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Synthesis of New Strigol Analogues

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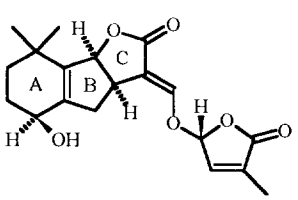
Abstract - 2-Cyclopenten-1-ylacetic acid has been converted into strigol seco-analogues.

Introduction

Germination of seeds of root parasitic flowering plants of the genera *Striga*, *Alectra* (Scrophulariaceae), and *Orobanche* (Orobanchaceae) is stimulated by substances from their host plants. Prominent examples are strigol (**1**) and its acetate [first isolated from cotton (*Gossypium hirsutum*) which is neither a host for *Striga* nor for *Orobanche*,[2] but recently also from the root exudates of *Striga*[3]], sorgolactone and alectrol [isolated from the root exudates of *Sorghum vulgare* (host for *Striga*) and *Vigna unguiculata* (host for *Striga* and *Alectra*), respectively].[4]

We and others have reported on a rather comprehensive set of structure-activity relations. There seem to exist very specific interactions between the stimulant and the binding site(s) at the seeds which are, in addition, species-dependent.[5] Both the absolute and the relative configuration at the butenolide C-2 (C-2") are of major importance as far as seed germination potency is concerned.[6,7,8]



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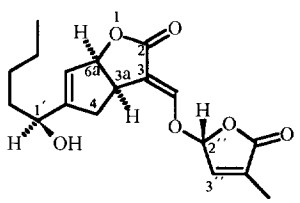


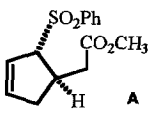
2

Scheme 1

For reasons that will be detailed in a later paper we became interested in compound **2** differing from strigol (**1**) mainly by the feature that to ring B instead of ring A an open-chain appendage is attached.[9] A new approach was envisaged with two palladium-mediated key reactions.

Results and Discussion

Compound *rac*-**4** was obtained from *rac*-**3** via iodo lactone **5** as described by Johnson et al.[10] Trost and Verhoeven have reported that the reaction of *rac*-**4** with sodium dimethyl malonate in the presence of catalytic quantities of $Pd[PPh_3]_4$ produced a single 4-alkylation product with cis configuration.[11]

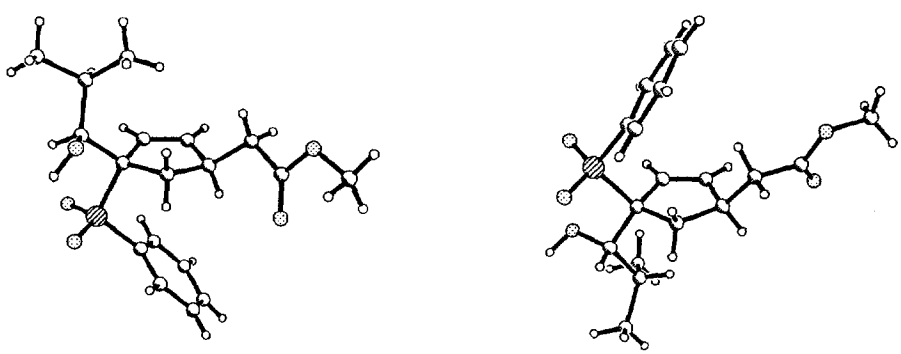


A

However, with sodium benzenesulfinate we observed the formation of a 1:1:1 mixture of *rac*-**6a**, *rac*-**6b**, and the 2-regioisomer *rac*-**A** (after methylester formation). Replacement of $Pd[PPh_3]_4$ by $Pd[P(OiPr)_3]_4$ improved the situation considerably. Under these conditions only the stereoisomers *rac*-**6a** and *rac*-**6b** were obtained (after methyl ester formation) in about 65% yield. The reaction was best performed in 2:1 THF-acetonitrile. Why the product ratio is so dependent on the catalyst has not been studied. In separate experiments it was found, however, that *rac*-**6a** and *rac*-**6b** were configurationally not completely stable both under the conditions of the sulfone and the ester formation.

When a mixture of *rac*-**6a** and *rac*-**6b** was treated with LDA and then with 1-isobutyryl-1H-imidazole[12] a mixture of the acylation products *rac*-**7a** and *rac*-**8a** was obtained. The configurational assignments are based on X-ray crystal structures (*vide infra*).

Reduction of *rac*-**7a** with sodium borohydride provided *rac*-**9a** and *rac*-**10a** in a 1:1.6, and from *rac*-**8a** the isomers *rac*-**11a** and *rac*-**12a** were obtained in a 1:2.5 ratio. The configuration of both *rac*-**9a** and *rac*-**11a** was determined by X-ray analysis (see Figures 1a and 1b).

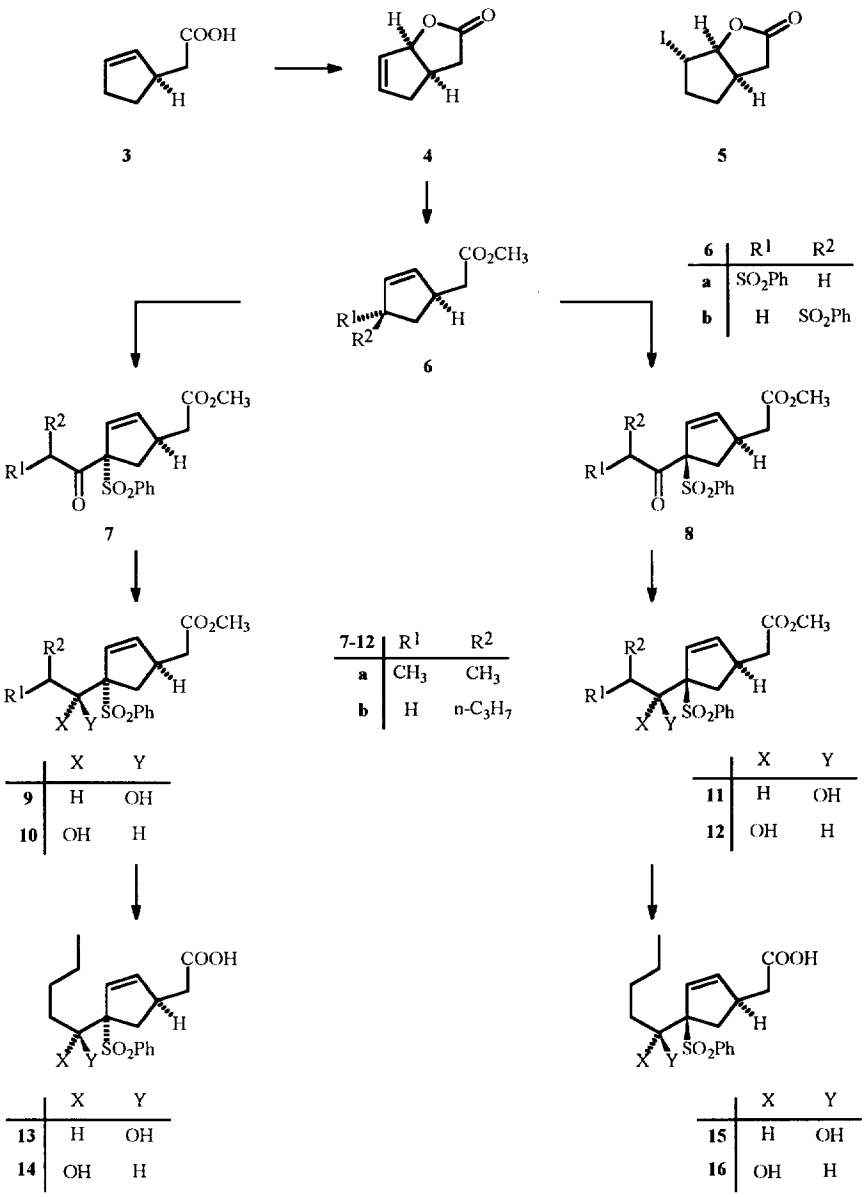


(a) (b)

Figure 1. X-ray structures of hydroxy sulfones *rac*-**9a** (a) and *rac*-**11a** (b)

The ^1H NMR spectra of the four hydroxy sulfones differ very characteristically from each other. In the series were the $PhSO_2$ group and 1-H are cis (*rac*-**9a** and *rac*-**10a**) the 1-H signal is much more shielded than in the

other series where the two groups are trans. This difference is probably caused by the ring current of the



Scheme 2

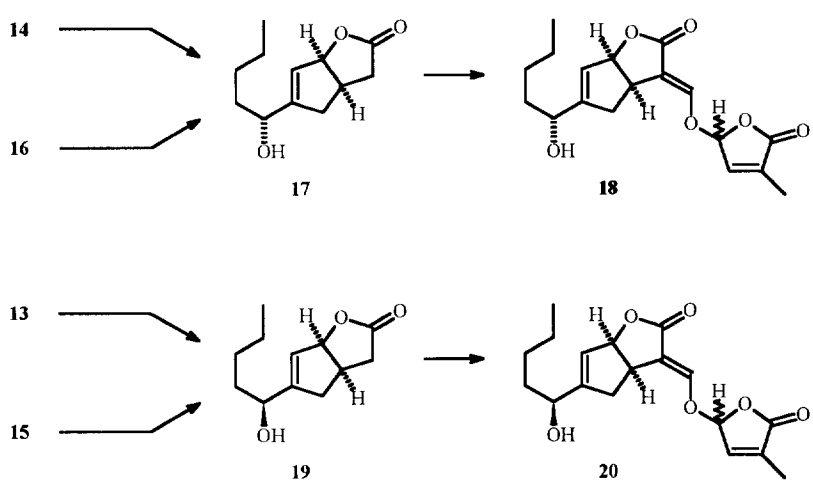
aromatic ring that can influence 1-H only in *rac*-**9a** and *rac*-**10a** (see Figure 1). On the other hand, the configuration at the carbinol C can be correlated with the chemical shift of 2-H which is more downfield in the *ul* (C-4 and C-1') compounds *rac*-**10a** and *rac*-**11a** than in the *l* isomers *rac*-**9a** and *rac*-**12a**.

Table 1. Characteristic ^{1}H NMR data of racemic hydroxy sulfones **9a - 12a** and **9b - 12b**

	1-H	2-H	3-H
rac- **9a**	≈ 2.20-2.35	5.56 (dd)	5.93 (dd)
rac- **10a**	≈ 2.10-2.41	5.87 (dd)	5.95 (dd)
rac- **11a**	≈ 3.06-3.15	5.91 (dd)	5.99 (dd)
rac- **12a**	≈ 3.11-3.22	5.50 (dd)	5.93 (dd)
rac- **9b**	≈ 2.36-2.47	5.35 (dd)	5.88 (dd)
rac- **10b**	≈ 2.15-2.20	5.79 (dd)	5.92 (dd)
rac- **11b**	≈ 2.99-3.09	5.87 (dd)	5.99 (dd)
rac- **12b**	≈ 3.07-3.17	5.33 (dd)	5.89 (dd)

When the anion derived from *rac*-**6** was treated with 1-pentanoyl-1H-imidazole,[13] the acylation products *rac*-**7b** and *rac*-**8b** were obtained. Each keto sulfone was reduced with $NaBH_4$ to give racemic **9b/10b** and **11b/12b**, respectively. In these hydroxy sulfones the configuration was easily assigned by comparison of their ^{1}H NMR spectra with those of *rac*-**9a** to *rac*-**12a** (see Table 1).

Ester hydrolysis converted *rac*-**11b** into *rac*-**15** and *rac*-**12b** into *rac*-**16**. Both compounds on exposure to freshly prepared $Pd[PPh_3]_4$ (THF, 60°C, 1.6 equiv. of DBU) underwent smooth cyclization to provide the bicyclic lactones *rac*-**19** and *rac*-**17**, respectively (yield ≈ 95%) in accord with the known stereochemistry of π-allylpalladium complex formation and substitution reactions.



Scheme 3

The stereoisomeric acids *rac*-**14** and *rac*-**13** (4-epimers of *rac*-**16** and *rac*-**15**) cyclized also under these conditions albeit much slower. The cyclisation products were, as expected, *rac*-**17** and *rac*-**19**, respectively. Finally, *rac*-**17** was formylated with ethyl formate and the hydroxymethylene derivative treated with racemic 5-bromo-3-methyl-5H-furan-2-one according to known procedures[14] to furnish a mixture of the two racemic 2"-isomers **18** which could be separated. As usual,[15] the NMR spectra were virtually superimposable and did not allow configurational assignment at C-2". In the same way *rac*-**19** was converted into the diastereomeric strigol analogues *rac*-**20**.

Experimental

General

All O_2 - or moisture-sensitive reactions were performed in oven-dried glassware under a positive pressure of argon. Liquids and solutions were transferred by syringe. Small-scale reactions were performed in Wheaton serum bottles sealed with aluminum caps with open top and Teflon-faced septum (Aldrich). Usual work-up means partitioning the reaction mixture between an aqueous phase and an organic solvent (given in parentheses), drying the combined organic solutions over Na_2SO_4, and removal of solvent by distillation using a rotatory evaporator (bath temperature 45°C). Solvents were purified by standard techniques.- The following materials and methods were used for chromatographic separations: preparative gravitational liquid chromatography (LC): silica gel 63-100 μm (ICN Biomedicals); Flash chromatography (FC) [16]: silica gel 32-63 μm (ICN Biomedicals); medium-pressure liquid chromatography (MPLC): silica gel 40-60 μm (Grace); Duramat pump (CfG), preparative HPLC: Jasco PU-987 pump and Jasco Lichrosorb column (Si 60, 10 μm, 250 x 25 mm), flow rate: 4.5 ml/min, detection with the multi wavelength UV detector Jasco 875-UV; analytical TLC: Merck precoated silica gel 60 F_{254} plates (0.2 mm), spots were identified under a UV lamp (Camag 29 200) and with a 2.22 mol/L H_2SO_4 solution which contained $Ce(SO_4)_2 \cdot 4H_2O$ (10 g/L) and $H_3[PO_4(Mo_3O_9)_4] \cdot H_2O$ (25 g/L)[17] and heating at 140°C; GC: HP 5890 Series II (Hewlett-Packard), 30 m x 0.2 mm phenyl methyl silicone column, carrier gas: H_2, FID; GC-MS: GC HP 5890 Series II (Hewlett-Packard), MS: 5972 Series (Hewlett-Packard), 30 m x 0.25 mm phenyl methyl silicone column (HP-5MS, Hewlett-Packard), 70°C (2 min), then 70°C → 270°C (25°C per min).- NMR and MS equipment: NMR: AM 400 (Bruker), UNITY 400 (Varian), GEMINI 200 (Varian), GEMINI 2000 (Varian), WP 80 (Bruker); MS: MAT-731 (Varian), VG-Autospec (Fisons).- IR: Perkin Elmer 1310 and 881, Carl Zeiss Specord M80, Genesis FTIR (ATI Mattson), solvent was in all cases $CDCl_3$, concentration 5 mg / 0.2 ml.- UV: Beckman DU 650.- X-ray: Siemes P4 diffractometer.

Reaction of *rac*-4 with sodium benzenesulfinate in the presence of $Pd[PPh_3]_4$

A solution of *rac*-**4** (1.09 g, 8.8 mmol) in THF (18.5 ml) was added at 20°C to a mixture of sodium benzenesulfinate (3.65 g, 22.3 mmol) and methanol (9.3 ml). Freshly prepared $Pd[PPh_3]_4$[18] (482.0 mg, 0.4 mmol) in THF (18.5 ml) was added, and the mixture was refluxed for 22 h. At 20°C water was added and the mixture was extracted with CH_2Cl_2, then the aqueous phase was acidified (pH 3) with 5 per cent HCl and then again extracted with CH_2Cl_2. The combined organic phases were worked up as usual. The crude product (4.17 g) was dissolved in acetonitrile (60 ml), DBU (2.4 ml, 16.1 mmol) and methyl iodide (980 μl, 15.7 mmol) were added and the mixture was left at 20°C for 1 h. After water addition and extraction with CH_2Cl_2 the aqueous phase was acidified with 5 per cent HCl (pH 1) and extracted with CH_2Cl_2. 619.4 mg of non-esterified reaction product were isolated which was submitted to the methylation conditions described above. After LC

($CHCl_3$ - acetone 100:1) a 1:1:1 mixture of *rac*-**6a**, *rac*-**6b** and *rac*-**A** (2.33 g, 94%) was obtained. Analytical samples of the three sulfones were obtained by MPLC (petrol - ethyl acetate 3:1).

Reaction of *rac*-4 with sodium benzenesulfinate in the presence of $Pd[P(O^iPr)_3]_4$

To a suspension of sodium benzenesulfinate (262.9 mg, 1.603 mmol) in acetonitrile (2 ml) a solution of *rac*-**4** (79.6 mg, 0.641 mmol) in THF (2 ml) and a solution of tetrakis(triisopropylphosphite)palladium(0) (0.096 mmol), prepared from a solution of palladium(II) acetate (21.6 mg, 0.096 mmol) in THF (2 ml) by addition of triisopropylphosphite (237 µl, 0.960 mmol) and butyllithium (1.6 M in hexane, 120 µl, 0.192 mmol) in THF (2 ml)[19] were added at 0°C. The mixture was stirred at 70°C for 6 d. Water was added. After extraction with ether, acidification of the aqueous phase with 5 per cent HCl to pH 2, further extraction with ether, drying of the combined organic phases, solvent evaporation, the crude product was dryed at 80°C at 1 Pa. This material was dissolved in acetonitrile (3 ml) and treated with DBU (173 µl, 1.154 mmol) and methyl iodide (72 µl, 1.154 mmol). The reaction mixture was stirred for 2 h at 40°C then again DBU (96 µl, 0.641 mmol) and methyl iodide (40 µl, 0.641 mmol) were added. After another 90 min at 40°C water was added. Usual work-up (CH_2Cl_2) followed by LC ($CHCl_3$ - acetone 100:1) and MPLC (cyclohexane - ^{t}butyl methyl ether - 2-propanol 35:5:1) furnished *rac*-**6b** (77.5 mg, 43%), *rac*-**6a** (12.0 mg, 7%) and a fraction containing *rac*-**6b** and *rac*-**6a** (31.2 mg, 18%).

Methyl [(1S*, 4S*)-4-benzenesulfonyl-2-cyclopenten-1-yl] acetate (*rac*-6a)

^{1}H NMR (400 MHz, $CDCl_3$, cis or trans refers to 1-H): δ = 1.76-1.84 (ddd, 1H, 5_t-H); 2.20-2.29 (dd, 1H, -C$\underline{H}_a$-CO_2CH_3); 2.31-2.38 (dd, 1H, -C$\underline{H}_b$-CO_2CH_3); 2.55-2.65 (ddd, 1H, 5_c-H); 2.92-3.02 (m, 1H, 1-H); 3.64 (s, 3H, OCH_3); 4.27-4.34 (m, 1H, 4-H); 5.65-5.71 (m, 1H, 2-H); 6.00-6.05 (m, 1H, 3-H); 7.50-7.56 (m, 2H, Ar-H's); 7.60-7.67 (m, 1H, Ar-H); 7.82-7.88 (m, 2H, Ar-H's). $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5c}$ = 8.0 Hz; $J_{1,5t}$ = 6.5 Hz; $J_{1,C\underline{H}_aH_bCO_2CH_3}$ + $J_{1,CH_a\underline{H}_bCO_2CH_3}$ = 14.0 Hz; $J_{2,3}$ = 5.5 Hz; $J_{2,4}$ = 2.0 Hz; $J_{3,4}$ = 2.0 Hz; $J_{4,5c}$ = 3.0 Hz; $J_{4,5t}$ = 9.5 Hz; J_{5gem} = 14.5 Hz; $J_{C\underline{H}_aH_bCO_2CH_3}$ = 15.5 Hz.- IR ($CHCl_3$): 1730, 1440, 1305, 1150, 1085 cm^{-1}.- MS: m/z (%) = 249 (2), 207 (6), 139 (95), 107 (58), 97 (15), 79 (100), 77 (29).- HRMS calc. for $C_{13}H_{13}O_3S$: 249.0585, found 249.0590.- $C_{14}H_{16}O_4S$ (280.3) calc. C 59.98, H 5.75, found C 60.03, H 5.79.

Methyl [(1S*, 4R*)-4-benzenesulfonyl-2-cyclopenten-1-yl] acetate (*rac*-6b)

^{1}H NMR (400 MHz, $CDCl_3$, cis or trans refers to 1-H): δ = 1.88-1.95 (ddd, 1H, 5_c-H); 2.15-2.22 (dd, 1H, -C$\underline{H}_a$-CO_2CH_3); 2.25-2.34 (dd, 1H, -C$\underline{H}_b$-CO_2CH_3); 2.41-2.50 (ddd, 1H, 5_t-H); 3.08-3.18 (m, 1H, 1-H); 3.63 (s, 3H, OCH_3); 4.22-4.30 (m, 1H, 4-H); 5.60-5.65 (ddd, 1H, 2-H); 5.99-6.04 (ddd, 1H, 3-H); 7.49-7.56 (m, 2H, Ar-H's); 7.59-7.68 (m, 1H, Ar-H); 7.82-7.88 (m, 2H, Ar-H's); $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5c}$ = 4.5 Hz; $J_{1,5t}$ = 9.0 Hz; $J_{1,C\underline{H}_aH_bCO_2CH_3}$ + $J_{1,CH_a\underline{H}_bCO_2CH_3}$ = 15.0 Hz; $J_{2,3}$ = 5.5 Hz; $J_{2,4}$ = 2.0 Hz; $J_{3,4}$ = 2.0 Hz; $J_{4,5c}$ = 4.5 Hz; $J_{4,5t}$ = 9.0 Hz; J_{5gem} = 15.0 Hz; $J_{CH_a\underline{H}_bCO_2CH_3}$ = 16.5 Hz.- IR ($CHCl_3$): 1725, 1440, 1300, 1145 cm^{-1}.- MS: m/z (%) = 279 (3), 249 (2,5), 167 (8), 149 (18), 139 (90), 107 (57), 79 (100).- $C_{14}H_{16}O_4S$ (280.3) calc C 59.98, H 5.75, found C 59.97, H 5.70.

Methyl [(1S*, 2S*)-2-benzenesulfonyl-3-cyclopenten-1-yl] acetate (*rac*-A)

^{1}H NMR (400 MHz, $CDCl_3$, H,H COSY, cis or trans refers to 1-H): δ = 1.98-2.07 (m, 1H, 5_t-H); 2.30-2.39 (dd, 1H, -C$\underline{H}_a$-CO_2CH_3); 2.40-2.49 (dd, 1H, -C$\underline{H}_b$-CO_2CH_3); 2.50-2.60 (m, 1H, 5_c-H); 2.99-3.08 (m, 1H, 1-H); 3.60 (s, 3H, OCH_3); 4.03-4.10 (m, 1H, 2-H); 5.55-5.62 (m, 1H, 4-H); 5.98-6.04 (m, 1H, 3-H); 7.50-7.57 (m, 2H, Ar-H's); 7.59-7.68 (m, 1H, Ar-H); 7.82-7.88 (m, 2H, Ar-H's). $J_{1,C\underline{H}_aH_bCO_2CH_3}$ + $J_{1,CH_a\underline{H}_bCO_2CH_3}$ = 14.0 Hz; J_{5gem} = 17.5 Hz; $J_{C\underline{H}_aH_bCO_2CH_3}$ = 15.0 Hz.- IR ($CHCl_3$): 1730, 1440, 1305, 1150, 1135, 1085 cm^{-1}.-

MS: m/z (%) = 249 (4); 139 (96); 107 (63); 97 (17); 79 (100);77 (36).- HRMS calc for $C_{13}H_{13}O_3S$: 249.0585, found 249.0593.- $C_{14}H_{16}O_4S$ (280.3).

Treatment of *rac*-6b with DBU

A solution of ***rac*-6b** (2.9 mg, 0.010 mmol) in acetonitrile (300 µl) was treated with DBU (2.8 µl, 0.018 mmol) and the mixture was left at 20°C for 3 h. After usual work-up (diethyl ether) the formation of ***rac*-6a** could be detected by TLC (cyclohexane - ^{t}butyl methyl ether - 2-propanol 25 : 5 : 1).

Treatment of *rac*-6b with tetrakis(triisopropylphosphite)palladium(0)

To a suspension of sodium benzenesulfinate (17.2 mg, 0.105 mmol) in acetonitrile (1.2 ml) a solution of ***rac*-6b** (14.7 mg, 0.052 mmol) in THF (1.5 ml) and then $Pd[P(O^iPr)_3]_4$ {freshly prepared from palladium(II) acetate (2.9 mg, 0.013 mmol), triisopropyl phosphite (32 µl, 0.130 mmol) and a 1.6 mol/L solution of butyllithium in hexan (16 µl, 0.026 mmol)} were added. The mixture was stirred at 70°C for 5 d. The formation of rac-**6a** was detected by TLC (cyclohexane - ^{t}butyl methyl ether - 2-propanol 25 : 5 : 1.

Conversion of *rac*-6a and *rac*-6b into *rac*-7a and *rac*-8a

To a solution of ***rac*-6a** and ***rac*-6b** (735.9 mg, 2.625 mmol) in THF (70 ml) cooled to -105°C a solution of LDA (-78°C, 0.5 mol/L in THF/hexane, 5.8 ml, 2.887 mmol) and 1-isobutyryl-1H-imidazole (3.62 g, 26.2 mmol) were added. The mixture was allowed to warm to -78°C. After 5h and 30 min the cooling bath was removed and sat. aq. NH_4Cl (10 ml) was added. Usual work-up (CH_2Cl_2), followed by LC (petrol - ethyl acetate = 5 : 1) and MPLC (cyclohexane - ^{t}butyl methyl ether - 2-propanol 75 : 5 : 1) furnished ***rac*-8a** (141.7 mg, 16%), ***rac*-7a** (164.4 mg, 19%) and a fraction containing ***rac*-8a** and ***rac*-7a** (254.8 mg, 29%).

Methyl [(1S*, 4S*)-4-benzenesulfonyl-4-(2-methyl-propanoyl)-2-cyclopenten-1-yl] acetate (*rac*-7a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, 3H, 2´- CH_3); 1.17 (d, 3H, 2´- CH_3); 2.11 (dd, 1H, 5-H_a); 2.19-2.35 (m, 2H, C$\underline{H}_2CO_2CH_3$, AB of ABX, J_{AB} = 16.0 Hz); 2.80 (dd, 1H, 5-H_b); 2.88-2.96 (m, 1H, 1-H), 3.38 (sept, 1H, 2´-H); 3.63 (s, 3H, OCH_3); 6.01 (dd, 1H, 2-H); 6.10 (dd, 1H, 3-H); 7.48-7.59 (m, 2H, Ar-H´s); 7.63-7.70 (m, 1H, Ar-H); 7.73-7.80 (m, 2H, Ar-H´s); $J_{1,2}$ = 2.5 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5\text{-}Ha}$ = 6.0 Hz; $J_{1,5\text{-}Hb}$ = 8.0 Hz; $J_{2,3}$ = 5.5 Hz; J_{5gem} = 15.0 Hz; $J_{2'\text{-}CH3,2'}$ = 7.0 Hz.- IR ($CHCl_3$): 1740, 1715, 1455, 1445, 1325, 1150, 1090 cm^{-1}.- $C_{18}H_{22}O_5S$ (350.4).- MS: m/z (%) = 350 (2), 280 (10), 209 (73), 77 (47), 71 (82), 43 (100).- HRMS: calc. 350.1188, found 350.1213.

Methyl [(1S*, 4R*)-4-benzenesulfonyl-4-(2-methyl-propanoyl)-2-cyclopenten-1-yl] acetate (*rac*-8a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, 3H, 2´- CH_3); 1.14 (d, 3H, 2´- CH_3); 2.08 (dd, 1H, 5-H_a); 2.20-2.35 (m, 2H, C$\underline{H}_2CO_2CH_3$, AB of ABX, J_{AB} = 16.0 Hz); 2.79 (dd, 1H, 5-H_b); 3.06-3.19 (m, 1H, 1-H), 3.30 (sept, 1H, 2´-H); 3.75 (s, 3H, OCH_3); 6.06 (dd, 1H, 2-H); 6.13 (dd, 1H, 3-H); 7.50-7.56 (m, 2H, Ar-H´s); 7.61-7.68 (m, 1H, Ar-H); 7.71-7.78 (m, 2H, Ar-H´s); $J_{1,2}$ = 2.5 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5\text{-}Ha}$ = 5.5 Hz; $J_{1,5\text{-}Hb}$ = 8.5 Hz; $J_{2,3}$ = 5.5 Hz; J_{5gem} = 15.0 Hz; $J_{2'\text{-}CH3,2'}$ = 7.0 Hz.- IR ($CHCl_3$): 1735, 1715, 1455, 1445, 1320, 1150, 1085 cm^{-1}.- $C_{18}H_{22}O_5S$ (350.4).- MS: m/z (%) = 350 (3), 280 (8), 209 (60), 77 (31), 71 (78), 43 (100).- HRMS: calc. 350.1188, found 350.1190.

Reduction of *rac*-8a

To a solution of ***rac*-8a** (202.0 mg, 0.576 mmol) in methanol (3 ml) at 20°C $NaBH_4$ (43.6 mg, 1.153 mmol) was added and the mixture was stirred at 20°C for 3 h. Excess $NaBH_4$ was destroyed with 5% per cent HCl.

Usual work-up (CH_2Cl_2) and MPLC (petrol - ethyl acetate 4 : 1) gave *rac*-**12a** (47.0 mg, 23%) and *rac*-**11a** (116.9 mg, 58%).

Methyl [(1S*, 4R*)-4-benzenesulfonyl-4-{(S*)-1-hydroxy-2-methyl-propyl}-2-cyclopenten-1-yl] acetate (*rac*-11a)

M.p. 112-114°C (petrol-CH_2Cl_2).- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (d, 3H, 2′- CH_3); 1.03 (d, 3H, 2′-CH_3); 1.74 (dd, 1H, 5-H_a), 1.87 (dd, 1H, $C\underline{H}_aCO_2CH_3$); 1.93-2.03 (m, 2H, 2′-H and $C\underline{H}_bCO_2CH_3$); 2.33 (dd, 1H, 5-H_b); 3.06-3.15 (m, 1H, 1-H); 3.25-3.33 (m, 1H, OH); 3.63 (s, 3H, OCH_3); 4.11-4.16 (m, 1H, 1′-H); 5.91 (dd, 1H, 2-H); 5.99 (dd, 1H, 3-H); 7.48-7.58 (m, 2H, Ar-H′s); 7.60-7.66 (m, 1H, Ar-H); 7.80-7.86 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5\text{-}Ha}$ = 8.5 Hz; $J_{1,5\text{-}Hb}$ = 9.0 Hz; $J_{2,3}$ = 5.5 Hz; J_{5gem} = 15.5 Hz; $J_{2'\text{-}CH3,2'}$ = 7.0 Hz; $J_{C\underline{H}aCO2CH3,1}$ = 5.5 Hz; $J_{C\underline{H}bCO2CH3,1}$ = 6.5 Hz; $J_{C\underline{H}a\underline{H}bCO2CH3}$ = 16.0 Hz.- IR ($CHCl_3$): 3540, 2970, 1735, 1455, 1445, 1290, 1270, 1160, 1090, 1010 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4).- MS: m/z (%) = 280 (10, $[M\text{-}(CH_3)_2CHCHO]^{+\cdot}$), 211 (9), 207 (15), 193 (51), 179 (32), 71 (100), 43 (80).

X-ray structural analysis of *rac*-11a

rac-**11a**, $C_{18}H_{24}O_5S$, colorless prisms, monoclinic, space group C2/c, with $\underline{a}$ = 29.894(5) Å, $\underline{b}$ = 8.907(2) Å, $\underline{c}$ = 15.362(3) Å, β = 120.13(2) °, V = 3537.8(17) $Å^3$, Z = 8, D_c = 1.323 $g{\cdot}cm^3$. The structure was refined to R = 0.042, R_w = 0.038 for 1615 independent reflexions with $F_0^2 > 2\sigma(F_0^2)$ from 2572 collected on a Siemens P4 diffractometer (MoKα, 2θ≤46°, ω-scan). Nonhydrogen atoms were assigned anisotropic temperature factors; hydrogen atoms were refined isotropically. Further details of the structure investigation may be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76012 Eggenstein-Leopoldshafen (Germany), on quoting the deposition number CSD - 405237. Any request should be accompanied by the full literature citation of this paper.

Methyl [(1S*, 4R*)-4-benzenesulfonyl-4-{(R*)-1-hydroxy-2-methyl-propyl}-2-cyclopenten-1-yl] acetate (*rac*-12a)

^{1}H NMR (400 MHz, $CDCl_3$); H,H COSY: δ = 0.81 (d, 3H, 2′- CH_3); 1.01 (d, 3H, 2′- CH_3); 1.59-1.73 (m, 2H, 2′-H and $C\underline{H}_aCO_2CH_3$); 1.82 (dd, 1H, 5-H_a); 1.92 (dd, 1H, $C\underline{H}_bCO_2CH_3$); 2.88 (dd, 1H, 5-H_b); 3.11-3.21 (m, 1H, 1-H), 3.29-3.35 (m, 1H, OH); 3.63 (s, 3H, OCH_3); 4.46-4.51 (m, 1H, 1′-H), J = 3.0 Hz; 5.50 (dd, 1H, 2-H); 5.93 (dd, 1H, 3-H); 7.51-7.60 (m, 2H, Ar-H′s); 7.65-7.71 (m, 1H, Ar-H); 7.78-7.86 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.5 Hz; $J_{1,3}$ = 2.5 Hz; $J_{1,5\text{-}Ha}$ = 7.0 Hz; $J_{1,5\text{-}Hb}$ = 9.5 Hz; $J_{2,3}$ = 5.5 Hz; J_{5gem} = 16.5 Hz; $J_{2'\text{-}CH3,2'}$ = 7.0 Hz; $J_{C\underline{H}aCO2CH3,1}$ = 8.5 Hz; $J_{C\underline{H}bCO2CH3,1}$ = 4.0 Hz; $J_{C\underline{H}a\underline{H}bCO2CH3}$ = 16.5 Hz.- IR ($CHCl_3$): 3550, 2970, 1735, 1455, 1445, 1290, 1270, 1155, 1135, 1010 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4) .- MS: m/z (%) = 280 (8, $[M\text{-}(CH_3)_2CHCHO]^{+\cdot}$), 211 (8), 207 (8), 193 (46), 179 (31), 71 (100), 43 (85).

Reduction of *rac*-7a

The reduction was performed as described for *rac*-**8a**. MPLC (petrol - ethyl acetate 4 : 1) furnished *rac*-**9a** (28%) and *rac*-**10a** (45%).

Methyl [(1S*, 4S*)-4-benzenesulfonyl-4-{(S*)-1-hydroxy-2-methyl-propyl}-2-cyclopenten-1-yl] acetate (*rac*-9a)

M.p. 82-84°C (petrol-CH_2Cl_2).-^{1}H NMR (400 MHz, $CDCl_3$; H,H COSY): δ = 0.88 (d, 3H, 2′-CH_3); 1.02 (d, 3H, 2′-CH_3); 1.70-1.83 (m, 1H, 2′-H); 2.09 (dd, 1H, 5-H_a); 2.20-2.35 (m, 3H, $C\underline{H}_2CO_2CH_3$, AB of ABX, J_{AB} = 17.3 Hz and 1-H); 2.63 (dd, 1H, 5-H_b); 3.28-3.30 (d broad, 1H, OH); 3.61 (s, 3H, OCH_3); 4.38-4.42 (m, 1H, 1′-H); 5.56 (dd, 1H, 2-H); 5.93 (dd, 1H, 3-H); 7.50-7.58 (m, 2H, Ar-H′s); 7.63-7.70 (m, 1H, Ar-H);

7.80-7.88 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 1.5 Hz; $J_{1,5\text{-}Ha}$ = 7.0 Hz; $J_{1,5\text{-}Hb}$ = 7.0 Hz; $J_{2,3}$ = 5.5 Hz; J_{5gem} = 16.0 Hz; $J_{1',2'}$ = 3.5 Hz; $J_{2'\text{-}CH3,2'}$ = 7.0 Hz.- IR ($CHCl_3$): 3550, 2970, 1737, 1455, 1445, 1290, 1265, 1135, 1085 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4).- MS: m/z (%) = 280 (3, $[M\text{-}(CH_3)_2CHCHO]^{+\cdot}$), 211 (12), 207 (6), 193 (48), 179 (35), 71 (100), 43 (76).

X-ray structural analysis of *rac*-9a

rac-**9a**, $C_{18}H_{24}O_5S$, white prisms, monoclinic, space group $P2_1/n$, with a = 11.627(2) Å, b = 15.043(3) Å, c = 11.715(2) Å, β = 114.12(2) °, V = 1869.9(6) $Å^3$, Z = 4, Dc = 323 $g \cdot cm^3$. The structure was refined to R = 0.049, R_w = 0.048 for 1353 independent reflexions with $F_0^2 > 2\sigma(F_0^2)$ from 2309 collected on a Siemens P4 diffractometer (MoKα, 2θ≤45°, ω-scan). Anisotropic and isotropic temperature factors were assigned as for *rac*-**11a**. Further details of the structure investigation may be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76012 Eggenstein-Leopoldshafen (Germany), on quoting the deposition number CSD - 405236. Any request should be accompanied by the full literature citation of this paper.

Methyl [(1S*, 4S*)-4-benzenesulfonyl-4-{(R*)-1-hydroxy-2-methyl-propyl}-2-cyclopenten-1-yl] acetate (*rac*-10a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, 3H, 2′-CH_3); 1.07 (d, 3H, 2′-CH_3); 1.76 (dd, 1H, 5-H_a); 2.10-2.41 (m, 4H, 2′-H; $CH_2CO_2CH_3$ and 1-H); 2.63 (dd, 1H, 5-H_b); 2.99-3.06 (bs, 1H, OH); 3.60 (s, 3H, OCH_3); 4.08-4.13 (m, 1H, 1′-H); 5.87 (dd, 1H, 2-H); 5.95 (dd, 1H, 3-H); 7.45-7.55 (m, 2H, Ar-H′s); 7.59-7.68 (m, 1H, Ar-H); 7.83-7.90 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 2.5 Hz; $J_{1,5\text{-}Ha}$ = 7.0 Hz; $J_{1,5\text{-}Hb}$ = 8.0 Hz; $J_{2,3}$ = 5.5 Hz; J_{5gem} = 15.5 Hz; $J_{2'\text{-}CH3,2'}$ = 7.0 Hz; $J_{1',2'}$ = 3.0 Hz.- IR ($CHCl_3$): 3540, 2970, 1737, 1455, 1445, 1290, 1270, 1140, 1085 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4).- MS: m/z (%) = 280 (4, $[M\text{-}(CH_3)_2CHCHO]^{+\cdot}$), 211 (12), 207 (10), 193 (49), 179 (36), 71 (100), 43 (78).

Conversion of *rac*-6a and *rac*-6b into *rac*-7b and *rac*-8b

This reaction was performed as described for the conversion of *rac*-**6a** and *rac*-**6b** into *rac*-**7a** and *rac*-**8a**. LC (petrol - ethyl acetate 5 : 1) and MPLC (cyclohexane - ^{t}butyl methylether - 2-propanol 75 : 5 : 1) furnished *rac*-**8b** (29%), *rac*-**7b** (16%) and a fraction containing both compounds (21%). 13% of a mixture of *rac*-**6a** and *rac*-**6b** were reisolated. Later it was found that the separation can be accomplished by prep. HPLC (Jasco-Lichrosorb Si 60, flow rate 4.5 ml min^{-1}, cyclohexane - ^{t}butyl methylether - 2-propanol 75 : 5 : 1).

Methyl [(1S*, 4S*)-(4-benzenesulfonyl-4-(1-pentanoyl)-2-cyclopenten-1-yl] acetate (*rac*-7b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, 3H, 5′-CH_3); 1.26-1.37 (m, 2H, 4′-CH_2); 1.51-1.61 (m, 2H, 3′-CH_2); 2.06 (dd, 1H, 5-H_a); 2.18-2.34 (m, 2H, $CH_2CO_2CH_3$, AB of ABX, J_{AB} = 16.0 Hz); 2.77 (dt, 1H 2′-H_a); 2.84 (dd, 1H, 5-H_b); 2.91 (dt, 1H, 2′-H_b); 2.89-2.98 (m, 1H, 1-H); 3.62 (s, 3H, OCH_3); 5.96 (dd, 1H, 2-H); 6.07 (dd, 1H, 3-H); 7.48-7.54 (m, 2H, Ar-H′s); 7.61-7.67 (m, 1H, Ar-H); 7.72-7.76 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.2 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5\text{-}Ha}$ = 6.4 Hz; $J_{1,5\text{-}Hb}$ = 8.3 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 14.9 Hz; $J_{2'gem}$ = 18.4 Hz; $J_{2'\text{-}Ha,3'}$ = 7.3 Hz; $J_{2'\text{-}Hb,3'}$ = 7.3 Hz; $J_{4',5'}$ = 7.3 Hz.- IR ($CHCl_3$): 2963, 1734, 1439, 1308, 1263, 1169, 1144, 1082 cm^{-1}.- $C_{19}H_{24}O_5S$ (364.4).- MS: m/z (%) = 364 (1), 333 (2, $[M\text{-}OCH_3]^+$), 280 (9), 223 (56), 207 (14), 163 (36), 85 (100) ($C_5H_9O^+$), 77 (40), 57 (93), 41 (42), 29 (33).

Methyl [(1S*, 4R*)-(4-benzenesulfonyl-4-(1-pentanoyl)-2-cyclopenten-1-yl] acetate (*rac*-8b)

^{1}H NMR (400 MHz, $CDCl_3$, H,H COSY): δ = 0.85 (t, 3H, 5′-CH_3); 1.21-1.34 (m, 2H, 4′-CH_2); 1.46-1.56 (m, 2H, 3′-CH_2); 2.11 (dd, 1H, 5-H_a); 2.21-2.34 (m, 2H, $CH_2CO_2CH_3$, AB of ABX, J_{AB} = 16.0 Hz); 2.67 (dt, 1H, 2′-H_a); 2.78 (dd, 1H, 5-H_b); 2.86 (dt, 1H, 2′-H_b); 3.06-3.16 (m, 1H, 1-H); 3.64 (s, 3H, OCH_3); 5.99 (dd, 1H,

2-H); 6.09 (dd, 1H, 3-H); 7.48-7.54 (m, 2H, Ar-H′s); 7.61-7.67 (m, 1H, Ar-H); 7.70-7.74 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.2 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5\text{-Ha}}$ = 5.1 Hz; $J_{1,5\text{-Hb}}$ = 8.5 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 14.9 Hz; $J_{2',3'}$ = 7.3 Hz; $J_{2'gem}$ = 18.3 Hz; $J_{4',5'}$ = 7.3 Hz.- IR ($CHCl_3$): 2962, 1730, 1439, 1308, 1263, 1166, 1146, 1083 cm^{-1}.- $C_{19}H_{24}O_5S$ (364.4).- MS: m/z (%) = 364 (1), 333(1, $[M\text{-}OCH_3]^+$), 280 (14), 223 (55), 207 (16), 163 (26), 85 (100) ($C_5H_9O^+$), 77 (36), 57 (94), 41 (31), 29 (35).

Reduction of β-ketosulfone *rac*-8b

The reaction was performed as described for *rac*-**8a**. MPLC (petrol - ethyl acetate 4 : 1) yielded *rac*-**12b** (26%) and *rac*-**11b** (54%).

Methyl [(1S*, 4R*)-4-benzenesulfonyl-4-{(S*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetate (*rac*-11b)

^1H NMR (400 MHz, $CDCl_3$, H,H COSY): δ = 0.85 (t, 3H, 5′-CH_3); 1.19-1.60 (m, 6H, 4′-CH_2, 3′-CH_2 and 2′-CH_2); 1.77 (dd, 1H, C$\underline{H}_a$$CO_2CH_3$); 1.81 (dd, 1H, 5-$H_a$); 1.97 (dd, 1H, C$\underline{H}_b$$CO_2CH_3$); 2.18 (dd, 1H, 5-$H_b$); 2.99-3.09 (m, 1H, 1-H); 3.50-3.61 (4H, broad s, OH and 3.60 s, OCH_3); 4.08-4.14 (m, 1H, 1′-H), J = 9.6 Hz; 5.87 (dd, 1H, 2-H); 5.95 (dd, 1H, 3-H); 7.49-7.55 (m, 2H, Ar-H′s); 7.60-7.66 (m, 1H, Ar-H); 7.79-7.84 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5\text{-Ha}}$ = 5.6 Hz; $J_{4',5'}$ = 7.2 Hz; $J_{1,5\text{-Hb}}$ = 8.6 Hz; $J_{1,C\underline{H}aCO2CH3}$ = 8.4 Hz; $J_{1,C\underline{H}bCO2CH3}$ = 6.8 Hz; $J_{2,3}$ = 5.7 Hz; J_{5gem} = 15.4 Hz; $J_{C\underline{H}a\underline{H}bCO2CH3}$ = 16.0 Hz.- IR ($CHCl_3$): 3534, 2961, 1732, 1447, 1438, 1286, 1148, 1084 cm^{-1}.- $C_{19}H_{26}O_5S$ (366.4).- MS: m/z (%) = 280 (11, $[M\text{-}CH_3CH_2CH_2CH_2CHO]^{+\cdot}$), 225 (9), 207 (61), 193 (29), 85 (100) ($C_5H_9O^+$), 77 (29), 57 (46), 41 (24).

Methyl [(1S*, 4R*)-4-benzenesulfonyl-4-{(R*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetate (*rac*-12b)

^1H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, 3H, 5′-CH_3); 1.15-1.33 (m, 5H) and 1.43-1.57 (m, 1H) (4′-CH_2, 3′-CH_2 and 2′-CH_2); 1.83 (dd, 1H, 5-H_a); 1.89-1.99 (m, 2H, C$\underline{H}_2CO_2CH_3$, AB of ABX, J_{AB} = 12.5 Hz); 2.72 (dd, 1H, 5-H_b); 3.07-3.17 (m, 1H, 1-H); 3.61 (s, 3H, OCH_3); 3.67-3.76 (bs, 1H, OH); 4.26-4.32 (m, 1H, 1′-H), J = 3.3 Hz, J = 8.8 Hz; 5.33 (dd, 1H, 2-H); 5.89 (dd, 1H, 3-H); 7.51-7.57 (m, 2H, Ar-H′s); 7.63-7.69 (m, 1H, Ar-H); 7.79-7.84 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 2.2 Hz; $J_{1,5\text{-Ha}}$ = 8.3 Hz; $J_{1,5\text{-Hb}}$ = 9.4 Hz; $J_{2,3}$ = 5.9 Hz; J_{5gem} = 16.2 Hz; $J_{4',5'}$ = 7.2 Hz.- IR ($CHCl_3$): 3538, 2960, 1733, 1447, 1438, 1290, 1136, 1081 cm^{-1}.- $C_{19}H_{26}O_5S$ (366.4).- MS: m/z (%) = 280 (10, $[M\text{-}CH_3CH_2CH_2CH_2CHO]^{+\cdot}$), 225 (10), 207 (61), 193 (29), 85 (100) ($C_5H_9O^+$), 77 (24), 57 (44), 41 (22).

Reduction of *rac*-7b

The reaction was performed as described for *rac*-**8a**. MPLC (petrol - ethyl acetate 4 : 1) provided *rac*-**9b** (38%) and *rac*-**10b** (40%).

Methyl [(1S*, 4S*)-4-benzenesulfonyl-4-{(S*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetate (*rac*-9b)

^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, 3H, 5′-CH_3); 1.10-1.35 (m, 5H) and 1.50-1.65 (m, 1H) (4′-CH_2, 3′-CH_2 and 2′-CH_2); 1.87, (dd, 1H, 5-H_a); 2.18-2.32 (m, 2H, C$\underline{H}_2CO_2CH_3$, AB of ABX, J_{AB} = 15.8 Hz); 2.36-2.47 (m, 1H, 1-H); 2.64 (dd, 1H, 5-H_b); 3.61 (s, 3H, OCH_3); 3.67-3.71 (m, 1H, OH); 4.41-4.46 (m, 1H, 1′-H); 5.35 (dd, 1H, 2-H); 5.88 (dd, 1H, 3-H); 7.50-7.56 (m, 2H, Ar-H′s); 7.63-7.68 (m, 1H, Ar-H); 7.80-7.84 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.4 Hz; $J_{1,3}$ = 1.8 Hz; $J_{1,5\text{-Ha}}$ = 7.1 Hz; $J_{1,5\text{-Hb}}$ = 8.2 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 15.8 Hz, $J_{4',5'}$ = 7.1 Hz.- IR ($CHCl_3$): 3535, 2960, 1732, 1448, 1439, 1287, 1144, 1084 cm^{-1}.- $C_{19}H_{26}O_5S$ (366.4.- MS: m/z (%) = 280 (5, $[M\text{-}CH_3CH_2CH_2CH_2CHO]^{+\cdot}$, 225 (11), 207 (47), 193 (28), 85 (100) ($C_5H_9O^+$), 77 (34), 57 (50), 41 (29).

Methyl [(1S*, 4S*)-4-benzenesulfonyl-4-{(R*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetate (*rac*-10b)
^{1}H NMR (400 MHz, $CDCl_3$); H,H COSY: δ = 0.88 (t, 3H, 5′-CH_3); 1.20-1.34 (m, 3H) and 1.47-1.76 (m, 4H) (4′-CH_2, 3′-CH_2, 2′-CH_2, and at 1.69, dd, 5-H_a); 2.15-2.40 (m, 3H, C$\underline{H}_2CO_2CH_3$, AB of ABX, J_{AB} = 15.3 Hz and 1-H); 2.61 (dd, 1H, 5-H_b); 3.11 (bd, 1H, OH); 3.60 (s, 3H, OCH_3); 3.96-4.02 (m, 1H, 1′-H); 5.79 (dd, 1H, 2-H); 5.92 (dd, 1H, 3-H); 7.47-7.53 (m, 2H, Ar-H′s); 7.59-7.65 (m, 1H, Ar-H); 7.81-7.86 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.5 Hz; $J_{1,3}$ = 2.0 Hz; $J_{1,5\text{-Ha}}$ = 6.8 Hz; $J_{1,5\text{-Hb}}$ = 8.1 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 15.4 Hz; $J_{1',OH}$ = 5.6 Hz; $J_{4',5'}$ = 7.1 Hz.- IR ($CHCl_3$): 3540, 2961, 1734, 1439, 1413, 1290, 1265, 1136, 1082 cm^{-1}.- $C_{19}H_{26}O_5S$ (366.4).- MS: m/z (%) = 280 (4, [M-$CH_3CH_2CH_2CH_2CHO$]$^{+\cdot}$), 225 (10), 207 (50), 193 (32), 85 (100) ($C_5H_9O^+$), 77 (34), 57 (51), 41 (29).

(1S*, 4R*)-[4-Benzenesulfonyl-4-{(S*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetic acid (*rac*-15)
To a solution of *rac*-**11b** (19.7 mg, 0.054 mmol) in THF (2 ml) at 0°C freshly prepared LiOH solution (0.3 mol/L in water, 215 µl, 0.065 mmol) was added. The mixture was stirred for 90 min at 0°C and for 19 h at 20°C. Another portion of the LiOH solution (90 µl, 0.027 mmol) was added. After 2h at 20°C freshly regenerated cation exchange resin (Dowex 50 W X 2, H^+ form) was added and the mixture was stirred for 30 min. Decantation of the solution and washing of the resin, addition of water and usual work-up (CH_2Cl_2) gave *rac*-**15** (17.0 mg, 90%).- ^{1}H NMR (400 MHz, $CDCl_3$); H,H COSY: δ = 0.86 (t, 3H, 5′-CH_3); 1.10-1.63 (m, 6H, 4′-CH_2, 3′-CH_2, and 2′-CH_2); 1.77 (dd, 1H, C$\underline{H}_a$$CO_2H$); 1.85 (dd, 1H, 5-$H_a$), 2.03 (dd, 1H, C$\underline{H}_b$$CO_2H$); 2.21 (dd, 1H, 5-$H_b$); 3.00-3.10 (m, 1H, 1-H); 4.13 (dd, 1H, 1′-H); 4.50-5.50 (bs, 1H, OH); 5.90 (dd, 1H, 2-H); 5.98 (dd, 1H, 3-H); 7.52-7.58 (m, 2H, Ar-H′s); 7.63-7.68 (m, 1H, Ar-H); 7.81-7.86 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.2 Hz; $J_{1,3}$ = 2.1 Hz; $J_{1,5\text{-Ha}}$ = 6.0 Hz; $J_{1,5\text{-Hb}}$ = 8.8 Hz; $J_{1,CHaCO2H}$ = 8.5 Hz; $J_{1,CHbCO2H}$ = 6.6 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 15.4 Hz; $J_{1',2'\text{-Ha}}$ = 2.7 Hz, $J_{1',2'\text{-Hb}}$ = 9.5 Hz; $J_{4',5'}$ = 7.1 Hz; $J_{CHaHbCO2H}$ = 16.4 Hz.- IR ($CHCl_3$): 3520, 2962, 1711, 1447, 1408, 1286, 1149, 1083 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4).- MS: m/z (%) = 266 (3), 248 (2), 211 (6), 193 (33), 153 (30), 142 (20), 125 (25), 85 (100), 77 (68), 57 (66), 51 (28), 41 (52).

(1S*, 4R*)-[4-Benzenesulfonyl-4-{(R*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetic acid (*rac*-16)
The hydrolysis was performed as described for *rac*-**11b** → *rac*-**15**. Yield: 82%.- ^{1}H NMR (200 MHz, $CDCl_3$); H,H COSY: δ = 0.85 (t, 3H, 5′-CH_3); 1.14-1.40 (m, 5H) and 1.42-1.65 (m, 1H) (4′-CH_2, 3′-CH_2 and 2′-CH_2); 1.90 (dd, 1H, 5-H_a); 1.92-2.11 (m, 2H, C$\underline{H}_2CO_2H$, AB of ABX, J_{AB} = 11.5 Hz); 2.76 (dd, 1H, 5-H_b); 3.05-3.19 (m, 1H, 1-H); 4.30-4.41 (m, 1H, 1′-H); 5.40 (dd, 1H, 2-H); 5.93 (dd, 1H, 3-H); 7.54-7.64 (m, 2H, Ar-H′s); 7.66-7.76 (m, 1H, Ar-H); 7.82-7.90 (m, 2H, Ar-H′s); $J_{1,2}$ = 2.1 Hz; $J_{1,3}$ = 2.3 Hz; $J_{1,5\text{-Ha}}$ = 4.8 Hz; $J_{1,5\text{-Hb}}$ = 9.4 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 16.0 Hz; $J_{4',5'}$ = 6.8 Hz.- IR ($CHCl_3$): 3520, 1710, 1280, 1230, 1140, 1080 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4).- MS: m/z (%) = 266 (11), 248 (2), 211 (16), 193 (42), 153 (39), 142 (39), 125 (31), 85 (100), 77 (99), 57 (57), 51 (43), 41 (47).

(1S*, 4S*)-[4-Benzenesulfonyl-4-{(R*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetic acid (*rac*-14)
The hydrolysis was performed as described for *rac*-**11b** → *rac*-**15**. Yield: 84%.- ^{1}H NMR (200 MHz, $CDCl_3$); H,H COSY: δ = 0.92 (t, 3H, 5′-CH_3); 1.22-1.82 (m, 8 H, 4′-CH_2, 3′-CH_2, 2′-CH_2, 1-H, and at 1.74 dd, C$\underline{H}_a$$CO_2H$); 2.16-2.50 (m, 2H, C$\underline{H}_b$$CO_2H$ and 5-H_a); 2.68 (dd, 1H, 5-H_b); 4.01 (dd, 1H, 1′-H); 5.84 (dd, 1H, 2-H); 5.96 (dd, 1H, 3-H); 7.48-7.58 (m, 2H, Ar-H′s); 7.64-7.72 (m, 1H, Ar-H); 7.86-7.92 (m, 2H, Ar H′s); $J_{1,2}$ = 2.0 Hz; $J_{1,3}$ = 1.5 Hz; $J_{1,5\text{-Hb}}$ = 7.5 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 15.1 Hz; $J_{1',2'\text{-Ha}}$ = 2.0 Hz; $J_{1',2'\text{-Hb}}$ = 10.2 Hz; $J_{4',5'}$ = 6.9 Hz.- IR ($CHCl_3$): 3520, 1715, 1450, 1280, 1240, 1140 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4).- MS: m/z (%) = 266 (3), 248 (1), 211 (12), 193 (27), 153 (43), 142 (42), 125 (26), 85 (81), 77 (100), 57 (63), 51 (49), 41 (59).

(1S*, 4S*)-[4-Benzenesulfonyl-4-{(S*)-1-hydroxy-pentyl}-2-cyclopenten-1-yl] acetic acid (*rac*-13)
The hydrolysis was performed as described for *rac*-**11b** → *rac*-**15**. Yield: 86%.- ^{1}H NMR (200 MHz, $CDCl_3$); H,H COSY: δ = 0.88 (t, 3H, 5′-CH_3); 1.10-1.42 (m, 5H, 2′-H_a, 3′-CH_2, 4′- CH_2); 1.46-1.68 (m, 1H, 2′-H_b); 1.92 (dd, 1H, 5-H_a); 2.20-2.58 (m, 3H, 1-H and $C\underline{H}_2CO_2H$); 2.71 (dd, 1H, 5-H_b); 3.50-4.00 (bs, 1H, OH); 4.43 (dd, 1H, 1′-H); 5.39 (dd, 1H, 2-H); 5.92 (dd, 1H, 3-H); 7.52-7.64 (m, 2H, Ar-H′s); 7.68-7.74 (m, 1H, Ar-H); 7.84-7.88 (m, 2H, Ar-H′s); $J_{1,2}$= 2.3 Hz; $J_{1,3}$ = 1.7 Hz; $J_{1,5\text{-}Ha}$ = 6.9 Hz; $J_{1,5\text{-}Hb}$ = 7.9 Hz; $J_{2,3}$ = 5.6 Hz; J_{5gem} = 15.5 Hz; $J_{1',2'\text{-}Ha}$ = 3.1 Hz; $J_{1',2'\text{-}Hb}$ = 9.3 Hz; $J_{4',5'}$ = 7.1 Hz.- IR ($CHCl_3$): 3520, 1715, 1450, 1280, 1230, 1140 cm^{-1}.- $C_{18}H_{24}O_5S$ (352.4).- MS: m/z (%) = 266 (5), 211 (22), 193 (60), 153 (23), 142 (17), 125 (21), 85 (100), 77 (52), 57 (46), 51 (22), 41 (31).

(3aR*, 6aS*)-5-[(R*)-1-Hydroxy-pentyl]-3, 3a, 4, 6a-tetrahydro-cyclopenta[b]-furan-2-one (*rac*-17)
a) To a solution of *rac*-**16** (37.5 mg, 0.106 mmol) in THF (2 ml) at 20°C DBU (24 µl, 0.159 mmol) and after 30 min a solution of freshly prepared $Pd[PPh_3]_4$ (838.6 mg) in THF (20 ml) (1.46 ml, 0.053 mmol) were added. The mixture was stirred at 60°C for 20 h. Additional $Pd[PPh_3]_4$ (838.6 mg) dissolved in THF (20 ml) (0.73 ml, 0.027 mmol) was added and heating to 60°C was continued for 4 h. Usual work-up (CH_2Cl_2) and LC (petrol - ethyl acetate 2 : 1) furnished *rac*-**17** (21.3 mg, 96%).
b) *rac*-**17** was obtained from *rac*-**14** as described for *rac*-**16** → *rac*-**17**.- LC (petrol - ethyl acetate 2 : 1) furnished *rac*-**17** (47%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 3H, 5′-CH_3); 1.22-1.41 (m, 4H, 4′-CH_2 and 3′-CH_2); 1.51-1.64 (m, 3H, 2′-CH_2 and OH); 2.26-2.36 (m, 2H, 3-H_a and 4-H_a); 2.66-2.75 (m, 1H, 4-H_b); 2.82 (dd, 1H, 3-H_b); 3.10-3.20 (m, 1H, 3a-H); 4.25 (bt, 1H, 1′-H); 5.44-5.49 (m, 1H, 6a-H); 5.71-5.74 (m, 1H, 6-H); $J_{3\text{-}Ha,3a}$ = 7.6 Hz; $J_{3\text{-}Hb,3a}$ = 10.5 Hz; J_{3gem} = 18.3 Hz; $J_{3a,4\text{-}Hb}$ = 8.3 Hz; J_{4gem} = 17.1 Hz; $J_{1',2'}$ = 6.4 Hz; $J_{4',5'}$ = 7.0 Hz.- IR ($CHCl_3$): 1770, 1170, 1010 cm^{-1}.- $C_{12}H_{18}O_3$ (210.2).- MS: m/z (%) = 210 (5), 192 (8), 168 (11), 153 (100, $[M\text{-}C_4H_9]^+$), 126 (38), 125 (42), 107 (41), 85 (38), 79 (58), 57 (46), 41 (99).- HRMS: calc 210.1256, found 210.1253.- GC (200°C): retention time: 7.88 min.

(3aR*, 6aS*)-5-[(S*)-1-Hydroxy-pentyl]-3, 3a, 4, 6a-tetrahydro-cyclopenta[b]-furan-2-one (*rac*-19)
a) *rac*-**19** was obtained from *rac*-**15** as described for *rac*-**16** → *rac*-**17**.- FC (petrol - ethyl acetate 1 : 1) provided *rac*-**19** (95%).
b) *rac*-**19** was obtained from *rac*-**13** as described for *rac*-**16** → *rac*-**17**.- LC (petrol - ethyl acetate 2 : 1) furnished *rac*-**19** (37%).
^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, 3H, 5′-CH_3); 1.22-1.74 (m, 7H, 4′-CH_2, 3′-CH_2, 2′-CH_2 and OH); 2.18-2.42 (m, 2H, 4-H_a and at 2.31, dd, 3-H_a); 2.68-2.94 (m, 2H, 4-H_b and at 2.85, dd, 3-H_b); 3.08-3.30 (m, 1H, 3a-H); 4.29 (t, 1H, 1′-H); 5.48-5.56 (m, 1H, 6a-H); 5.74-5.80 (m, 1H, 6-H); $J_{3\text{-}Ha,3a}$ = 5.7 Hz; $J_{3\text{-}Hb,3a}$ = 10.3 Hz; J_{3gem} = 18.3 Hz; $J_{1',2'}$ = 6.1 Hz; $J_{4',5'}$ = 6.5 Hz.- IR ($CHCl_3$): 1770, 1175, 1010 cm^{-1}.- $C_{12}H_{18}O_3$ (210.2).- MS: m/z (%) = 210 (5), 192 (7), 168 (12), 153 (100, $[M\text{-}C_4H_9]^+$), 125 (43), 107 (48), 85 (54), 57 (56).- HRMS: calc 210.1256, found 210.1264.-GC (200°C): retention time: 7.75 min.

(3aR*, 6aS*)-5-[R*)-1-Hydroxy-pentyl]-3-(4-methyl-5-oxo-2,5-dihydrofuran-2-yloxymethylene)-3, 3a, 4, 6a-tetrahydrocyclopenta[b]furan-2-one (*rac*-18), two stereoisomers
To a suspension of sodium hydride (21.8 mg, 0.909 mmol) in THF (2 ml) a solution of *rac*-**17** (29.4 mg, 0.139 mmol) in THF (3 ml) and methyl formate (112 µl, 1.388 mmol) were added. The resulting mixture was stirred at 20°C for 26 h. 5 per cent aq. HCl was added. Usual work-up (CH_2Cl_2) and LC (gel, petrol - ethyl acetate =

1 : 1) provided the hydroxymethylene derivative of *rac*-**17** (22.3 mg, 67%).- ^{1}H NMR (200 MHz, $CDCl_3$) : δ = 0.80-0.98 (m, 3H, side-chain CH_3); 1.10-1.70 (m, 7H, 4′-CH_2, 3′-CH_2, 2′-CH_2 and OH); 3.41-3.82 (m, 2H), 4.18-4.41 (m, 1H, 3a-H); 5.38-5.80 (m, 2H, 6-H and 6a-H); 7.09 (d, C<u>H</u>OH of the enol form); 9.83 (s, aldehyde H).

A mixture containing this compound (22.3 mg, 0.094 mmol) , potassium carbonate (25.8 mg, 0.187 mmol), 5-bromo-3-methyl-5H-furan-2-one (17 µl), N-methylpyrrolidone (2 ml) was stirred at 20°C for 24 h. 5 per cent HCl was added. Usual work-up, followed by preparative HPLC (Jasco-Lichrosorb Si 60, flow rate 2 ml min^{-1}; $CHCl_3$ - acetone 100 : 1) provided 6.4 mg (15%) of the less polar and 6.5 mg (15%) of the more polar stereoisomer *rac*-**18**.

Spectral data of the less polar isomer: ^{1}H NMR (200 MHz, $CDCl_3$, H,H COSY): δ = 0.82-0.92 (m, 3H, 5′-CH_3); 1.21-1.70 (m, 7H, 4′-CH_2, 3′-CH_2, 2′-CH_2 and OH); 2.04 (t, 3H, 4′′-CH_3); 2.41-2.57 (m, 1H, 4-H_a); 2.72-2.92 (m, 1H, 4-H_b); 3.66-3.80 (m, 1H, 3a-H); 4.18-4.31 (m, 1H, 1′-H); 5.47-5.57 (m, 1H, 6a-H); 5.70-5.76 (m, 1H, 6-H); 6.13-6.17 (m, 1-H, 2′′-H); 6.91-6.96 (m, 1H, 3′′-H); 7.46 (d, 1H, =CHO); $J_{3a,=CHO}$ = 2.6 Hz; $J_{2'',3''} = J_{2'',4''\text{-}CH3} = J_{3'',4''\text{-}CH3}$ = 1.5 Hz.- IR ($CHCl_3$): 1787, 1744, 1683, 1338, 1224, 1217, 1180, 1093, 1021 cm^{-1}.- $C_{18}H_{22}O_6$ (334.4).- MS: m/z (%) = 334 (2), 317 (2, $[M\text{-}OH]^+$), 316 (2), 277 (3), 219 (19), 135 (10), 97 (100).- HRMS: calc 334.1416, found 334.1415.

Spectral data of the more polar isomer: ^{1}H NMR (200 MHz, $CDCl_3$); H,H COSY: δ = 0.82-0.93 (m, 3H, 5′-CH_3); 1.16-1.77 (m, 7H, 4′-CH_2, 3′-CH_2, 2′-CH_2 and OH); 2.00 (t, 3H, 4′′-CH_3); 2.41-2.58 (m, 1H, 4-H_a); 2.71-2.88 (m, 1H, 4-H_b); 3.63-3.79 (m, 1H, 3a-H); 4.19-4.30 (m, 1H, 1′-H); 5.46-5.54 (m, 1H, 6a-H); 5.68-5.73 (m, 1H, 6-H); 6.11-6.16 (m, 1-H, 2′′-H); 6.89-6.95 (m, 1H, 3′′-H); 7.44 (d, 1H, =CHO); $J_{3a,=CHO}$ = 2.6 Hz; $J_{2'',3''} = J_{2'',4''\text{-}CH3} = J_{3'',4''\text{-}CH3}$ = 1.5 Hz.- IR ($CHCl_3$): 1787, 1743, 1683, 1225, 1221, 1217, 1180, 1092, 1021 cm^{-1}.- $C_{18}H_{22}O_6$ (334.4).- MS: m/z (%) = 334 (3), 316 (18), 277 (7), 259 (26), 219 (14), 135 (18), 97 (100).- HRMS: calc 334.1416, found 334.1416.

(3aR*, 6aS*)-5-[(S*)-1-Hydroxy-pentyl]-3-(4-methyl-5-oxo-2,5-dihydrofuran-2-yloxymethylen)-3, 3a, 4, 6a-tetrahydrocyclopenta[b]furan-2-one (*rac*-20), two stereoisomers

rac-**19** was converted to *rac*-**20** as described for *rac*-**17** → *rac*-**18**.- FC (petrol - ethyl acetate 1 : 1) and HPLC (Jasco Lichrosorb Si 60, flow rate 4.5 ml min^{-1}; petrol - ethyl acetate 1 : 1) furnished 12.5 mg (24%) of the less polar and 11.3 mg (22%) of the more polar stereoisomer *rac*-**20**.

Spectral data of the less polar isomer: ^{1}H NMR (200 MHz, $CDCl_3$, H,H COSY): δ = 0.84-0.96 (m, 3H, 5′-CH_3); 1.24-1.77 (m, 7H, 4′-CH_2, 3′-CH_2, 2′-CH_2 and OH); 2.02 (t, 3H, 4′′-CH_3); 2.33-2.52 (m, 1H, 4-H_a); 2.75-2.94 (m, 1H, 4-H_b); 3.67-3.82 (m, 1H, 3a-H); 4.20-4.31 (m, 1H, 1′-H); 5.49-5.58 (m, 1H, 6a-H); 5.72-5.78 (m, 1H, 6-H); 6.13-6.19 (m, 1-H, 2′′-H); 6.91-6.96 (m, 1H, 3′′-H); 7.44 (d, 1H, =CHO); $J_{3a,=CHO}$ = 2.6 Hz, $J_{2'',3''} = J_{2'',4''\text{-}CH3} = J_{3'',4''\text{-}CH3}$ = 1.5 Hz.- IR ($CHCl_3$): 1787, 1744, 1683, 1348, 1337, 1225, 1215, 1207, 1180, 1155, 1093, 1044, 1020 cm^{-1}.- $C_{18}H_{22}O_6$ (334.4).- MS: m/z (%) = 334 (2), 316 (10), 277 (10), 259 (40), 258 (28), 219 (14), 135 (21), 97 (100).- HRMS: calc 334.1416, found 334.1420.

Spectral data of the more polar isomer: ^{1}H NMR (200 MHz, $CDCl_3$, H,H COSY): δ = 0.83-0.97 (m, 3H, 5′-CH_3); 1.21-1.72 (m, 7H, 4′-CH_2, 3′-CH_2, 2′-CH_2 and OH); 2.04 (t, 3H, 4′′-CH_3); 2.34-2.49 (m, 1H, 4-H_a); 2.74-2.92 (m, 1H, 4-H_b); 3.66-3.82 (m, 1H, 3a-H); 4.21-4.33 (m, 1H, 1′-H); 5.48-5.59 (m, 1H, 6a-H); 5.72-5.79 (m, 1H, 6-H); 6.11-6.19 (m, 1-H, 2′′-H); 6.91-6.96 (m, 1H, 3′′-H); 7.46 (d, 1H, =CHO); $J_{3a,=CHO}$ = 2.6 Hz, $J_{2'',3''} = J_{2'',4''\text{-}CH3} = J_{3'',4''\text{-}CH3}$ = 1.6 Hz.- IR ($CHCl_3$): 1787, 1744, 1684, 1337, 1225, 1180, 1093, 1021 cm^{-1}.- $C_{18}H_{22}O_6$ (334.4).- MS: m/z (%) = 334 (2), 316 (12, $[M\text{-}H_2O]^+$), 277 (22), 259 (55), 219 (17), 135 (21), 97 (100).- HRMS: calc 334.1416, found 334.1417.

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