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Convergent Synthesis of (*R*,*R*)-6,12-Dimethylpentadecan-2-one, the Female Sex Pheromone of the Banded Cucumber Beetle by Iron Mediated Chirality Transfer

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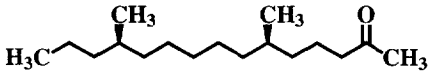
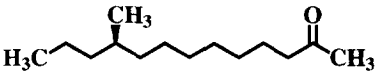
Abstract: The highly convergent synthesis of (*R*,*R*)-6,12-dimethylpentadecan-2-one [(*R*,*R*)-**1**], the bioactive form of the sex pheromone produced by female adults of the banded cucumber beetle *Diabrotica balteata* LeConte, in high enantio- and diastereomeric purity (*ee* ≥ 99%, *de* ≥ 98 %) and good overall yield (13 steps, 39%) is described. The stereogenic centres were generated by nucleophilic addition of allyltrimethylsilane to an enantiopure planar chiral (π–allyl)-tetracarbonyliron(1+)-complex.

The banded cucumber beetle (BCB) *Diabrotica balteata* LeConte and the spotted cucumber beetle *Diabrotica undecimpunctata howardi* Barber are polyphagous insects (*Coleoptera: Chrysomelidae*) belonging to the *Fucata* species group of the genus *Diabrotica* , confined to North America from Canada to Cuba.[1] The larvae of these beetles are a pest of several crop plants, particularly sweet potatoes and seedling cucurbits. The chemical structures of sex pheromones included in the *Fucata* species group are characterised by the methyl ketone functionality and a methyl group on the fourth carbon from the hydrocarbon end of the chain (scheme 1).



(*R*,*R*)-6,12-dimethylpentadecan-2-one

Diabrotica balteata LeConte



(*R*)-10-methyltridecane-2-one

Diabrotica undecimpunctata howardi Barber

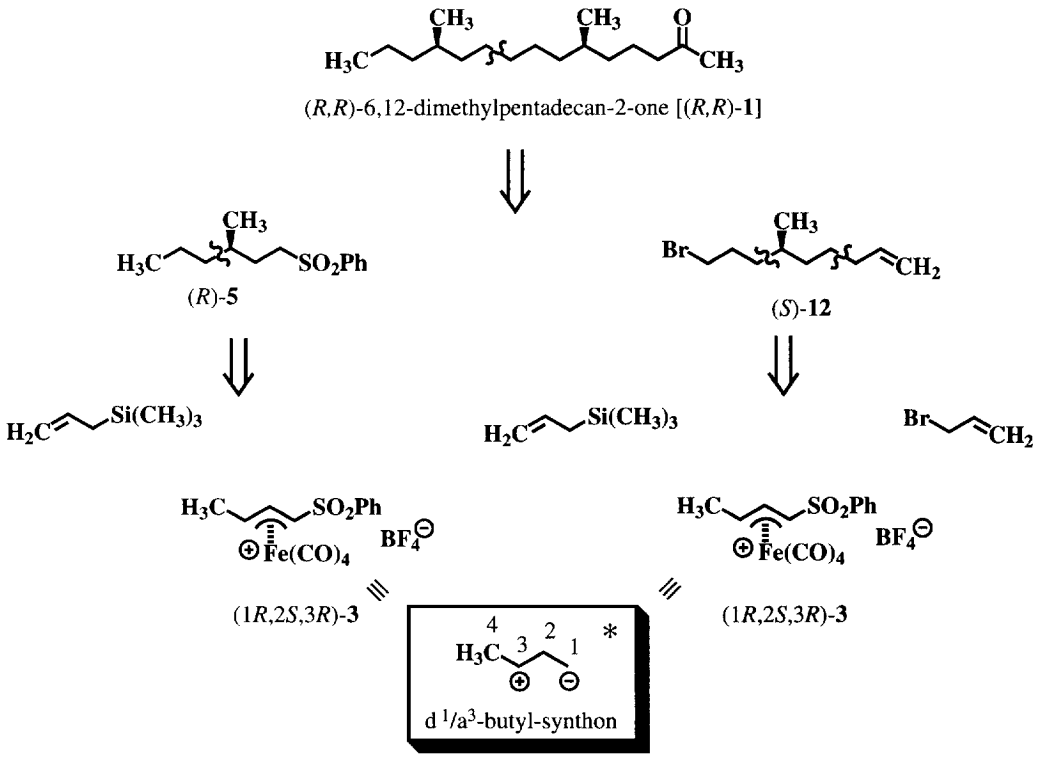
Scheme 1. Sex pheromones of the *Fucata* species group

The female produced sex pheromone of the BCB *Diabrotica balteata* LeConte has been isolated and identified as 6,12-dimethylpentadecan-2-one. Its structure has been elucidated by spectroscopic analyses and was confirmed by comparison with the material synthesised in racemic form.[1a] Field trapping experiments generally demonstrated that the *R* stereoisomers show the highest attractive bioactivity towards males of the BCB *Diabrotica balteata* LeConte [1a,2] as well as the spotted cucumber beetle *Diabrotica undecimpunctata howardi* Barber [1b,c] and closely related variants. However, only one synthesis of all four possible stereoisomers of **1** in high optical purity has been reported in the literature. The synthesis of these isomers included cross-coupling reactions of two different chiral building blocks, which have been prepared starting from either (*R*)-(+)- or (*S*)-(−)-citronellol.[3,4]

Recently, we have reported the synthesis of acceptor-substituted, cationic (π-allyl)-carbonyliron complexes in their diastereo- and enantiomerically pure forms, easily obtainable from the natural precursor (*S*)-lactic acid, which undergo addition reactions with a wide range of "soft"- carbon and heteroatom nucleophiles to allow regio- and stereocontrolled functionalisations of the allyl unit.[5,6] Employing benzenesulfonyl-substituted (π-allyl)tetracarbonyliron complexes as chiral starting material access to highly enantiomerically enriched alkenyl sulfones with a multitude of substituents at the γ-position is efficiently provided.[7]

In this paper we report on a highly convergent synthesis of (*R*,*R*)-6,12-dimethylpentadecan-2-one [(*R*,*R*)-**1**], the female sex pheromone of *Diabrotica balteata* LeConte in high enantio- and diastereomeric purity (*ee* ≥ 99%, *de* ≥ 98%) and good overall yield (13 steps, 39%). Key steps in our synthesis are the regio- and stereocontrolled addition of allyltrimethylsilane to the planar chiral tetracarbonyliron-(1+)-complex (1*R*,2*S*,3*R*)-**3**, the alkylation of the sulfone (*R*)-**8** with allyl bromide for the synthesis of the subunit (*S*)-**12** and the coupling reaction of the bromide (*S*)-**12** with the sulfone (*R*)-**5** for the final construction of the carbon backbone.

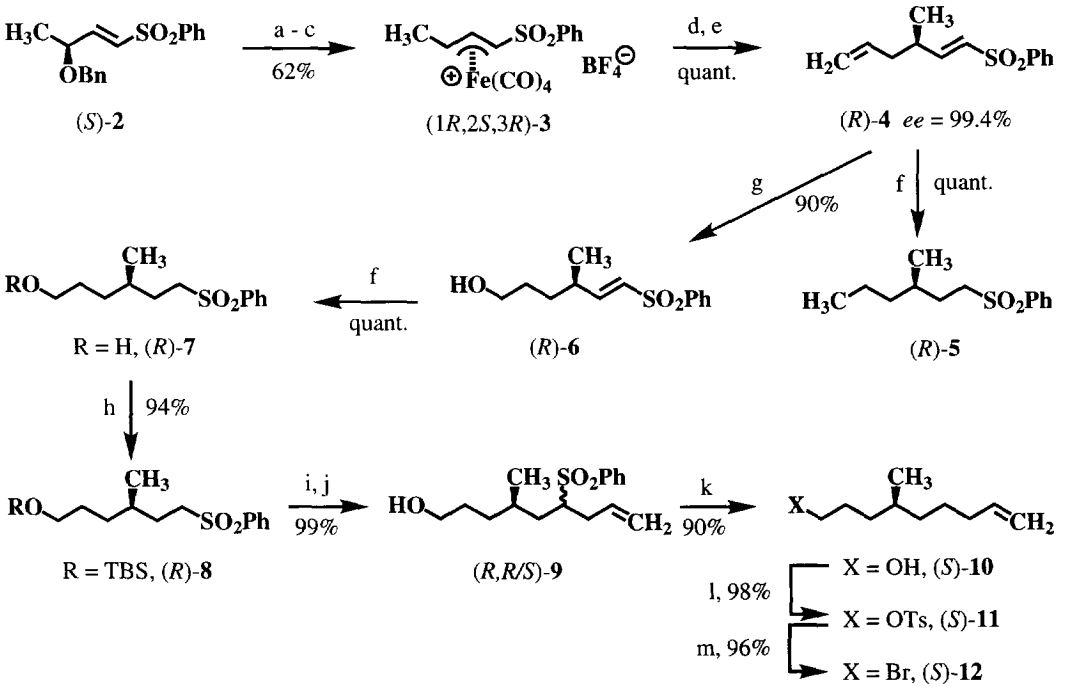
The synthetic strategy is shown in scheme 2. The target molecule can be disconnected into the two subunits (*R*)-**5** and (*S*)-**12**. Recently, the synthesis of the sulfone (*R*)-**5** has been reported,[8b] while the bromide (*S*)-**12** can be prepared from allyltrimethylsilane, the planar chiral, cationic benzenesulfonyl-substituted (η^3-allyl)tetracarbonyliron complex (1*R*,2*S*,3*R*)-**3** and allyl bromide. A crucial step for the construction of the carbon chain of the title compound was the alkylation of the sulfone (*R*)-**5** with the bromide (*S*)-**12**.



Scheme 2. Retrosynthetic analysis of (*R*,*R*)-**1**

The organometallic iron complex (1*R*,2*S*,3*R*)-**3** represents the synthetic equivalent of a d^1/a^3-butyl synthon due to its bifunctionality: on the one hand, the electrophilic allylic reactivity at the γ-position and on the other, the nucleophilic reactivity after hydrogenation and α-metalation to the sulfonyl group.[8] Subsequent removal of the auxiliary sulfonyl group completes the reaction sequence.

The iron complex (1*R*,2*S*,3*R*)-**3** was used as the starting material for the synthesis of the two chiral building blocks, the sulfone (*R*)-**5** and the bromide (*S*)-**12**. The complex **3** was readily obtained in 62% yield from the vinylic sulfone (*S*)-**2** according to literature procedures.[7] As illustrated in scheme 3, the γ-propenyl-substituted alkenyl-sulfone (*R*)-**4** was prepared in quantitative yield by nucleophilic addition of allyltrimethylsilane in dichloromethane to the electrophilic iron complex (1*R*,2*S*,3*R*)-**3**, followed by oxidative cleavage of the tetracarbonyliron fragment with aqueous ceric ammonium nitrate solution.



Reagents and conditions: a-c: ref.[7] - d: $C_3H_5Si(CH_3)_3$ (3 equiv.), CH_2Cl_2, –10 °C to room temperature, 6 h. - e: $(NH_4)_2Ce(NO_3)_6/H_2O$ (4 equiv.), 12 h. - f: 10% Pd/C, H_2 (atmospheric pressure), MeOH, room temperature. - g: 9-BBN (1.1 equiv.), 0 °C to room temperature, 3 h, then excess H_2O_2, NaOAc/H_2O, 0 °C to room temperature, 3 h. - h: $[(H_3C)_3C](H_3C)_2SiCl$ (2.4 equiv.), imidazole (3 equiv.), DMF, room temperature, 15 h. - i: *n*-butyllithium, THF, cosolvent: HMPA, –30 °C, 1 h then C_3H_5Br (3 equiv.), –78 °C to room temperature - j: HF, H_2O, CH_3CN, room temp., 6 h. - k: 6% Na(Hg) (10 equiv.), Na_2HPO_4 (10 equiv.), MeOH, –10 °C to room temperature, 14 h. - l: $H_3CC_6H_4SO_2Cl$ (2 equiv.), pyridine, room temperature, 16 h. - m: LiBr (2.7 equiv.), acetone, Δ, 16 h.

Scheme 3. Synthesis of the sulfone (*R*)-**5** and the bromide (*S*)-**12**

The nucleophilic addition of allyltrimethylsilane proceeded with complete regioselectivity and due to the overriding *anti*-directing effect of the $Fe(CO)_4$ moiety highly stereoselectively *anti* to the metal fragment. The stereogenic centre could be assigned the (*R*)-configuration, as it has been proved by previous results of our research group and can be concluded from the sign of the optical rotation of the final product (*vide supra*). For the determination of the enantiomeric purity of (*R*)-**4** (*ee* = 99.4%), the product was analysed by GC employing a chiral stationary phase (Lipodex E) and by comparison with the racemic material, which was synthesised by an analogous route making use of the racemic iron complex **3** (Fig. 1).

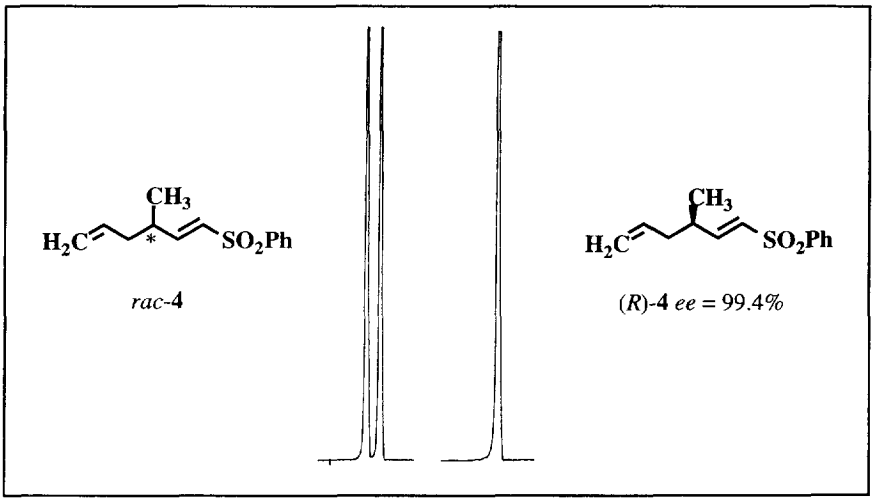
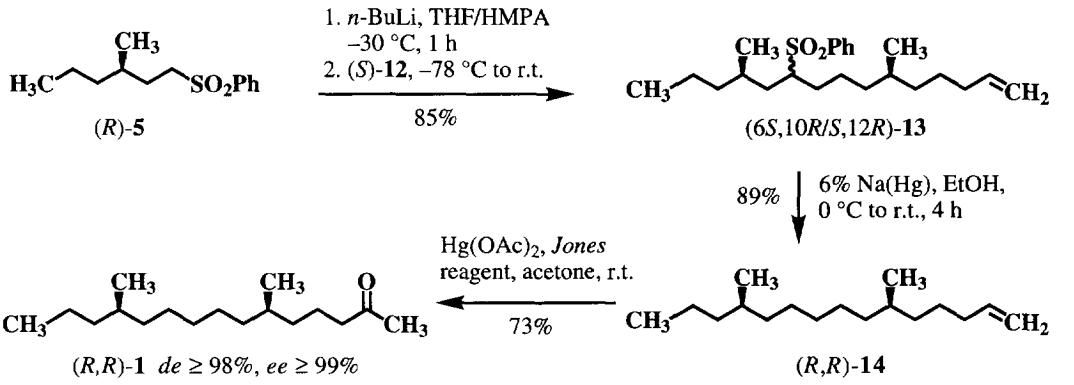


Figure 1. Determination of the enantiomeric excess of (*R*)-**4** by comparative GC_{CSP} on Lipodex E

Catalytic hydrogenation of (*R*)-**4** with palladium on charcoal in methanol under an atmospheric pressure of hydrogen completed the final construction of the sulfone (*R*)-**5** in quantitative yield. For the preparation of the subunit (*S*)-**12**, the regioselective hydroboration of terminal double bond of (*R*)-**4** was achieved by treatment of (*R*)-**4** with borabicyclononane (9-BBN), followed by oxidative work up of the alkylborane with H_2O_2 in the presence of sodium acetate at 0 °C to furnish the alcohol (*R*)-**6** in 90% yield. Reduction of the double bond of (*R*)-**6** under similar conditions as employed for (*R*)-**4** yielded the saturated hydroxy sulfone (*R*)-**7** in quantitative yield. Protection of hydroxy group using *t*-butyldimethylsilyl chloride in the presence of excess imidazole in DMF afforded the silyl ether (*R*)-**8** in 94% yield after purification by column chromatography. The sulfone (*R*)-**8** was deprotonated at –30 °C with *n*-butyllithium in THF/HMPA and the resulting α-lithiosulfone alkylated with allylbromide at –78 °C to afford the sulfone after aqueous work up.[9] The crude sulfone was directly deprotected by treatment with aqueous hydrofluoric acid in acetonitrile at room temperature to yield the hydroxy sulfone (*R,R/S*)-**9** as a mixture of α-epimers in 99% yield (two steps).[10] For reductive removal of the sulfonyl group, a solution of (*R,R/S*)-**9** in methanol was treated with an excess of sodium amalgam in the presence of anhydrous disodium hydrogenphosphate to afford (*S*)-**10** in 90% yield.[11] The alcohol (*S*)-**10** was converted into the corresponding tosylate (*S*)-**11** in 98% yield with tosyl chloride in pyridine according to conventional procedures. Treatment of (*S*)-**11** with lithium bromide in acetone under reflux conditions for 16 h completed the preparation of the bromide (*S*)-**12** in 96% yield after purification by column chromatography.[12]

The final construction of the hydrocarbon chain was achieved by connection of the two building blocks (*R*)-**5** and (*S*)-**12** as shown in scheme 4.



Scheme 4. Synthesis of the title compound (*R*,*R*)-**1** by cross coupling of (*R*)-**5** and (*S*)-**12**

Metalation of the sulfone (*R*)-**5** with *n*-butyllithium in THF/HMPA at –30 °C, followed by alkylation with bromide (*S*)-**12** at –78 °C gave the sulfone (*S*,*R*/*S*,*R*)-**13** in 85% yield as a mixture of diastereoisomers.[9] According to ref.[3] the resulting sulfone **13** was reduced with sodium amalgam under similar conditions as employed for (*S*)-**10** to afford (*R*,*R*)-**14** in 93% yield after purification by column chromatography. However, in this case, GC analysis of the purified product (*R*,*R*)-**14** indicated about 7% of a mixture of β-elimination side products derived from hydrobenzenesulfonyl elimination.[9] Finally, conversion of the terminal double bond into the methyl ketone was carried out by oxymercuration in the presence of catalytic amounts of mercury(II)acetate and *in situ* oxidation of (*R*,*R*)-**14** with excess *Jones* reagent to afford crude (*R*,*R*)-**1**.[13] The products of the β-elimination side reaction, generated during the desulfurisation step, were removed by ozonolysis of the mixture in dichloromethane at –78 °C followed by oxidative work up with H_2O_2 to furnish the pure pheromone (*R*,*R*) in 73% yield. The product was identical in all spectroscopic and analytical details with the naturally occurring substance.[1] Since the above described synthetic operations did not cause marked racemisation at the stereogenic centres, the enantio- and diastreomeric purity of (*R*,*R*)-**1** is expected to be greater than 98%. The value for the optical rotation $[\alpha]_D^{20} = -0.5$ (c = 0.60, $CHCl_3$) {ref.[3]: $[\alpha]_D^{22} = -0.5$ (c = 1.13, $CHCl_3$)} is in excellent agreement with data reported for the enantiopure pheromone synthesised from (+)-(*R*)-citronellol.

In conclusion, starting from readily available, inexpensive starting materials, the first stereocontrolled, efficient and highly convergent synthesis of the sex pheromone (*R*,*R*)-(–)-6,12-dimethylpentadecan-2-one [(*R*,*R*)-**1**] of female banded cucumber beetles *Diabrotica balteata* LeConte in its naturally occurring absolute configuration and of high enantiomeric (*ee* ≥ 99%) and diastereomeric (*de* ≥ 98%) purity in good overall yield (39%, 13 steps) is reported. Subsequent connection of five allylic subunits with stereocontrol of the newly generated stereocentres has allowed the construction of the carbon skeleton. This synthesis again demonstrates clearly the broadness and flexibility of the iron-mediated chirality transfer method in allylic substitution reactions. As an extension of this method we are now investigating novel synthetic applications to take advantage of the bifunctionality of the cationic sulfonyl iron complex, representing the synthetic equivalent of a

d^1/a^3-synthon, for the synthesis of other enantiopure natural or bioactive compounds by variation of the nucleophilic and electrophilic components.

EXPERIMENTAL

General. All reactions were carried out using standard Schlenk techniques unless otherwise stated. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran (THF) was freshly distilled from potassium, dichloromethane and dimethylformamide (DMF) from CaH_2 under argon. Light petroleum refers to the fraction with b.p. 40 - 80 °C. Reagents of commercial quality were used from freshly opened containers unless otherwise stated. Allyltrimethylsilane was purchased from ACROS Chimica, Belgium; *n*-butyllithium (1.6 M in *n*-hexane) was purchased from Merck, Darmstadt. Allyl bromide was freshly distilled and handled under argon. 6% Sodium amalgam [Na(Hg)] was freshly prepared prior to use. The iron complex (1*R*,2*S*,3*R*)-**3** has been prepared according to a literature procedure.[7] - Analytical TLC: Merck glass-backed silica gel 60 F_{254} plates. - Preparative column chromatography: Merck silica gel 60, particle size 0.040 - 0.063 mm (230 - 400 mesh) (flash). - Analytical GC: Siemens Sichromat 2 or 3 equipped with a SE-54-CB-column (25 m x 0.25 mm), carrier gas nitrogen, FID. - Optical rotations: Perkin-Elmer P 241 polarimeter; solvents of Merck UVASOL quality. - IR spectra: Perkin-Elmer 1420 and Perkin-Elmer FT/IR 1750. - ^{1}H NMR spectra (300 MHz), ^{13}C NMR spectra (75 MHz): Varian VXR 300 and Gemini 300 (solvent: $CDCl_3$, TMS as internal standard). - Mass spectra: Varian MAT 212 (EI 70 eV) (relative intensities in parenthesis). High resolution mass spectra: Finnigan MAT, MAT 95. - GC-HRMS: GC: Varian 3400, SGE 25QC2/BP5-column (25 m x 0.25 mm); HRMS: MAT 95. - Microanalyses: Heraeus CHN-O-Rapid.

(R,E)-1-Benzenesulfonyl-3-methylhexa-1,5-diene [(*R*)-**4**]: To a stirred suspension of the tetracarbonyliron complex (1*R*,2*S*,3*R*)-**3** (3.60 g, 8.0 mmol) in CH_2Cl_2 (85 ml) a solution of allyltrimethylsilane (2.74 g, 24.0 mmol) in CH_2Cl_2 (15 ml) was added dropwise with a syringe at –10 °C. The reaction mixture was allowed to warm to room temp. and stirring was continued until the yellow suspension had dissolved to yield a clear yellow solution (ca. 5 - 6 h) of the neutral product complex. Oxidative demetalation was achieved by treatment of the reaction mixture with an aqueous solution of ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$] (17.48 g, 32.0 mmol in 35 ml H_2O) for 12 h at room temp. The organic layer was separated, the aqueous phase extracted with CH_2Cl_2 (5 x 50 ml) and the combined organic extracts were washed with saturated NH_4F solution (40 ml) and brine (40 ml). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, light petroleum / diethyl ether, 3:1) to afford 1.89 g (quantitative) of a pale yellow oil. - R_f = 0.27 (light petroleum diethyl ether, 3:1). - $[\alpha]_D^{24}$: –4.4 (*c* = 1.10, $CHCl_3$). - *ee* = 99.4 %, determined by GC_{CSP} analysis on a 25 m Lipodex E phase, 170 °C iso, 1 bar H_2, $R_{t(R)\text{-}4}$ = 24.4 min, [$R_{t(S)\text{-}4}$ = 25.6 min]). - IR (film): $\tilde{\nu}$ = 3065 (m, =CH), 2970, 2928 (m, CH_2), 1641, 1622 (m, C=C), 1585 (w, C_{Ar}=C_{Ar}), 1447 (s), 1318 (s), 1308 (s, S=O), 1288 (s), 1148 (vs, S=O), 1087 (s), 820 (m), 745 (s), 719 (s), 689 (s), 592 (s) cm^{-1}. - ^{1}H NMR: δ = 1.07 (d, *J* = 6.7 Hz, 3H, 3-CHC*H*$_3$), 2.13 (dtt, *J* = 14.1 Hz, *J* = 7.0 Hz, *J* = 1.4 Hz, 1H, 4-C*H*H), 2.18 (dtt, *J* = 14.1 Hz, *J* = 7.0 Hz, *J* = 1.4 Hz, 1H, 4-CH*H*), 2.46 (sept.d, *J* = 7.0 Hz, *J* = 1.4 Hz, 1H, 3-C*H*CH$_3$), 5.01 (m, 2H, 6-CH_2), 5.67 (ddt, *J* = 17.5 Hz, *J* = 9.7 Hz, *J* = 7.0 Hz, 1H, 5-CH), 6.25 (dd, *J* = 15.1 Hz, *J* = 1.3 Hz, 1H, 1-CH), 6.95 (dd, *J* = 15.1 Hz, *J* = 7.1 Hz, 1H, 2-CH), 7.50-7.57 (m, 2H, C_{meta}-H), 7.58-7.65 (m, 1H, C_{para}-H), 7.85-7.90 (m, 2H, C_{ortho}-H). - ^{13}C NMR: δ = 18.32 (3-CH*C*H$_3$), 35.68 (3-*C*HCH$_3$), 39.86 (4-CH_2), 117.41 (6-CH_2), 127.56 (C_{ortho}), 129.23 (C_{meta}), 129.30 (1-CH), C133.24 (C_{para}), 135.05 (5-CH),

140.77 (C_{ipso}), 151.35 (2-CH). - MS (70 eV), *m/z* (%): 143 (3), 125 (54), 95 (100) [M^+–$C_6H_5SO_2$], 79 (26), 77 (32) [$C_6H_5^+$], 67 (40), 55 (15), 53 (17), 51 (22), 41 (21), 39 (22). - $C_{13}H_{16}O_2S$ (236.3): calcd. C 66.07, H 6.82; found C 65.88, H 6.73.

(R)-1-Benzenesulfonyl-3-methylhexane [(*R*)-**5**]: To a solution of (*R*)-**4** (0.220 g, 0.93 mmol) in MeOH (15 ml) was added a catalytic amount of 10 % Pd/C. The reaction mixture was stirred at room temperature under an atmosphere of hydrogen for 1 h, then filtered over Celite® and the filtrate concentrated under reduced pressure to yield 0.224 g (quantitative) (*R*)-**5** as a light green oil. - R_f = 0.31 (light petroleum / diethyl ether, 3:1). - $[\alpha]_D^{26}$: –6.2 (*c* = 1.28, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3065 (w, =CH), 2958, 2930, 2872 (s, CH_2), 1586 (w, C_{Ar}=C_{Ar}), 1448 (s), 1307 (vs, S=O), 1147 (vs, S=O), 1088 (s), 743 (m), 690 (m), 596 (m) cm^{-1}. - ^1H NMR: δ = 0.84 (t/d, superimposed, *J* = 7.0 Hz / *J* = 6.7 Hz, 6H, 6-CH_3, 3-CHC*H*$_3$), 1.02-1.38 (m, 4H, 4-CH_2, 5-CH_2), 1.42-1.60 (m, 2H, 3-C*H*CH_3, 2-C*H*H), 1.72 (m, 1H, 2-CH*H*), 3.06 (ddd, *J* = 13.1 Hz, *J* = 10.0 Hz, *J* = 5.8 Hz, 1H, 1-C*H*H), 3.12 (ddd, *J* = 13.1 Hz, *J* = 10.0 Hz, *J* = 5.8 Hz, 1H, 1-CH*H*), 7.54-7.61 (m, 2H, C_{meta}-H), 7.65-7.70 (m, 1H, C_{para}-H), 7.89-7.94 (m, 2H, C_{ortho}-H). - ^{13}C NMR: δ = 14.17 (6-CH_3), 19.11 (3-CH*C*H$_3$), 19.83 (5-CH_2), 29.16 (2-CH_2), 31.58 (3-*C*HCH$_3$), 38.57 (4-CH_2), 54.40 (1-CH_2), 128.00 (C_{ortho}), 129.26 (C_{meta}), 133.64 (C_{para}), 139.25 (C_{ipso}). - MS (70 eV), *m/z* (%): 240 (2) [M^+], 143 (100), 142 (12), 98 (62) [M^+–$C_6H_5SO_2H$], 78 (13), 77 (21) [$C_6H_5^+$], 70 (24), 69 (19), 57 (76), 56 (13), 55 (23). - $C_{13}H_{20}O_2S$ (240.4): calcd. C 64.96, H 8.39; found C 65.07, H 8.67.

(R,E)-1-Benzenesulfonyl-3-methylhex-1-en-6-ol [(*R*,*E*)-**6**]: To a stirred solution of 9-borabicyclononane (9-BBN) (0.58 g, 5.0 mmol) in THF (15 ml) was added dropwise a solution of the diene (*R*)-**4** (0.53 g, 2.20 mmol) in THF (3 ml) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirring was continued for 3 h after removal of the cooling bath. Oxidative cleavage of the alkylborane was achieved by hydrogen peroxide (3.6 ml, 30% H_2O_2) and an aqueous solution of sodium acetate (1.00 g in 2.5 ml) for 3 h at 0 °C. After dilution with diethyl ether (100 ml), followed by separation of the organic layer, the aqueous phase was extracted with CH_2Cl_2 (3 x 20 ml). The organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, eluent: light petroleum / diethyl ether, 1:3) to afford alcohol (*E*,*R*)-**6** (0.52 g, 90%) as a colourless oil. - R_f = 0.17 (light petroleum / diethylether, 1:3). - $[\alpha]_D^{24}$ = –23.3 (*c* = 0.86, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3500-3380 (br. m, OH), 3060 (m, =CH), 2920 (s, CH_2, CH_3), 1620 (m, C=C), 1585 (w, C_{Ar}=C_{Ar}), 1442 (m), 1318 (s), 1303 (s, S=O), 1283 (s), 1140 (vs, S=O), 1083 (s), 815 (m), 750 (m), 715 (m), 684 (s) cm^{-1}. - ^1H NMR: δ = 1.05 (d, *J* = 7.0 Hz, 3H, 3-CHC*H*$_3$), 1.38-1.58 (m, 4H, 4-CH_2, 5-CH_2), 2.38 (m, 1H, 3-C*H*CH_3), 3.3 (br. s, 1H, OH), 3.57 (t, *J* = 6.1 Hz, 2H, 6-CH_2), 6.33 (dd, *J* = 15.1 Hz, *J* = 1.4 Hz, 1H, 1-CH), 6.93 (dd, *J* = 15.1 Hz, *J* = 7.4 Hz, 1H, 2-CH), 7.51-7.58 (m, 2H, C_{meta}-H), 7.59-7.65 (m, 1H, C_{para}-H), 7.84-7.89 (m, 2H, C_{ortho}-H). - ^{13}C NMR: δ = 19.36 (3-CH*C*H$_3$), 30.48 (5-CH_2), 32.30 (4-CH_2), 36.35 (3-*C*HCH$_3$), 62.75 (6-CH_2), 127.99 (C_{ortho}), 129.52 (1-CH), 129.86 (C_{meta}), 133.91 (C_{para}), 141.05 (C_{ipso}), 152.59 (2-CH). - MS (70 eV), *m/z* (%): 255 (0.8) [M^++1], 209 (4) [M^+–C_2H_4OH], 196 (6) [M^++1–C_3H_6OH], 182 (8), 169 (56), 143 (33), 125 (36), 113 (23), 112 (81) [M^+–$C_6H_5SO_2H$], 95 (100), 77 (44) [$C_6H_5^+$], 67 (47), 53 (23), 41 (50). - $C_{13}H_{18}O_3S$ (254.3): calcd. C 61.38, H 7.13; found C 61.37, H 7.28.

(R)-1-Benzenesulfonyl-3-methylhexan-6-ol [(*R*)-**7**]: To a solution of alkene (*R*)-**6** (0.9 g, 3.53 mmol) in methanol (40 ml) was added a catalytic amount of 10% Pd/C. The reaction mixture was stirred at room temperature under an atmosphere of hydrogen for 1 h, then filtered through Celite® and the filtrate concentrated under reduced pressure to yield 0.91 g (quantitative) (*R*)-**7** as a light green oil. - R_f = 0.12 (light petroleum / diethyl ether, 1:3). - $[\alpha]_D^{24}$ = –4.2 (*c* = 1.28, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3524-3397 (br., m, OH), 1586 (w,

C_{Ar}=C_{Ar}), 1448 (m), 1383 (w), 1306 (s, S=O), 1217 (m), 1147 (s, S=O), 1087 (m), 756 (s), 689 (m), 668 (m) cm^{-1}. - ^1H NMR: δ = 0.87 (d, J = 6.3 Hz, 1H, 3-CHC*H*$_3$), 1.09-1.80 (m, 7H, 2-CH_2, 3-C*H*CH_3, 4-CH_2, 5-CH_2), 2.05 (br. s, 1H, OH), 3.01-3.19 (m, 2H, 1-CH_2), 3.59 (t, J = 6.3 Hz, 2H, 6-CH_2), 7.54-7.61 (m, 2H, C_{meta}-H), 7.65 (m, 1H, C_{para}-H), 7.88-7.92 (m, 2H, C_{ortho}-H). - ^{13}C NMR: δ = 19.11 (4-CH*C*H_3), 29.11, 29.83 (2-CH_2, 5-CH_2), 31.69 (3-*C*HCH_3), 32.29 (4-CH_2), 54.32 (1-CH_2), 62.76 (6-CH_2), 127.99 (C_{ortho}), 129.28 (C_{meta}), 133.68 (C_{para}), 139.1 (C_{ipso}). - MS (70 eV), *m/z* (%): 256 (1) [M^+], 226 (6), 169 (13), 143 (38), 115 (11) [M^+–$C_6H_5SO_2$], 96 (48), 77 (30) [$C_6H_5^+$], 70 (23), 69 (65), 56 (11), 55 (100), 51 (15), 43 (17), 41 (59). - HRMS: calcd. for $C_{13}H_{20}O_3S$ 256.1133; found 256.1132. - $C_{13}H_{20}O_3S$ (256.4): calcd. C 60.91, H 7.86; found C 61.18, H 7.90.

(R)-1-Benzenesulfonyl-6-(tert-butyldimethylsiloxy)-3-methylhexane [(*R*)-**8**]: Following the protocol of *Corey*,[14] 0.95 g (3.71 mmol) of (*R*)-**7** was treated with *tert*-butyldimethylsilyl chloride (1.33 g, 8.82 mmol) in dimethylformamide (15 ml) in the presence of an excess of imidazole (0.78 g, 11.44 mmol) at room temperature for 15 h (TLC control) until the starting alcohol (*R*)-**7** was comletely converted. The reaction mixture was diluted with light petroleum (100 ml) and water (50 ml). The aqueous phase was extracted with light petroleum (4 x 50 ml) and diethyl ether (1 x 50 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. Final purification by column chromatography (silica gel, eluent: light petroleum / diethyl ether, 5:1) afforded (*R*)-**8** as a pale green liquid (1.30 g, 94%). - R_f = 0.27 (light petroleum / diethyl ether, 5:1). - $[\alpha]_D^{20}$ = –3.6 (c = 1.15, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 2954, 2931, 2884 (s, CH_2, CH_3), 1586 (w, C_{Ar} =C_{Ar}), 1471 (m), 1463 (m), 1448 (s), 1318 (s), 1307 (s, S=O), 1255 (s), 1149 (vs, S=O), 1089 (s), 836 (s), 777 (s), 757 (s), 690 (m), 596 (m), 538 (m). - ^1H NMR: δ = 0.03 [s, 6H, $Si(CH_3)_2$], 0.85 (d, J = 6.6 Hz, 3H, 3-CHC*H*$_3$), 0.88 [s, 9H, $SiC(CH_3)_3$], 1.07-1.80 (m, 7H, 2-CH_2, 3-C*H*CH_3, 4-CH_2, 5-CH_2), 3.00-3.18 (m, 2H, 1-CH_2), 3.55 (t, J = 6.3 Hz, 2H, 6-CH_2), 7.54-7.61 (m, 2H, C_{meta}-H), 7.66 (m, 1H, C_{para}-H), 7.89-7.93 (m, 2H, C_{ortho}-H). - ^{13}C NMR: δ = –5.29 [$Si(CH_3)_2$], 18.31 [$SiC(CH_3)_3$], 19.16 (3-CH*C*H_3), 25.94 [$SiC(CH_3)_3$], 29.12, 29.25 (4-CH_2, 5-CH_2), 31.71 (3-*C*HCH_3), 32.39 (2-CH_2), 54.39 (1-CH_2), 63.11 (6-CH_2), 128.00 (C_{ortho}), 129.25 (C_{meta}), 133.61 (C_{para}), 139.16 (C_{ipso}). - MS (70 eV), *m/z* (%): 370 (0.15) [M^+], 355 (2.5) [M^+–CH_3], 313 (100) [M^+–C_4H_9], 199 (26), 135 (34), 125 (5), 97 (6), 77 (5) [$C_6H_5^+$], 75 (13), 73 (10), 55 (19). - $C_{19}H_{34}O_3SSi$ (370.6): calcd. C 61.57, H 9.25; found C 61.62, H 9.30.

(4R,6R/S)-6-Benzenesulfonyl-4-methylnon-8-enol [(*R,R/S*-**9**)]: To a solution of (*R*)-**8** (1.00 g, 2.7 mmol) in dry THF (11 ml) containing dry HMPA (3 ml) under argon was added dropwise a solution of *n*-butyllithium in hexane (2.05 ml, 1.6 M) at –30 °C and the resulting yellow-orange solution was stirred at –30 °C for 1 h. After cooling to –78 °C, a solution of allyl bromide (0.98 g, 8.1 mmol) in THF (6 ml) was added dropwise with a syringe. The cooling bath was removed and stirring was continued for 12 h. The reaction was quenched with saturated NH_4Cl solution (5 ml), diluted with water (15 ml) and the aqueous phase was extracted with diethyl ether (5 x 30 ml). The combined organic extracts were washed with brine (20 ml), dried ($MgSO_4$), and concentrated *in vacuo*. According to ref.[11], 1.75 g of the crude pale yellow alkylated silyl ether were treated at room temperature by acetonitrile (50 ml) containing 40% aqueous solution of HF (2.5 ml). When the deprotection was complete by TLC (ca. 6 h), chloroform (20 ml) and water (20 ml) were added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 x 30 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. Final purification by column chromatography (silica gel, eluent: light petroleum / diethyl ether, 1:2) afforded 0.80 g (99%) of the alcohol (*R,S/R*)-**9**. - R_f = 0.15 (light petroleum / diethyl ether, 1:2).- IR (film): $\tilde{\nu}$ = 3520-3200 (br., m, OH), 3060 (m, =CH), 2920, 2860 (CH_2, CH_3), 1680 (m, C=C), 1585 (w, C_{Ar}=C_{Ar}), 1445 (m),

1380 (m), 1300 (vs, S=O), 1140 (vs, S=O), 1080 (s), 920 (m), 730 (s), 680 (s) cm^{-1}. - ^1H NMR (epimer 1/epimer 2): δ = 0.86/0.87 (d/d, superimposed, J = 6.6 Hz, 3H, 4-CHC*H*$_3$), 1.00-1.18 (m, 7H, 2-CH_2, 3-CH_2, 4-C*H*CH_3, 5-CH_2), 1.80-1.89 (t/t, J = 6.0 Hz, 1H, OH), 2.17-2.39 (m, 1H, 7-C*H*H), 2.47-2.68 (m, 1H, 7-CH*H*), 3.03-3.16 (m, 1H, 6-CH), 3.58/3.60 (t/t, superimposed, J = 6.9 Hz, 2H, 1-CH_2), 5.01-5.18 (m, 2H, 9-CH_2), 5.62-6.18 (m, 1H, 8-CH), 7.54-7.62 (m, 2H, C_{meta}-H), 7.64-7.71 (m, 1H, C_{para}-H), 7.87-7.94 (m, 2H, C_{ortho}-H). - ^{13}C NMR (epimer 1/epimer 2): δ = 18.94/19.53 (4-CH*C*H$_3$), 29.50/29.86 (7-CH_2), 29.79/30.29 (4-*C*HCH$_3$), 32.08/32.99 (5-CH_2), 32.99/33.72 (3-CH_2), 33.55/34.64 (2-CH_2), 61.96/62.04 (6-CH), 62.76/62.85 (1-CH_2), 118.41/118.58 (9-CH_2), 128.89/128.93 (C_{ortho}), 129.17 (C_{meta}) 133.34/133.41 (8-CH), 133.71 (C_{para}), 137.72 (C_{ipso}). - MS (70 eV), *m/z* (%): 297 (0.1) [M^++1], 209 (3), 155 (27) [M^+–$SO_2C_6H_5$], 154 (23), 143 (25), 137 (25), 136 (12), 125 (10), 121 (4), 113 (10), 109 (18), 95 (100), 93 (9), 85 (31), 81 (72), 77 (28) [$C_6H_5^+$], 69 (52), 67 (57), 55 (70), 53 (13), 51 (13), 41 (93). - $C_{16}H_{24}O_3S$ (296.4): calcd. C 64.84, H 8.16; found C 64.81, H 8.46.

(S)-4-Methl-non-8-en-1-ol [(*S*)-**10**]: According to ref.[10], a solution of (*R,R/S*)-**9** (0.24 g, 0.8 mmol) in dry methanol (3 ml) was added to a stirred suspension of sodium amalgam [freshly prepared from 0.37 g (16.1 mmol) of sodium and 6.2 g (30.9 mmol) of mercury] and Na_2HPO_4 (2.28 g, 16.1 mmol) in methanol (10 ml) under argon. The conversion was monitored by TLC (ca. 14 h). The mixture was then filtered and the filter cake was washed with ether. The combined filtrate and washings were evaporated (at room temperature) *in vacuo*. The residue was diluted with water (40 ml) and extracted with ether (3 x 15 ml). The ethereal phase was washed with water (15 ml) and brine (15 ml), dried ($MgSO_4$) and concentrated *in vacuo* (at room temperature). The residue was purified by flash column chromatography (silica gel, eluent: light petroleum, diethyl ether, 2:1) to give the alcohol (*S*)-**10** (0.11 g, 90%) as a colourless oil. - R_f = 0.19 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{23}$ = –1.8 (c = 1.23, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3400-3200 (br., m, OH), 3078 (m, =CH), 2920, 2860 (s, CH_2, CH_3), 1640 (m, C=C), 1405 (m), 1373 (m), 1055 (s), 990 (m), 905 (s) cm^{-1}. - ^1H NMR: δ = 0.88 (d, J = 6.3 Hz, 3H, 4-CHC*H*$_3$), 1.07-1.68 (m, 7H, 6-CH_2, 5-CH_2, 4-CH, 3-CH_2), 1.96-2.07 (m, 3H, 7-CH_2, OH), 3.60 (t, J = 6.3 Hz, 2H, 1-CH_2), 4.90-5.04 (m, 2H, 9-CH_2), 5.81 (ddt, J = 17.0 Hz, J = 10.5 Hz, J = 6.6 Hz, 1H, 8-CH). - ^{13}C NMR: δ = 19.61 (4-CH*C*H$_3$), 26.37 (7-CH_2), 30.29 (5-CH_2), 32.55 (4-*C*HCH$_3$), 32.94 (3-CH_2), 34.11 (6-CH_2), 36.47 (2-CH_2), 63.27 (1-CH_2), 114.23 (9-CH_2), 139.14 (8-CH). - MS (70 eV), *m/z* (%): 156 (0.6) [M^+], 123 (3), 112 (14), 97 (22), 95 (40), 82 (22), 81 (37), 70 (24), 69 (67), 55 (100), 41 (85). - $C_{10}H_{20}O$ (156.3): calcd. C 76.85, H 12.90; found C 76.71, H 13.03.

(S)-1-(p-Methylbenzenesulfonyloxy)-4-methylnonan-8-ene [(*S*)-**11**]: To a cooled (0 °C) solution of the alcohol (*S*)-**10** (0.30 g, 1.9 mmol) in dry pyridine (10 ml) was added *p*-toluenesulfonyl chloride (0.74 g, 4.0 mmol). The mixture was stirred at 0-5 °C for 14 h. The reaction was quenched with methanol (4 ml) and then the reaction mixture was poured into water (20 ml). The aqueous phase was extracted with diethyl ether (5 x 10 ml). The combined organic extracts were washed with diluted (5%) hydrochloric acid solution (3 x 10 ml), with saturated $NaHCO_3$ solution (3 x 10 ml), brine (20 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, light petroleum / diethyl ether, 4:1) to afford the tosylate (*S*)-**11** (0.57 g, 98%) as a colourless oil. - R_f = 0.45 (light petroleum / diethylether, 4:1) - $[\alpha]_D^{20}$ = + 0.7 (c = 4.02, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3070 (m, =CH), 2920, 2840 (s, CH_2, CH_3), 1678 (m, C=C), 1598 (m, C_{Ar}=C_{Ar}), 1498 (w), 1455 (m), 1360 (vs, S=O), 1180 (vs), 1170 (vs), 1085 (s), 960 (s), 920 (s), 820 (s), 730 (m), 660 (s) cm^{-1} - ^1H NMR: δ = 0.81 (d, J = 6.6 Hz, 3H, 4-CHC*H*$_3$), 1.01-1.44 (m, 7H, 6-CH_2, 5-CH_2, 4-C*H*CH_3, 3-CH_2), 1.52-1.74 (m, 2H, 2-CH_2), 1.93-2.06 (m, 2H, 7-CH_2), 2.44 (s, 3H, CH_3*tosyl*), 4.01(t, J = 6.6 Hz, 2H, 1-CH_2), 4.89-5.03 (m, 2H, 9-CH_2), 5.79 (ddt, J = 16.8 Hz, J = 10.2 Hz, J = 6.6

Hz, 1H, 8-CH), 7.35 (d, J = 8.0 Hz, 2H, C_{meta}-H), 7.79 (d, J = 8.2 Hz, 2H, C_{ortho}-H). - ^{13}C NMR: δ = 19.36 (4-$CHCH_3$), 21.62 (CH_{3tosyl}), 26.21 (5-CH_2), 26.43 (7-CH_2), 32.13 (4-$CHCH_3$), 32.42, 33.98 (6-CH_2, 3-CH_2), 36.16 (2-CH_2), 71.04 (1-CH_2), 114.30 (9-CH_2), 127.86 (C_{ortho}), 133.23 ($C_{ipso}CH_3$), 138.96 (8-CH), 144.64 ($C_{ipso}SO_2$). - MS (70 eV), *m/z* (%): 310 [M^+], 173 (19), 172 (12), 155 (17), 138 (98) [M^+–$H_3CC_6H_4SO_3$], 110 (29), 109 (33), 96 (41), 95 (87), 91 (72) [$C_7H_7^+$], 84 (20), 82 (100), 68 (75), 55 (86) 41 (71). - $C_{17}H_{26}O_3S$ (310.4): calcd. C 65.78, H 8.44; found C 66.01, H 8.91.

(S)-1-Bromo-4-methylnon-8-ene [(*S*)-**12**]: Lithium bromide (0.29 g, 3.45 mmol) was added to a solution of (*S*)-**11** (0.40 g, 1.28 mmol) in dry acetone (20 ml). The reaction mixture was heated to reflux for 14 h (monitored by TLC). Upon complete consumption of the starting material, the mixture was poured into water (20 ml) and the aqueous layer was extracted with diethyl ether (5 x 10 ml). The ethereal extracts were washed with water (15 ml) and brine (15 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography (silicagel, eluent: light petroleum / diethyl ether, 8:1) afforded the bromide (*S*)-**12** as a colourless liquid (0.27 g, 96%). - R_f = 0.60 (light petroleum / diethyl ether, 8:1). - $[\alpha]_D^{20}$ = +2.5 (c = 1.37, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3070 (m, =CH), 2980, 2860 (s, CH_2, CH_3), 1630 (m, C=C), 1455 (s), 1435 (s), 1375 (m), 1250 (m), 1205 (w), 990 (m), 905 (s), 640 (m) cm^{-1}. - ^1H NMR: δ = 0.87 (d, J = 6.6 Hz, 3H, 4-$CHCH_3$), 1.09-1.50 (m, 7H, 3-CH_2, 4-$CHCH_3$, 5-CH_2, 6-CH_2), 1.75-1.94 (m, 2H, 2-CH_2), 1.98-2.08 (m, 2H, 7-CH_2), 3.39 (t, J = 6.9 Hz, 2H, 1-CH_2), 4.51-5.04 (m, 2H, 9-CH_2), 5.81 (ddt, J = 17.0 Hz, J = 10.2 Hz, J = 6.9 Hz, 1H, 8-CH). - ^{13}C NMR: δ = 19.48 (4-$CHCH_3$), 26.29 (7-CH_2), 30.50 (5-CH_2), 32.12 (4-$CHCH_3$), 34.04, 34.29, 35.44 (6-CH_2, 3-CH_2, 2-CH_2), 36.29 (1-CH_2), 114.29 (9-CH_2), 139.04 (8-CH). - MS (70 eV), *m/z* (%): 219 (1.5) [M^+], 164 (24), 162 (26), 97 (54), 83 (27), 69 (74), 55 (100), 41 (80). - GC/HRMS: calcd. for [M^+–C_4H_7,–H] $C_6H_{11}Br$ 162.0044; found 162.0041.

(6S,10R/S,12R)-10-Benzenesulfonyl-6,12-dimethylpentadecene [(*S,R/S,R*)-**13**]: To a solution of sulfone (*R*)-**5** (0.12 g, 0.51 mmol) in THF (10 ml) containing dry HMPA (0.67 ml) under argon was added dropwise a solution of *n*-butyllithium in hexane (1.6 M, 0.38 ml, 0.62 mmol) at –30 °C and the resulting yellow solution was stirred at –30 °C for 1 h. After cooling to –78 °C, a solution of bromide (*S*)-**12** (0.14 g. 0.62 mmol) in THF (2 ml) was added dropwise with a syringe. The reaction mixture was slowly allowed to warm to room temperature and then quenched with saturated NH_4Cl solution (3 ml). The mixture was diluted with water (6 ml) and the aqueous phase was extracted with diethyl ether (5 x 20 ml). The combined organic extracts were washed with brine (20 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (silicagel, eluent: light petroleum / diethyl ether, 8:1), yielding 0.17 g (85 %) (*S,R/S,R*)-**13** as a colourless oil. - R_f = 0.16 (light petroleum / diethyl ether, 8:1). - IR (film): $\tilde{\nu}$ = 3070 (w, =CH), 2950, 2920, 2860 (s, CH_2, CH_3), 1680 (w, C=C), 1585 (w, C_{Ar}=C_{Ar}),1455 (m), 1443 (m), 1379 (w), 1300 (s, S=0), 1140 (s, S=0), 1072 (m), 905 (m), 725 (s), 690 (s) cm^{-1}. - ^1H NMR (epimer 1/epimer 2): δ = 0.73-0.90 (m, 9H, 6-$CHCH_3$, 12-$CHCH_3$, 15-CH_3), 0.92-1.90 (m, 18H, chain-CH_2, 6-$CHCH_3$, 12-$CHCH_3$), 1.94-2.06 (m, 2H, 3-CH_2), 2.92-3.01 (m, 1H, 10-CH), 4.90-5.04 (m, 2H, 1-CH_2), 5.72-5.88 (m, 1H, 2-CH), 7.52-7.60 (m, 2H, C_{meta}-H), 7.61-7.68 (m, 1H, C_{para}-H), 7.85 - 7.91 (m, 2H, C_{ortho}-H). - ^{13}C NMR (epimer 1/epimer 2): δ = 14.76/14.83 (15-CH_3), 19.57/20.07 (12-$CHCH_3$), 20.15/20.38 (6-$CHCH_3$), 20.17/20.51, 24.69/24.73, 26.85/26.89, 29.40/29.98 (3-CH_2, 5-CH_2, 7-CH_2, 13-CH_2), 30.69/30.93, 32.90 (6-$CHCH_3$, 12-$CHCH_3$), 34.60, 35.91/36.44,38.82/36.96, 37.37/37.49, 39.04/40.16 (4-CH_2, 8-CH_2, 9-CH_2, 11-CH_2, 14-CH_2), 63.14/63.24 (10-CH), 144.81 (1-CH_2), 129.39/129.45 (C_{ortho}), 134.03 (2-CH), 138.72/138.76 (C_{ipso}), 139.61/139.64 (C_{para}). - MS (70 eV), *m/z* (%): = 378 (1.7) [M^+], 237 (21) [M^+–$C_6H_5SO_2$], 236 (36), 153 (13), 143 (34), 139 (18), 125 (32), 111 (52), 97 (100), 85 (31), 83 (74), 77 (13),

71 (48), 69 (73), 57 (73), 55 (97), 43 (67), 41 (42). - $C_{24}H_{38}SO_2$ (390.6): calcd. C 72.96, H 10.11; found C 73.32, H 10.23.

(6R,12R)-6,12-Dimethylpentadecene [(*R,R*)-**14**]: According to ref.[3] , a solution of (*S,R/S,R*)-**13** (0.22 g, 0.58 mmol) in dry ethanol (2 ml) was added to a stirred suspension of sodium amalgam [freshly prepared from 0.33 g (14.5 mmol) of sodium and 5.2 g (25.9 mmol) of mercury] in ethanol (3 ml) at 0 °C under argon. The conversion was monitored by TLC (ca. 4 h). The mixture was then filtered (Celite®/Florisil®) and the filter cake was washed with ether. The combined filtrate and washings were concentrated to about a half of the original volume *in vacuo* at room temperature. The ethereal extracts were washed with water (10 ml) and brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* at room temperature. The residue was purified by flash column chromatography (silicagel, eluent: light petroleum / diethyl ether) to give (0.124 g, 89%) as a colourless liquid. - R_f = 0.76 (pentane). - $[\alpha]_D^{20}$ = –4.1 (*c* = 0.90, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3078 (w, =CH), 2950, 2920, 2860 (s, CH_2, CH_3), 1640 (m, C=C), 1455 (s), 1375 (s), 990 (m), 905 (s), 738 (w) cm^{-1}. - ^1H NMR: δ = 0.80-0.92 (m, 9H, 15-CH_3, 6-CHC*H*$_3$, 12-CHC*H*$_3$), 1.04-1.44 (m, 20H, chain CH_2, 6-C*H*CH_3, 12-C*H*CH_3), 1.96-2.08 (m, 2H, 3-CH_2), 4.90-5.04 (m, 2H, 1-CH_2), 5.81 (ddt, *J* = 17.0 Hz, *J* = 10.4 Hz, *J* = 6.6 Hz, 1H, 2-CH). - ^{13}C NMR: δ = 14.44 (15-CH_3), 19.71 (6-CH*C*H$_3$, 12-CH*C*H$_3$), 20.18, 26.47, 26.95, 27.15, 30.40, 34.19, 36.58, 37.09, 37.14, 39.46 (3-5-CH_2, 7-11-CH_2, 13-CH_2, 14-CH_2), 32.53, 32.69 (6-*C*HCH_3, 12-*C*HCH_3), 114.11 (1-CH_2), 139.27 (2-CH). - MS (70 eV), *m/z* (%): 238 (13) [M^+], 139 (14), 125 (13), 112 (37), 97 (100), 84 (72), 69 (55), 57 (65), 55 (67), 43 (44). - $C_{17}H_{34}$ (238.4): calcd. C 85.62, H 14.37; found C 85.69, H 14.39.

(6R,12R)-6,12-Dimethylpentadecan-2-one [(*R,R*)-**1**]: To the stirred yellow solution of mercury(II) acetate (0.43 g, 0.13 mmol) in acetone (2 ml) and water (0.1 ml) was added (*R,R*)-**14** (0.16 g, 0.64 mmol) in one portion. Jones reagent (2 ml of a 0.7 M solution) was added during 20 h. The dark, green to brown solution was stirred for an additional 20 h, then poured into water, and extracted with diethyl ether (4 x 15 ml). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. To remove small amounts of β-elimination side products the crude reaction product was subjected to ozonolysis in CH_2Cl_2 at –78 °C for 15 min with subsequent H_2O_2 oxidation (3%, 5 ml) at room temperature (2 h) to furnish pure (*R,R*)-**1** after extraction with diethyl ether (4 x 30 ml), drying ($MgSO_4$), evaporation and final purification by column chromatography (silicagel, eluent: pentane / diethyl ether, 50:1) as a colourless liquid (0.12 g, 73%). - R_f = 0.50 (pentane / diethyl ether, 8:1). - $[\alpha]_D^{20}$ = –0.5 (*c* = 0.6, $CHCl_3$) {ref.[3]: $[\alpha]_D^{22}$ = –0.5 (*c* = 1.13, $CHCl_3$) - IR (film): $\tilde{\nu}$ = 2960, 2920, 2850 (br., CH_2, CH_3), 1718 (C=O), 1460 (m), 1440 (w), 1370 (m), 1355 (m), 1225 (w), 1165 (w) cm^{-1}. - ^1H NMR: δ = 0.81-0.92 (m, 9H, 15-CH_3, 6-CHC*H*$_3$, 12-CHC*H*$_3$), 1.00-1.68 (m, 20H, chain-CH_2, 6-$CHCH_3$, 12-$CHCH_3$), 2.13 (s, 3H, 1-CH_3), 2.40 (t, *J* = 7.7 Hz, 3-CH_2). - ^{13}C NMR: δ = 14.98 (15-CH_3), 20.12, 20.24 (6-CH*C*H$_3$, 12-CH*C*H$_3$), 20.71, 22.00, 27.63, 27.66, 30.90, 37.07, 37.47, 37.65, 39.99 (4-CH_2, 5-CH_2, 7-11-CH_2, 13-CH_2, 14-CH_2), 30.43 (1-CH_3), 33.04, 33.22 (6-*C*HCH_3, 12-*C*HCH_3), 44.71 (3-CH_2), 209.97 (C=O). - MS (70 eV), *m/z* (%): 254 (3) [M^+], 236 (10), 211 (12), 196 (3), 165 (2), 137 (2), 123 (4), 110 (16), 95 (9), 85 (12), 71 (30), 58 (100), 57 (27), 43 (35). - HRMS: calcd. for $C_{17}H_{34}O$ 254.2610; found 254.2611.

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