Supporting Information

Sulfur Dioxide Mediated Syntheses of

Polyfunctional Alkenes,

(*E,Z*)-, and (*E,E*)-2,4-Dien-1-ones

*Laure C. Bouchez, Cotinica Craita and Pierre Vogel**

Laboratoire de Glycochimie et de Synthèse Asymétrique, BCH, École Polytechnique Fédérale de Lausanne (EPFL) BCH, CH-1015 Lausanne-Dorigny, Switzerland
Tel.: +41/ 21/ 693/ 9371. Fax.: +41/ 21/ 693/ 9355.

e-mail: pierre.vogel@epfl.ch

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Material and Methods

All solvents were distilled prior to use: THF and Et₂O from Na and benzophenone; DMF, CH₂Cl₂, and toluene from P₂O₅. Solvent after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040-0.63 μ m, silica gel 60,240-400 mesh). Thin layer chromatography (TLC) for reaction monitoring; detection by UV light. *Pancaldi* reagent ((NH₄)₆MoO₄, Ce(SO₄)₂, H₂SO₄, H₂O), or KMnO₄. M.p.: uncorrected; IR Spectra : spectrometer; ν in cm⁻¹. ¹H-NMR Spectra: 400 MHz spectrometer; δ (H) in ppm rel.to internal Me₄Si (= 0.00 ppm) or to the solvent's residual ¹H-signal (CH-Cl₃, δ (H) 7.27; C₆HD₅, δ (H) 7.16; CHD₂COCD₃, δ (H) 1.95; CD₂H₂CN, δ (H) 2.50; CHD₂SOCD₃, δ (H) 2.50, CH₂OD, δ (H) 3.31) as internal reference, all ¹H-signal assignments were confirmed by double irradiation experiments or by 2D COSY-DQF or COSY-45 spectra. ¹³C-NMR Spectra: same instruments as above (101.61MHz); δ (C) in ppm rel. to internal Me₄Si (= 0.00 ppm) or to solvents ¹³C-signal (CDCl₃, C₆D₆, δ (C) 128.4; (CD₃)₂CO, δ (C) 29.8; CD₃CN, δ (C) 1.3; (CD₃)₂SO, δ (C) 39.5, CD₃OD, δ (C) 49.2) as internal reference; coupling constants J in Hz ($\pm$ 0.5 Hz). Ms, chemical ionization (NH₃) mode m/z amu [% relative base peak(100%)].

General procedure 1 for the syntheses of 2,4-dinitro-phenylsulfone derivatives

HNTf₂ (0.5 M in CH₂Cl₂, 2 mL, 1 mmol, 0.5 equiv) in anh. CH₂Cl₂ (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO₂ (20 mL, 457 mmol, 205 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CH₂Cl₂ solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 10 min at this temperature a solution of 1,3-diene (1 equiv) and the enoxysilane (2 to 5 equiv) in CH₂Cl₂ (2 mL) were added dropwise under vigorous stirring and Ar atmosphere. The mixture was stirred at -78 °C for 10 h. Then the excess of SO₂ and the solvent were evaporated under reduced pressure (10⁻¹ Torr) to dryness (ca. 1h) while temperature slowly reached 20 °C. A 1 M solution of Bu₄NF in THF (1 equiv) and 2,4-dinitrofluorobenzene (1.47 g, 14 mmol, 7 equiv) in CH₃CN (2 mL) were added under Ar at -78 °C. The resulting mixture was stirred at -10 °C for 1 h, and gradually allowed to reach 20 °C in about 8 h. After the addition of H₂O (20 mL), and neutralization with saturated aqueous solution of NaHCO₃, the mixture was extracted with Et₂O (15 mL, 2 times). The combined organic extracts were washed with brine (20 mL, 5 times), dried (Na₂SO₄) and the solvent eliminated under reduced pressure. The residue was purified by FC.

General procedure 2 for the syntheses of Z-sulfones

HN(SO₂CF₃)₂ (0.5 M in CH₂Cl₂, 1.35 mL, 0.68 mmol, 0.2 equiv) in anh. CH₂Cl₂ (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO₂ (5 mL, 114.0 mmol, 34 equiv), dried through a column packed with basic alumina and phosphorus pentoxide, was transferred on the vacuum line to the CH₂Cl₂ solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 1 h at this temperature a solution of 1,3-diene (1 equiv) and the enoxysilane (2 to 5 equiv) in CH₂Cl₂ (3 mL) was added slowly. The mixture was stirred at -78 °C for 12 h. Excess of SO₂ and solvent were evaporated under reduced pressure (10⁻¹ Torr) to dryness, while temperature was rising to 25 °C (ca. 1h). A 1 M solution of Bu₄NF in THF (1 equiv) and electrophile (2.5 to 7 equiv) in a 4:1 mixture of DMF (40 eq) /CH₃CN were added under Argon atmosphere. The mixture was stirred at this temperature for 1 h, then at -40 °C for 1 h, and gradually allowed to reach 20 °C in about 10 h. After the addition of H₂O (40 mL), and neutralization with aqueous saturated solution of NaHCO₃ (10 mL), the mixture was extracted with CH₂Cl₂ (30 mL, 3 times). The combined organic extracts were washed with brine (30 mL, 2 times), dried (Na₂SO₄) and the solvent eliminated under reduced pressure. The residue was purified by FC.

General procedure 3 for the syntheses of E-sulfones

Same procedure as procedure 2, except for the amount of $\text{HN}(\text{SO}_2\text{CF}_3)_2$ (0.5 M in CH_2Cl_2 , 3.4 mL, 1.17 mmol, 0.5 equiv) which was introduced.

General procedure 4 for the syntheses of dienones

Same procedure as procedures 2 or 3, then a catalytic amount of TfOH (80%) was added at -20°C . Evolution of reaction was monitored by ^1H NMR. The reaction mixture was then allowed to warm to 20°C and stirred for 20 h. It was diluted with CH_2Cl_2 (10 mL), washed with aqueous saturated solution of NaHCO_3 (5 mL, 4 times), aqueous solution of 0.1 M HCl (5 mL, 3 times), brine (5 mL, 3 times), dried over Na_2SO_4 , and concentrated under vacuum.

(1E,3E)-2-Methyl-1-[[trimethylsilyl]oxy]-1,3-pentadiene (1a).

To neat NaI (61.1 g, 0.41 mol, 0.8 equiv, dried overnight under vacuum 10^{-2} Torr, 120°C), Et_3N (113.4 mL, 0.82 mol, 1.6 equiv) was added followed by anh. CH_3CN (40 mL) at 0°C under Ar atmosphere. Then 2-methyl-2-pentenal (50 g, 0.51 mol, 1 equiv) in 20 mL anh. CH_3CN , and anh. pentane (80 mL) and then TMSCl (64.6 mL, 0.45 mol, 0.88 equiv) were added sequentially. Reaction mixture was then heated to 40°C for 2 h and stirred vigorously at 20°C overnight. After dilution with cold pentane (50 mL), the sodium salt was quickly removed by suction filtration through a pad of Celite. The reaction vessel and filter cake were rinsed thoroughly with cold pentane (10 mL). The organic filtrate was concentrated under reduced pressure. The crude residue was purified by distillation, $\text{bp}^{56} = 91^\circ\text{C}$, and gave 66g (60%) of **1a** as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 6.32 (s, 1H, H-C(1)), 5.98 (dq, 1H, $^3J(\text{H}_3-\text{H}_4) = 15.4$, $^4J(\text{H}_3-\text{Me}_4) = 0.8$, H-C(3)), 5.98 (dq, 1H, $^3J(\text{H}_4-\text{H}_3) = 15.4$, $^3J(\text{H}_4-\text{Me}_4) = 6.6$, H-C(4)), 1.78 (dd, 3H, $^3J(\text{Me}_4-\text{H}_4) = 6.6$, $^4J(\text{Me}_4-\text{H}_3) = 0.8$, Me-C(4)), 1.71 (d, 3H, $^4J(\text{Me}_2-\text{H}_1) = 0.8$, Me-C(2)), 0.21 (s, 9H, Me_3Si).

8:6:1 Mixture of (Z)- and (E)-2- [(triethylsilyl)oxy]but-2-ene (7a) and 2- [(triethylsilyl)oxy]but-1-ene (7b).

WARNING reaction mixture can explode!

Scheme 1.

This mixture (**Z**) was prepared following the procedure described by Ojima *et al*¹ (Scheme 1). However, it is important to point out that this reaction should not be run with more than 0.3 mol of but-3-en-2-one. We have performed this reaction 5 times with 1 mol of but-3-en-2-one, but the sixth time the reaction ran out of control and exploded, causing significant damage. The cause of the explosion has not been elucidated. Neither the presence of peroxides, nor the eventual cyclodimerization of the methyl vinyl ketones can be excluded.

¹ Igarashi, M. Sugihara, Y. Fuchikami, T. *Tetrahedron Lett*, **1999**, 40(4), 711. (b) Johnson, C. R.; Raheja, R. K. *J. Org. Chem.*, **1994**, 59, 2287. (c) Tius, M. A.; Ousset, J. B.; Astrab, D. P.; Fauq, A. H.; Trehan, S. *Tetrahedron Lett.*, **1989**, 30(8), 923. (d) Ojima, I. *Organometallics*, **1982**, 1, 1390, (e) Ojima, I.; Korgue, T. *Tetrahedron Lett.*, **1972**, 49, 5085.

1:1 Mixture of ($\pm$)-(3*RS*,4*RS*,5*Z*,7*SR*)-4-hydroxy-3,5-dimethyl-7-[(methyl)sulfonyl]oct-5-en-2-one (($\pm$)-*syn*-3a**) and ($\pm$)-(3*RS*,4*SR*,5*Z*,7*RS*)-4-hydroxy-3,5-dimethyl-7-[(methyl)sulfonyl]oct-5-en-2-one (($\pm$)-*anti*-**3a**).**

The mixture was prepared as described above in the **general procedure 2** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (100 mg, 0.59 mmol, 1 equiv) and a mixture of (*E/Z*)-2-trimethylsilyloxybut-2-ene (**7**) (190 mg, 1.11 mmol, 2 equiv). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (0.59 mL, 0.59 mmol, 1 equiv) and 1-iodomethane (208 mg, 1.47 mmol, 3 equiv) in CH₂Cl₂ (2 mL). FC (petroleum ether / ethyl acetate 3:7, R_f = 0.32) gives 78 mg (53%) of a 1:1 mixture of ($\pm$)-*syn*-**3a** and ($\pm$)-*anti*-**3a** as a colorless oil. **IR (film):** ν 3455, 3000, 2980, 2970, 1705, 1610, 1470, 1405, 1360, 1290, 1120, 890 cm⁻¹. **¹H NMR (400 MHz, CDCl₃) of ($\pm$)-*syn*-3a:** δ 5.28 (dq, 1H, ³*J*(H₆-H₇) = 10.3, ⁴*J*(H₆-Me₅) = 1.3, H-C(6)), 4.61 (d, 1H, ³*J*(H₄-H₃) = 7.1, H-C(4)), 4.32 (dq, 1H, ³*J*(H₇-H₆) = 10.3, ³*J*(H₇-H₈) = 7.1, H-C(7)), 2.92 (m, 1H, H-C(3)), 2.87 (s, 3H, MeSO₂), 2.30 (s, 3H, H-C(1)), 1.85 (d, 3H, ⁴*J*(Me₅-H₆) = 1.3, Me-C(5)), 1.52 (d, 3H, ³*J*(H₈-H₇) = 7.1, H-C(8)), 1.30 (d, 3H, ³*J*(Me₃-H₃) = 7.1, Me-C(3)). **¹³C NMR (100.6 MHz, CDCl₃) of ($\pm$)-*syn*-3a:** δ 213.0 (s, CO), 145.4 (s, C(5)), 122.2 (d, ¹*J*(C,H) = 148, C(6)), 71.7 (t, ¹*J*(C,H) = 145, C(4)), 57.9 (d, ¹*J*(C,H) = 140, C(3)), 48.9 (d, ¹*J*(C,H) = 131, C(7)), 37.8 (d, ¹*J*(C,H) = 132, C(1')), 31.1 (q, ¹*J*(C,H) = 132, C(1)), 19.6 (q, ¹*J*(C,H) = 129, Me-C(5)), 15.0 (q, ¹*J*(C,H) = 129, C(8)), 14.9 (q, ¹*J*(C,H) = 132, Me-C(3)). **¹H NMR (400 MHz, CDCl₃) of ($\pm$)-*anti*-3a:** δ 5.11 (dq, 1H, ³*J*(H₆-H₇) = 10.8, ⁴*J*(H₆-Me₅) = 1.3, H-C(6)), 4.58 (d, 1H, ³*J*(H₄-H₃) = 7.1, H-C(4)), 4.16 (dq, 1H, ³*J*(H₇-H₆) = 10.8, ³*J*(H₇-H₈) = 7.1, H-C(7)), 2.92 (m, 1H, H-C(3)), 2.86 (s, 3H, MeSO₂), 2.18 (s, 3H, H-C(1)), 1.80 (d, 3H, ⁴*J*(Me₅-H₆) = 1.3, Me-C(5)), 1.51 (d, 3H, ³*J*(H₈-H₇) = 7.1, H-C(8)), 1.30 (d, 3H, ³*J*(Me₃-H₃) = 7.1, Me-C(3)). **¹³C NMR (100.6 MHz, CDCl₃) of ($\pm$)-*anti*-3a:** δ 213.0 (s, CO), 144.4 (s, C(5)), 120.8 (d, ¹*J*(C,H) = 146, C(6)), 70.9 (t, ¹*J*(C,H) = 149, C(4)), 57.5 (d, ¹*J*(C,H) = 144, C(3)), 46.8 (d, ¹*J*(C,H) = 131, C(7)), 37.6 (d, ¹*J*(C,H) = 132, C(1')), 30.1 (q, ¹*J*(C,H) = 139, C(1)), 18.9 (q, ¹*J*(C,H) = 131, Me-C(5)), 14.8 (q, ¹*J*(C,H) = 129, C(8)), 14.4 (q, ¹*J*(C,H) = 136, Me-C(3)). **CI-MS (NH₃) of 1:1 mixture of ($\pm$)-*syn* and *anti*-3a:** m/z 266 (100,

$[M+18]^+$, 249 (3, $[M+1]^+$). *Anal. Calcd for* $C_{11}H_{20}O_4S$ (248.11): C, 53.20, H, 8.12. Found: C, 53.22, H, 8.18.

2:1 Mixture of ($\pm$)-(3*RS*,4*RS*,5*Z*,7*SR*)-4-benzyloxy-7-(methylsulfonyl)-2,4-dimethyloct-5-en-2-one ($\pm$)-*syn*-3c and ($\pm$)-(3*RS*,4*SR*,5*Z*,7*RS*)-4-benzyloxy-7-(methylsulfonyl)-2,4-dimethyloct-5-en-2-one ($\pm$)-*anti*-3c.

($\pm$)-*syn*-3c, Major

($\pm$)-*anti*-3c, minor

The mixture was prepared as described above in the **general procedure 2** from (*E,E*)-2-methyl-1-benzyloxy-1,3-pentadiene (300 mg, 1.59 mmol, 1 equiv) and a 1:1 mixture of (*E/Z*)-2-trimethylsilyloxybut-2-ene (890 mg, 4.78 mmol, 3 equiv) in CH_2Cl_2 (2 mL). The reaction mixture was quenched with a 1 M solution of Bu_4NF in THF (1.59 mL, 1.59 mmol, 1 equiv) and iodo-methane (3.18 mmol, 2 equiv) in CH_2Cl_2 (3 mL). FC (light petroleum ether/EtOAc 7:3, R_f 0.25) gives 335 mg (62%) of 2:1 mixture of ($\pm$)-*syn*-3c and ($\pm$)-*anti*-3c as a colorless oil. *UV* (CH_3CN): λ_{max} = 212 nm (ϵ = 9607). *IR* (*film*): ν 2980, 1672, 1407, 1378, 1209, 1119, 1064, 954, 840 cm^{-1} . *¹H NMR* (400 MHz, $CDCl_3$) of (($\pm$)-*syn*-3c and ($\pm$)-*anti*-3c: δ 7.41-7.29 (m, 5H, H_{Bn}), 5.41 (d, 1H, $^3J(H_6-H_7)$ = 10.2, H-C(6)), 4.57 (d, 1H, 2J = 11.8, Ha- CH_2Bn), 4.40 (d, 1H, 2J = 11.8, Hb- CH_2Bn), 4.29 (d, 1H, $^3J(H_4-H_3)$ = 9.9, H-C(4)), 4.24 (dq, 1H, $^3J(H_7-H_6)$ = 10.2, $^3J(H_7-H_8)$ = 6.7, H-C(7)), 3.03 (qd, 1H, $^3J(H_3-H_4)$ = 9.9, $^3J(H_3-Me_3)$ = 7.3, H-C(3)), 2.74 (s, 3H, Me-C(1')), 2.14 (s, 3H, H-C(1)), 2.01 (s, 3H, Me-C(5)), 1.86 (s, 3H, Me-C(2')), 1.42 (d, 3H, $^3J(H_8-H_7)$ = 6.7, H-C(8)), 1.26 (d, 3H, $^3J(Me_3-H_3)$ = 7.3, Me-C(3)). *¹³C NMR* (100.6 MHz, $CDCl_3$) of ($\pm$)-*syn*-3c and ($\pm$)-*anti*-3c: δ 210.0 (s, CO), 133.3 (s, C(5)), 128.8- 127.4 (m, 6C(Bn)), 120.5 (d, $^1J(C,H)$ = 160, C(6)), 77.9 (t, $^1J(C,H)$ = 148, CH_2-Bn), 58.1 (d, $^1J(C,H)$ = 139, C(4)), 56.2 (d, $^1J(C,H)$ = 149, C(7)), 50.1 (d, $^1J(C,H)$ = 139, C(3)), 42.9 (q, $^1J(C,H)$ = 158, Me-C(1')), 30.9 (q, $^1J(C,H)$ = 142, C(1)), 19.0 (q, $^1J(C,H)$ = 150, Me-C(5)), 15.5 (q, $^1J(C,H)$ = 132, C(8)), 14.5 (q, $^1J(C,H)$ = 127, Me-C(3)). *CI-MS* (NH_3): $C_{18}H_{26}O_4S$, m/z 356 (56, $[M+18]^+$), 339 (7, $[M+1]^+$). *Anal. Calcd for* $C_{18}H_{26}O_4S$ (338.16): C, 63.88, H, 7.74. Found: C, 63.80, H, 7.69.

1:1 Mixture of ($\pm$)-(3*RS*,4*RS*,5*E*,7*RS*)-4-hydroxy-3,5-dimethyl-7-[(methyl)sulfonyl]oct-5-en-2-one ($\pm$)-*syn*-4a and ($\pm$)-(3*RS*,4*SR*,5*E*,7*SR*)-4-hydroxy-3,5-dimethyl-7-[(methyl)sulfonyl]oct-5-en-2-one, respectively ($\pm$)-*anti*-4a.

The mixture was prepared as described above in the **general procedure 3** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (10 g, 58.7 mmol, 1 equiv) and 1:1 mixture of (*E/Z*)-2-trimethylsilyloxybut-2-ene (19 g, 101.9 mmol, 2 equiv). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (58.7 mL, 58.7 mmol, 1 equiv) and 1-iodomethane (20.8 g, 146.8 mmol, 3 equiv) in CH₂Cl₂ (20 mL). FC (petroleum ether / ethyl acetate 3:7, R_f = 0.30) gives 11.4 g (79 %) of 1:1 mixture of ($\pm$)-*syn*-4a and ($\pm$)-*anti*-4a as an orange oil. **IR (film):** ν 3440, 3000, 2980, 2970, 1705, 1610, 1470, 1405, 1360, 1290, 1120, 780 cm⁻¹. **¹H NMR (400 MHz, CDCl₃) of ($\pm$)-*syn*-4a:** δ 5.55 (dq, 1H, ³*J*(H₆-H₇) = 13.4, ⁴*J*(H₆-Me₅) = 1.3, H-C(6)), 4.47 (m, 1H, H-C(4)), 3.89 (dq, 1H, ³*J*(H₇-H₆) = 13.4, ³*J*(H₇-H₈) = 6.4, H-C(7)), 2.80 (s, 3H, MeSO₂), 2.76 (m, 1H, H-C(3)), 2.26 (s, 3H, H-C(1)), 1.75 (d, 3H, ⁴*J*(Me₅-H₆) = 1.3, Me-C(5)), 1.54 (d, 3H, ³*J*(H₈-H₇) = 6.4, H-C(8)), 1.13 (d, 3H, ³*J*(Me₃-H₃) = 7.6, Me-C(3)). **¹³C NMR (100.6 MHz, CDCl₃) of ($\pm$)-*syn*-4a:** δ 213.0 (s, CO), 140.1 (s, C(5)), 128.5 (d, ¹*J*(C,H) = 160, C(6)), 69.9 (t, ¹*J*(C,H) = 155, C(4)), 58.5 (d, ¹*J*(C,H) = 148, C(3)), 50.1 (d, ¹*J*(C,H) = 136, C(7)), 38.8 (d, ¹*J*(C,H) = 139, C(1')), 30.1 (q, ¹*J*(C,H) = 129, C(1)), 19.8 (q, ¹*J*(C,H) = 126, Me-C(5)), 16.1 (q, ¹*J*(C,H) = 133, C(8)), 15.0 (q, ¹*J*(C,H) = 127, Me-C(3)). **¹H NMR (400 MHz, CDCl₃) of ($\pm$)-*anti*-4a:** δ 5.54 (dq, 1H, ³*J*(H₆-H₇) = 13.4, ⁴*J*(H₆-Me₅) = 1.3, H-C(6)), 4.47 (m, 1H, H-C(4)), 3.89 (dq, 1H, ³*J*(H₇-H₆) = 13.4, ³*J*(H₇-H₈) = 6.4, H-C(7)), 2.80 (s, 3H, MeSO₂), 2.76 (m, 1H, H-C(3)), 2.24 (s, 3H, H-C(1)), 1.74 (d, 3H, ⁴*J*(Me₅-H₆) = 1.3, Me-C(5)), 1.49 (d, 3H, ³*J*(H₈-H₇) = 6.4, H-C(8)), 1.13 (d, 3H, ³*J*(Me₃-H₃) = 7.6, Me-C(3)). **¹³C NMR (100.6 MHz, CDCl₃) of ($\pm$)-*anti*-4a:** δ 211.0 (s, CO), 140.1 (s, C(5)), 125.4 (d, ¹*J*(C,H) = 161, C(6)), 69.9 (t, ¹*J*(C,H) = 155, C(4)), 58.5 (d, ¹*J*(C,H) = 148, C(3)), 50.1 (d, ¹*J*(C,H) = 136, C(7)), 38.8 (d, ¹*J*(C,H) = 139, C(1')), 30.1 (q, ¹*J*(C,H) = 129, C(1)), 19.8 (q, ¹*J*(C,H) = 126, Me-C(5)), 15.6 (q, ¹*J*(C,H) = 137, C(8)), 15.0 (q, ¹*J*(C,H) = 127, Me-C(3)). **CI-MS (NH₃):** *m/z* 266 (100, [M+18]⁺), 249 (23, [M+1]⁺). **Anal. Calcd for C₁₁H₂₀O₄S** (248.11): C, 53.20, H, 8.12. Found: C, 53.25, H, 8.13.

Elucidation of the structure by 2D-NOESY ^1H -NMR experiments of the 1:1 mixture of ($\pm$)-(*syn*)-**4a** and ($\pm$)-(*anti*)-**4a** and corresponding spectrum.

1:1 mixture of ($\pm$)-(3*RS*,4*RS*,7*SR*)

and ($\pm$)-(3*RS*,4*SR*,7*SR*)-(E)-**4a**

NOEs found for:

δ_{H} (H-4) = 4.47 ppm (with Me₃, H-5)

δ_{H} (H-6) = 5.55 ppm (with H-8)

δ_{H} (H-7) = 3.89 ppm (with Me₅)

δ_{H} (H-8) = 1.54 ppm (with H-6)

δ_{H} (H-Me₃) = 1.13 ppm (with H-4)

δ_{H} (H-Me₅) = 1.75 ppm (with H-4, H-7)

(±)-(4*E*,6*E*,8*RS*)-3,5-Dimethyl-8-[(2,4-dinitrophenyl)sulfonyl]nona-4,6-dien-3-one ((±)-**5b**).

(±)-**5b**

5b was prepared as described above in the **general procedure 4** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (100 mg, 0.59 mmol, 1 equiv) and a 83:7 mixture of (*E*) or (*Z*)-3-trimethylsilyloxy-2-pentene (350 mg, 1.76 mmol, 3 equiv) in CH₂Cl₂ (2 mL). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (0.59 mL, 0.59 mmol, 1 equiv) and 2,4-dinitrofluorobenzene (0.73 g, 3.91 mmol, 6.5 equiv), and TfOH (1M solution in CH₂Cl₂, 0.47 mL, 80%). FC petroleum ether/ ethyl acetate 9:1 (R_f = 0.25) gives 145 mg (62%) of (±)-**5b**. Structure was confirmed with 2D-NOESY ¹H-NMR experiments. NOE's between H-C(5)↔H-C(7), Me-C(4)↔Me-C(6) and H-C(5)↔Me-C(2) were observed. **IR** (*KBr*, *cm*⁻¹): 2960, 1690, 1560, 1540, 1470, 1350, 1200, 1150, 1095, 970, 910, 750. **¹H NMR** (400 MHz, CDCl₃, 283K) of (±)-**5b**: δ 8.66 (d, 1H, ⁴*J*(H₃'-H₅') = 1.9, H-C(3')), 8.57 (dd, 1H, ³*J*(H₅'-H₆') = 8.6, ⁴*J*(H₅'-H₃') = 1.9, H-C(5')), 8.30 (d, 1H, ³*J*(H₆'-H₅') = 8.6, H-C(6')), 6.84 (*br. s*, 1H, H-C(5)), 5.45 (d, 1H, ³*J*(H₇-H₈) = 9.8, H-C(7)), 4.96 (dq, 1H, ³*J*(H₈-H₇) = 9.8, ³*J*(H₈-H₉) = 6.7, H-C(8)), 2.70 (dd, 2H, ²*J* = 14.2, ³*J*(H₂-H₁) = 7.4, H-C(2)), 1.91 (*s*, 3H, *Me*-C(4)), 1.77 (*s*, 3H, *Me*-C(6)), 1.58 (d, 3H, ³*J*(H₉-H₈) = 6.7, H-C(9)), 1.12 (*t*, 3H, ³*J*(H₉-H₈) = 7.4, H-C(1)). **¹³C NMR** (100 MHz, CDCl₃, 283K) of (±)-**5b**: δ 192.1 (*s*, C(3)), 153.0 (*s*, C(ar)), 152.1 (*s*, C(ar)), 138.6 (*s*, C(4)), 136.9 (*s*, C(ar)), 135.6 (*s*, C(6)), 135.2 (*d*, ¹*J*(H,C) = 170, C(ar)), 132.2 (*d*, ¹*J*(H,C) = 150, C(5)), 130.0 (*d*, ¹*J*(H,C) = 165, C(ar)), 123.4 (*d*, ¹*J*(H,C) = 146, C(7)), 118.9 (*d*, ¹*J*(H,C) = 168, C(ar)), 58.0 (*d*, ¹*J*(H,C) = 143, C(8)), 28.9 (*t*, ¹*J*(H,C) = 141, C(2)), 27.7 (*q*, ¹*J*(H,C) = 129, *Me*-C(4)), 26.4 (*q*, ¹*J*(H,C) = 131, *Me*-C(6)), 17.4 (*q*, ¹*J*(H,C) = 133, C(9)), 11.5 (*q*, ¹*J*(H,C) = 132, C(1)). **MALDI-HRMS**: Calcd. for C₁₇H₂₀N₂O₇S+Na⁺: 419.0889 found: 419.0891.

(3*E*,5*E*)-7-(butylsulfonyl)-3-methylhept-3,5-dien-2-one (**5a**).

Same procedure as for the preparation of dienone ((±)-**5b**). FC (cyclohexan / ethyl acetate 4:1, Rf 0.35), gives 75 mg (52%) of **5a** as a colorless oil. Structure was confirmed with 2D-NOE ^1H NMR experiments: NOE's between H-C(4) $\leftrightarrow$ H-C(6); H-C(4) $\leftrightarrow$ H-C(1) and H-C(5) $\leftrightarrow$ Me-C(3) were observed. **IR (film, cm^{-1})**: 2965, 1670, 1655, 1635, 1440, 1370, 1320, 1255, 1130, 995, 975. **^1H NMR (400 MHz, CDCl_3 , 283K)**: δ 7.02 (d, 1H, $^3J(\text{H}_4\text{-H}_5) = 10.9$, H-C(4)), 6.72 (dd, 1H, $^3J(\text{H}_5\text{-H}_6) = 15.4$, $^3J(\text{H}_5\text{-H}_4) = 10.9$, H-C(5)), 6.12 (dt, 1H, $^3J(\text{H}_6\text{-H}_5) = 15.4$, $^3J(\text{H}_6\text{-H}_7) = 7.6$, H-C(6)), 3.86 (d, 2H, $^3J(\text{H}_7\text{-H}_6) = 7.6$, H-C(7)), 2.96 (dd, 2H, $^3J(\text{H}_{1'}\text{-H}_{2a'}) = 7.7$, $^3J(\text{H}_{1'}\text{-H}_{2b'}) = 8.0$, H-C(1')), 2.32 (s, 3H, H-C(1)), 1.87 (s, 3H, Me-C(3)), 1.79 (dddd, 2H, $^3J(\text{H}_2\text{-H}_{1'}) = 7.7$, $^3J(\text{H}_2\text{-H}_{3'}) = 7.4$, H-C(2')), 1.46 (qdd, 2H, $^3J(\text{H}_3\text{-H}_{2'}) = 7.4$, $^3J(\text{H}_3\text{-H}_{4'}) = 7.4$, H-C(3')), 0.93 (t, 3H, $^3J(\text{H}_4\text{-H}_{3'}) = 7.4$, H-C(4')). **^{13}C NMR (100 MHz, CDCl_3 , 283K)**: δ 197.6 (s, C(2)), 136.5 (s, C(3)), 134.6 (d, $^1J(\text{H,C}) = 156$, C(4)), 132.5 (d, $^1J(\text{H,C}) = 158$, C(5)), 123.8 (d, $^1J(\text{H,C}) = 164$, C(6)), 55.1 (t, $^1J(\text{H,C}) = 140$, C(7)), 49.8 (t, $^1J(\text{H,C}) = 144$, C(1')), 41.1 (q, $^1J(\text{H,C}) = 132$, C(1)), 23.7 (t, $^1J(\text{H,C}) = 129$, C(2')), 21.8 (t, $^1J(\text{H,C}) = 135$, C(3')), 19.7 (q, $^1J(\text{H,C}) = 126$, Me-C(3)), 9.7 (q, $^1J(\text{H,C}) = 138$, C(4')). **MALDI-HRMS**: Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{S}+\text{Na}^+$: 267.1031; found 267.1047.

((±)-**(3E,5Z,7RS)**-3,5-Dimethyl-7-[(2-methylprop-2-enyl)sulfonyl]octa-3,5-dien-2-one ((±)-**6b**).

((±)-**6b**)

The mixture was prepared as described above in the **general procedure 2** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (200 mg, 1.17 mmol, 1 equiv) and mixture of (*Z*)-2-trimethylsilyloxybut-2-ene (**7**) (440 mg, 2.34 mmol, 2 equiv). The reaction mixture was quenched with a 1 M solution of Bu_4NF in THF (1.17 mL, 1.17 mmol, 1 equiv) and 3-bromo-2-methylpropene (394 mg, 2.93 mmol, 3 equiv) in CH_2Cl_2 (2 mL). FC (petroleum ether / ethyl acetate 3:2 (Rf 0.32) gives 250 mg (75 %) of a 1:1 mixture of intermediate β -hydroxy-sulfone as a yellow oil. To a solution of 1:1 mixture of the latest sulfone (50 mg, 0.17 mmol, 1 equiv) in CH_2Cl_2 (4 mL) under Ar atmosphere, a catalytic amount of HNTf_2 (0.5 M in CH_2Cl_2 , 0.17 mL, 0.08 mmol, 0.5 equiv) was added at -80°C . Evolution of reaction was monitored by ^1H NMR. After 10 h at -80°C no change was observed. Then reaction mixture was allowed to

warm to 20 °C and stirred for 48 h. It was diluted with CH₂Cl₂ (10 mL), washed with aqueous saturated solution of NaHCO₃ (5 mL, 4 times), aqueous solution of 0.1 M HCl (5 mL, 3 times), brine (5 mL, 3 times), dried over Na₂SO₄, and concentrated under vacuum. FC (petroleum ether / ethyl acetate 7:3, R_f 0.24), gives 43 mg (94%) of ((±)-**6b**) as a colorless oil. Structure was confirmed with its 2D-NOE ¹H NMR spectrum. NOE's between H-C(4)↔H-C(7), Me-C(3)↔Me-C(5), H-C(6)↔Me-C(5) and H-C(6)↔H-C(8) were observed. **IR (film)**: ν 2967, 2890, 1715, 1630, 1605, 1460, 1415, 1360, 1295, 1120, 1011 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)**: δ 7.00 (*br.s*, 1H, H-C(4)), 5.50 (d, 1H, ³J(H₆-H₇) = 10.9, H-C(6)), 5.20 (*br.s*, 1H, Ha-C(3')), 5.05 (*br.s*, 1H, Hb-C(3')), 3.77 (dq, 1H, ³J(H₇-H₆) = 10.9, ³J(H₇-H₈) = 7.1, H-C(7)), 3.70 (d, 1H, ²J = 13.4, Ha-C(1')), 3.56 (d, 1H, ²J = 13.4, Hb-C(1')), 2.38 (s, 3H, MeCO), 1.98 & 1.97 (2s, 6H, Me-C(3) & Me-C(5)), 1.80 (s, 3H, Me-C(2')), 1.48 (d, 3H, ³J(H₈-H₇) = 7.1, H-C(8)). **¹³C NMR (100.6 MHz, CDCl₃)**: δ 201.0 (s, CO), 140.4 (s, C(3)), 139.4 (d, ¹J(C,H) = 142, C(4)), 137.9 (s, C(5)), 134.5 (s, C(2')), 122.4 (t, ¹J(C,H) = 152, C(3')), 120.0 (d, ¹J(C,H) = 149, C(6)), 58.7 (d, ¹J(C,H) = 142, C(1')), 57.4 (t, ¹J(C,H) = 137, C(7)), 29.9 (q, ¹J(C,H) = 145, C(1)), 26.1 (q, ¹J(C,H) = 162, Me-C(2')), 23.2 (q, ¹J(C,H) = 147, Me-C(3)), 23.2 (q, ¹J(C,H) = 147, Me-C(5)), 13.6 (q, ¹J(C,H) = 128, C(8)). **CI-MS (NH₃)**: m/z 288 (100, [M+18]⁺), 271 (54, [M+1]⁺). **Anal. Calcd for C₁₄H₂₂O₃S** (270.13): C, 62.19, H, 8.20. Found: C, 62.26, H, 8.22.

(±)-(3E,5Z,7RS)-6b

NOEs found for :

- $\delta_{\text{H}}(\text{H-4}) = 7.0 \text{ ppm}$ (with H-7, H-1)
- $\delta_{\text{H}}(\text{H-6}) = 5.50 \text{ ppm}$ (with Me₅, H-8)
- $\delta_{\text{H}}(\text{H-7}) = 3.77 \text{ ppm}$ (with H-4)
- $\delta_{\text{H}}(\text{H-8}) = 1.48 \text{ ppm}$ (with H-6)
- $\delta_{\text{H}}(\text{H}_a\text{-3}') = 5.20 \text{ ppm}$ (with Me₂)
- $\delta_{\text{H}}(\text{H-Me}_2) = 1.80 \text{ ppm}$ (with H-3')
- $\delta_{\text{H}}(\text{H-1}) = 2.38 \text{ ppm}$ (with H-4)
- $\delta_{\text{H}}(\text{H-Me}_3) = 1.98 \text{ ppm}$ (with Me₅)
- $\delta_{\text{H}}(\text{H-Me}_5) = 1.97 \text{ ppm}$ (with Me₃)

((±)-(3*E*,5*E*,7*RS*)-3,5-Dimethyl-7-[(methyl)sulfonyl]octa-3,5-dien-2-one ((±)-5c).

Same procedure as for the preparation of sulfone ((±)-6b). FC (petroleum ether / ethyl acetate 7:3, $R_f = 0.24$) gives 40 mg (59%) of ((±)-5c) as a colorless oil. Structure was also confirmed with 2D-NOE ^1H NMR experiments. NOE's between $\text{H-C}(4) \leftrightarrow \text{H-C}(6)$, $\text{Me-C}(3) \leftrightarrow \text{Me-C}(5)$ were observed. **IR (film):** ν 2980, 2900, 1715, 1610, 1460, 1415, 1360, 1290, 1120, 895 cm^{-1} .

UV (CH_3CN): $\lambda_{\text{max}} = 270 \text{ nm}$ ($\epsilon = 8400$). **^1H NMR** (400 MHz, CDCl_3 , 283K): δ 6.95 (s, 1H, H-C(4)), 5.54 (d, 1H, $^3J(\text{H}_6\text{-H}_7) = 11.5$, H-C(6)), 4.0 (dq, 1H, $^3J(\text{H}_7\text{-H}_6) = 11.5$, $^3J(\text{H}_7\text{-H}_8) = 7.1$, H-C(7)), 2.87 (s, 3H, H-C(1')), 2.38 (s, 3H, H-C(1)), 1.98 (s, 3H, Me-C(3)), 1.96 (s, 3H, Me-C(5)), 1.55 (d, 3H, $^3J(\text{H}_8\text{-H}_7) = 7.1$, H-C(8)). **^{13}C NMR** (100 MHz, CDCl_3 , 283K): δ 200.7 (s, C(2)), 141.5 (d, $^1J(\text{H,C}) = 158$, C(4)), 139.5 (s, C(3)), 138.0 (s, C(5)), 127.3 (d, $^1J(\text{H,C}) = 162$, C(6)), 59.1 (d, $^1J(\text{H,C}) = 141$, C(7)), 38.4 (q, $^1J(\text{H,C}) = 132$, C(1')), 26.3 (q, $^1J(\text{H,C}) = 135$, C(1)), 17.8 (q, $^1J(\text{H,C}) = 128$, Me-C(3)), 13.9 (q, $^1J(\text{H,C}) = 130$, Me-C(5)), 13.4 (q, $^1J(\text{H,C}) = 130$, C(8)). **MALDI-HRMS**: Calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_3\text{S} + \text{Na}^+$ 253.0874, found: 253.0879. **Anal. Calcd for** $\text{C}_{11}\text{H}_{18}\text{O}_3\text{S}$ (270.13): C, 57.36, H, 7.88. Found: C, 57.31, H, 7.92.

(±)-(3E,5E,7RS)-5c

NOEs found for :

- δ_{H} (H-4) = 6.95 ppm (with H-6, H-1)
- δ_{H} (H-6) = 5.54 ppm (with H-8, H-4)
- δ_{H} (H-7) = 4.00 ppm (with Me₅)
- δ_{H} (H-8) = 1.55 ppm (with H-6)
- δ_{H} (H-1) = 2.38 ppm (with H-4)
- δ_{H} (H-Me₃) = 1.98 ppm (with Me₅)
- δ_{H} (H-Me₅) = 1.96 ppm (with Me₃, H-7)

(±)-(2*E*,4*E*,6*RS*)-4-Methyl-6-[(2,4-dinitrophenyl)sulfonyl]phenylhepta-2,4-dien-1-one
((±)-6c).

6c was prepared as described above in the **general procedure 4** from (*E,E*)-2-methyl-1-[(trimethylsilyl)oxy]-1,3-pentadiene (100 mg, 0.59 mmol, 1 equiv) and 1-phenyl-1-trimethylsilyloxy-ethylene (339 mg, 1.76 mmol, 3 equiv) in CH₂Cl₂ (1 mL). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (0.59 mL, 0.59 mmol, 1 equiv) and 2,4-dinitrofluorobenzene (327 mg, 1.76 mmol, 3 equiv) and TfOH (1M solution in CH₂Cl₂, 0.47 mL, 80%). FC (hexane / ethyl acetate 10:1, R_f = 0.20) gives 171 mg (68%) of (±)-**6c** as brown solid. Structure was also confirmed with 2D-NOESY ¹H-NMR experiments. NOE's between H-C(6)↔H-C(3), H-C(2)↔Me-C(4), H-C(3)↔H-C(7) and H-C(5)↔Me-C(4) were observed. **IR (KBr, cm⁻¹):** 2930, 1670, 1605, 1560, 1545, 1465, 1350, 1265, 1150, 1095, 1005, 995. **¹H NMR (400 MHz, CDCl₃, 283K):** δ 8.55 (d, 1H, ⁴J(H₃-H₅) = 1.9, H-C(3')), 8.40 (dd, 1H, ³J(H₅-H₆) = 8.9, ⁴J(H₅-H₃) = 1.9, H-C(5')), 8.09 (d, 1H, ³J(H₆-H₅) = 8.9, H-C(6')), 7.8 (d, 1H, ³J = 7.1, H-C(ar)), 7.61 (t, 1H, ³J = 7.7, H-C(ar)), 7.48 (dd, 1H, ³J = 7.7, ³J = 7.1, H-C(ar)), 7.32 (d, 1H, ³J(H₂-H₃) = 15.8, H-C(2)), 6.76 (d, 1H, ³J(H₃-H₂) = 15.8, H-C(3)), 5.71 (d, 1H, ³J(H₅-H₆) = 9.6, H-C(5)), 5.24 (dq, 1H, ³J(H₆-H₅) = 9.6, ³J(H₆-H₇) = 7.1, H-C(6)), 1.98 (s, 3H, Me-C(4)), 1.74 (d, 3H, ³J(H₇-H₆) = 7.1, H-C(7)). **¹³C NMR (100 MHz, CDCl₃, 283K):** δ 190.1 (s, C(1)), 150.9 & 150.8 (s, 2 C(ar)), 140.0 (d, ¹J(H,C) = 166, C(2)), 139.3 (s, C(ar)), 137.7 (s, C(ar)), 136.7 (d, ¹J(H,C) = 165, C(ar)), 135.6 (d, ¹J(H,C) = 158, C(ar)), 134.1 (d, ¹J(H,C) = 155, C(ar)), 133.9 (d, ¹J(H,C) = 170, C(3)), 133.9 (s, C(4)), 129.3 (d, ¹J(H,C) = 160, C(ar)), 129.2 (d, ¹J(H,C) = 156, C(ar)), 128.7 (d, ¹J(H,C) = 162, C(ar)), 128.6 (d, ¹J(H,C) = 168, C(ar)), 126.2 (d, ¹J(H,C) = 160, C(ar)), 121.7 (d, ¹J(H,C) = 165, C(5)), 60.1 (d, ¹J(H,C) = 140, C(6)), 20.6 (q, ¹J(H,C) = 137, C(7)), 12.9 (q, ¹J(H,C) = 130, Me-C(4)). **MALDI-HRMS:** Calcd. for C₂₀H₁₈N₂O₇S+Na⁺: 453.4209 found: 453.4214.

3:1 Mixture of ($\pm$)-(2*RS*,3*RS*,4*Z*,6*SR*)-3-hydroxy-2,4-dimethyl-6-[(methyl)sulfonyl]-1-phenylhept-4-en-1-one ($\pm$)-*syn*-8 and ($\pm$)-(2*RS*,3*SR*,4*Z*,6*RS*)-3-hydroxy-2,4-dimethyl-6-[(methyl)sulfonyl]-1-phenylhept-4-en-1-one ($\pm$)-*anti*-8.

This mixture was prepared as described above in the **general procedure 2** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (100 mg, 0.59 mmol, 1 equiv) and (*Z*)-1-phenyl-1-trimethylsilyloxy-propylene (303 mg, 1.47 mmol, 2.5 equiv). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (0.59 mL, 0.59 mmol, 1 equiv) and 1-iodomethane (251 mg, 1.77 mmol, 3 equiv) in CH₂Cl₂ (1 mL). FC (pure EtOAc, R_f = 0.4) gives 101 mg (55%), of 3:1 mixture of ($\pm$)-*syn*-8 and ($\pm$)-*anti*-8 as colorless oil. **IR (film):** ν 3050, 2975, 2935, 1679, 1455, 1303, 1138, 1070, 968, 739 cm⁻¹. **¹H NMR (400 MHz, CDCl₃) of ($\pm$)-*syn*-8 and ($\pm$)-*anti*-8:** δ 7.95 (d, 2H, ³*J* = 8.1, H-C(ar)), 7.60 (t, 1H, ³*J* = 8.9, H-C(ar)), 7.51 (t, 2H, ³*J* = 7.7, H-C(ar)), 5.06 (d, 1H, ³*J*(H₅-H₆) = 9.1, H-C(5)), 4.83 (d, 1H, ³*J*(H₃-H₂) = 9.4, H-C(3)), 4.41 (dq, 1H, ³*J*(H₆-H₅) = 9.1, ³*J*(H₆-H₇) = 6.8, H-C(6)), 3.82 ((dq, 1H, ³*J*(H₂-H₃) = 9.4, ³*J*(H₂-Me₂) = 7.0, H-C(2)) 2.87 (s, 3H, C(1')), 1.73 (s, 3H, Me-C(4)), 1.54 (d, 3H, ³*J*(H₇-H₆) = 6.8, H-C(7)), 1.42 (d, 3H, ³*J*(Me₂-H₂) = 7.0, Me-C(2)). **¹³C NMR (100.6 MHz, CDCl₃) of ($\pm$)-*syn*-8 and ($\pm$)-*anti*-8:** δ 163.8 (s, C(1)), 145.2 (s, C(ar)), 129.8 (m, C(ar)), 122.3 (s, C(4)), 120.3 (d, ¹*J*(C,H) = 160, C(5)), 71.3 (d, ¹*J*(C,H) = 167, C(6)), 57.8 (d, ¹*J*(C,H) = 138, C(3)), 43.9 (d, ¹*J*(C,H) = 147, C(2)), 46.9 (q, ¹*J*(C,H) = 125, C(1')), 23.7 (q, ¹*J*(C,H) = 126, Me-C(4)), 18.6 (q, ¹*J*(C,H) = 132, C(7)), 15.8 (q, ¹*J*(C,H) = 126, Me-C(2)). **CI-MS (NH₃):** m/z 328 (100, [M+18]⁺, 311 (41, [M+1]⁺).

6:1 Mixture of ($\pm$)-(2*RS*,3*RS*,4*E*,6*RS*)-3-[[(*tert*-butyl)dimethylsilyl]oxy]-6-[(methyl)sulfonyl]-2,4-dimethyl-1-(2,4,6-trimethoxyphenyl)hept-4-en-1-one ($\pm$)-*syn*-9 and ($\pm$)-(2*RS*,3*SR*,4*E*,6*SR*)-3-[[(*tert*-butyl)dimethylsilyl]oxy]-6-[(methyl)sulfonyl]-2,4-dimethyl-1-(2,4,6-trimethoxyphenyl)hept-4-en-1-one ($\pm$)-*anti*-9.

(±)-syn-9, Major **(±)-anti-9**, minor

The mixture was prepared as described above in the **general procedure 3** from (*E,E*)-2-methyl-1-[(terbutyldimethylsilyl)oxy]-1,3-pentadiene (724 mg, 3.41 mmol, 1 equiv) and trimethyl{[(1*E*)-1-(2,4,6-trimethoxyphenyl)prop-1-enyl]oxy}silane (1.7 g, 5.8 mmol, 1.7 equiv) in CH₂Cl₂ (3 mL). Excess of SO₂ and solvent were evaporated under reduced pressure (10⁻¹ Torr) to dryness, while temperature was rising to 0 °C (ca. 1h). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (3.41 mL, 3.41 mmol, 1 equiv) and iodomethane (8.52 mmol, 2.5 equiv) in CH₂Cl₂ (5 mL). The mixture was stirred at -60 °C for 4 h. FC (light petroleum ether / EtOAc 4:2, R_f = 0.20) gives 1.59 g (90%) of a 6:1 mixture of (±)-**syn-9** and (±)-**anti-9** as a yellow oil. **UV (CH₃CN)**: λ_{max} = 209 nm (ε = 7920). **IR (film)**: ν 2987, 1694, 1606, 1456, 1421, 1305, 1266, 1157, 1132, 898, 740 cm⁻¹. **¹H NMR (400 MHz, CDCl₃) of (±)-syn-9**: δ 6.09 (s, 2H, Har), 5.54 (d, 1H, ³J(H₅-H₆) = 10.5, H-C(5)), 4.58 (d, 1H, ³J(H₃-H₂) = 6.2, H-C(3)), 3.92 (dq, 1H, ³J(H₆-H₅) = 10.5, ³J(H₆-H₇) = 7.1, H-C(6)), 3.82 (s, 3H, H-OMe), 3.77 (s, 6H, H-OMe), 3.2 (qd, 1H, ³J(H₂-Me₂) = 7.4, ³J(H₂-H₃) = 6.2, H-C(2)), 2.79 (s, 3H, Me-C(1')), 1.97 (s, 3H, Me-C(4)), 1.42 (d, 3H, ³J(H₇-H₆) = 7.1, H-C(7)), 1.11 (d, 3H, ³J(Me₂-H₂) = 7.4, Me-C(2)). **¹³C NMR (100.6 MHz, CDCl₃) of (±)-syn-9**: δ 209.2 (s, CO), 162.3-158.4 (s, 4C, C(ar)), 133.1 (s, C(4)), 117.9 (d, ¹J(C,H) = 161, C(5)), 90.6 & 90.5 (d, 2C, ¹J(C,H) = 161, C(ar)), 58.1 (d, ¹J(C,H) = 148, C(3)), 56.9 (d, ¹J(C,H) = 133, C(6)), 55.6 (q, ¹J(C,H) = 151, C(OMe)), 51.6 (d, ¹J(C,H) = 146, C(2)), 44.1 (q, ¹J(C,H) = 154, C(1')), 25.8 (q, ¹J(C,H) = 142, *t*-Bu), 18.3 (q, ¹J(C,H) = 132, Me-C(4)), 15.1 (s, Cquat-*t*Bu), 14.6 (q, ¹J(C,H) = 131, Me-C(6)), 12.6 (q, ¹J(C,H) = 139, Me-C(2)), -4.2 (q, ¹J(C,H) = 127, Me₂Si-C(3)), -5.0 (q, ¹J(C,H) = 129, Me₂Si-C(3)). **¹H NMR (400 MHz, CDCl₃) of (±)-anti-9**: δ 6.09 (s, 2H, H-C(ar)), 5.54 (d, 1H, ³J(H₅-H₆) = 10.5, H-C(5)), 4.80 (d, 1H, ³J(H₃-H₂) = 7.6, H-C(3)), 4.4 (qd, 1H, ³J(H₆-H₅) = 10.5, ³J(H₆-H₇) = 6.5, H-C(6)), 3.82 (s, 3H, H-OMe), 3.77 (s, 6H, H-OMe), 3.2 (dq, 1H, ³J(H₂-Me₂) = 7.4, ³J(H₂-H₃) = 6.5, H-C(2)), 2.79 (s, 3H, Me-C(1')), 2.01 (s, 3H, Me-C(4)), 1.37 (d, 3H, ³J(H₇-H₆) = 6.5, H-C(7)), 1.11 (d, 3H, ³J(Me₂-H₂) = 7.4, Me-C(2)). **¹³C NMR (100.6 MHz, CDCl₃) of (±)-anti-9**: δ 209.1 (s, CO), 162.3-158.4 (s, 4C, C(ar)), 133.3 (s, C(4)), 117.9 (d, ¹J(C,H) = 161, C(5)), 90.6 & 90.5 (d, 2C, ¹J(C,H) = 161, C(ar)), 57.6 (d, ¹J(C,H) = 143, C(3)), 56.7 (d, ¹J(C,H) = 131, C(6)), 55.6 (q, ¹J(C,H) = 151,

C(OMe)), 53.4 (d, $^1J(\text{C,H}) = 139$, C(2)), 44.1 (q, $^1J(\text{C,H}) = 154$, C(1')), 25.8 (q, $^1J(\text{C,H}) = 142$, *t*-Bu), 18.2 (q, $^1J(\text{C,H}) = 129$, *Me*-C(4)), 15.4 (q, $^1J(\text{C,H}) = 128$, *Me*-C(6)), 15.0 (s, Cquat-*t*Bu), 13.8 (q, $^1J(\text{C,H}) = 132$, *Me*-C(2)), -4.7 (q, $^1J(\text{C,H}) = 126$, *Me*Si-C(3)), -5.3 (q, $^1J(\text{C,H}) = 129$, *Me*Si-C(3)). **CI-MS** (NH_3): $\text{C}_{25}\text{H}_{42}\text{SSiO}_7$, m/z 515 (25, $[\text{M}+1]^+$), 108 (100). **Anal. Calcd for** $\text{C}_{25}\text{H}_{42}\text{O}_7\text{SSi}$ (514.24): C, 58.33, H, 8.22. Found: C, 58.60, H, 8.39.

(±)-(5*RS*,6*Z*,8*SR*)-8-(Ethylsulfonyl)-5-hydroxy-2,2,6-trimethylnon-6-en-3-one ((±)-12).

(±)-12

12 was prepared as described above in the **general procedure 2** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (200 mg, 1.17 mmol, 1 equiv) and [(1-*tert*-butyl)vinyl]oxy]trimethylsilane (605 mg, 3.51 mmol, 3 equiv) in CH_2Cl_2 (2 mL). The reaction mixture was quenched with a 1 M solution of Bu_4NF in THF (1.17 mL, 1.17 mmol, 1 equiv) and iodoethane (1.37 g, 8.78 mmol, 7.5 equiv) in CH_3CN (2 mL) DMF (10 mL). FC (petroleum ether/ ethyl acetate 3:2, R_f 0.31) gives 260 mg (77%) of (±)-**12**, yellow solid, mp = 78.2-79°C. **UV** (CH_3CN): $\lambda_{\text{max}} = 225$ nm ($\epsilon_{\text{max}} = 5000$). **IR** (KBr , cm^{-1}): 3200, 3050, 2975, 2935, 1700, 1650, 1455, 1330, 1290, 1120, 1030, 735. **^1H NMR** (400 MHz, CDCl_3 , 283K): δ 5.21 (dq, 1H, $^3J(\text{H}_7\text{-H}_8) = 9.6$, $^4J(\text{H}_7\text{-Me}_{(6)}) = 1.3$, H-C(7)), 4.92 (ddd, 1H, $^3J(\text{H}_5\text{-H}_4) = 6.7$, $^3J(\text{H}_5\text{-OH}) = 2.5$, H-C(5)), 4.33 (dq, 1H, $^3J(\text{H}_8\text{-H}_7) = 9.6$, $^3J(\text{H}_8\text{-H}_9) = 7.0$, H-C(8)), 3.19 (d, 1H, $^3J(\text{OH-H}_5) = 2.5$, H-(OH)), 3.02 (q, 2H, $^3J(\text{H}_{1'}\text{-H}_{2'}) = 7.4$, H-C(1')), 2.90 & 2.75 (dd, 2H, $^2J = 17.9$, $^3J(\text{H}_{4a}\text{-H}_5) = 7.7$, $^3J(\text{H}_{4b}\text{-H}_5) = 5.4$, H-C(4)), 1.82 (d, 3H, $^4J(\text{Me}_{(6)}\text{-H}_7) = 1.3$, *Me*-C(6)), 1.49 (d, 3H, $^3J(\text{H}_9\text{-H}_8) = 7.0$, H-C(9)), 1.42 (t, 3H, $^3J(\text{Me}_{2'}\text{-H}_{1'}) = 7.4$, *Me*-C(2')), 1.17 (s, 9H, H-C(1)). **^{13}C NMR** (100 MHz, CDCl_3 , 283K): δ 215.8 (s, C(3)), 145.0 (s, C(6)), 120.7 (d, $^1J(\text{H,C}) = 162$, C(7)), 66.6 (d, $^1J(\text{H,C}) = 144$, C(8)), 55.9 (d, $^1J(\text{H,C}) = 139$, C(5)), 44.8 (s, C(2)), 44.6 (t, $^1J(\text{H,C}) = 135$, C(1')), 41.4 (t, $^1J(\text{H,C}) = 130$, C(4)), 26.7 (q, $^1J(\text{H,C}) = 129$, C(1)), 26.7 (q, $^1J(\text{H,C}) = 129$, *Me*-C(2)), 19.2 (q, $^1J(\text{H,C}) = 128$, *Me*-C(6)), 15.0 (q, $^1J(\text{H,C}) = 134$, C(9)), 6.4 (q, $^1J(\text{H,C}) = 132$, C(2')). **MALDI-HRMS**: Calc. for $\text{C}_{14}\text{H}_{26}\text{O}_4\text{S}+\text{Na}^+$, 313.1449. Found: 313.1466. **Anal. Calcd. for** $\text{C}_{14}\text{H}_{26}\text{O}_4\text{S}$ (290.16): C, 57.90, H, 9.02. Found: C, 57.86, H, 9.02.

(±)-(5*RS*,6*Z*,8*SR*)-5-(Benzyloxy)-8-(butylsulfonyl)-2,2,6-trimethylnon-6-en-3-one ((±)-**13**).

((±)-**13**)

13 was prepared as described above in the **general procedure 2** from 1-benzyloxy-1,3-pentadiene (200 mg, 1.06 mmol, 1 equiv) and [(1-*tert*-butyl)vinyl]oxy]trimethylsilane (493 mg, 2.65 mmol, 2.5 equiv) in CH₂Cl₂ (2 mL). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (1.06 mL, 1.06 mmol, 1 equiv) and 1-iodobutane (975 mg, 5.3 mmol, 5 equiv) in CH₃CN (1 mL) DMF (8 mL). FC (petroleum ether/ ethyl acetate 4:1, R_f = 0.35) gives 350 mg (81%) of (±)-**13** as a colorless oil. Structure was also confirmed with a 2D-NOE ¹H NMR experiments. NOE's between H-C(5)↔H-C(8), and H-C(7)↔Me-C(6) were observed. This is consistent with a *Z* double bond. **UV** (CH₃CN): λ_{max} = 242 nm (ε_{max} = 9000). **IR** (KBr, cm⁻¹): 2955, 2880, 1710, 1655, 1455, 1300, 1240, 1270, 1110, 1045, 920, 745. **¹H NMR** (400 MHz, CDCl₃, 283K): δ 7.36-7.28 (m, 5H, H-C(ar)), 5.42 (dq, 1H, ³J(H₇-H₈) = 9.1, ⁴J(H₇-Me₆) = 0.9, H-C(7)), 4.83 (t, 1H, ³J(H₅-H₄) = 6.7, H-C(5)), 4.39 (dd, AB, 2H, ²J = 11.5, H-CH₂Bn), 4.34 (dq, 1H, ³J(H₈-H₇) = 9.1, ³J(H₈-H₉) = 6.7, H-C(8)), 2.97 (dd, 1H, ²J = 16.9, ³J(H_{4a}-H₅) = 6.7, Ha-C(4)), 2.95 (ddd, 2H, ²J = 14.1, ³J(H_{1'}-H_{2a'}) = 8.0, ³J(H_{1'}-H_{2b'}) = 7.7, H-C(1')), 2.71 (dd, 1H, ²J = 16.9, ³J(H_{4b}-H₅) = 6.7, Hb-C(4)), 1.84 (d, 3H, ⁴J(Me₆-H₇) = 0.9, Me-C(6)), 1.47 (ddt, 2H, ³J(H_{2'}-H_{1a'}) = 8.0, ³J(H_{2'}-H_{1b'}) = 7.7, ³J(H_{2'}-H_{3'}) = 7.7, H-C(2')), 1.41 (d, ³J(H₉-H₈) = 6.7, H-C(9)), 1.14 (br. s, 11H, H-C(1), H-C(3')), 0.97 (t, 3H, ³J(H_{4'}-H_{3'}) = 7.7, H-C(4')). **¹³C NMR** (100 MHz, CDCl₃, 283K): δ 213.3 (s, C(3)), 142.8 (s, C(6)), 138.6 (s, C(ar)), 128.7 (d, ¹J(H,C) = 166, C(ar)), 127.9 (d, ¹J(H,C) = 158, C(ar)), 127.9 (d, ¹J(H,C) = 158, C(ar)), 122.4 (d, ¹J(H,C) = 159, C(7)), 74.4 (d, ¹J(H,C) = 145, C(8)), 71.1 (t, ¹J(H,C) = 146, C(1')), 56.5 (d, ¹J(H,C) = 144, C(5)), 50.2 (t, ¹J(H,C) = 140, C(4)), 44.7 (s, C(2)), 41.8 (t, ¹J(H,C) = 139, C(CH₂Bn)), 26.3 (q, ¹J(H,C) = 137, C(1)), 26.1 (q, ¹J(H,C) = 131, Me-C(2)), 24.2 (q, ¹J(H,C) = 130, C(2')), 22.3 (q, ¹J(H,C) = 132, C(3')), 19.2 (q, ¹J(H,C) = 139, Me-C(6)), 15.2 (q, ¹J(H,C) = 132, C(9)), 13.9 (q, ¹J(H,C) = 136, C(4')). **MALDI-HRMS**: Calcd. for C₂₃H₂₆O₄S+ Na⁺ 431.2232, found : 431.2058. **Anal. Calcd.** for C₂₃H₂₆O₄S (408.23): C, 67.61, H, 8.88. Found: C, 67.80, H, 8.93.

1:1 Mixture of ($\pm$)-(3*RS*,4*RS*,5*Z*,7*SR*)-4-hydroxy-7-(2-methylpropane-1-sulfonyl)-3,5-dimethyloct-5-en-2-one ($\pm$)-*syn*-14 and ($\pm$)-(3*RS*,4*SR*,5*Z*,7*RS*)-4-hydroxy-7-(2-methylpropane-1-sulfonyl)-3,5-dimethyloct-5-en-2-one ($\pm$)-*anti*-14.

14 was prepared as described above in the **general procedure 2** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (200 mg, 1.07 mmol, 1 equiv) and 3-trimethylsilyloxy-2-pentene (455 mg, 2.67 mmol, 2.5 equiv). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (1.07 mL, 1.07 mmol, 1 equiv) and 1-iodo-2-methylpropane (1.38 g, 7.5 mmol, 7 equiv) in CH₃CN (1 mL) and HMPA (8 mL). FC (petroleum ether / ethyl acetate 1:1, R_f 0.28) gives 525 mg (62%) of 1:1 mixture of ($\pm$)-*syn*-14 and ($\pm$)-*anti*-14 as a yellowish oil. Structure was confirmed with a 2D-NOE ¹H NMR experiment. NOEs between H-C(4)↔H-C(7), and H-C(6)↔Me-C(5) were observed. **UV (CH₃CN):** λ = 220 nm ε=4300.

IR (film, cm⁻¹): 3470, 2970, 2935, 2855, 1710, 1630, 1460, 1370, 1295, 1135, 1030, 830. **¹H NMR (400 MHz, CDCl₃, 283K) of ($\pm$)-*syn*-14 and ($\pm$)-*anti*-14:** δ 5.21 (dq, 1H, ³J(H₇-H₈) = 10.9, ⁴J(H₇-Me₆) = 1.16, H-C(7)), 4.73 (dd, 1H, ³J(H₅-H₄) = 9.6, ³J(H₅-H_{OH}) = 3.2, H-C(5)), 4.35 (dq, 1H, ³J(H₈-H₇) = 10.9, ³J(H₈-H₉) = 6.9, H-C(8)), 3.06 (dq, 1H, ³J(H₄-H₅) = 9.6, ³J(H₄-Me₄) = 6.6, H-C(4)), 2.94 (d, 2H, ³J(H_{1'}-H_{2'}) = 6.6, H-C(1')), 2.92 (d, 1H, ³J(H_{OH}-H₅) = 3.2, H-OH), 2.72 (dq, 1H, ²J = 17.9, ³J(H₂-H₁) = 7.2, H-C(2)), 2.56 (m, 3H, H-C(2), H-C(2')), 1.94 (d, 3H, ⁴J(Me₆-H₇) = 1.16, Me-C(6)), 1.72 (*br.s*, 1H, H-OH), 1.57 (d, 3H, ³J(H₈-H₉) = 6.9, H-C(9)), 1.42 (d, 3H, ³J(Me₄-H₄) = 6.6, Me-C(4)), 1.29 (d, 3H, ³J(H₃-H₂) = 6.4, H-C(3')), 1.27 (d, 3H, ³J(H₃-H₂) = 6.4, H-C(3')), 1.16 (t, 3H, ³J(H₁-H₂) = 6.4, H-C(1)). **¹³C NMR (100 MHz, CDCl₃, 283K) of ($\pm$)-*syn*-14 and ($\pm$)-*anti*-14:** δ 211.1 (s, C(3)), 145.2 (s, C(6)), 120.1 (d, ¹J(H,C) = 150, C(7)), 70.9 (d, ¹J(H,C) = 143, C(8)), 57.5 (d, ¹J(H,C) = 139, C(5)), 56.5 (t, ¹J(H,C) = 132, C(1')), 49.9 (d, ¹J(H,C) = 132, C(2')), 41.6 (d, ¹J(H,C) = 142, C(4)), 35.5 (t, ¹J(H,C) = 141, C(2)), 23.3 (q, ¹J(H,C) = 133, Me-C(6)), 23.2 (q, ¹J(H,C) = 134, C(9)), 18.3 (q, ¹J(H,C) = 132, C(1)), 15.4 (q, ¹J(H,C) = 132, Me-C(4)), 14.5 (q, ¹J(H,C) = 129, C(3')), 12.9 (q, ¹J(H,C) = 130, C(3')). **MALDI-HRMS of ($\pm$)-*syn*-14 and ($\pm$)-*anti*-14:** Calcd.

for $C_{15}H_{28}O_4S + Na^+$: 327.1606, found: 327.1598. *Anal. Calcd for* $C_{15}H_{28}O_4S$ (304.17): C, 59.18, H, 9.27. Found: C, 59.46, H, 9.35.

1:1 Mixture of ($\pm$)-(3*RS*,4*RS*,5*Z*,7*SR*)-4-(benzyloxy)-3,5-dimethyl-7-(2-methyl-prop-1-yl-sulfonyl)oct-5-en-2-one ($\pm$)-syn-15 and ($\pm$)-(3*RS*,4*SR*,5*Z*,7*RS*)-4-(benzyloxy)-3,5-dimethyl-7-(2-methyl-prop-1-yl-sulfonyl)oct-5-en-2-one ($\pm$)-anti-15.

($\pm$)-syn-15 Major

($\pm$)-anti-15 minor

The mixture was prepared as described above in the **general procedure 2** from 1-benzyloxy-1,3-pentadiene (990 mg, 5.26 mmol, 1 equiv) and mixture of 2-[(triethylsilyl)oxy]-2-butene **7** (1.96 g, 10.52 mmol, 2 equiv). The reaction mixture was quenched with a 1 M solution of Bu_4NF in THF (5.26 mL, 5.26 mmol, 1 equiv) and 1-iodo-2-methylpropane (4.84 g, 26.3 mmol, 5 equiv) in CH_3CN (3 mL) DMF (17 mL). FC (petroleum ether / ethyl acetate 75:25, R_f = 0.22), gives 1.56 g (78%) of a 1:1 mixture of ($\pm$)-syn-15 and ($\pm$)-anti-15 as a yellow oil. Structure was confirmed with 2D-NOE 1H NMR experiments. NOE's between $H-C(4) \leftrightarrow H-C(7)$, and $H-C(6) \leftrightarrow Me-C(5)$ were observed. *UV* (CH_3CN): λ_{max} = 240 nm (ϵ_{max} = 6700). *IR* (*film*, cm^{-1}): 2960, 2930, 2855, 1710, 1650, 1460, 1350, 1265, 1195, 1135, 1060, 740. *1H NMR* (400 MHz, $CDCl_3$, 283K) of ($\pm$)-syn-15 and ($\pm$)-anti-15: δ 7.38-7.27 (m, 5H, H-C(ar)), 5.41 (d, 1H, $^3J(H_6-H_7)$ = 10.9, H-C(6)), 4.53 & 4.42 (d, AB, 2H, 2J = 12.2, H-C(CH_2Bn)), 4.30 (d, 1H, $^3J(H_4-H_3)$ = 9.6, H-C(4)), 4.06 (dq, 1H, $^3J(H_7-H_6)$ = 10.9, $^3J(H_7-H_8)$ = 7.1, H-C(7)), 3.05 (dq, 1H, $^3J(H_3-H_4)$ = 10.9, $^3J(H_3-Me_3)$ = 7.1, H-C(3)), 2.86 (dd, 2H, 2J = 17.9, $^3J(H_{1'}-H_{2'})$ = 6.4, H-C(1')), 2.46 (tqq, 1H, $^3J(H_{2'}-H_{1'})$ = 6.4, $^3J(H_{2'}-H_{3a'})$ = 6.4, $^3J(H_{2'}-H_{3b'})$ = 6.4, H-C(2')), 2.14 (s, 3H, H-C(1)), 1.86 (s, 3H, Me-C(5)), 1.39 (d, 3H, $^3J(H_7-H_8)$ = 7.1, H-C(8)), 1.26 (d, 3H, $^3J(Me_3-H_3)$ = 7.1, Me-C(3)), 1.16 (d, 3H, $^3J(H_3-H_{2'})$ = 6.4, H-C(3')), 1.14 (d, 3H, $^3J(H_3-H_{2'})$ = 6.4, H-C(3')). *^{13}C NMR* (100 MHz, $CDCl_3$, 283K) of ($\pm$)-syn-15 and ($\pm$)-anti-15: δ 211.2 (s, C(2)), 142.4 (s, C(5)), 138.7 (s, C(ar)), 128.7 (d, $^1J(H,C)$ = 160, C(ar)), 128.1 (d, $^1J(H,C)$ = 164, $^1J(H,C)$ = 164, C(ar)), 127.9 (d, $^1J(H,C)$ = 159, C(6)), 78.5 (d, $^1J(H,C)$ =

140, C(7)), 71.3 (t, $^1J(\text{H,C}) = 145$, C-(CH₂Bn)), 58.2 (d, $^1J(\text{H,C}) = 142$, C(4)), 57.6 (t, $^1J(\text{H,C}) = 136$, C(1')), 54.1 (d, $^1J(\text{H,C}) = 135$, C(3)), 50.5 (d, $^1J(\text{H,C}) = 131$, C(2')), 31.4 (q, $^1J(\text{H,C}) = 130$, C(1)), 23.6 (q, $^1J(\text{H,C}) = 140$, Me-C(5)), 23.4 (q, $^1J(\text{H,C}) = 133$, C(8)), 19.3 (q, $^1J(\text{H,C}) = 131$, Me-C(3)), 15.7 (q, $^1J(\text{H,C}) = 132$, C(3')), 15.1 (q, $^1J(\text{H,C}) = 133$, C(3')). **MALDI-*HRMS*** : Calcd for C₂₁H₃₂O₄S+ Na⁺ : 403.1919, found : 403.1909. **Anal. Calcd** for C₂₁H₃₂SO₄ (318.19): C, 66.28, H, 8.48. Found: C, 66.57, H, 8.63.

(±)-(3*RS*,4*Z*,6*SR*)-6-[(2,4-Dinitrophenyl)sulfonyl]-3-hydroxy-4-methyl-1-phenylhept-4-en-1-one ((±)-16**).**

(±)-16

16 was prepared as described above in the **general procedure 1** from (*E,E*)-2-methyl-1-[(trimethylsilyl)oxy]-1,3-pentadiene (1 g, 5.87 mmol, 1 equiv) and 1-phenyl-1-[(trimethylsilyl)oxy]-ethylene (3.39 g, 17.6 mmol, 3 equiv) in CH₂Cl₂ (7 mL). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (1.17 mL, 1.17 mmol, 1 equiv) and 2,4-dinitrofluorobenzene (3.27 g, 17.6 mmol, 3 equiv). FC (petroleum ether / ethyl acetate 7:3, R_f = 0.31) gives 456 mg (87%) of **(±)-16** as light yellow oil. Structure was confirmed with 2D-NOESY ¹H-NMR experiments. NOE's between H-C(6)↔H-C(3), H-C(5)↔H-C(7), H-C(2)↔Me-C(4) and H-C(5)↔Me-C(4) were observed. **UV (CH₃CN)**: λ₁ = 258 nm (ε₁ = 14420), λ₂ = 240 nm (ε₂ = 5960). **IR (KBr, cm⁻¹)**: 3530, 3020, 1730, 1690, 1590, 1560, 1540, 1350, 1220, 1145, 1030, 835, 755. **¹H NMR (400 MHz, CDCl₃, 283K)**: δ 8.63 (d, 1H, $^4J(\text{H}_{3'}-\text{H}_{5'}) = 1.9$, H-C(3')), 8.60 (dd, 1H, $^3J(\text{H}_{5'}-\text{H}_{6'}) = 8.6$, $^4J(\text{H}_{5'}-\text{H}_{3'}) = 1.9$, H-C(5')), 8.30 (d, 1H, $^3J(\text{H}_{6'}-\text{H}_{5'}) = 8.6$, H-C(6')), 7.91 (d, 1H, $^3J = 7$, H-C(ar)), 7.60 (t, 1H, $^3J = 7$, H-C(ar)), 7.48 (t, 1H, $^3J = 7$, H-C(ar)), 5.25 (m, 2H, H-C(5), H-C(6)), 5.02 (m, 1H, H-C(3)), 3.27 & 3.19 (dd, 2H, AB, $^2J = 17.2$, $^3J(\text{H}_{2a}-\text{H}_3) = 7.6$, $^3J(\text{H}_{2b}-\text{H}_3) = 5.6$, H-C(2)), 2.81 (d, 1H, $^3J(\text{H}_{\text{OH}}-\text{H}_3) = 2.8$, H-OH), 1.82 (s, 3H, Me-C(4)), 1.49 (d, 3H, $^3J(\text{H}_7-\text{H}_6) = 6.4$, H-C(7)). **¹³C NMR (100 MHz, CDCl₃, 283K)**: δ 199.4 (s, C(1)), 151.1 & 150.3 (s, 2 C(ar)), 147.5 (s, C(4)), 147.3 (s, C(ar)), 137.7 (s, C(ar)), 136.7 (d, $^1J(\text{H,C}) = 165$, C(ar)), 135.6 (d, $^1J(\text{H,C}) = 158$, C(ar)), 134.1 (d, $^1J(\text{H,C}) = 155$, C(ar)), 129.2 (d, $^1J(\text{H,C}) = 160$, C(ar)), 129.1 (d, $^1J(\text{H,C})$

= 154, C(ar)), 128.4 (d, $^1J(\text{H},\text{C}) = 165$, C(ar)), 128.3 (d, $^1J(\text{H},\text{C}) = 160$, C(ar)), 126.6 (d, $^1J(\text{H},\text{C}) = 161$, C(ar)), 120.7 (d, $^1J(\text{H},\text{C}) = 168$, C(5)), 67.1 (d, $^1J(\text{H},\text{C}) = 143$, C(6)), 60.7 (d, $^1J(\text{H},\text{C}) = 144$, C(3)), 43.5 (t, $^1J(\text{H},\text{C}) = 128$, C(2)), 19.2 (q, $^1J(\text{H},\text{C}) = 128$, C(7)), 14.6 (q, $^1J(\text{H},\text{C}) = 135$, *Me*-C(4)). **MALDI-HRMS:** Calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_8\text{S}+\text{K}^+$: 487.0577 found : 487.0571. **Anal. Calcd.** for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_8\text{S}$ (448.09): C, 53.57, H, 4.50. Found: C, 53.33, H, 4.73.

(±)-(5*RS*,6*Z*,8*SR*)-8-[(2,4-Dinitrophenyl)sulfonyl]-5-hydroxy-2,2,6-trimethylnon-6-en-3-one ((±)-**17**).

(±)-**17**

(±)-**17** was prepared as described above in the **general procedure 1** from (*E,E*)-2-methyl-1-[(trimethylsilyl)oxy]-1,3-pentadiene (400 mg, 2.23 mmol, 1 equiv) and [(1-*tert*-butylvinyl)oxy]trimethylsilane (1.51 g, 8.92 mmol, 4 equiv) in CH₂Cl₂ (4 ml). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (2.23 mL, 2.23 mmol, 1 equiv) and 2,4-dinitrofluorobenzene (2.91 g, 15.61 mmol, 7 equiv). FC (petroleum ether/ ethyl acetate 1:1; R_f = 0.25 and recrystallization from pentane / CH₂Cl₂ gives light yellow crystals (*X-Ray* available) of (±)-**17**, light yellow crystals, 814 mg (81%), mp = 70.0-71.7 °C.

UV (CH₃CN): λ_{max} = 233 nm (ε_{max} = 28000). **IR** (KBr, cm⁻¹): 3520, 2970, 1700, 1605, 1555, 1545, 1350, 1270, 1145, 1030, 905, 755. **¹H NMR** (400 MHz, CDCl₃, 283K): δ 8.65 (d, 1H, ⁴*J*(H_{3'}-H_{5'}) = 1.9, H-C(3')), 8.55 (dd, 1H, ³*J*(H_{5'}-H_{6'}) = 8.9, ⁴*J*(H_{5'}-H_{3'}) = 1.9, H-C(5')), 8.29 (d, 1H, ³*J*(H_{6'}-H_{5'}) = 8.9, H-C(6')), 5.23 (m, 2H, H-C(7), H-C(8)), 4.79 (ddd, 1H, ³*J*(H₅-H_{4a}) = 7.3, ³*J*(H₅-H_{4b}) = 6.7, ³*J*(H₅-OH) = 2.9, H-C(5)), 2.75 (m, 3H, H-C(4), H-OH), 1.77 (s, 3H, Me-C(6)), 1.51 (d, 3H, ³*J*(H₉-H₈) = 6.4, H-C(9)), 1.15 (s, 9H, H-C(1)). **¹³C NMR** (100 MHz, CDCl₃, 283K): δ = 216.2 (s, C(3)), 151.0 (s, C(ar)), 150.3 (s, C(ar)), 147.5 (s, C(6)), 137.7 (s, C(ar)), 135.6 (d, ¹*J*(H,C) = 170, C(ar)), 130.0 (d, ¹*J*(H,C) = 165, C(ar)), 120.7 (d, ¹*J*(H,C) = 136, C(7)), 118.9 (d, ¹*J*(H,C) = 168, C(ar)), 67.2 (d, ¹*J*(H,C) = 144, C(8)), 60.0 (d, ¹*J*(H,C) = 145, C(5)), 44.8 (s, C(2)), 41.6 (t, ¹*J*(H,C) = 142, C(4)), 26.5 (q, ¹*J*(H,C) = 134, C(1)), 19.2 (q, ¹*J*(H,C) = 129, C(9)), 14.6 (q, ¹*J*(H,C) = 134, Me-C(6)). **MALDI-HRMS**: Calcd. for C₁₈H₂₄N₂O₈S+Na⁺: 451.1151. Found: 451.1199. **Anal. Calcd.** for C₁₈H₂₄N₂O₈S (428.13): C, 50.46, H, 5.65. Found: C, 50.53, H, 5.74.

2:1 Mixture of (±)-(4*RS*,5*RS*,6*E*,8*RS*)-8-[(2,4-dinitrophenyl)sulfonyl]-5-hydroxy-4,6-dimethylnon-6-en-3-one (±)-*syn*-18 and (±)-(4*RS*,5*SR*,6*E*,8*SR*)-8-[(2,4-Dinitrophenyl)sulfonyl]-5-hydroxy-4,6-dimethylnon-6-en-3-one (±)-*anti*-18.

(±)-syn-18- Major **(±)-anti-18**-minor

(±)-18 was prepared as described above in the **general procedure 1** from (*E,E*)-2-methyl-1-[(trimethylsilyl)oxy]-1,3-pentadiene (200 mg, 1.17 mmol, 1 equiv) and 3-[(trimethylsilyl)oxy]-2-pentene (700 mg, 3.51 mmol, 3 equiv) in CH₂Cl₂ (2 mL). The reaction mixture was quenched with a 1 M solution of Bu₄NF in THF (1.17 mL, 1.17 mmol, 1 equiv) and 2,4-dinitrofluorobenzene (1.45 g, 7.81 mmol, 6.5 equiv). FC petroleum ether/ ethyl acetate 2:1 (R_f = 0.30), and recrystallisation from pentane /CH₂Cl₂ gives 365 mg (76%) of a 3:2 mixture of **(±)-syn-18** and **(±)-anti-18**, yellow crystals (*X-Ray* of **(±)-syn-18** available) mp = 69.8-70.2 °C. *UV* (CH₃CN): λ_{max} = 234 nm (ε_{max} = 22000). *IR* (KBr, cm⁻¹): 3395, 2965, 2935, 1710, 1610, 1460, 1345, 1265, 1195, 1145, 1060, 1030, 835, 755, 740. *¹H NMR* (400 MHz, CDCl₃, 283K) of **(±)-syn-18**: δ 8.65 (d, 1H, ⁴*J*(H_{3'}-H_{5'}) = 1.9, H-C(3')), 8.55 (dd, 1H, ³*J*(H_{5'}-H_{6'}) = 8.9, ⁴*J*(H_{5'}-H_{3'}) = 1.9, H-C(5')), 8.29 (d, 1H, ³*J*(H_{6'}-H_{5'}) = 8.9, H-C(6')), 5.59 (dq, 1H, ³*J*(H₇-H₈) = 8.9, ⁴*J*(H₇-Me₆) = 0.9, H-C(7)), 4.79 (m, H-C(5)), 3.43 (*br. s*, 1H, H-OH), 2.75-2.44 (m, 4H, H-C(2), H-C(4), H-C(8)), 1.77 (d, 3H, ⁴*J*(Me₆-H₇) = 0.9, *Me*-C(6)), 1.53 (d, 3H, ³*J*(H₉-H₈) = 6.4, H-C(9)), 1.20 (t, 3H, ³*J*(H₉-H₈) = 7.1, H-C(1)), 0.98 (d, 3H, ³*J*(Me₄-H₄) = 7.1, *Me*-C(4)). *¹³C NMR* (100 MHz, CDCl₃, 283K) of **(±)-syn-18**: δ 216.7 (s, C(3)), 151.0 (s, C(ar)), 150.3 (s, C(ar)), 145.9 (s, C(6)), 135.9 (s, C(ar)), 135.6 (d, ¹*J*(H,C) = 170, C(ar)), 130.0 (d, ¹*J*(H,C) = 165, C(ar)), 120.8 (d, ¹*J*(H,C) = 136, C(7)), 118.9 (d, ¹*J*(H,C) = 168, C(ar)), 74.4 (d, ¹*J*(H,C) = 144, C(8)), 54.5 (d, ¹*J*(H,C) = 145, C(5)), 41.6 (d, ¹*J*(H,C) = 142, C(4)), 35.5 (t, ¹*J*(H,C) = 141, C(2)), 19.2 (q, ¹*J*(H,C) = 129, C(9)), 18.3 (q, ¹*J*(H,C) = 132, C(1)), 15.4 (q, ¹*J*(H,C) = 132, *Me*-C(4)), 14.6 (q, ¹*J*(H,C) = 134, *Me*-C(6)). *¹H NMR* (400 MHz, CDCl₃, 283K) of **(±)-anti-18**: δ 8.65 (d, 1H, ⁴*J*(H_{3'}-H_{5'}) = 1.9, H-C(3')), 8.55 (dd, 1H, ³*J*(H_{5'}-H_{6'}) = 8.9, ⁴*J*(H_{5'}-H_{3'}) = 1.9, H-C(5')), 8.29 (d, 1H, ³*J*(H_{6'}-H_{5'}) = 8.9, H-C(6')), 5.59 (dq, 1H, ³*J*(H₇-H₈) = 8.9, ⁴*J*(H₇-Me₆) = 0.9, H-C(7)), 4.79 (m, H-C(5)), 3.09 (*br. s*, 1H, H-OH), 2.75-2.44 (m, 4H, H-C(2), H-C(4), H-C(8)), 1.77 (d, 3H, ⁴*J*(Me₆-H₇) = 0.9, *Me*-C(6)), 1.50 (d, 3H, ³*J*(H₉-H₈) = 6.4, H-C(9)), 1.18 (t, 3H, ³*J*(H₉-H₈) = 7.1, H-C(1)), 0.98 (d, 3H, ³*J*(Me₄-H₄) = 7.1, *Me*-C(4)). *¹³C NMR* (100 MHz, CDCl₃, 283K) of **(±)-anti-18**: δ 216.7 (s, C(3)), 151.0 (s, C(ar)), 150.3 (s, C(ar)), 144.3 (s, C(6)), 135.5 (s, C(ar)), 135.3 (d, ¹*J*(H,C) = 170, C(ar)), 130.0 (d, ¹*J*(H,C) =

165, C(ar)), 120.8 (d, $^1J(\text{H,C}) = 136$, C(7)), 118.9 (d, $^1J(\text{H,C}) = 168$, C(ar)), 74.1 (d, $^1J(\text{H,C}) = 148$, C(8)), 54.5 (d, $^1J(\text{H,C}) = 145$, C(5)), 41.2 (d, $^1J(\text{H,C}) = 139$, C(4)), 35.5 (t, $^1J(\text{H,C}) = 141$, C(2)), 18.9 (q, $^1J(\text{H,C}) = 130$, C(9)), 18.3 (q, $^1J(\text{H,C}) = 132$, C(1)), 15.0 (q, $^1J(\text{H,C}) = 130$, *Me*-C(4)), 12.1 (q, $^1J(\text{H}_6\text{-C}_6) = 128$, *Me*-C(6)). **CI-MS** (NH_3): 415 (10), 432 (100). **Anal. Calcd.** for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_8\text{S}$ (414.11): C, 49.27, H, 5.35. Found: C, 49.31, H, 5.48.

2:1 Mixture of ($\pm$)-(2*RS*)-2-[(1*RS*,2*E*)-1-hydroxy-2-methyl-4-[(2,4-dinitrophenyl)sulfonyl]pent-2-enyl]cyclohexanone ($\pm$)-*syn*-19 and ($\pm$)-(2*SR*)-2-[(1*RS*,2*E*)-1-Hydroxy-2-methyl-4-[(2,4-dinitrophenyl)sulfonyl]pent-2-enyl]cyclohexanone ($\pm$)-*anti*-19.

19 was prepared as described above in the **general procedure 1** from (*E,E*)-2-methyl-1-trimethylsilyloxy-1,3-pentadiene (100 mg, 0.59 mmol, 1 equiv) and enoxysilane derived from cyclohexanone (300 mg, 1.76 mmol, 3 equiv) in CH_2Cl_2 (7 mL). Reaction-mixture was quenched with a 1 M solution of Bu_4NF in THF (0.59 mL, 0.59 mmol, 1 equiv) and 2,4-dinitrofluorobenzene (327 mg, 1.76 mmol, 3 equiv). FC (petroleum ether / ethyl acetate 1:1, *R_f* 0.4), gives 138 mg (55%) of a 2:1 mixture of (($\pm$)-*syn*-19 and ($\pm$)-*anti*-19) as a light orange solid, mp = 72.2-72.5°C. **IR** (*KBr*, cm^{-1}): 3530, 2940, 2870, 1720, 1690, 1650, 1450, 1555, 1380, 1220, 1135, 1030, 955, 750. **^1H NMR** (400 MHz, CDCl_3 , 283K) of ($\pm$)-($\pm$)-*syn*-19: δ 8.63 (d, 1H, $^4J(\text{H}_{3''}-\text{H}_{5''}) = 1.9$, H-C(3'')), 8.58 (dd, 1H, $^3J(\text{H}_{5''}-\text{H}_{6''}) = 8.8$, $^4J(\text{H}_{5''}-\text{H}_{3''}) = 1.9$, H-C(5'')), 8.37 (d, 1H, $^3J(\text{H}_{6''}-\text{H}_{5''}) = 8.8$, H-C(6'')), 5.40 (m, 1H, H-C(4')), 5.20 (d, 1H, $^3J(\text{H}_{5'}-\text{H}_{6'}) = 8.6$, H-C(3')), 4.81 (d, 1H, $^3J(\text{H}_{1'}-\text{H}_2) = 7.4$, H-C(1')), 2.71-1.4 (m, 9H, H-C(2), 2H-C(3), 2.1 (s, 3H, *Me*-C(2')), 1.36 (d, 3H, $^3J(\text{H}_{5'}-\text{H}_{4'}) = 7.1$, H-C(5')). **^{13}C NMR** (100 MHz, CDCl_3 , 283K) of ($\pm$)-($\pm$)-*syn*-19: δ = 212.3 (s, C(3)), 150.9 (s, C(ar)), 149.7 (s, C(ar)), 140.1 (s, C(2')), 137.7 (s, C(ar)), 135.6 (d, $^1J(\text{H,C}) = 171$, C(ar)), 130.0 (d, $^1J(\text{H,C}) = 168$, C(ar)), 120.7 (d, $^1J(\text{H,C}) = 139$, C(7)), 118.9 (d, $^1J(\text{H,C}) = 168$, C(ar)), 70.3 (d, $^1J(\text{H,C}) = 140$, C(1')), 57.0 (d, $^1J(\text{H,C}) = 140$, C(4')), 55.6 (d, $^1J(\text{H,C}) = 128$, C(2)), 43.2 (t, $^1J(\text{H,C}) = 135$, C(6)), 28.7, 27.2, 26.7 (3t, $^1J(\text{H,C}) = 132$, C(3), C(4), C(5)), 19.0 (q, $^1J(\text{H,C}) = 131$, *Me*-

C(2')), 16.4 (q, $^1J(\text{H},\text{C}) = 130$, C(5')). **^1H NMR (400 MHz, CDCl_3 , 283K) of ($\pm$)-anti-19:** δ 8.65 (d, 1H, $^4J(\text{H}_{3''}-\text{H}_{5''}) = 1.9$, H-C(3'')), 8.55 (dd, 1H, $^3J(\text{H}_{5''}-\text{H}_{6''}) = 8.8$, $^4J(\text{H}_{5''}-\text{H}_{3''}) = 1.9$, H-C(5'')), 8.36 (d, 1H, $^3J(\text{H}_{6''}-\text{H}_{5''}) = 8.8$, H-C(6'')), 5.40 (m, 1H, H-C(4')), 5.20 (d, 1H, $^3J(\text{H}_{5'}-\text{H}_{6'}) = 8.6$, H-C(3')), 4.45 (d, 1H, $^3J(\text{H}_{1'}-\text{H}_2) = 7.4$, H-C(1')), 2.71-1.4 (m, 9H, H-C(2), 2H-C(3), 2.1 (s, 3H, *Me*-C(2')), 1.34 (d, 3H, $^3J(\text{H}_{5'}-\text{H}_{4'}) = 7.1$, H-C(5')). **^{13}C NMR (100 MHz, CDCl_3 , 283K) of ($\pm$)-anti-19:** δ = 212.3 (s, C(3)), 150.9 (s, C(ar)), 149.7 (s, C(ar)), 140.1 (s, C(2')), 137.7 (s, C(ar)), 135.3 (d, $^1J(\text{H},\text{C}) = 171$, C(ar)), 130.0 (d, $^1J(\text{H},\text{C}) = 168$, C(ar)), 120.5 (d, $^1J(\text{H},\text{C}) = 139$, C(7)), 117.4 (d, $^1J(\text{H},\text{C}) = 168$, C(ar)), 70.3 (d, $^1J(\text{H},\text{C}) = 140$, C(1')), 56.8 (d, $^1J(\text{H},\text{C}) = 141$, C(4')), 55.5 (d, $^1J(\text{H},\text{C}) = 128$, C(2)), 43.2 (t, $^1J(\text{H},\text{C}) = 135$, C(6)), 28.7, 27.3, 25.3 (3t, $^1J(\text{H},\text{C}) = 132$, C(3), C(4), C(5)), 18.7 (q, $^1J(\text{H},\text{C}) = 131$, *Me*-C(2')), 16.3 (q, $^1J(\text{H},\text{C}) = 130$, C(5')). **MALDI-HRMS:** Calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_8\text{S}+\text{Na}^+$: 449.0995, found : 449.0990. **Anal. Calcd.** for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_8\text{S}$ (426.11): C, 50.70, H, 5.20. Found: C, 50.80, H, 5.24.