)-**3** of 2,4-dimethylfuran and 1-cyanovinyl acetate was converted stereoselectively into benzyl 6-(4-chlorophenylsulfonyl)-1,3-*exo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl (**26**) and -2-*endo*-yl ether (**36**). Addition of $LiAlH_4$ to the latter led to the 3-*O*-benzyl derivatives **28** and **37** of (1*RS*,2*SR*,3*SR*,6*SR*)- and (1*RS*,2*SR*,3*RS*,6*SR*)-5-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diol, respectively. Methylenation of 6-*exo*-(4-chlorophenylthio)-1-methyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-one (**16**), obtained by reaction of (±)-**3** with 4-Cl-C_6H_4SCl and saponification gave, 6-*exo*-(4-chlorophenylthio)-1-methyl-3,5-dimethylidene-7-oxabicyclo[2.2.1]heptan-2-one (**43**), the reduction of which with *K-Selectride* afforded 6-*exo*-(4-chlorophenylthio)-1,3-*endo*-dimethyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (**44**). The 3-*O*-benzyl derivative **48** of (1*RS*,2*RS*,3*RS*,6*SR*)-5-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diol was derived from **44** *via* based-induced oxa-ring opening of benzyl 6-*endo*-(4-chlorophenylsulfonyl)-1,3-*endo*,5-*endo*-trimethyl-7-oxabicyclo[2.2.1]hept-2-*endo*-yl ether (**49**). Benzylation of **28**, followed by reductive desulfonylation and oxidative cleavage of the cyclohexene moiety afforded (2*RS*,3*SR*,4*RS*,5*RS*)-3,5-bis(benzyloxy)-2,4-dimethyl-6-oxoheptanal (**32**).

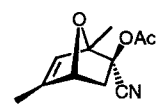
Introduction. – In the preceding paper [2], we demonstrated that the optically pure *Diels-Alder* adducts (+)-**1** and (−)-**2** (naked sugars of the second generation) [3] of 2,4-dimethylfuran [4] to 1-cyanovinyl (1*R*)-camphanate and (1*S*)-camphanate, respectively, can be converted with high stereoselectivity into polypropionate fragments with four or five contiguous stereogenic centers. Cross-aldolisations with 7-oxabicyclo[2.2.1]heptan-2-ones allowed one to generate long-chain polypropionate fragments containing up to eleven contiguous stereogenic centers and tertiary-alcohol moieties. The method relies on the high *exo*-face selectivity of the reactions of endocyclic π functions of the 7-oxabicyclo[2.2.1]heptene systems [5] and on the high regioselectivity of the *Baeyer-*



(+)-**1**



(−)-**2**



(±)-**3**

R* = (1*R*)-camphanoyl R′ = (1*S*)-camphanoyl

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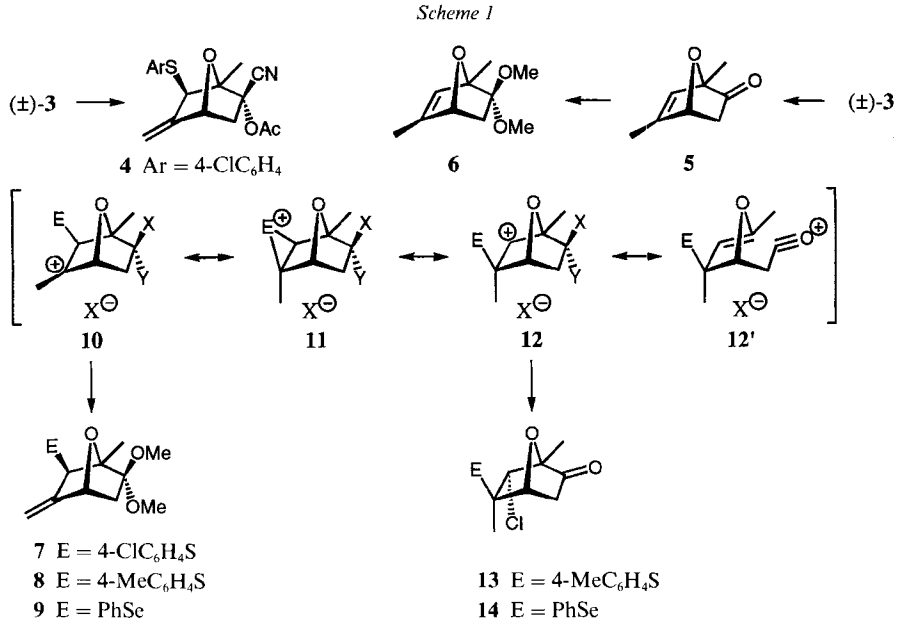
Villiger oxidation of 7-oxabicyclo[2.2.1]heptan-2-ones into the corresponding 2,8-dioxabicyclo[3.2.1]octan-3-ones [6]. In this report, we disclose further exploratory studies on the chemistry of the naked sugars of the second generation [2] [3]. Inspired by the work of *Plumet* and coworkers [7] on the sulfone-directed alkylative oxa-ring opening of 7-oxabicyclo[2.2.1]heptenes with organolithium reagents, we have developed a method based on the S_N2' hydride displacement of 2-(4-chlorophenylsulfonyl)-3-methyl-7-oxabicyclo[2.2.1]hept-2-enes to convert the racemic *Diels-Alder* adduct (±)-**3** of 2,4-dimethylfuran and 1-cyanovinyl acetate into a variety of 4,6-dihydroxy-1,3,5-trimethylcyclohexene derivatives with high stereoselectivity. These compounds can be transformed by C=C bond oxidative cleavage into 6-oxoheptanals that are polypropionate fragments containing four contiguous stereogenic centres.

Results and Discussion. – In the presence of 1 equiv. of 4-chlorobenzenesulfenyl chloride in tetrahydrofuran (THF), followed by workup with aqueous $NaHCO_3$ solution, the *Diels-Alder* adduct (±)-**3** gave the allylic sulfide **4** nearly quantitatively (*Scheme 1*). Analogous reaction of trisubstituted alkenes with sulfenyl halides were already described [8]. The dimethyl acetal **6** [3a] derived from (±)-**3** *via* ketone **5** [3b] led to the corresponding allylic sulfide **7** (99%) under the above conditions. Similarly, the reaction of **6** with 4-MeC_6H_4SSCl (obtained by reaction of *p*-thiocresol and SCl_2 in CS_2 [9]), followed by workup with aqueous $NaHCO_3$ solution also furnished the corresponding allylic sulfenyl derivative **8** (80%). The allylic selenenyl derivative **9** (56%) was formed on reacting **6** with benzeneselenenyl chloride. In contrast with these additions/eliminations that involve probably cationic intermediates of type **10** and **11**, enone **5** added to 4-MeC_6H_4SSCl (THF, −78 to 20°) and to PhSeCl (in CH_2Cl_2, −15 to 20°; followed by workup with aqueous $NaHCO_3$ solution) to give the corresponding adducts **13** (72%) and **14** (75%)

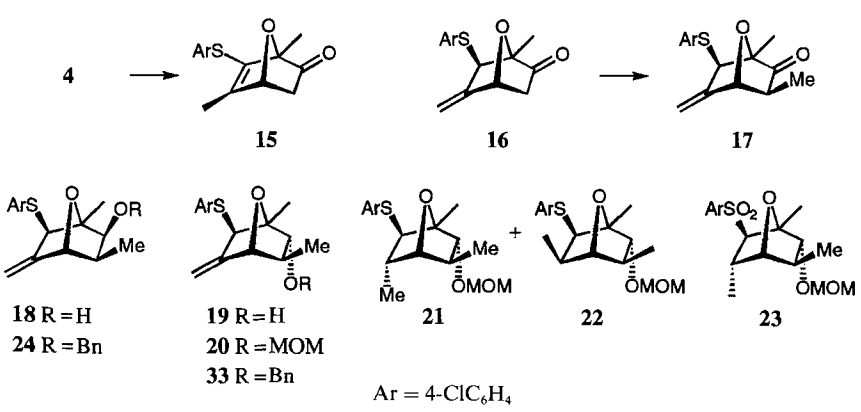
Scheme 1



together with unreacted starting material (10–15%). No trace of any regioisomeric adducts or of the corresponding products of HCl elimination could be detected by 400-MHz ^{1}H-NMR of the crude reaction mixture. These results suggest that the bridged intermediates of type **11** maintain a significant positive charge at the secondary center C(6) due to the electron-releasing ability of the homoconjugated carbonyl group [10], which completes with the cation-stabilizing effect of the Me substituent at C(5). In the electrophilic additions of (±)-**3** and **6**, the limiting structures **10**↔**11** are sufficient to describe the properties of the intermediate leading to the products, whereas, with enone **5**, limiting structures **11**↔**12**↔**12′** must be retained.

Saponification of the cyanoacetate moiety of **4** under usual conditions (MeONa/MeOH, then H_2CO [11]) led to olefin isomerisation and formation of enone **15** (96%; *Scheme 2*)[3]). Under milder conditions ($NaHCO_3$/MeOH, then aqueous H_2CO solution), the γ-methylideneketone **16** was obtained in 92% yield. The lithium enolate of **16**, obtained by deprotonation with $(Me_3Si)_2NLi$ (THF, −78°), was quenched with MeI (−78°) and afforded the product of mono-α-methylation **17** (80%)[4]). The high *exo*-facial selectivity of this alkylation was expected for steric reasons [12]. Depending on the nature of the reducing agent, ketone **17** could be transformed either into *exo*-alcohol **18** or its *endo*-isomer **19**. With *L-Selectride* ($LiB[CH(Me)Et]_3$) at −78° in THF, only the *exo*-alcohol **18** was formed, and it was isolated in 87% yield. In this case, the *exo*-Me group at C(3) impedes the approach of the reagent to the carbonyl moiety onto its *exo*-face [13]. The structure of **18**, as that of the new compounds described in this report, was established by its ^{1}H-NMR spectrum [14] (see *Exper. Part*). The NOESY experiment with **18** showed interactions between protons H–C(2), H–C(3), and H–C(6) and thus established the *exo*-configuration of the substituents at C(2), C(3), and C(6) in this compound. With $LiAlH(t\text{-BuO})_3$ (THF, 20°), the selectivity of the reduction of ketone **17** was somewhat lower, giving a 5.5:1 mixture **18**/**19** (95% yield). With the smaller reducing agent $NaBH_4$ ($EtOH/H_2O$, 20°), a 2.2:1 mixture **18**/**19** (97%) was obtained. With reagents such as

Scheme 2



[3]) This ketone could not be α-methylated without decomposition.

[4]) Attempts to monomethylate 1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**5**) under similar conditions led only to aldolization.

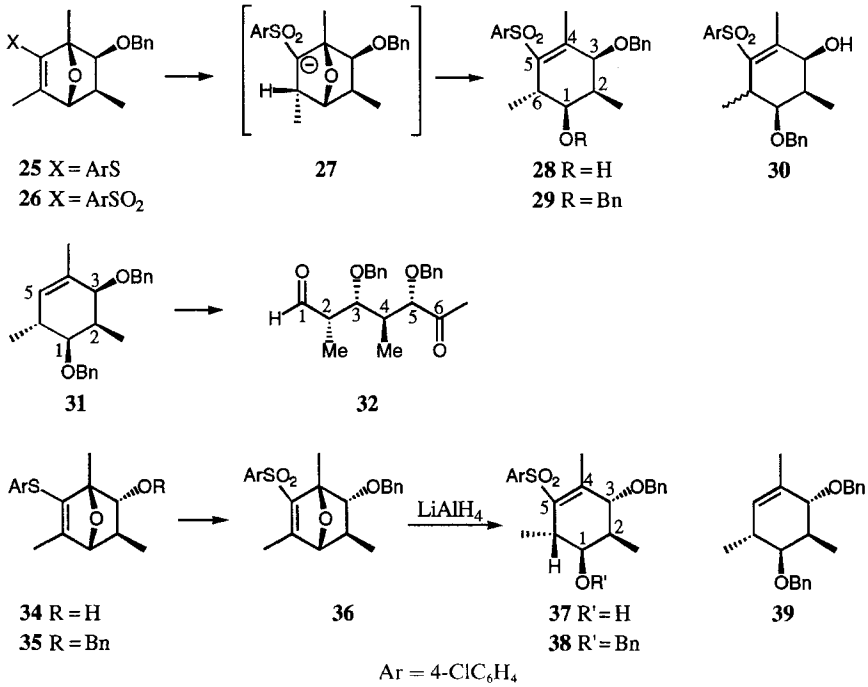
DIBAH (diisobutylaluminium hydride) or mixed hydrides resulting from the combination of $NaBH_4$ with *Lewis* acids, concurrent attack onto the *exo*-face of the bicyclic ketone becomes possible, perhaps because of coordination with the 7-oxa bridge. The best yield (73%) of *endo*-alcohol **19** was obtained with a 4:1 mixture of $ZnCl_2 \cdot Et_2O$ and $NaBH_4$ in dry Et_2O at 0°. Under the *Luche* conditions [15] ($NaBH_4$, $CeCl_3$), no selectivity was observed, and the reaction was very slow.

Treatment of **19** with $(MeO)_2CH_2$ and P_2O_5 [16] (reaction with $(MeO)_2CH_2$/TsOH/LiBr [17] led to low conversion) furnished the corresponding methoxymethyl (MOM) ether **20** (*Scheme 2*). The reduction of its exocyclic olefinic moiety with diimide generated by treatment with $TsNHNH_2$/NaOAc [18] (reaction with $N_2(COOK)_2$/AcOH [19] failed) afforded a 7:1 mixture of the 5-*endo*- and 5-*exo*-methyl derivatives **21**/**22**. Oxidation of this mixture with 3-chloroperbenzoic acid ($3\text{-}ClC_6H_4CO_3H$) gave a sulfone mixture from which **23** could be isolated pure in 56% yield (based on alcohol **19**). The *endo*-MOMO (*endo*-$MeOCH_2O$) moiety in **20** is probably responsible for the relatively high *exo*-face selectivity of the dyotropic transfer of hydrogen onto the methylidene group. The *endo*-MOMO group completes with the *exo*-sulfenyl substituent at C(6) for the diastereoselectivity of this reduction. Attempts to induce oxa-ring opening in **23** by treatment with $(Me_3Si)_2NLi$/THF (−78 to 20°), BuLi/THF (−78 to 20°), KH/THF (−78 to 20°), *t*-BuOK/THF (20°), or 50% NaOH/$Bu_4N(HSO_4)$/toluene (20°) all failed to give the expected cyclohexenol. On treating **23** with MeONa/MeOH, the 4-Cl group of the ArS moiety was substituted by a 4-MeO group. Quenching of the reaction mixture resulting from the treatment of **23** with BuLi at −78° with AcOD led to deuteration at the *ortho*-position of the ArS moiety. These negative results demonstrate the low kinetic acidity of the C−H moiety α to the sulfonyl group of **23**. This is probably due to steric hindrance by the *endo*-MOMO and -Me groups that impedes the *endo*-face approach of the base [20].

Benzylations of alcohol **18** under phase-transfer-catalysis conditions (BnBr, toluene, 50% NaOH/H_2O, Bu_4NBr [21]) furnished **24** which was isomerized into the 7-oxanorbornene derivative **25** (86% based on **18**) on treatment with MeONa in refluxing MeOH (*Scheme 3*). The reaction was accompanied by the formation of 2–5% of the C(2)-epimer of **25**. Oxidation of **25** with H_2O_2 in AcOH (20°) afforded the corresponding sulfone **26** (95%). Treatment of **26** with $LiAlH_4$ in THF at −78° yielded the cyclohexenediol derivative **28** (86%) with high stereoselectivity. This reaction proceeds probably by hydride addition onto the *exo* face of the methylidene moiety with formation of a carbanion intermediate **27** stabilized by the arylsulfonyl group. The latter undergoes then 7-oxa-ring opening. The vinyl sulfide **25** was unreactive toward $LiAlH_4$ in THF. The high *exo*-face selectivity of the hydride addition **26**→**27** can be interpreted in terms of steric factors and of possible precoordination of $LiAlH_4$ to the sulfonyl moiety or/and to the 7-oxa ethereal bridge. The structure of **28** was given by its spectral data and those of the corresponding dibenzyl ether **29**, obtained in 76% yield by treatment with benzyl 2,2,2-trichloroacetimidate in the presence of a catalytic amount of CF_3SO_3H [22]. The latter reaction was accompanied by the formation of **30** (*ca.* 5%). Benzylation under alkaline conditions [21] led to the formation of benzene derivatives.

Attempts to cleave the C=C bond of **29** with ozone, $KMnO_4$/[18]crown-6, OsO_4/pyridinium dichromate (PDC), $NaIO_4/RuCl_3$ [23], or $H_2Cr_2O_4$ were not met with success. Desulfonation with Al/Hg [24] or sodium dithionite [25] also failed. Finally, we found that treatment of **29** with butylmagnesium chloride in THF in the presence of $[Pd(acac)_2]$ or

Scheme 3

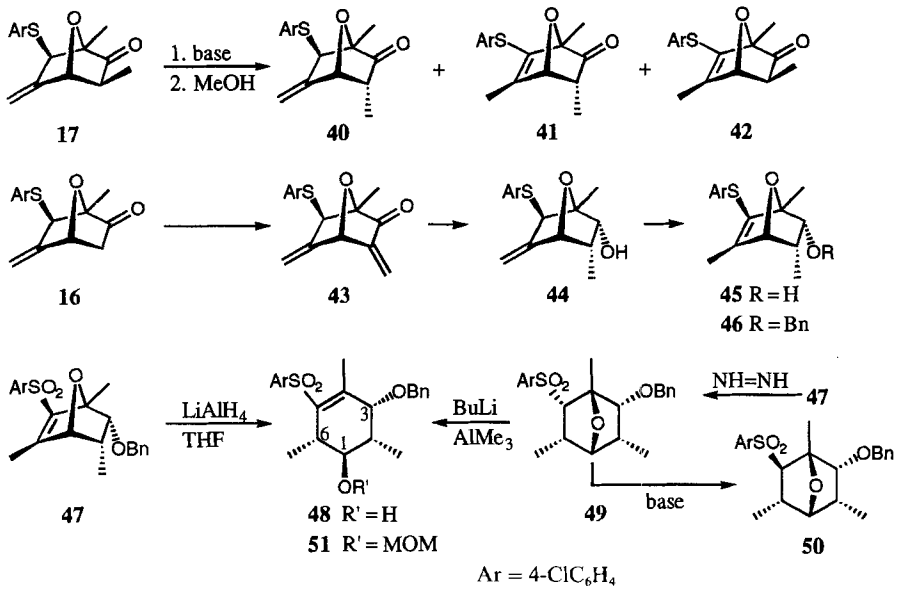


$[Pd(CF_3COO)_2]$ [26] afforded **31** (56%). Direct cleavage of the C=C bond of **31** with O_3, $RuCl_3/NaIO_4$ [23], or $OsO_4/NaIO_4$ led to untractable product mixtures. Double hydroxylation of **31** with *N*-methylmorpholine *N*-oxide and a catalytic amount of OsO_4 (THF/*t*-BuOH/H_2O 12:10:1, 20°) gave a 4:3 mixture of diastereoisomeric diols the oxidation of which with $NaIO_4/NH_4Cl$/MeOH yielded the 6-oxoheptanal derivative **32** (70% based on **31**), a polypropionate fragment with four contiguous stereogenic centers. Homochiral **32** is a potential intermediate in the synthesis of aplysiatoxin [27].

Benzylation [21] of the bicyclic *endo*-alcohol **19** afforded **33** (*Scheme 2*); the base-induced C=C bond migration was a slower process than reaction **24**→**25**, probably because of steric hindrance to the approach of the *endo*-H at C(6). In contrast, treatment of *endo*-alcohol **19** with MeONa/MeOH (reflux) led to fast isomerisation into **34** (*Scheme 3*). After benzylation [21] of **34** into **35** and oxidation with H_2O_2/AcOH, sulfone **36** was obtained pure in 75% yield (based on **19**). As for the reductive oxa-ring opening corresponding to **26**→**28**, treatment of **36** with $LiAlH_4$ in THF furnished the cyclohexenol **37** (79%). Benzylation of **37** with benzyl 2,2,2-trichloroacetimidate and CF_3SO_3H [22] afforded **38** (79%), and reductive desulfonylation [26] gave a moderate yield of cyclohexene derivative **39**.

In the preceding paper, we showed that 4-*exo*-methyl-2,8-dioxabicyclo[3.2.1]octan-3-one derivatives can be isomerized with good yield and high stereoselectivity into the corresponding 4-*endo*-methyl derivative. A similar technology applied to bicyclic ketone **17** was less successful and led to a mixture of isomerized derivatives **40**–**42** from which the desired 3-*endo*-methyl-substituted oxanorbornanones **40** and **41** were isolated in

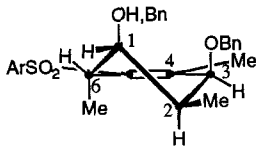
Scheme 4



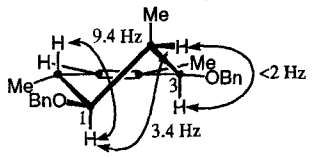
mediocre yields (*Scheme 4*). This was the case when treating **17** with $(i\text{-Pr})_2NLi$, then with MeOH, or with Et_2NLi/THF, then MeOH, or with $(Me_3Si)_2NLi$/THF, then MeOH, or with MeONa/MeOH. Dienone **43** was obtained in 65% yield by deprotonation of enone **16** with $(Me_3Si)_2NK$ in THF (−78°), quenching the corresponding enolate with Me_3SiCl, and reacting the enoxysilane in DMF with *Eschenmoser*'s salt ($Me_2N^+=CH_2I^-$), followed by *Hoffmann*'s elimination (MeI, $NaHCO_3$). Other methods of methylenation [28–31] all failed. Reduction of **43** with *K-Selectride* ($KB[CH(Me)Et]_3H$) in EtOH (−78°) afforded the 3-*endo*-methyl-substituted *endo*-alcohol **44** (91%). Olefin isomerisation was induced with MeONa/MeOH (65°, 3 days) giving **45** in 72% yield. After benzylation under phase-transfer-catalysis conditions [21] into **46**, oxidation with H_2O_2/AcOH gave the corresponding sulfone **47** (100%). Contrary to the vinyl sulfones **26** and **36** that reacted with $LiAlH_4$ at −78°, no reaction of **47** was observed with $LiAlH_4$ in THF at −78°. At higher temperature, complex mixtures were formed containing low amounts of the expected cyclohexene **48**.

Reduction of alkene **47** with diimide ($TsNHNH_2$/AcONa/H_2O/DME (dimethoxyethane), 100°) gave the all-*endo*-tetrasubstituted 7-oxanorbornane derivative **49** (84% based on **46**; recovery of 12% of **47**; *Scheme 4*). Treatment of **49** with BuLi (THF, −78°) and then with Me_3Al (2M in toluene) as electrophilic promoter of the 7-oxa-ring opening afforded cyclohexenol **48** (73%; MOM derivative **51**) and the *exo*-sulfonyl derivative **50** (1%).

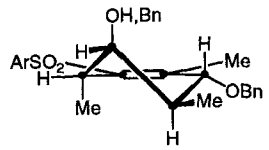
The structures of the new compounds described in this work were established by their 250-MHz ^{1}H-NMR and 100-MHz ^{13}C-NMR spectra and were consistent with their mode of formation. ^{1}H-NMR-signal attributions were confirmed by double-irradiation experiments and by NOE measurements. The (arylsulfonyl)cyclohexene derivatives **28** and



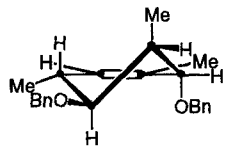
A (28, 29)



B (31)



C (37, 38)



D

E F (48, 51) X=SO_2Ar

29 (cyclohex-4-ene-1,3-diol numbering) adopt probably the pseudo-chair configuration **A** as suggested by the vicinal coupling constant between protons H–C(1)/H–C(6) (2.1 Hz in **28**, 4.4 Hz in **29**), H–C(1)/H–C(2) (1.4 Hz in **28**, 2.9 Hz in **29**), and H–C(2)/H–C(3) (4.1 Hz in **28**, 5.7 Hz in **29**). This was confirmed also by the observation of significant NOE's between the proton signals of Me–C(6) and H–C(2). In contrast, the ^{1}H-NMR data of the desulfonylated derivative **31** showed a relatively large ^3J(H–C(1),H–C(6)) = 9.4 Hz typical of two pseudo-axial vicinal protons as shown in **B**. *Gauche* interactions between the arylsulfonyl substituent at C(5) and the Me group at C(6) render conformation **A** more stable than **B** although it places three substituents at C(1), C(3), and C(6) in pseudo-axial positions. This is the case for **28** and **29**. With **31**, the absence of the arylsulfonyl group allows for the expected conformation **B** in which three substituents occupy pseudo-equatorial positions.

In the cases of the (arylsulfonyl)cyclohexene derivatives **37** and **38** that are 3-epimers of **28** and **29**, respectively, the conformation **C** (analogous to **A**, with pseudo-equatorial Me–C(2), and BnO–C(3) and pseudo-axial OH–C(1) (or BnO–C(1)) and Me–C(6)) is consistent with the coupling constants measured for H–C(1)/H–C(6) (2.6 Hz in **37**, 2.8 Hz in **38**), H–C(1)/H–C(2) (1.7 Hz in **37**, 2.0 Hz in **38**), and H–C(2)/H–C(3) (9.6 Hz in **37**, 9.7 Hz in **38**). The ^{1}H-NMR data collected for the desulfonylated cyclohexene derivative **39** were consistent with conformations **C** or **D**, both conformations implying two pseudo-axial and two pseudo-equatorial substituents at the tetragonal C-atoms.

Interestingly, the ^{1}H-NMR data of the (arylsulfonyl)cyclohexenes **48** and **51** showed relatively large coupling constants between the vicinal protons H–C(1)/H–C(2) (9.5 Hz

in **48**, 7.7 Hz in **51**), typical for protons occupying quasi-pseudo-axial positions. The other coupling constants (^3J(H–C(1)/H–C(6)) = 5.1 Hz in **48**, 2.5 Hz in **51**; ^3J(H–C(2)/H–C(3)) = 3.4 Hz in **48**, 3.6 Hz in **51**) were typical of vicinal protons making dihedral angles of 50–70° or 140–160°. These data were more consistent with conformation **F** (distorted pseudo-chair or nearly envelope with three substituents in pseudo-equatorial positions and nearly eclipsing $ArSO_2$ and Me–C(6) groups) than with conformation **E** (three pseudo-axial substituents and nearly eclipsing BnO–C(3) and Me–C(4) groups).

Conclusion. – The *Diels-Alder* adduct of 2,4-dimethylfuran and 1-cyanovinyl acetate was converted into 2,4,6-trimethylcyclohex-4-ene-1,3-diol derivatives with complete control of the configuration at C(1), C(2), C(3), and C(6). The method relies on the 7-oxa-ring opening of the conjugate base of arylsulfonylated 7-oxabicyclo[2.2.1]heptane derivatives; the latter can be obtained, in some cases, by hydride addition on the corresponding 2-(arylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-enes. Hydride reduction of 3-*exo*-methyl-7-oxabicyclo[2.2.1]heptan-2-ones can be either *exo*- or *endo*-face-selective depending on the nature of the reagent. The double reduction of 3-methylidene-7-oxabicyclo[2.2.1]heptan-2-ones leads stereoselectively to the corresponding 3-*endo*-methyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ols. In one case, the 1,3-di-*O*-benzylated-2,4,6-trimethylcyclohex-4-ene-1,3-diol, *i.e.*, (1*RS*,2*RS*,3*SR*,6*RS*)-**31**, was cleaved oxidatively into (2*RS*,3*SR*,4*RS*,5*RS*)-3,5-bis(benzyloxy)-2,4-dimethyl-6-oxoheptanal (**32**), a polypropionate fragment with four contiguous stereogenic centers. Since both enantiomeric forms of the starting *Diels-Alder* adduct are readily available, the methodologies described in these work should be applicable to the synthesis of all kinds of homochiral polypropionate fragments. In principle, the method allows one to introduce orthogonal protective groups [32] of the alcoholic moieties.

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Experimental Part

General. See [2] [33]. None of the procedures were optimized. All solvents were distilled before use, THF and Et_2O from Ph_2CO/Na. DMF, cyclohexane, and CH_2Cl_2 were dried over 3-Å molecular sieves. Flash column chromatography (FC): *Merck* silica gel *60* (63–200 μm).

*6-*exo*-(4-Chlorophenylthio)-2-*exo*-cyano-1-methyl-5-methylidene-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Acetate* (**4**). A soln. of (±)-**3** (0.207 g, 1 mmol) in THF (2 ml) was added to 4-chlorobenzenesulfenyl chloride (0.179 g, 1 mmol) dissolved in THF (5 ml) at –70° under Ar. The cooling bath was removed and stirring was continued for 1 h at 20°. Aq. $NaHCO_3$ soln. (10 ml) and CH_2Cl_2 (10 ml) were added. The aq. layer was extracted with CH_2Cl_2 (3 ml, 3 times) and the combined org. extract dried ($MgSO_4$) and evaporated: white solid 0.346 g (99%). M.p. 108–109°. IR (KBr): 3010, 2990, 2020, 1760, 1475, 1215, 1190, 1060, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.37–7.30 (*m*, 4 H); 5.26, 5.19 (2*m*, CH_2=C(5)); 4.80 (*d*, *J* = 5.8, H–C(4)); 4.38 (*s*, H–C(6)); 3.01 (*dd*, *J* = 14.3, 5.8, H_{exo}–C(3)); 2.18 (*s*, Ac); 2.01 (*d*, *J* = 14.3, H_{endo}–C(3)); 1.79 (*s*, Me). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 168.4 (*s*, CO); 148.9 (*s*, C(5)); 133.9, 133.0 (*s*); 131.3 (*d*, ^1J(C,H) = 164); 129.2 (*d*, ^1J(C,H) = 166); 117.1 (*s*, CN); 109.1 (*t*, ^1J(C,H) = 161, CH_2=C(5)); 90.5 (*s*, C(1)); 79.7 (*d*, ^1J(C,H) = 170, C(4)); 77.9 (*s*, C(2)); 52.2 (*d*, ^1J(C,H) = 153, C(6)); 45.8 (*t*, ^1J(C,H) = 140, C(3)); 20.6 (*q*, ^1J(C,H) = 131, *Me*COO); 16.3 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 351 (35, (^{37}Cl)M^+), 349 (63, (^{35}Cl)M^+), 308 (25), 306 (21), 264 (28), 209 (31), 134 (25), 109 (39), 95 (100). Anal. calc. for $C_{17}H_{16}ClNO_3S$ (349.05): C 58.37, H 4.61, N 4.00; found: C 58.40, H 4.71, N 4.30.

*6-*exo*-(4-Chlorophenylthio)-1-methyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* (**7**). A soln. of **6** (0.184 g, 1 mmol) in THF (2 ml) was added dropwise to a stirred soln. of 4-chlorobenzenesulfenyl chloride

(0.179 g, 1 mmol) in THF (5 ml), at −78° under Ar (5 min). The cooling bath was removed, and after 0.5 h, sat. aq. $NaHCO_3$ soln. (10 ml) was added at 20°. The aq. layer was extracted with CH_2Cl_2 (3 ml, 5 times). The combined org. extract was washed with brine (10 ml), which was extracted with CH_2Cl_2 (3 ml, 3 times). Drying ($MgSO_4$) and evaporation yielded 0.322 g (99%) of colourless oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.47 (*m*, 2 H); 7.28 (*m*, 2 H); 5.18, 5.13 (2*m*, CH_2=C(5)); 4.66 (*d*, *J* = 5.6, H–C(4)); 4.27 (*s*, H–C(6)); 3.22, 3.09 (2*s*, 2 MeO); 2.32 (*dd*, *J* = 12.4, 5.9, H_{exo}–C(3)); 1.62 (*d*, *J* = 12.4, H_{endo}–C(3)); 1.49 (*s*, Me). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 151.4 (*s*, C(5)); 134.7, 133.0 (2*s*); 132.9 (*d*, ^1J(C,H) = 166); 129.0 (*d*, ^1J(C,H) = 168); 108.5 (*s*, C(2)); 107.7 (*t*, ^1J(C,H) = 159, CH_2=C(5)); 91.1 (*s*, C(1)); 79.4 (*d*, ^1J(C,H) = 161, C(4)); 54.2 (*d*, ^1J(C,H) = 145, C(6)); 50.3 (*q*, ^1J(C,H) = 142, MeO); 49.1 (*q*, ^1J(C,H) = 143, MeO); 43.0 (*t*, ^1J(C,H) = 134, MeO); 15.6 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 297 (5, [(^{37}Cl)*M* − MeO]$^+$), 295 (13, [(^{35}Cl)*M* − MeO]$^+$), 265 (3), 263 (3), 221 (3), 183 (52), 151 (4), 95 (100).

*1-Methyl-5-methylidene-6-*exo-*(4-tolylthio)-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* (**8**). A soln. of *p*-thiocresol (0.027 g, 0.22 mmol) in CS_2 (1 ml) was added dropwise under stirring (7 min) to SCl_2 (0.42 ml, 6.6 mmol) at −78°. After stirring for 0.5 h, the cooling bath was removed, and 20° was reached in 0.5 h. The solvent was evaporated, THF (1 ml) added, and after cooling to −78°, **6** (0.037 g, 0.2 mmol) in THF (1 ml) was added dropwise during 5 min. After stirring for 1 h, the cooling bath was removed, MeOH (1 ml) was added, followed by aq. $NaHCO_3$ soln. (20 ml) and CH_2Cl_2 (10 ml). The aq. layer was extracted with CH_2Cl_2 (3 ml, 3 times). The combined org. extracts were washed with brine (10 ml) which was extracted with CH_2Cl_2 (3 ml, 3 times). Drying ($MgSO_4$), evaporation, and FC ($CHCl_3$) gave 0.049 g (80%) of colourless oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.43 (*m*, 2 H); 7.11 (*m*, 2 H); 5.16, 5.13 (2*m*, CH_2=C(5)); 4.66 (*d*, *J* = 5.80, H–C(4)); 4.26 (*s*, H–C(6)); 3.20, 3.06 (2*s*, 2 MeO); 2.33 (*s*, Me); 2.31 (*dd*, *J* = 12.4, 5.8, H_{exo}–C(3)); 1.60 (*d*, *J* = 12.3, H_{endo}–C(3)); 1.51 (*s*, Me). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 151.9 (*s*, C(5)); 137.0, 132.5, 132.0 (3*d*, ^1J(C,H) = 160); 129.7 (*d*, ^1J(C,H) = 157); 108.5 (*s*, C(2)); 107.4 (*t*, ^1J(C,H) = 159, CH_2=C(5)); 91.1 (*s*, C(1)); 79.4 (*d*, ^1J(C,H) = 159, C(4)); 54.4 (*d*, ^1J(C,H) = 149, C(6)); 50.2 (*q*, ^1J(C,H) = 142, MeO); 49.0 (*q*, ^1J(C,H) = 143, MeO); 43.2 (*t*, ^1J(C,H) = 134, C(3)); 21.0 (*q*, ^1J(C,H) = 127, Me); 15.6 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 275 (5, [*M* − MeO]$^+$), 243 (7), 183 (28), 123 (5), 109 (11), 95 (100). Anal. calc. for $C_{17}H_{22}O_3S$ (306.43): C 66.63, H 7.24, S 10.46; found: C 66.81, H 7.24, S 10.69.

*1-Methyl-5-methylidene-6-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* (**9**). A soln. of **6** (0.037 g, 0.2 mmol) in THF (0.5 ml) was added to benzeneselenenyl chloride (0.038 g, 0.2 mmol) in THF (1 ml) at −78° under Ar. The cooling bath was removed and stirring continued for 3 h at 20°. Sat. aq. $NaHCO_3$ soln. (10 ml) and CH_2Cl_2 (10 ml) were added. The aq. layer was extracted with CH_2Cl_2 (3 ml, 3 times). The org. phase was washed with brine (10 ml), which was then extracted with CH_2Cl_2 (3 ml, twice). Drying, evaporation and FC (CH_2Cl_2) yielded 0.038 g (56%) of **9** and 5 mg (8%) of the corresponding ketone.

Data of **9**: Yellowish oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.69–7.65 (*m*, 2 H); 7.31–7.29 (*m*, 3 H); 5.14, 5.11 (2*m*, CH_2=C(5)); 4.65 (*d*, *J* = 5.8, H–C(4)); 4.44 (*s*, H–C(6)); 3.20, 3.03 (2*s*, 2 MeO); 2.31 (*dd*, *J* = 12.2, 5.8, H_{exo}–C(3)); 1.60 (*d*, *J* = 12.2, H_{endo}–C(3)); 1.52 (*s*, Me). CI-MS (NH_3): 309 (11, [(^{80}Se)*M* − MeO]$^+$), 307 (8, [(^{78}Se)*M* − MeO]$^+$), 183 (49), 109 (15), 95 (100).

*Data of 1-Methyl-5-methylidene-6-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one.* ^{1}H-NMR (250 MHz, $CDCl_3$): 7.61–7.57 (*m*, 2 H); 7.31–7.28 (*m*, 3 H); 5.32, 5.26 (2*m*, CH_2=C(5)); 5.00 (*d*, *J* = 5.7, H–C(4)); 3.98 (*s*, H–C(6)); 2.64 (*dd*, *J* = 17.2, 5.7, H_{exo}–C(3)); 2.18 (*d*, *J* = 17.2, H_{endo}–C(3)); 1.47 (*s*, Me). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 211.4 (*s*, C(2)); 150.2 (*s*, C(5)); 134.0 (*d*, ^1J(C,H) = 162); 129.6 (*s*); 129.2 (*d*, ^1J(C,H) = 158); 127.8 (*d*, ^1J(C,H) = 161); 110.2 (*t*, ^1J(C,H) = 160); 89.2 (*s*, C(1)); 78.5 (*d*, ^1J(C,H) = 168, C(4)); 48.7 (*d*, ^1J(C,H) = 149, C(6)); 44.5 (*t*, ^1J(C,H) = 136, C(3)); 14.6 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 312 (20, [(^{80}Se)*M* + NH_4]$^+$), 310 (9, [(^{78}Se)*M* + NH_4]$^+$), 295 (18, [(^{80}Se)*M* + H]$^+$), 294 (7, (^{80}Se)*M*$^+$), 293 (9, [(^{78}Se)*M* + H]$^+$), 292 (6, (^{78}Se)*M*$^+$), 137 (8), 109 (100).

6-endo-*Chloro-1,5-*endo-*dimethyl-5-*exo-*(4-tolylthio)-7-oxabicyclo[2.2.1]heptan-2-one* (**13**). As described for **8**, with *p*-thiocresol (0.137 g, 1.1 mmol) in CS_2 (2 ml; in 20 min), SCl_2 (2.1 ml, 63 mmol), then THF (5 ml) and **5** (0.138 g, 1 mmol) in THF (2 ml; within 10 min). Workup with $NaHCO_3$ soln. (20 ml), CH_2Cl_2 (5 ml and 5 × 3 ml), brine (20 ml), and CH_2Cl_2 (3 ml, 3 times). FC (Et_2O/light petroleum ether 1:4) yielded 0.214 g (72%) of **9** and 9 mg (7%) of **5**. **9**: White crystals. M.p. 127°. IR (KBr): 2970, 2925, 2910, 1755, 1440, 1395, 1075, 1050, 890, 810, 795. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.48 (*m*, 2 H); 7.20 (*m*, 2 H); 4.65 (*d*, *J* = 6.1, H–C(4)); 4.08 (*d*, *J* = 0.9, H–C(6)); 2.53 (*ddd*, *J* = 18.2, 5.9, 0.6, H_{exo}–C(3)); 2.39 (*s*, Me); 2.38 (*dd*, *J* = 18.1, 0.5, H_{endo}–C(3)); 1.50, 1.36 (2*s*, 2 Me). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 206.5 (*s*, C(2)); 140.1 (*s*); 137.0 (*d*, ^1J(C,H) = 162); 129.9 (*d*, ^1J(C,H) = 158); 127.4 (*s*); 89.4 (*s*, C(1)); 81.9 (*d*, ^1J(C,H) = 164, C(4)); 67.3 (*d*, ^1J(C,H) = 164, C(6)); 57.6 (*s*, C(5)); 39.2 (*t*, ^1J(C,H) = 135, C(3)); 21.9, 21.2, 12.9 (3*q*, ^1J(C,H) = 127–129, 3 Me). CI-MS (NH_3): 298 (28, (^{37}Cl)*M*$^{+\cdot}$), 296 (60, (^{35}Cl)*M*$^{+\cdot}$), 261 (21), 233 (21), 124 (100), 109 (99). Anal. calc. for $C_{15}H_{17}ClO_2S$ (296.824): C 60.70, H 5.77, S 10.78; found: C 60.68, H 5.82, S 10.80.

6-endo-*Chloro-1,5*-endo-*dimethyl-5*-exo-*(4-tolylthio)-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal.* Ketone **13** (0.060 g, 0.2 mmol) was heated in MeOH (2 ml) under reflux with trimethyl orthoformate (0.11 ml, 1 mmol) and a catalytic amount of TsOH for 18 h. Charcoal was added and heating continued for 5 min. After cooling to 20° and filtration, sat. aq. $NaHCO_3$ soln. (10 ml) and CH_2Cl_2 (10 ml) were added. The aq. layer was extracted with CH_2Cl_2 (3 ml, 3 times). The combined org. extracts were washed with brine which was extracted with CH_2Cl_2 (3 ml, twice). FC ($CHCl_3$) yielded 42 mg (61%) of colourless oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.46 (*m*, 2 H); 7.16 (*m*, 2 H); 4.42 (*d*, J = 6.3, H–C(4)); 4.00 (*s*, H–C(6)); 3.22, 3.19 (2*s*, 2 MeO); 2.37 (*s*, Me); 2.18 (*dd*, J = 13.3, 6.3, H_{exo}–C(3)); 1.85 (*d*, J = 13.3, H_{endo}–C(3)); 1.52 (*s*, Me–C(1)); 1.37 (*s*, Me–C(5)). CI-MS (NH_3): 344 (1, (^{37}Cl)$M^{+\cdot}$), 342 (2, (^{35}Cl)$M^{+\cdot}$), 313 (2), 311 (6), 219 (3), 184 (15), 183 (100), 109 (34).

6-endo-*Chloro-1,5*-endo-*dimethyl-5*-exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* (**14**). Benzeneselenenyl chloride (0.038 g, 0.2 mmol) dissolved in dry CH_2Cl_2 (1 ml) was added dropwise in 25 min to a soln. of **5** (0.027 g, 0.2 mmol) in CH_2Cl_2 (1 ml) at −15° under Ar. After stirring at −15° for 10 min, the cooling bath was removed and the mixture stirred overnight at 20°. CH_2Cl_2 (10 ml) and brine (10 ml) were added. The aq. layer was extracted with CH_2Cl_2 (3 ml, 3 times). The combined org. extracts were dried ($MgSO_4$). FC (Et_2O/light petroleum ether) gave 0.048 g (75%) of white solid recrystallized from CH_2Cl_2/heptane. M.p. 109°. IR ($CHCl_3$): 2980, 2920, 1765, 1430, 1405, 1380, 1145, 1110, 1075, 955, 900, 840. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.72–7.68 (*m*, 2 H); 7.45–7.35 (*m*, 3 H); 4.74 (*dm*, J = 5.1, H–C(4)); 4.23 (*s*, H–C(6)); 2.47–2.44 (*m*, CH_2(3)); 1.48, 1.45 (2*s*, 2 Me). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 206.0 (*s*, C(2)); 137.9 (*d*, ^1J(C,H) = 163); 129.5, 129.2 (2*d*, ^1J(C,H) = 161); 127.4 (*s*); 89.4 (*s*, C(1)); 83.0 (*d*, ^1J(C,H) = 165, C(4)); 67.8 (*d*, ^1J(C,H) = 168, C(6)); 52.9 (*s*, C(5)); 39.7 (*t*, ^1J(C,H) = 136, C(3)); 22.4, 12.8 (2*q*, ^1J(C,H) = 129, 2 Me). CI-MS (NH_3): 332 (13, (^{80}Se,^{37}Cl)$M^{+\cdot}$), 330 (32, (^{80}Se,^{35}Cl)$M^{+\cdot}$), 328 (15, (^{78}Se,^{35}Cl)$M^{+\cdot}$), 297 (12, [(^{82}Se)M − Cl]$^+$), 295 (40, [(^{80}Se)M − Cl]$^+$), 293 (19, [(^{78}Se)M − Cl]$^+$), 157 (12), 109 (100). Anal. calc. for $C_{14}H_{15}ClO_2Se$ (329.69): C 51.00, H 4.59; found: C 51.62, H 4.69.

6-(4-Chlorophenylthio)-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**15**). MeONa (5.4M in MeOH, 0.93 ml) was added dropwise to a stirred soln. of **4** (0.147 g, 0.42 mmol) in MeOH (6 ml) at 20°. After stirring for 1 h, 36% aq. H_2CO soln. (0.19 ml, 2.5 mmol) was added. The mixture was stirred for 1 h and quenched with brine (10 ml) and CH_2Cl_2 (10 ml). The aq. layer was extracted with CH_2Cl_2 (3 ml, 3 times), and the combined org. extracts were washed with brine (10 ml), which was then extracted with CH_2Cl_2 (3 ml, 3 times). Drying ($MgSO_4$) and evaporation yielded 0.113 g (96%) of white solid. M.p. 67–69°. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.26–7.18 (*m*, 4 H); 5.08 (*d*, J = 4.4, H–C(4)); 2.35 (*dd*, J = 16.0, 4.4, H_{exo}–C(3)); 1.98 (*s*, Me–C(5)); 1.95 (*d*, J = 16.0, H_{endo}–C(3)); 1.27 (*s*, Me–C(1)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 206.7 (*s*, C(2)); 159.4 (*s*, C(5)); 133.3, 132.7 (2*s*); 130.1 (*d*, ^1J(C,H) = 165); 129.4 (*s*); 129.1 (*d*, ^1J(C,H) = 167); 90.9 (*s*, C(1)); 80.3 (*d*, ^1J(C,H) = 167, C(4)); 33.5 (*t*, ^1J(C,H) = 138, C(3)); 13.1, 11.4 (2*q*, ^1J(C,H) = 129, 2 Me).

6-exo-*(4-Chlorophenylthio)-1-methyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-one* (**16**). Sat. aq. $NaHCO_3$ soln. (0.71 g, 8.4 mmol) and 36% aq. H_2CO soln. (6.5 ml, 84 mmol) in H_2O (10 ml) were added to a stirred soln. of **4** (0.984 g, 2.8 mmol) in MeOH (50 ml). After stirring at 20° for 1 h, H_2O (50 ml) and Et_2O (50 ml) were added. The aq. layer was extracted with Et_2O (5 ml, 6 times). The combined extracts were dried ($MgSO_4$). FC (Et_2O/light petroleum ether 1:2) gave 0.727 g (92%) of yellow crystals. M.p. 76°. IR (KBr): 2910, 1750, 1470, 1385, 1090, 1060, 1005, 915, 805. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.38–7.27 (*m*, 4 H); 5.36, 5.27 (2*m*, CH_2=C(5)); 5.04 (*d*, J = 5.6, H–C(4)); 3.84 (*s*, H–C(6)); 2.67 (*dd*, J = 17.3, 5.6, H_{exo}–C(3)); 2.20 (*d*, J = 17.3, H_{endo}–C(3)); 1.45 (*s*, Me). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 211.5 (*s*, C(2)); 149.2 (*s*, C(5)); 133.3 (*s*); 132.3 (*d*, ^1J(C,H) = 164); 131.8 (*s*); 129.2 (*d*, ^1J(C,H) = 167); 110.7 (*t*, ^1J(C,H) = 160, CH_2=C(5)); 89.3 (*s*, C(1)); 78.3 (*d*, ^1J(C,H) = 153, C(4)); 53.1 (*d*, ^1J(C,H) = 150, C(6)); 44.4 (*t*, ^1J(C,H) = 136, C(3)); 13.1 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 283 (5, [(^{37}Cl)M + H]$^+$), 282 (7, (^{37}Cl)$M^{+\cdot}$), 281 (17, [(^{35}Cl)M + H]$^+$), 280 (7, (^{35}Cl)$M^{+\cdot}$), 252 (13), 237 (13), 209 (20), 125 (17), 109 (100). Anal. calc. for $C_{14}H_{13}ClO_2S$ (280.78): C 59.89, H 4.65; found: C 59.87, H 4.85.

6-exo-*(4-Chlorophenylthio)-1,3*-exo-*dimethyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-one* (**17**). A soln. of $(Me_3Si)_2NH$ (1.26 ml, 6 mmol) in THF (50 ml) and BuLi (1.9M in hexane; 2.76 ml, 5.25 mmol) was stirred under Ar at 0° for 0.5 h, then cooled to −78°. A soln. of **16** (1.404 g, 5 mmol) in THF (10 ml) was added dropwise in 20 min. Stirring at −78° was continued for 1 h, and then MeI (0.93 ml, 15 mmol) was added. After stirring at −78° for 1 h, the cooling bath was removed and, at 0°, brine (30 ml) was added. The aq. layer was extracted with Et_2O (5 ml, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (Et_2O/light petroleum ether 1:6): 1.179 g (80%) of yellow crystals. M.p. 81–82°. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.36, 7.27 (2*m*, 2 H); 5.35, 5.27 (2*m*, CH_2=C(5)); 4.61 (*s*, H–C(4)); 3.82 (*s*, H–C(6)); 2.22 (*q*, J = 7.4, H–C(3)); 1.44 (*s*, Me–C(1)); 1.26 (*d*, J = 7.4, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 214.4 (*s*, C(2)); 149.2 (*s*, C(5)); 133.5, 133.2 (2*s*); 132.3 (*d*, ^1J(C,H) = 165); 129.2 (*d*, ^1J(C,H) = 167); 110.5 (*t*, ^1J(C,H) = 160, CH_2=C(5)); 89.4 (*s*, C(1)); 83.6 (*d*,

^1J(C,H) = 163, C(4)); 53.0 (*d*, ^1J(C,H) = 148, C(6)); 48.6 (*d*, ^1J(C,H) = 136, C(3)); 13.8, 13.4 (2*q*, ^1J(C,H) = 129, 2 Me). CI-MS (NH_3): 296 (2, (^{37}Cl)M^+), 294 (7, (^{35}Cl)M^+), 266 (8), 238 (6), 223 (14), 188 (7), 123 (100). Anal. calc. for $C_{15}H_{15}ClO_2S$ (294.81): C 61.11, H 5.13; found: C 60.97, H 5.24.

6-exo-*(4-Chlorophenylthio)-1,3-*exo-*dimethyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-*exo-*ol* (**18**). To a stirred soln. of **17** (0.924 g, 3.1 mmol) in THF (20 ml), *L-Selectride* (1M in THF; 3.9 ml, 3.9 mmol) was added dropwise in 5 min at −78° under Ar. After stirring for 1 h, the cooling bath was removed and 3M aq. NaOH (5.2 ml, 15.6 mmol), then 30% aq. H_2O_2 soln. (1.6 ml, 15.6 mmol) were added at 20° (cooling with H_2O bath). After stirring at 20° for 4 h, brine (10 ml) was added and the mixture extracted with Et_2O (3 ml, 3 times). After drying ($MgSO_4$) and evaporation, FC (Et_2O/light petroleum ether 1:2) yielded 0.810 g (87%). M.p. 143–144°. IR (KBr): 3380, 2960, 2920, 1475, 1090, 1045, 1010, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.36, 7.26 (2*m*, 2 H); 5.16, 5.07 (2*m*, CH_2=C(5)); 4.24 (*s*, H–C(4)); 3.79 (*dd*, *J* = 9.8, 7.4, H–C(2)); 3.71 (*s*, H–C(6)); 2.23 (*dd*, *J* = 7.4, 7.3, H–C(3)); 1.55 (*d*, *J* = 9.8, OH); 1.46 (*s*, Me–C(1)); 1.05 (*d*, *J* = 7.3, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 150.8 (*s*, C(5)); 134.6, 132.6 (2*s*); 131.9 (*d*, ^1J(C,H) = 164); 129.0 (*d*, ^1J(C,H) = 167); 107.8 (*t*, ^1J(C,H) = 160, CH_2=C(5)); 90.8 (*s*, C(1)); 85.0 (*d*, ^1J(C,H) = 159, C(4)); 77.1 (*d*, ^1J(C,H) = 149, C(2)); 55.1 (*d*, ^1J(C,H) = 144, C(6)); 44.0 (*d*, ^1J(C,H) = 133, C(3)); 14.7 (*q*, ^1J(C,H) = 128, Me); 11.8 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 298 (3, (^{37}Cl)M^+), 296 (8, (^{35}Cl)M^+), 253 (6), 224 (8), 223 (11), 222 (11), 144 (46), 109 (100). Anal. calc. for $C_{15}H_{16}ClO_2S$ (296.82): C 60.70, H 5.77; found: C 61.03, H 5.63.

6-exo-*(4-Chlorophenylthio)-1,3-*exo-*dimethyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-*endo-*ol* (**19**). A soln. of 2.2M $ZnCl_2 \cdot Et_2O$ in CH_2Cl_2 (4.3 ml, 9.5 mmol) was added to a stirred mixture of $NaBH_4$ (0.093 g, 2.5 mmol) and Et_2O (50 ml) under Ar at 0°. After stirring for 10 min, **17** (0.926 g, 3.1 mmol) in Et_2O (10 ml) was added to the slurry. Stirring at 0° was continued for 1 h, then 1M aq. HCl (12 ml) was added and the cooling bath removed. After stirring at 20° for 1 h, brine (30 ml) was added, the aq. phase extracted with Et_2O (5 ml, 3 times), and the combined extract dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:2, then 2:1) gave 0.678 g (73%) of **19** and 93 mg (10%) of **18**. **19**: M.p. 102–105°. IR (KBr): 3420, 2010, 1465, 1220, 1090, 890, 805. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.38, 7.25 (2*m*, 2 H); 5.19, 5.13 (2*m*, CH_2=C(5)); 4.53 (*s*, H–C(6)); 4.19 (*s*, H–C(4)); 3.60 (*m*, H–C(2)); 1.96 (*d*, *J* = 4.4, OH); 1.76 (*qd*, *J* = 7.1, 2.8, H–C(3)); 1.47 (*s*, Me–C(1)); 1.18 (*d*, *J* = 7.1, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 151.7 (*s*, C(5)); 135.3, 132.0 (2*s*); 130.8 (*d*, ^1J(C,H) = 164); 128.9 (*d*, ^1J(C,H) = 167); 107.3 (*t*, ^1J(C,H) = 159, CH_2=C(5)); 89.0 (*s*, C(1)); 86.0 (*d*, ^1J(C,H) = 160, C(4)); 85.1 (*d*, ^1J(C,H) = 150, C(2)); 50.4 (*d*, ^1J(C,H) = 148, C(6)); 48.2 (*d*, ^1J(C,H) = 135, C(3)); 18.7 (*q*, ^1J(C,H) = 125, Me); 17.6 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 317 (7), 316 (38, [(^{37}Cl)M + NH_4]$^+$), 315 (20), 314 (100, [(^{35}Cl)M + NH_4]$^+$), 299 (4), 298 (8, (^{37}Cl)M^+), 297 (11), 296 (17, (^{35}Cl)M^+), 279 (25), 152 (19). Anal. calc. for $C_{15}H_{16}ClO_2S$ (296.82): C 60.70, H 5.77; found: C 61.00, H 5.76.

6-exo-*(4-Chlorophenylthio)-1,3-*exo-*dimethyl-5-methylidene-7-oxabicyclo[2.2.1]hept-2-*endo-*yl Methoxymethyl Ether* (**20**). A soln. of **19** (0.678 g, 2.3 mmol) in $CHCl_3$ (10 ml), dimethoxymethane (10 ml, 113 mmol), and P_2O_5 (3.2 g, 23 mmol) was stirred at 20° for 2 h. Sat. aq. K_2CO_3 soln. (25 ml) and Et_2O (50 ml) were added. The aq. phase was extracted (5 ml, 6 times). Drying ($MgSO_4$) and evaporation gave yellowish oil (0.883 g) which contained 85% of **20** and unidentified product $C_{20}H_{29}ClO_5S$. **20**: ^{1}H-NMR (250 MHz, $CDCl_3$): 7.36, 7.24 (2*m*, 2 H); 5.17, 5.11 (2*m*, CH_2=C(5)); 4.64 (*m*, OCH_2O); 4.46 (*s*, H–C(6)); 4.21 (*s*, H–C(4)); 3.39 (*d*, *J* = 2.6, H–C(2)); 3.33 (*s*, MeO); 1.81 (*qd*, *J* = 7.2, 2.6, H–C(3)); 1.48 (*s*, Me–C(1)); 1.17 (*d*, *J* = 7.2, Me–C(3)).

6-exo-*(4-Chlorophenylthio)-1,3-*exo,*5-*endo-*trimethyl-7-oxabicyclo[2.2.1]hept-2-*endo-*yl Methoxymethyl Ether* (**21**). A soln. of crude **20** obtained above (0.663 g, 1.9 mmol) in DME (10 ml) was heated under reflux with $TsNHNH_2$ (1.28 g, 6.9 mmol). Aq. AcONa soln. (0.75 g, 9 mmol, in 5 ml of H_2O) was added dropwise within 5 h. Then more $TsNHNH_2$ (1.28 g) was added followed by the same amount of aq. AcONa soln. (dropwise in *ca.* 1 h). Heating was continued for 14 h. After cooling to 20°, CH_2Cl_2 (25 ml) was added. Separation, extraction with CH_2Cl_2 (3 ml, 3 times), drying ($MgSO_4$), evaporation, and FC (Et_2O/light petroleum ether 1:6) yielded 0.584 g (75%) of **21**, yellowish oil, containing *ca.* 12% of **22** (by ^{1}H-NMR). **21**: ^{1}H-NMR (250 MHz, $CDCl_3$): 7.31, 7.22 (2*m*, 2 H); 4.67 (*m*, OCH_2O); 3.78 (*d*, *J* = 5.1, H–C(4)); 3.52 (*d*, *J* = 6.7, H–C(6)); 3.36 (*s*, MeO); 3.33 (*d*, *J* = 3.0, H–C(2)); 2.14 (*m*, H–C(5)); 2.00 (*dq*, *J* = 7.1, 3.0, H–C(3)); 1.41 (*s*, Me–C(1)); 1.15 (*d*, *J* = 7.1, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 136.2, 131.4 (2*s*); 130.1 (*d*, ^1J(C,H) = 164); 128.8 (*d*, ^1J(C,H) = 166); 96.6 (*t*, ^1J(C,H) = 163, OCH_2O); 90.6 (*d*, ^1J(C,H) = 146, C(2)); 86.0 (*d*, ^1J(C,H) = 151, C(4)); 55.4 (*q*, ^1J(C,H) = 142, MeO); 52.6 (*d*, ^1J(C,H) = 143, C(6)); 46.6 (*d*, ^1J(C,H) = 132, C(3)); 37.7 (*d*, ^1J(C,H) = 131, C(5)); 19.3, 17.5, 13.5 (3*q*, ^1J(C,H) = 127, 3 Me).

6-exo-*(4-Chlorophenylsulfonyl)-1,3-*exo,*5-*endo-*trimethyl-7-oxabicyclo[2.2.1]hept-2-*endo-*yl Methoxymethyl Ether* (**23**). A mixture of **21** (0.584 g, 1.7 mmol; containing 12% of **22**), $CHCl_3$ (20 ml), 80% 3-$ClC_6H_4CO_3H$ (1.1 g, 5.1 mmol), and $NaHCO_3$ (0.86 g, 10.2 mmol) was stirred at 20° for 11 h. Sat. aq. NaI soln. (25 ml) and AcOEt

(25 ml) were added. The org. layer was washed with sat. aq. $Na_2S_2O_3$ soln. (10 ml) and the combined aq. layer extracted with AcOEt (5 ml, 5 times). Washing with NaI and $Na_2S_2O_3$ soln. was repeated, then the org. extracts were washed with sat. aq. K_2CO_3 soln. (10 ml, twice) and brine (10 ml), each of them being reextracted with Et_2O (3 ml, 3 times). The combined org. extract was dried ($MgSO_4$), filtered through silica gel, evaporated, and the white solid recrystallized from Et_2O/heptane: 0.476 g (56% based on **20**). M.p. 106–108°. IR (KBr): 2960, 2880, 1300, 1275, 1140, 1080, 1040, 750. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.87, 7.56 (*2m*, 2 H); 4.65 (*m*, OCH_2O); 3.88 (*d*, *J* = 5.3, H–C(4)); 3.46 (*d*, *J* = 6.8, H–C(6)); 3.36 (*s*, MeO); 3.21 (*d*, *J* = 2.8, H–C(2)); 2.52 (*m*, H–C(5)); 1.88 (*qd*, *J* = 7.1, 2.8, H–C(3)); 1.82 (*s*, Me–C(1)); 1.11 (*d*, *J* = 7.1, Me–C(3)); 0.56 (*d*, *J* = 7.0, Me–C(5)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 140.2, 138.1 (*2s*); 130.0 (*d*, ^1J(C,H) = 168); 129.5 (*d*, ^1J(C,H) = 169); 96.6 (*t*, ^1J(C,H) = 163, OCH_2O); 91.6 (*d*, ^1J(C,H) = 149, C(2)); 88.0 (*s*, C(1)); 85.6 (*d*, ^1J(C,H) = 162, C(4)); 68.5 (*d*, ^1J(C,H) = 145, C(6)); 55.5 (*q*, ^1J(C,H) = 142, MeO); 41.5 (*d*, ^1J(C,H) = 133); 38.1 (*d*, ^1J(C,H) = 132); 19.1, 17.8, 13.6 (*3q*, ^1J(C,H) = 127, 3 Me). CI-MS (NH_3): 394 (15, $[(^{37}Cl)M + NH_4]^+$), 392 (36, $[(^{35}Cl)M + NH_4]^+$), 377 (11, $[(^{37}Cl)M + H]^+$), 375 (32, $[(^{35}Cl)M + H]^+$), 329 (18), 199 (70), 97 (100). Anal. calc. for $C_{17}H_{23}ClO_5S$ (374.894): C 54.47, H 6.18; found: C 54.86, H 6.10.

*Benzyl 6-*exo*-(4-Chlorophenylthio)-1,3-*exo*-dimethyl-5-methylidene-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Ether* (**24**). A mixture of benzyl bromide (1.08 ml, 9 mmol), **18** (0.895 g, 3 mmol), Bu_4NBr (0.097 g, 0.3 mmol), toluene (75 ml), and 50% aq. NaOH soln. (4 ml) was stirred at 20° for 30 h. Brine (25 ml) was added, the aq. layer extracted with Et_2O (5 ml, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (Et_2O/light petroleum ether 1:8, then 1:2): **24** containing *ca.* 3% of **18** and 2% of **25**. The product was used directly in the synthesis of **25**. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.38–7.23 (*m*, 9 H); 5.15, 5.02 (*2m*, CH_2=C(5)); 4.52 (*m*, PhCH_2); 4.27 (*s*, H–C(4)); 3.67 (*s*, H–C(6)); 3.55 (*d*, *J* = 7.3, H–C(2)); 2.28 (*dq*, *J* = 7.3, 7.3, H–C(3)); 1.51 (*s*, Me–C(1)); 1.11 (*d*, *J* = 7.3, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 151.2 (*s*, C(5)); 138.1, 134.6, 132.6 (*3s*); 132.3 (*d*, ^1J(C,H) = 164); 128.9 (*d*, ^1J(C,H) = 167); 128.3 (*d*, ^1J(C,H) = 160); 127.6 (*d*, ^1J(C,H) = 161); 127.4 (*d*, ^1J(C,H) ≈ 155); 108.0 (*t*, ^1J(C,H) = 159, CH_2=C(5)); 90.4 (*s*, C(1)); 85.1 (*d*, ^1J(C,H) = 160, C(4)); 83.9 (*d*, ^1J(C,H) = 143, C(2)); 73.6 (*t*, ^1J(C,H) = 142, PhCH_2); 56.1 (*d*, ^1J(C,H) = 146, C(6)); 44.2 (*d*, ^1J(C,H) = 135, C(3)); 14.9 (*q*, ^1J(C,H) = 128, Me); 12.7 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 407 (11), 406 (43, $[(^{37}Cl)M + NH_4]^+$), 405 (18), 404 (67, $[(^{35}Cl)M + NH_4]^+$), 388 (20, $(^{37}Cl)M^{+\cdot}$), 387 (10), 386 (4, $(^{35}Cl)M^{+\cdot}$), 326 (11), 262 (28), 243 (35), 237 (23), 223 (17), 221 (19), 95 (68), 91 (100).

*Benzyl 6-(4-Chlorophenylthio)-1,3-*exo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl Ether* (**25**). MeONa (5.4M in MeOH; 5.4 ml, 29 mmol) was added to the soln. of **24** (1.125 g, 2.9 mmol) in MeOH (20 ml). The mixture was heated under reflux for 60 h. The soln. was cooled to 20°, and brine (30 ml) and Et_2O (30 ml) were added. Separation, extraction of the aq. layer with Et_2O (5 ml, 3 times), drying ($MgSO_4$), evaporation, and FC (Et_2O/light petroleum ether 1:12) yielded 1.004 g (86% based on **18**) of **25**, colourless oil, 24 mg (2%) of **24** and 60 mg (5%) of 6-epi-**24**.

Data of **25**: IR ($CHCl_3$): 2970, 2920, 2860, 1440, 1085, 1005, 955. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.34–7.18 (*m*, 9 H); 4.53 (*s*, PhCH_2); 4.31 (*s*, H–C(4)); 3.40 (*d*, *J* = 6.8, H–C(2)); 2.00 (*m*, H–C(3)); 1.90 (*s*, Me–C(5)); 1.34 (*s*, Me–C(1)); 1.12 (*d*, *J* = 7.2, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 157.4, 138.3, 134.4, 132.0, 130.8 (*5s*); 129.7, 128.9 (*2d*, ^1J(C,H) = 165); 128.2 (*d*, ^1J(C,H) = 160); 127.5 (*d*, ^1J(C,H) = 159); 93.2 (*s*, C(1)); 87.2 (*d*, ^1J(C,H) = 162, C(4)); 80.8 (*d*, ^1J(C,H) = 148, C(2)); 73.8 (*t*, ^1J(C,H) = 141, PhCH_2); 37.3 (*d*, ^1J(C,H) = 134, C(3)); 14.1, 13.6, 12.3 (*3q*, ^1J(C,H) = 127, 3 Me). CI-MS (NH_3): 406 (2, $[(^{37}Cl)M + NH_4]^+$), 404 (3, $[(^{35}Cl)M + NH_4]^+$), 389 (1, $[(^{37}Cl)M + H]^+$), 387 (3, $[(^{35}Cl)M + H]^+$), 279 (5), 240 (38), 239 (16), 238 (100), 209 (7), 204 (6). Anal. calc. for $C_{22}H_{23}ClO_2S$ (386.95): C 68.29, H 5.99; found: C 68.75, H 6.10.

*Data of Benzyl 6-*endo*-(4-Chlorophenylthio)-1,3-*exo*-dimethyl-5-methylidene-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Ether* (6-epi-**24**): ^{1}H-NMR (250 MHz, $CDCl_3$): 7.39–7.23 (*m*, 9 H); 5.10 (*m*, CH_2=C(5)); 4.54 (*m*, PhCH_2); 4.26 (*s*, H–C(4)); 4.22 (*d*, ^1J(C,H) = 7.4, H–C(2)); 3.78 (*t*, *J* = 2.7, H–C(6)); 2.26 (*m*, H–C(3)); 1.20 (*s*, Me–C(1)); 1.11 (*d*, *J* = 7.2, Me–C(3)).

*Benzyl 6-(4-Chlorophenylsulfonyl)-1,3-*exo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl Ether* (**26**). Aq. H_2O_2 soln. (30%; 1.95 ml, 19 mmol) was added to **25** (0.736 g, 1.9 mmol) in AcOH (10 ml), and the mixture was kept at 20° for 3 days. H_2O (20 ml) and Et_2O (20 ml) were added. After separation and extraction of the aq. layer with Et_2O (3 ml, 5 times), the combined org. extracts were washed 3 times with sat. aq. $NaHCO_3$ soln. (20 ml). Each of the aq. layers was reextracted with Et_2O (3 ml, 5 times). Drying ($MgSO_4$) of the combined org. extracts, evaporation, and FC (Et_2O/light petroleum ether 1:2) yielded 0.753 g (99%) of colourless crystals. M.p. 108–110°. IR (KBr): 2980, 2930, 1640, 1450, 1305, 1140, 1080, 750, 665, 610. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.79, 7.50 (*2m*, 4 H); 7.33 (*m*, 5 H); 4.56 (*m*, PhCH_2); 4.24 (*s*, H–C(4)); 3.67 (*d*, *J* = 6.9, H–C(2)); 2.29 (*s*, Me–C(5)); 2.07 (*m*, H–C(3)); 1.47 (*s*, Me–C(1)); 1.10 (*d*, *J* = 7.2, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 163.8 (*s*, C(5)); 140.4,

140.0, 138.0, 137.0, 137.4 (4*s*); 129.5 (*d*, ^1J(C,H) ≈ 169); 128.5 (*d*, ^1J(C,H) = 167); 128.3, 127.6 (2*d*, ^1J(C,H) = 160); 91.6 (*s*, C(1)); 88.5 (*d*, ^1J(C,H) = 163, C(4)); 80.9 (*d*, ^1J(C,H) = 151, C(2)); 74.0 (*t*, ^1J(C,H) = 141, Ph*C*H$_2$); 36.4 (*d*, ^1J(C,H) = 134, C(3)); 14.1, 13.6 (2*q*, ^1J(C,H) = 128, 2 Me); 12.5 (*q*, ^1J(C,H) = 130, Me). CI-MS (NH_3): 438 (5, [(^{37}Cl)*M* + NH_4]$^+$), 437 (5), 436 (9, [(^{35}Cl)*M* + NH_4]$^+$), 270 (2), 148 (5), 119 (6), 108 (6), 91 (100). Anal. calc. for $C_{22}H_{23}ClO_4S$ (418.95): C 63.07, H 5.53; found: C 63.60, H 5.59.

*(1*RS,*2*SR,*3*SR,*6*SR*)-3-*O*-Benzyl-5-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diol* (= *(1*RS,*2*SR,*5*SR,*6*SR*)-5-(Benzyloxy)-3-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-3-en-1-ol*; **28**). $LiAlH_4$ (1M in THF; 8.6 ml, 8.6 mmol) was added dropwise to a stirred soln. of **26** (0.718 g, 1.7 mmol) in THF (20 ml) at −78° under Ar. After stirring at −78° for 2 h, a mixture of AcOH (3 ml) and MeOH (6 ml) was added. The temp. rose to −50°, and the cooling bath was removed. At 0°, brine (20 ml) was added. The aq. layer was extracted with Et_2O (5 ml, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (Et_2O/light petroleum ether 1:2, then 1:1): 0.623 g (86%) of **28** and 0.016 g (2%) of **30**. **28**: M.p. 125–127°. IR (KBr): 3500, 2960, 2880, 1300, 1140, 1080, 750, 740. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.82, 7.49 (2*m*, 2 H); 7.33–7.31 (*m*, 3 H); 7.17–7.13 (*m*, 2 H); 4.68 (*m*, PhCH_2); 3.78 (*d*, *J* = 4.1, H–C(3)); 3.65 (*ddd*, *J* = 2.1, 8.7, H–C(1)); 3.43 (*d*, *J* = 8.7, OH); 3.18 (*m*, H–C(6)); 2.15 (*m*, H–C(2)); 1.97 (*d*, *J* = 1.2, Me–C(4)); 1.33 (*d*, *J* = 7.1, Me–C(2)); 1.26 (*d*, *J* = 7.0, Me–C(6)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 144.7 (C(4)); 140.9, 140.4, 139.3, 136.9 (4*s*); 129.2 (*d*, ^1J(C,H) = 170); 128.5 (*d*, ^1J(C,H) = 159); 128.2 (*d*, ^1J(C,H) = 167); 128.2 (*d*, ^1J(C,H) ≈ 160); 127.5 (*d*, ^1J(C,H) ≈ 165); 82.5 (*d*, ^1J(C,H) = 143, C(3)); 77.0 (*t*, ^1J(C,H) = 143, Ph*C*H$_2$); 75.8 (*d*, ^1J(C,H) ≈ 140, C(1)); 41.1 (*d*, ^1J(C,H) = 134, C(6)); 32.3 (*d*, ^1J(C,H) = 124, C(2)); 19.5, 19.2 (2*q*, ^1J(C,H) = 129, 2 Me); 14.2 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 441 (10), 440 (39, [(^{37}Cl)*M* + NH_4]$^+$), 439 (28), 438 (100, [(^{35}Cl)*M* + NH_4]$^+$), 422 (1, (^{37}Cl)*M*$^+$), 420 (2, (^{35}Cl)*M*$^+$), 403 (5), 332 (9), 331 (9), 330 (8), 298 (7), 296 (7), 245 (6), 91 (45). Anal. calc. for $C_{22}H_{25}ClO_4S$ (420.97): C 62.77, H 5.99; found: C 62.72, H 5.95.

*Dibenzyl (1*RS,*2*SR,*3*SR,*6*SR*)-5-(4-Chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diyl Diether* (**29**). Trifluoromethanesulfonic acid (0.032 ml, 0.36 mmol) was added to a soln. of **28** (0.772 g, 1.8 mmol) and benzyl 2,2,2-trichloroacetimidate (1.03 ml, 5.5 mmol) in cyclohexane (10 ml) and CH_2Cl_2 (5 ml) at 20° under Ar. Stirring was continued for 3 h. Addition of brine (25 ml) and Et_2O (25 ml), extraction of the aq. phase with Et_2O (5 ml, 3 times), drying ($MgSO_4$), evaporation, and FC (Et_2O/light petroleum ether 1:8) gave an oil which was subsequently purified by FC ($CHCl_3$/light petroleum ether/acetone): 0.709 g (76%) of **29** and 34 mg (5%) of *(5*RS,*6*RS*)-5-(benzyloxy)-1-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohexa-1,3-diene* (anhydro-**30**).

Data of **29**: Colourless oil. IR ($CHCl_3$): 2960, 2860, 1440, 1300, 1140, 1080. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.73 (*m*, 2 H); 7.33–7.23 (*m*, 12 H); 4.56–4.53 (*m*, 4 H); 3.92 (*d*, *J* = 5.7, H–C(3)); 3.37 (*dd*, *J* = 4.4, 2.9, H–C(1)); 3.13 (*m*, H–C(6)); 2.38 (*m*, H–C(2)); 1.97 (br. *s*, Me–C(4)); 1.34 (*d*, *J* = 6.8, Me–C(6)); 1.11 (*d*, *J* = 7.0, Me–C(2)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 147.7 (C(4)); 141.4, 139.1, 138.3, 138.1 (5*s*); 129.1 (*d*, ^1J(C,H) = 170); 128.2 (*d*, ^1J(C,H) = 160); 128.0 (*d*, ^1J(C,H) = 168); 127.5, 127.4, 127.3 (3*d*, ^1J(C,H) = 160); 81.4 (*d*, ^1J(C,H) = 142); 78.9 (*d*, ^1J(C,H) = 136); 73.2 (*t*, ^1J(C,H) = 143); 71.4 (*t*, ^1J(C,H) = 141); 35.8 (*d*, ^1J(C,H) = 132, C(6)); 32.4 (*d*, ^1J(C,H) = 124, C(2)); 19.8, 18.0, 10.9 (3*q*, ^1J(C,H) = 128, 3 Me). CI-Ms (NH_3): 529 (1, [(^{35}Cl)*M* + H + NH_4]$^+$), 404 (1), 299 (1), 298 (2), 297 (2), 296 (3), 212 (3), 211 (3), 92 (67), 91 (100). Anal. calc. for $C_{29}H_{31}ClO_4S$ (511.09): C 68.15, H 6.11; found: C 67.95, H 6.21.

*Data of anhydro-***30**: ^{1}H-NMR (250 MHz, $CDCl_3$): 7.80 (*m*, 2 H); 7.38–7.22 (*m*, 7 H); 5.83 (*d*, *J* = 1.6, H–C(3)); 4.32 (*m*, PhCH_2); 3.48 (*d*, *J* = 1.5, H–C(5)); 3.23 (*m*, H–C(6)); 2.19 (*s*, Me–C(2)); 1.91 (*d*, *J* = 1.6, Me–C(4)); 1.16 (*d*, *J* = 7.1, Me–C(6)).

*(1*RS,*2*SR,*3*SR,*6*SR/RS*)-1-*O*-Benzyl-5-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diol* (= *(1*RS,*4*RS/SR,*5*SR,*6*RS*)-5-(Benzyloxy)-3-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-2-en-1-ol*; **30**). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.73 (*m*, 2 H); 7.41–7.15 (*m*, 7 H); 4.44 (*m*, PhCH_2); 3.66 (*dd*, *J* = 11.4, 4.6, H–C(3)); 3.55 (*m*, H–C(1)); 3.30 (*m*, H–C(6)); 2.95 (*d*, *J* = 11.4, OH); 2.11 (*d*, *J* = 1.0, Me–C(4)); 2.09 (*m*, H–C(2)); 1.31 (*d*, *J* = 7.0, Me–C(6)); 1.23 (*d*, *J* = 7.1, Me–C(2)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 149.5, 141.0, 139.3, 136.9 (4*s*); 129.2 (*d*, ^1J(C,H) = 169); 128.6 (*d*, ^1J(C,H) = 161); 128.1 (*d*, ^1J(C,H) = 167); 127.5 (*d*, ^1J(C,H) ≈ 165); 84.0 (*d*, ^1J(C,H) = 145, C(3)); 73.5 (*d*, ^1J(C,H) = 148, C(1)); 72.3 (*t*, ^1J(C,H) = 142, Ph*C*H$_2$); 35.4 (*d*, ^1J(C,H) = 133, C(6)); 31.2 (*d*, ^1J(C,H) = 124, C(2)); 19.4, 19.3, 13.7 (3*q*, ^1J(C,H) ≈ 128, 3 Me).

*Dibenzyl (1*RS,*2*RS,*3*RS,*6*SR*)-2,4,6-Trimethylcyclohex-4-ene-1,3-diyl Diether* (**31**). BuMgCl (2M in THF, 0.9 ml, 1.8 mmol) was added to a soln. of **29** (0.457 g, 0.89 mmol) and [Pd(CF_3COO)$_2$] (0.015 g, 0.045 mmol) in THF (30 ml). The mixture was stirred at 20° under Ar for 36 h, then brine (30 ml) was added. Filtration through *Celite*, separation, extraction of the aq. layer with Et_2O (3 ml, 5 times), drying ($MgSO_4$), evaporation, and FC (Et_2O/light petroleum ether 1:30) gave 0.169 g (56%) of colourless oil. IR ($CHCl_3$): 2960, 2920, 2860, 1440, 1095, 1055. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.45–7.36 (*m*, 10 H); 5.22 (*m*, H–C(5)); 4.64, 4.61 (*m*, 2 PhCH_2); 4.05 (*m*,

H–C(3)); 3.20 (*dd*, *J* = 9.4, 3.5, H–C(1)); 2.78 (*m*, H–C(6)); 2.39 (*m*, H–C(2)); 1.81 (*m*, Me–C(4)); 1.12, 1.04 (2*d*, *J* = 6.9, Me–C(2), Me–C(6)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 138.7, 133.0 (2*s*); 128.3 (*d*, ^1J(C,H) = 160, C(5)); 127.7, 127.6, 127.5, 127.4, 127.2 (5*d*, ^1J(C,H) = 160); 82.7 (*d*, ^1J(C,H) = 140); 79.2 (*d*, ^1J(C,H) = 144); 70.8, 70.5 (2*t*, ^1J(C,H) = 141); 32.8 (*d*, ^1J(C,H) = 125); 31.8 (*d*, ^1J(C,H) = 127); 19.3 (*q*, ^1J(C,H) = 127, Me); 18.4 (*q*, ^1J(C,H) = 130, Me); 6.5 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 337 (2, $[M + H]^+$), 336 (1, M^+), 245 (3), 188 (8), 123 (7), 91 (100). Anal. calc. for $C_{23}H_{28}O_2$ (336.48): C 82.10, H 8.39; found: C 82.28, H 8.45.

*(2*RS*,3*SR*,4*RS*,5*RS*)-3,5-Bis(benzyloxy)-2,4-dimethyl-6-oxoheptanal* (**32**). A mixture of **31** (0.089 g, 0.26 mmol), *N*-methylmorpholine *N*-oxide monohydrate (0.039 g, 0.29 mmol), OsO_4 (0.0065 g, 0.026 mmol), THF (1.25 ml), *t*-BuOH (1 ml), and H_2O (0.1 ml) was stirred at 20° for 54 h. Et_2O (20 ml) and H_2O (20 ml) were added. The aq. layer was extracted with Et_2O (3 ml, 3 times). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:2) yielded 0.071 g (72%) of colourless oil (mixture of diols). This product (0.051 g, 0.14 mmol) was dissolved in MeOH (2.5 ml) and stirred with $NaIO_4$ (0.065 g, 0.3 mmol), NH_4Cl (0.016 g, 0.3 mmol), and H_2O (1.5 ml) at 20° for 24 h. Et_2O (20 ml) and H_2O (20 ml) were added. Extraction of the aq. layer with Et_2O (3 ml, 3 times), washing with brine (20 ml) which was reextracted with Et_2O (3 ml, 3 times), drying ($MgSO_4$) of the combined org. extracts, and evaporation gave 0.049 g (97%) of yellowish oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 9.77 (*d*, *J* = 0.4, CHO); 7.39–7.21 (*m*, 10 H); 4.60, 4.34 (2*m*, 2 PhCH_2); 4.16 (*dd*, *J* = 9.0, 2.2, H–C(3)); 3.79 (*d*, *J* = 3.6, H–C(5)); 2.50 (*m*, H–C(2), H–C(4)); 2.06 (*s*, MeCO); 1.16 (*d*, *J* = 7.0, Me–C(4)); 1.00 (*d*, *J* = 7.1, Me–C(2)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 209.0 (*s*, C(6)); 204.0 (*d*, ^1J(C,H) = 167, CHO); 137.7, 137.6 (2*s*); 128.4, 128.2 (2*d*, ^1J(C,H) = 160); 128.0 (*d*, ^1J(C,H) = 156); 127.9 (*d*, ^1J(C,H) ≈ 160); 127.7 (*d*, ^1J(C,H) = 158); 127.5 (*d*, ^1J(C,H) = 160); 86.2 (*d*, ^1J(C,H) = 140); 77.5 (*d*, ^1J(C,H) = 136); 73.2, 72.5 (2*t*, ^1J(C,H) = 142, 2 PhCH_2); 48.9 (*dd*, $^n J$(C,H) = 122, 23, C(2)); 39.5 (*d*, ^1J(C,H) = 129, C(4)); 26,6 (*q*, ^1J(C,H) = 128, *Me*CO); 14.4, 6.9 (2*q*, ^1J(C,H) = 128, 2 Me).

*Benzyl 6-*exo*-(4-Chlorophenylthio)-1,3-*exo*-dimethyl-5-methylidene-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Ether* (**33**). A mixture of benzyl bromide (0.58 ml, 4.8 mmol), **19** (0.484 g, 1.6 mmol), Bu_4NBr (0.053 g, 0.16 mmol), toluene (20 ml), and 50% aq. NaOH soln. (2 ml) was stirred at 20° for 2 h. Brine (10 ml) was added, the aq. layer extracted with Et_2O (3 ml, 3 times), and the combined org. extract dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:8) yielded 0.488 g (77%) of **33**, colourless oil, and 0.06 g (12%) of **19**. **33**: ^{1}H-NMR (250 MHz, $CDCl_3$): 7.39 – 7.21 (*m*, 9 H); 5.18, 5.12 (2 *m*, CH_2=C(5)); 4.60 (*s*, H–C(6)); 4.54 (*m*, PhCH_2); 4.21 (*s*, H–C(4)); 3.33 (*d*, *J* = 2.6, H–C(2)); 1.90 (*qd*, *J* = 7.2, 2.6, H–C(3)); 1.48 (*s*, Me–C(1)); 1.15 (*d*, *J* = 7.2, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 151.7 (*s*, C(5)); 138.0, 135.7, 131.7 (3*s*); 130.4, 128.8 (2*d*, ^1J(C,H) ≈ 160); 128.4, 127.7, 127.2 (3*d*, ^1J(C,H) = 160); 107.2 (*t*, ^1J(C,H) = 160, CH_2=C(5)); 91.7 (*d*, ^1J(C,H) = 148, C(2)); 88.5 (*s*, C(1)); 86.3 (*d*, ^1J(C,H) = 160, C(4)); 72.6 (*t*, ^1J(C,H) = 142, PhCH_2); 50.8 (*d*, ^1J(C,H) = 149, C(6)); 45.4 (*d*, ^1J(C,H) = 133, C(3)); 19.4 (*q*, ^1J(C,H) = 125, Me); 18.1 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 389 (3, $[(^{37}Cl)M + NH_4]^+$), 388 (3, $(^{37}Cl)M^+$), 387 (6, $[(^{35}Cl)M + NH_4]^+$), 386 (5, $(^{35}Cl)M^+$), 295 (2), 243 (8), 109 (17), 91 (100).

*(1*RS*,5*RS*,6*SR*)-5-(Benzyloxy)-3-(4-chlorophenylthio)-4,6-dimethyl-2-methylidenecyclohex-3-en-1-ol.* BuLi (1.56M in hexane; 0.077 ml, 0.12 mmol) was added to the soln. of **33** (0.039 g, 0.01 mmol) in THF (2 ml) at –30° under Ar. After stirring at –30° for 1 h, AcOH (0.1 ml) was added and the cooling bath removed. Sat. aq. $NaHCO_3$ soln. (10 ml) and Et_2O (10 ml) were added at 0°. Separation, extraction with Et_2O (3 ml, 3 times), drying evaporation, and FC (Et_2O/light petroleum ether 1:2) yielded 10 mg (27%) of colourless oil (and 21 mg (54%) of **33**). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.40–7.31 (*m*, 5 H); 7.18, 7.06 (2*m*, 2 H); 5.67, 5.25 (2*s*, CH_2=C(2)); 4.63 (*m*, PhCH_2); 4.60 (*m*, H–C(1)); 3.92 (*d*, *J* = 4.9, H–C(5)); 2.38 (*m*, H–C(6)); 2.13 (*s*, Me–C(4)); 1.66 (*d*, *J* = 5.1, OH); 1.58 (*s*); 1.00 (*d*, *J* = 7.0, Me–C(6)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 145.6, 143.5, 137.9, 135.5, 130.8 (5*s*); 128.9 (*d*, ^1J(C,H) = 166); 128.4 (*d*, ^1J(C,H) = 160); 128.0, 127.9 (2*d*, ^1J(C,H) = 164); 113.9 (*t*, ^1J(C,H) = 160, CH_2=C(2)); 86.3 (*d*, ^1J(C,H) = 141); 72.0 (*t*, ^1J(C,H) = 143); 71.8 (*d*, ^1J(C,H) = 148); 37.2 (*d*, ^1J(C,H) = 130, C(5)); 20.2, 11.8 (2*q*, ^1J(C,H) = 128, 2 Me). CI-MS (NH_3): 388 (2, $(^{37}Cl)M^+$), 386 (6, $(^{35}Cl)M^+$), 335 (4), 295 (11), 282 (8), 281 (40), 280 (22), 279 (100), 249 (5).

*6-(4-Chlorophenylthio)-1,3-*exo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol* (**34**). MeONa (5.4M in MeOH; 2.26 ml, 12.2 mmol) was added to a soln. of **19** (0.724 g, 2.4 mmol) in MeOH (20 ml), and the mixture was heated under reflux for 3 days. Brine (20 ml) and Et_2O (20 ml) were added. The aq. layer was extracted with Et_2O (5 ml, 5 times) and the combined org. extract dried ($MgSO_4$) and evaporated giving an oil which was used directly in the next reaction. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.29–7.20 (*m*, 4 H); 4.27 (*s*, H–C(4)); 3.56 (*dd*, *J* = 6.1, 2.0, H–C(2)); 1.99 (*s*, Me–C(5)); 1.65 (*d*, *J* = 6.3, OH); 1.46 (*m*, H–C(3)); 1.39 (*s*, Me–C(1)); 1.29 (*d*, *J* = 6.9, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 156.4 (*s*, C(5)); 135.1, 131.7, 129.7 (3*s*); 129.2 (*d*, ^1J(C,H) = 164); 128.9 (*d*, ^1J(C,H) = 167); 90.1 (*s*, C(1)); 87.5 (*d*, ^1J(C,H) = 162, C(4)); 85.2 (*d*, ^1J(C,H) = 152, C(2)); 44.4 (*d*, ^1J(C,H) = 130, C(3)); 18.1 (*q*, ^1J(C,H) = 125, Me); 15.9 (*q*, ^1J(C,H) = 126, Me); 12.1 (*q*, ^1J(C,H) = 128, Me).

*Benzyl 6-(4-Chlorophenylthio)-1,3-*exo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Ether* (**35**). Benzyl bromide (0.87 ml, 7.3 mmol), crude **34**, and Bu_4NBr (0.079 g, 0.24 mmol) in toluene (50 ml) were stirred at 20° with 50% aq. NaOH soln. (3 ml) for 3 days. Brine (25 ml) was added, the aq. layer extracted with Et_2O (5 ml, 3 times), and the combined org. extract dried ($MgSO_4$), and evaporated. FC (Et_2O/light petroleum ether 1:8) gave 0.819 g (87% based on **19**) of colourless oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.35–7.17 (*m*, 9 H); 4.56 (*m*, PhCH_2); 4.27 (*s*, H–C(4)); 3.34 (*d*, *J* = 2.1, H–C(2)); 1.93 (*s*, Me–C(5)); 1.62 (*qd*, *J* = 7.1, 2.1, H–C(3)); 1.47 (*s*, Me–C(1)); 1.24 (*d*, *J* = 7.1, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 155.5 (C(5)); 138.3, 135.8, 131.1, 130.7 (4*s*); 128.7 (*d*, ^1J(C,H) = 166); 128.2, 127.5, 127.2 (3*d*, ^1J(C,H) ≈ 160); 91.8 (*d*, ^1J(C,H) = 149, C(2)); 87.7 (*d*, ^1J(C,H) = 162, C(4)); 72.4 (*t*, ^1J(C,H) = 142, PhCH_2); 42.2 (*d*, ^1J(C,H) = 134, C(3)); 18.8, 17.0, 12.1 (3*q*, ^1J(C,H) = 128, 3 Me).

*Benzyl 6-(4-Chlorophenylsulfonyl)-1,3-*exo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Ether* (**36**). Aq. H_2O_2 soln. (30%; 2.16 ml, 21 mmol) was added to a soln. of **35** (0.819 g, 2.1 mmol) in AcOH (20 ml) and the mixture was stirred at 20° for 3 days. Brine (30 ml) and Et_2O (30 ml) were added. The aq. layer was extracted with Et_2O (3 ml, 3 times) and the combined org. extract dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:2) yielded 0.767 g (75% based on **19**) of **35**. M.p. 76–77°. IR (KBr): 2950, 2920, 2860, 1615, 1310, 1145, 1080, 750, 610. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.84 (*m*, 2 H); 7.39–7.28 (*m*, 7 H); 4.45 (*m*, PhCH_2); 4.16 (*s*, H–C(4)); 3.26 (*d*, *J* = 2.2, H–C(2)); 2.24 (*s*, Me–C(5)); 1.72 (*s*, Me–C(1)); 1.58 (*qd*, *J* = 7.1, 2.2, H–C(3)); 1.17 (*s*, *J* = 7.1, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 160.7 (C(5)); 141.2, 140.1, 139.4, 137.9 (4*s*); 129.0 (*d*, ^1J(C,H) = 168); 128.3, 127.7, 127.6 (3*d*, ^1J(C,H) = 160); 90.5 (*d*, ^1J(C,H) = 145, C(2)); 88.3 (*d*, ^1J(C,H) = 164, C(4)); 72.6 (*t*, ^1J(C,H) = 141, PhCH_2); 41.6 (*d*, ^1J(C,H) = 135, C(3)); 18.7 (*q*, ^1J(C,H) = 130, Me); 17.4, 12.4 (2*q*, ^1J(C,H) = 128, 2 Me). CI-MS (NH_3): 439 (5), 438 (9, [(^{37}Cl)*M* + NH_4]$^+$), 437 (15), 426 (12, [(^{35}Cl)*M* + NH_4]$^+$), 421 (2, [(^{37}Cl)*M* + H]$^+$), 420 (2), 419 (5, [(^{35}Cl)*M* + H]$^+$), 290 (2), 289 (3), 288 (7), 270 (4), 149 (5), 148 (5), 91 (100). Anal. calc. for $C_{22}H_{23}ClO_4S$ (418.95): C 63.07, H 5.53; found: C 63.12, H 5.52.

(1RS,2SR,3RS,6SR)-3-O-Benzyl-5-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diol (= *(1RS,2SR,5RS,6SR)-5-(Benzyloxy)-3-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-3-en-1-ol*; **37**). To a soln. of **36** (0.753 g, 1.8 mmol) in THF (20 ml), $LiAlH_4$ (1M in THF; 9 ml, 9 mmol) was added dropwise over 10 min at −78° under Ar. After stirring at −78° for 2 h, a mixture of AcOH (3 ml) and MeOH (6 ml) was added. The temp. rose to −50°, and the cooling bath was removed. At 0°, brine (20 ml) was added and the layers separated. Extraction with Et_2O (5 ml, 3 times), drying of the combined extracts, evaporation, and FC (Et_2O/light petroleum ether 1:2, then 1:1) gave 0.112 g (15%) of **36** and a material which was subsequently purified by FC ($CHCl_3$/acetone 60:1); 0.601 g (79%) of **37**. M.p. 128–129°. IR (KBr): 3480, 3080, 2960, 2870, 1450, 1280, 1140, 1080, 750, 670. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.85, 7.48 (2*m*, 4 H); 7.37–7.30 (*m*, 5 H); 4.47 (*m*, PhCH_2); 3.93 (*d*, *J* = 9,6, H–C(3)); 3.75 (*m*, H–C(1)); 3.03 (*m*, H–C(6)); 2.58 (*s*, OH); 2.24 (*m*, H–C(2)); 2.02 (*s*, Me–C(4)); 1.35 (*d*, *J* = 6.9, Me–C(6)); 1.20 (*d*, *J* = 6.7, Me–C(2)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 148.7 (C(4)); 140.9, 139.6, 139.4, 137.6 (4*s*); 129.3 (*d*, ^1J(C,H) = 169); 128.5 (*d*, ^1J(C,H) = 160); 128.2 (*d*, ^1J(C,H) = 167); 127.9, 127.6 (2*d*, ^1J(C,H) ≈ 160); 82.5 (*d*, ^1J(C,H) = 145, C(3)); 76.5 (*d*, ^1J(C,H) ≈ 140, C(1)); 71.3 (*t*, ^1J(C,H) = 141, PhCH_2); 39.9 (*d*, ^1J(C,H) = 133, C(6)); 32.3 (*d*, ^1J(C,H) = 123, C(2)); 20.0, 16.6, 15.3 (3*q*, ^1J(C,H) = 128, 3 Me). CI-MS (NH_3): 441 (4), 440 (12, [(^{37}Cl)*M* + NH_4]$^+$), 439 (9), 438 (28, [(^{35}Cl)*M* + NH_4]$^+$), 404 (6), 332 (4), 245 (6), 91 (100). Anal. calc. for $C_{22}H_{25}ClO_4S$ (420.97): C 62.77, H 5.99; found: C 62.83, H 5.91.

Dibenzyl (1RS,2SR,3RS,6SR)-5-(4-Chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diyl Diether (**38**). Trifluoromethanesulfonic acid (0.012 ml, 0.14 mmol) was added to a soln. of **37** (0.132 g, 0.31 mmol) and benzyl 2,2,2-trichloroacetimidate (0.12 ml, 0.64 mmol) in cyclohexane (6 ml) and CH_2Cl_2 (3 ml). Stiring at 20° was continued for 4 h. Sat. aq. $NaHCO_3$ soln. (5 ml) and Et_2O (10 ml) were added. The aq. layer was extracted with Et_2O (3 ml, 3 times), which was washed with brine (10 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated: 0.148 g (92%) of colourless crystals. M.p. 113–115°. IR (KBr): 3020, 2950, 2920, 2870, 1450, 1300, 1145, 1075, 1055, 750. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.74 (*m*, 2 H); 7.38–7.22 (*m*, 12 H); 4.58–4.38 (*m*, 4 H); 3.96 (*d*, *J* = 9.7, H–C(3)); 3.47 (*m*, H–C(1)); 3.21 (*m*, H–C(6)); 2.33 (*m*, H–C(2)); 2.06 (*s*, Me–C(4)); 1.38 (*d*, *J* = 6.9, Me–C(6)); 1.21 (*d*, *J* = 6.6, Me–C(2)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 149.4 (C(4)); 141.0, 139.4, 139.2, 138.1, 137.8 (5*s*); 129.2 (*d*, ^1J(C,H) = 169); 128.5, 128.4 (2*d*, ^1J(C,H) = 160); 128.1 (*d*, ^1J(C,H) = 167); 127.8, 127.7, 127.6, 127.5 (4*d*, ^1J(C,H) = 160); 83.8 (*d*, ^1J(C,H) = 143); 83.0 (*d*, ^1J(C,H) = 141); 71.6 (*t*, ^1J(C,H) = 141, PhCh_2); 71.2 (*t*, ^1J(C,H) = 143, PhCH_2); 35.0 (*d*, ^1J(C,H) = 131, C(6)); 32.1 (*d*, ^1J(C,H) = 125, C(2)); 20.2, 16.6, 15.5 (3*q*, ^1J(C,H) = 128, 3 Me). CI-MS (NH_3): 531 (4), 530 (11, [(^{37}Cl)*M* + NH_4]$^+$), 529 (10), 528 (20, [(^{35}Cl)*M* + NH_4]$^+$), 494 (3), 354 (4), 246 (2), 188 (6), 91 (100). Anal. calc. for $C_{29}H_{31}ClO_4S$ (511.09): C 68.15, H 6.11; found: C 68.34, H 5.88.

Dibenzyl (1RS,2RS,3SR,6SR)-2,4,6-Trimethylcyclohex-4-ene-1,3-diyl Diether (**39**). BuMgCl (2M in THF; 0.15 ml, 0.3 mmol) was added to a soln. of **38** (0.051 g, 0.1 mmol) and [$Pd(CF_3COO)_2$] (0.0016 g, 0.005 mmol) in

THF (2 ml). The mixture was stirred at 20° under Ar for 4 days, then H_2O (10 ml) and Et_2O (10 ml) were added. Filtration through *Celite*, separation, extraction with Et_2O (3 ml, 3 times), drying ($MgSO_4$), evaporation, and FC (Et_2O/light petroleum ether 1:25, then 1:3) yielded **38** (27%) and **39** (20%) and unknown compounds. **39**: IR ($CHCl_3$): 2960, 2860, 1440, 1370, 1090, 1060. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.40–7.28 (*m*, 10 H); 5.29 (*s*, H–C(4)); 4.65–4.43 (*m*, 4 H); 3.52 (*d*, *J* = 2.2, H–C(3)); 3.43 (*dd*, *J* = 8.9, 3.8, H–C(1)); 2.43 (*m*, H–C(2)); 2.23 (*m*, H–C(6)); 1.72 (*s*, Me–C(4)); 1.08 (*d*, *J* = 7.0, Me–C(6)); 0.90 (*d*, *J* = 7.2, Me–C(2)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 138.9, 138.7, 130.5 (3*s*); 130.1 (*d*, ^1J(C,H) = 154, C(5)); 128.3, 128.2, 128.0, 127.9 (4*d*, ^1J(C,H) = 160); 127.6 (*d*, ^1J(C,H) = 167); 127.4 (*d*, ^1J(C,H) = 160); 82,6 (*d*, ^1J(C,H) = 139); 80.2 (*d*, ^1J(C,H) = 143); 72.0, 71.0 (2*t*, ^1J(C,H) = 141); 32.5, 32.2 (2*d*, ^1J(C,H) = 126); 21.0, 18.1, 10.9 (3*q*, ^1J(C,H) = 126, 3 Me).

Base-Induced Isomerisation of **17**. *E.g.* in MeOH containing MeONa, the products **40**–**42** were formed from **17** together with products of decomposition.

6-exo-*(4-Chlorophenylthio)-1,3*-endo-*dimethyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2-one* (**40**): ^{1}H-NMR (250 MHz, $CDCl_3$): 7.36, 7.28 (*m*, 4 H); 5.42, 5.32 (2*m*, CH_2=C(5)); 4.87 (*d*, *J* = 5.9, H–C(4)); 3.65 (*s*, H–C(6)); 2.69 (*dq*, *J* = 7.2, 5.9, H–C(3)); 1.45 (*s*, Me–C(1)); 1.02 (*d*, *J* = 7.2, Me–C(3)).

6-(4-Chlorophenylthio)-1,3-endo,*5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one* (**41**): ^{1}H-NMR (250 MHz, $CDCl_3$): 7.23 (*m*, 4 H); 4.99 (*d*, *J* = 4.5, H–C(4)); 2.46 (*dq*, *J* = 7.2, 4.5, H–C(3)); 2.01 (*s*, Me–C(5)); 1.29 (*s*, Me–C(1)); 1.04 (*d*, *J* = 7.2, Me–C(3)).

6-(4-Chlorophenylthio)-1,3-exo,*5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one* (**42**): ^{1}H-NMR (250 MHz, $CDCl_3$): 7.22 (*m*, 4 H); 4.68 (*s*, H–C(4)); 1.99 (*q*, *J* = 7.4, H–C(3)); 1.97 (*s*, Me–C(5)); 1.28 (*d*, *J* = 7.4, Me–C(3)); 1.27 (*s*, Me–C(1)).

6-exo-*(4-Chlorophenylthio)-1-methyl-3,5-dimethylidene-7-oxabicyclo[2.2.1]heptan-2-one* (**43**). $(Me_3Si)_2NK$ (15% in toluene; 3 ml, 2 mmol) was added to a soln. of **16** (0.280 g, 1 mmol) in THF (10 ml) stirred at −78° under Ar. After stirring at −78° for 1 h, Me_3SiCl (0.38 ml, 3 mmol) was added, and stirring was continued for 1 h. The cooling bath was removed, the solvent evaporated, and the residue dissolved in DMF (10 ml) and stirred with *N,N*-dimethylmethylideneammonium iodide (0.370, 2 mmol) at 20° for 24 h under Ar. Then MeI (0.31 ml, 5 mmol) was added and, after another 12 h of stirring, $NaHCO_3$ (0.84 g, 10 mmol) was added. Stirring at 20° was continued for further 24 h, then H_2O (50 ml) and Et_2O (25 ml) were added. The aq. layer was extracted with Et_2O (5 ml, 3 times) and the combined Et_2O extracts dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:8) gave 190 mg (65%) of yellowish crystals. M.p. 73°. IR (KBr): 1735, 1470, 1090, 1015, 940, 930, 915, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.37, 7.28 (2*m*, 2 H); 5.93 (*d*, *J* = 1.2, 1 H); 5.45 (*d*, *J* = 0.9, 1 H, CH_2=C(3)); 5.43, 5.33 (2*m*, 2 H, CH_2=C(5)); 5.21 (*d*, *J* = 0.7, H–C(4)); 3.88 (*s*, H–C(6)); 1.49 (*s*, Me–C(1)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 200.5 (*s*, C(2)); 147.9 (*s*, C(5)); 143.8 (*s*, C(3)); 133.5, 133.2 (2*s*); 132.1 (*d*, ^1J(C,H) = 165); 129.2 (*d*, ^1J(C,H) = 167); 114.3 (*t*, ^1J(C,H) = 163, CH_2=C); 111.2 (*t*, ^1J(C,H) = 160, CH_2=C); 89.7 (*s*, C(1)); 81.8 (*d*, ^1J(C,H) = 166, C(4)); 52.9 (*d*, ^1J(C,H) = 153, C(6)); 13.5 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 313 (5), 312 (6, $[(^{37}Cl)M + NH_4]^+$), 311 (16), 310 (12, $[(^{35}Cl)M + NH_4]^+$), 296 (24), 295 (41, $[(^{37}Cl)M + H]^+$), 294 (63, $[(^{37}Cl)M + H]^+$), 293 (67, $[(^{35}Cl)M + H]^+$), 292 (40, $(^{35}Cl)M^+$), 253 (11), 252 (35), 251 (29), 250 (100), 249 (18), 222 (10), 187 (7), 186 (7), 150 (16), 122 (13), 106 (58). Anal. calc. for $C_{15}H_{13}ClO_2S$ (292.79): C 61.53, H 4.48; found: C 61.36, H 4.44.

6-exo-*(4-Chlorophenylthio)-1,3*-endo-*dimethyl-5-methylidene-7-oxabicyclo[2.2.1]heptan-2*-endo-*ol* (**44**). *K-Selectride* (1M in THF; 6 ml, 6 mmol) was added dropwise to a stirred soln. of **43** (0.698 g, 2.4 mmol) in EtOH (35 ml) at −78° under Ar. After stirring at −78° for 1 h, the cooling bath was removed and at 0°, 3M aq. NaOH (8 ml, 24 mmol) and 30% aq. H_2O_2 soln. (2.5 ml, 24 mmol) were added. After stirring at 0° for 1 h, brine (25 ml) and Et_2O (25 ml) were added. The aq. phase was extracted with Et_2O (5 ml, 3 times) and the combined org. extract dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:2) yielded 0.643 (91%). M.p. 127–130°. IR (KBr): 3430, 2970, 2920, 1470, 1085, 1005, 890, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.35, 7.25 (2*m*, 4 H); 5.27, 5.12 (2*m*, CH_2=C(5)); 4.47 (*d*, *J* = 5.4, H–C(4)); 4.44 (*s*, H–C(6)); 3.99 (*dd*, *J* = 9.6, 4.5, H–C(2)); 2.38 (*m*, H–C(3)); 1.64 (*d*, *J* = 4.5, OH); 1.49 (*s*, Me–C(1)); 0.86 (*d*, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 148.1 (*s*, C(5)); 135.6, 131.8 (2*s*); 130.4 (*d*, ^1J(C,H) = 164); 128.9 (*d*, ^1J(C,H) = 166); 110.2 (*t*, ^1J(C,H) = 160, CH_2=C(5)); 89.1 (*s*, C(1)); 84.9 (*d*, ^1J(C,H) = 165, C(4)); 76.0 (*d*, ^1J(C,H) = 151, C(2)); 50.8 (*d*, ^1J(C,H) = 147, C(6)); 38.6 (*d*, ^1J(C,H) = 135, C(3)); 18.0, 9.7 (2*q*, ^1J(C,H) = 127, 2 Me). CI-MS (NH_3): 316 (4, $[(^{37}Cl)M + NH_4]^+$), 315 (4), 314 (14, $[(^{35}Cl)M + NH_4]^+$), 299 (2, $[(^{37}Cl)M + H]^+$), 298 (3, $(^{35}Cl)M^+$), 297 (5, $[(^{35}Cl)M + H]^+$), 296 (9, $(^{35}Cl)M^+$), 281 (4), 279 (9), 255 (4), 253 (7), 225 (3), 223 (7), 222 (6), 153 (31), 152 (32), 144 (36), 109 (100). Anal. calc. for $C_{15}H_{17}ClO_2S$ (296.82): C 60.70, H 5.77; found: C 60.62, H 5.91.

6-(4-Chlorophenylthio)-1,3-endo,*5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2*-endo-*ol* (**45**). MeONa (5.4M in MeOH; 2 ml, 10.8 mmol) was added to a stirred soln. of **44** (0.634 g, 2.1 mmol) in MeOH (20 ml). The mixture was heated under reflux for 3 days. Brine (20 ml) and Et_2O (20 ml) were added after cooling to 20° The aq. layer was

extracted with Et_2O (5 ml, 5 times) and the org. extract dried ($MgSO_4$) and evaporated. Crystallization from heptane/Et_2O yielded 0.459 g (72%) of **45**. M.p. 110°. IR (KBr): 3540, 2920, 1740, 1465, 1380, 1255, 1215, 1050, 1040, 1000, 960, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.25 (*m*, 4 H); 4.64 (*d*, *J* = 4.7, H–C(4)); 3.96 (*m*, C(2)); 2.53 (*m*, H–C(3)); 2.01 (*s*, Me–C(5)); 1.41 (*s*, Me–C(1)); 1.31 (*d*, *J* = 7.0, OH); 0.81 (*d*, *J* = 7.4, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 155.1 (*s*, C(5)); 134.9, 131.8, 130.8 (3*s*); 129.4 (*d*, ^1J(C,H) = 165); 128.9 (*d*, ^1J(C,H) = 167); 89.9 (*s*, C(1)); 85.4 (*d*, ^1J(C,H) = 162, C(4)); 76.0 (*d*, ^1J(C,H) = 158, C(2)); 38.8 (*d*, ^1J(C,H) = 135, C(3)); 16.5, 14.4, 10.2 (3*q*, ^1J(C,H) = 127, 3 Me). CI-MS (NH_3): 316 (2, $[(^{37}Cl)M + NH_4]^+$), 314 (5, $[(^{35}Cl)M + NH_4]^+$), 299 (19, $[(^{37}Cl)M + H]^+$), 298 (9), 297 (49, $[(^{35}Cl)M + NH]^+$), 281 (9), 279 (23), 240 (39), 238 (100). Anal. calc. for $C_{15}H_{17}ClO_2S$ (296.82): C 60.70, H 5.77; found: C 60.88, H 5.92.

*Benzyl 6-(4-Chlorophenylthio)-1,3-*endo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Ether* (**46**). Benzyl bromide (0.53 ml, 4.5 mmol), **45** (0.442 g, 1.5 mmol), Bu_4NBr (0.048 g, 0.15 mmol), toluene (25 ml), and 50% aq. NaOH soln. (3 ml) were stirred at 20° for 36 h. Brine (20 ml) was added, the aq. phase extracted with Et_2O (5 ml, 3 times), and the combined org. extract dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:8) gave 511 mg (88%) of **46** and 35 mg (8%) of starting material. IR (CH_2Cl_2): 2920, 1105, 1085, 1005, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.35–7.16 (*m*, 9 H); 4.66–4.53 (*m*, 3 H); 3.73 (*d*, *J* = 8.0, H–C(2)); 2.63 (*m*, H–C(3)); 1.94 (*s*, Me–C(5)); 1.46 (*s*, Me–C(1)); 0.84 (*d*, *J* = 7.3, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 153.9 (*s*, C(5)); 138.5, 135.6, 131.7, 131.1 (4*s*); 129.1, 128.7 (2*d*, ^1J(C,H) = 166); 128.2, 127.4, 127.3 (3*d*, ^1J(C,H) = 160); 89.5 (*s*, C(1)); 85.5 (*d*, ^1J(C,H) = 162, C(4)); 83.2 (*d*, ^1J(C,H) = 150, C(2)); 73.2 (*t*, ^1J(C,H) = 141, PhCH_2); 39.5 (*d*, ^1J(C,H) = 135, C(3)); 17.4, 14.4, 10.6 (3*q*, ^1J(C,H) = 127, 3 Me). CI-MS (NH_3): 406 (5, $[(^{37}Cl)M + NH_4]^+$), 405 (4), 404 (10, $[(^{35}Cl)M + NH_4]^+$), 390 (7), 389 (23, $[(^{27}Cl)M + H]^+$), 388 (17), 387 (52, $[(^{35}Cl)M + H]^+$), 353 (10), 281 (6), 279 (16), 240 (38), 238 (100), 204 (20), 91 (91). Anal. calc. for. $C_{22}H_{23}ClO_2S$ (386.95): C 68.29, H 5.99; found: C 68.52, H 6.03.

*Benzyl 6-(4-Chlorophenylsulfonyl)-1,3-*endo*,5-trimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Ether* (**47**). Aq. H_2O_2 soln. (30%; 1.3 ml, 13 mmol) was added to a stirred soln. of **46** (0.487 g, 1.3 mmol) in AcOH (10 ml) and kept at 20° for 3 days. H_2O (50 ml) and Et_2O (25 ml) were added. The aq. phase was extracted with Et_2O (5 ml, 3 times) and the extract washed with H_2O (50 ml) and sat. aq. K_2CO_3 soln. (25 ml), dried ($MgSO_4$), and evaporated: 0.527 g (100%) of colourless oil. IR (CH_2Cl_2): 2920, 1310, 1140, 1110, 1085. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.84 (*m*, 2 H); 7.36–7.30 (*m*, 7 H); 4.54 (*m*, 2 H); 4.50 (*d*, *J* = 5.0, H–C(4)); 3.70 (*d*, *J* = 8.2, H–C(2)); 2.62 (*m*, H–C(3)); 2.18 (*s*, Me–C(5)); 1.73 (*s*, Me–C(1)); 0.76 (*d*, *J* = 7.3, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 160.6 (*s*, C(5)); 141.3, 140.8, 139.2, 138.1 (4*s*); 129.0 (*d*, ^1J(C,H) = 167); 128.3, 127.9, 127.7 (3*d*, ^1J(C,H) = 160); 89.5 (*s*, C(1)); 86.0 (*d*, ^1J(C,H) = 164, C(4)); 82.0 (*d*, ^1J(C,H) = 150, C(2)); 73.4 (*t*, ^1J(C,H) = 142, PhCH_2); 38.8 (*d*, ^1J(C,H) = 136, C(3)); 17.9, 14.9, 10.4 (3*q*, ^1J(C,H) = 128, 3 Me).

*Benzyl 6-*endo*-(4-Chlorophenylsulfonyl)-1,3-*endo*,5-*endo*-trimethyl-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Ether* (**49**). Aq. AcONa soln. (0.108 g, 1.3 mmol) was added portionwise over 2 h to a soln. of **47** (0.138 g, 0.33 mmol) and $TsNHNH_2$ (0.184 g, 0.99 mmol) in DME (2 ml) heater under reflux. Heating was continued for 4 h, then the sequence was repeated twice: addition of $TsNHNH_2$ (0.184 g, 0.99 mmol), addition of AcONa (0.108 g, 1.3 mmol) in H_2O (1.5 ml) over 2 h, heating for 16 h, addition of $TsNHNH_2$ (0.184 g, 0.99 mmol) and DME (1 ml), addition of AcONa (0.108, 1.3 mmol) in H_2O (1.5 ml) over 2 h, heating for 24 h. After cooling to 20°, brine (25 ml) and Et_2O (25 ml) were added. The aq. layer was extracted with Et_2O (3 ml, 7 times) and the combined org. extract dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:3) gave 0.117 g (84% based on **46**) of **49** and 16 mg (12%) of **47**. **49**: M.p. 140–141°. IR (KBr): 3080, 2960, 2860, 1305, 1145, 1085, 990, 750. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.84 (*m*, 2 H); 7.51–7.46 (*m*, 4 H); 7.41–7.29 (*m*, 3 H); 4.76 (*m*, 2 H); 4.16 (*t*, *J* = 5.2, H–C(4)); 3.75 (*d*, *J* = 10.1, H–C(2)); 3.51 (*d*, *J* = 11.5, H–C(6)); 2.75–2.50 (*m*, H–C(3), H–C(5)); 1.68 (*s*, Me–C(1)); 1.46 (*d*, *J* = 7.9, Me–C(5)); 1.26 (*d*, *J* = 7.8, Me–C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 142.1, 139.4, 138.4 (3*s*); 129.4, 129.2 (2*d*, ^1J(C,H) = 168); 128.2, 128.1, 127.4 (3*d*, ^1J(C,H) = 160): 90.8 (*s*, C(1)); 84.3 (*d*, ^1J(C,H) = 156, C(4)); 82.5 (*d*, ^1J(C,H) = 149, C(2)); 73.8 (*t*, ^1J(C,H) = 143, PhCH_2); 71.7 (*d*, ^1J(C,H) = 135, C(6)); 40.8 (*d*, ^1J(C,H) = 129, C(5)); 39.4 (*d*, ^1J(C,H) = 132, C(3)); 22.4, 11.8, 9.8 (3*q*, ^1J(C,H) = 127, 3 Me). Anal. calc. for $C_{22}H_{25}ClO_4S$ (420.97): C 62.77, H 5.99; found: C 63.52, H 5.90.

*(1*RS*,2*RS*,3*RS*,6*SR*)-3-O-Benzyl-5-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diol* (= *(1*RS*,2SR,5*RS*,6*RS*)-5-(Benzyloxy)-3-(4-chlorophenylsulfonyl)-2,4,6-trimethylcyclohex-3-en-1-ol*; **48**). BuLi (1.86M in hexane; 0.52 ml, 0.97 mmol) was added dropwise to a stirred soln. of **49** (0.273 g, 0.65 mmol) in THF (10 ml) at −78° over 3 min. Stirring was continued at −78° for 15 min, then Me_3Al (2M in toluene; 0.97 ml, 1.94 mmol) was added dropwise over 3 min, and the cooling bath was removed. The soln. was stirred at 20° overnight (12 h), sat. aq. NH_4Cl soln. (25 ml) and Et_2O were added, and the mixture was filtered through *Celite* which was washed with Et_2O. The combined Et_2O soln. was dried ($MgSO_4$) and evaporated FC (Et_2O/light petroleum ether 1:1)

yielded 0.198 g (73%) of **48** and 2 mg (1%) of **50**. An anal. sample of **48** was obtained by FC ($CHCl_3$/AcOEt 50:1).

Data of **48**: colourless oil. IR ($CHCl_3$): 3600, 2960, 2870, 1575, 1390, 1300, 1140, 1085. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.79, 7.48 (2*m*, 2 H); 7.35–7.28 (*m*, 5 H); 4.60 (*m*, 2 H); 3.79 (*d*, *J* = 3.4, H–C(6)); 3.67 (*dd*, *J* = 9.5, 5.1, H–C(4)); 2.75 (*m*, H–C(3)); 2.07 (br. *s*, OH); 2.04 (*d*, *J* = 1.6, Me–C(1)); 1.77 (*m*, H–C(5)); 1.44 (*d*, *J* = 6.9, Me–C(3)); 1.17 (*d*, *J* = 6.9, Me–C(5)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 147.8 (*s*, C(1)); 141.3, 140.9, 139.3, 137.8 (4*s*); 129.3 (*d*, ^1J(C,H) = 169); 128.4 (*d*, ^1J(C,H) = 160); 128.1 (*d*, ^1J(C,H) = 167); 127.8, 127.5 (2*d*, ^1J(C,H) ≈ 160); 82.5 (*d*, ^1J(C,H) = 142, C(4) or C(6)); 76.3 (*d*, ^1J(C,H) ≈ 144, C(4) or C(6)); 74.1 (*t*, ^1J(C,H) = 142, Ph*C*H$_2$); 41.8 (*d*, ^1J(C,H) = 131); 39.6 (*d*, ^1J(C,H) = 125, C(3)); 20.8, 20.3, 14.0 (3*q*, ^1J(C,H) ≅ 127, 3 Me). Anal. calc. for $C_{22}H_{25}ClO_4S$ (420.97): C 62.77, H 5.99; found: C 63.73, H 6.05.

*Data of Benzyl 6-*exo*-(4-Chlorophenylsulfonyl)-1,3-*endo*,5-*endo*-trimethyl-7-oxabicyclo[2.2.1]hept-2-*endo*-yl Ether* (**50**). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.83, 7.53 (2*m*, 2 H); 7.39–7.28 (*m*, 5 H); 4.56 (*m*, 2 H); 4.16 (*t*, *J* = 5.1, H–C(4)); 3.74 (*d*, *J* = 7.4, H–C(6)); 3.60 (*d*, *J* = 9.6, H–C(2)); 2.66–2.47 (*m*, H–C(3), H–C(5)); 1.78 (*s*, Me–C(1)); 1.07 (*d*, *J* = 7.8, Me–C(3)); 0.72 (*d*, *J* = 7.5, Me–C(5)).

*(1*RS*,2*SR*,3*RS*,6*SR*)-3-*O*-Benzyl-5-(4-chlorophenylsulfonyl)-1-*O*-(methoxymethyl)-2,4,6-trimethylcyclohex-4-ene-1,3-diol* (= *(3*RS*,4*SR*,5*RS*,6*SR*)-3-(Benzyloxy)-1-(4-chlorophenylsulfonyl)-5-(methoxymethoxy)-2,4,6-trimethylcyclohex-1-ene*; **51**). A mixture of **48** (0.040 g, 0.095 mmol), dimethoxymethane (0.5 ml, 5.6 mmol), $CHCl_3$ (1.5 ml), and P_2O_5 (0.14 g, 0.98 mmol) was stirred at 20° for 1 h. H_2O (10 ml) and Et_2O (10 ml) were added. The aq. phase was extracted with Et_2O (3 ml, 3 times) and the combined org. extract dried ($MgSO_4$) and evaporated. FC (Et_2O/light petroleum ether 1:2) yielded 0.031 g (70%) of colourless oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.80, 7.49 (2*m*, 4 H); 7.36–7.28 (*m*, 5 H); 4.68, 4.53 (2*m*, 4 H); 3.83 (*d*, *J* = 3.6, H–C(6)); 3.66 (*dd*, *J* = 7.7, 2.5, H–C(4)); 3.38 (*s*, MeO); 2.99 (*m*, H–C(3)); 2.07 (*d*, *J* = 1.2, Me–C(1)); 1.88 (*m*, H–C(5)); 1.47 (*d*, *J* = 7.1, Me–C(3)); 1.13 (*d*, *J* = 7.0, Me–C(5)). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 148.5 (*s*, C(1)); 141.1, 140.8, 139.3, 137.8 (4*s*); 129.2 (*d*, ^1J(C,H) = 169); 128.4 (*d*, ^1J(C,H) = 160); 128.2 (*d*, ^1J(C,H) = 167); 127.8, 127.5 (2*d*, ^1J(C,H) ≈ 160); 96.0 (*t*, ^1J(C,H) = 163, OCH_2O); 82.7 (*d*, ^1J(C,H) = 146); 81.8 (*d*, ^1J(C,H) = 143, C(4), C(6)); 72.4 (*t*, ^1J(C,H) = 141, Ph*C*H$_2$); 55.7 (*q*, ^1J(C,H) = 142, MeO); 39.0 (*d*, ^1J(C,H) = 131); 38.1 (*d*, ^1J(C,H) = 127, C(3), C(5)); 22.0, 20.0, 14.7 (3*q*, ^1J(C,H) = 128, 3 Me).

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