Electronic Supporting Information for

Stereoselective Methylsulfanyl-Cyclization of 4-Pentenols via Aerobic Oxidation/Homolytic Substitution-Cascades

Patrick Fries, Melanie Kim Müller, and Jens Hartung*

Fachbereich Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany

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1 General Remarks
(i) The compound numbering in the Electronic Supporting information is consistent with the accompanying publication. (ii) References refer exclusively to the Electronic Supporting Information.
2 Instrumentation and Reagent Specification

$^1\text{H}$-, $^{13}\text{C}$- and $^{19}\text{F}$-NMR spectra were recorded with FT-NMR DPX 400 and DMX 600 instruments (Bruker). Chemical shifts refer to the $\delta$-scale (coupling constants $J$ are given in Hz). The resonances of residual protons and the corresponding carbons of deuterated solvents (CDCl$_3$: $\delta_H$ 7.26, $\delta_C$ 77.0) were used as internal standards for $^1\text{H}$-, and $^{13}\text{C}$-NMR. $^{19}\text{F}$-NMR chemical shifts were referenced versus $\alpha,\alpha,\alpha$-Trifluorotoluene ($\delta_F$ –63.72) as internal standard.

GC/MS Analysis were performed with a HP 6890 Series (Hewlett Packard) with a ZB5 column (Phenomenex, 30 m $\times$ 0.25 mm, 0.25 $\mu$m). Temperature program: 40 °C (3 min), linear temperature rise (10 °C min$^{-1}$) to 280 °C, final temperature 280 °C (10 min). Mass spectra (EI, 70 eV) were recorded with a Mass Selective Detector HP 6890 (Hewlett Packard).

Electrospray ionization mass spectrometry (ESI-MS) was performed with a Bruker amazonX ion trap instrument. The ion source was used in positive and negative electrospray ionization mode. Scan speed was 32500 m/z s$^{-1}$ in ultra scan mode (0.3 FWHM / m/z), 4650 m/z s$^{-1}$ in maximum resolution (<0.1 FWHM / m/z) scan range was 70 to 2200 m/z. Sample solutions in acetonitrile at concentrations of approx. 0.4 $\mu$M were continuously infused into the ESI chamber at a flow rate of 2 $\mu$L/min using a syringe pump. Nitrogen was used as drying gas with flow rate of 3.0 L/min at 220 °C. The solutions were sprayed at a nebulizer pressure of 4 psi (275.8 mbar) and the electrospray needle was typically held at 4.5 kV. The instrument was controlled by Bruker Trap Control 7.0 software. Data analysis was performed using Bruker Data Analysis 4.0 software.

Combustion analyses were performed with a vario Micro cube CHNS (Elementar Analysentechnik / Hanau).

Reaction progress was monitored via thin layer chromatography (TLC) on aluminium sheets coated with silica gel (60 F$_{254}$, Machery-Nagel). Compounds were detected by UV-light (254 nm) or by staining of developed TLC sheets with Ekkert’s reagent.

IR spectra were recorded from pelletized samples in KBr using a FT-IR 1000 spectrometer (Perkin Elmer).

All solvents were purified according to standard procedures.$^1$
1-Phenylpent-4-en-1-ol (1a), (E)-Methyl 6-hydroxy-6-phenylhex-2-enoate (1b), 1-phenylhex-4-en-1-ol (1c), cis-2-allylcyclopentanol (1d), cis-2-allylcyclohexanol (1e), rel-(1S,2R)-1,2-diphenylpent-4-en-1,2-diol (1f), 2-phenylpent-4-en-1-ol (1g), rel-(1S,2S)-1-phenylpent-4-en-1,2-diol (1h), and rel-(1R,2R)-1,2-diphenylpent-4-en-1-ol (1i) were prepared according to published procedures.
3 Cobalt Complexes and Alkenols

All cobalt complexes were prepared as reported previously.\textsuperscript{12}

3.1.1 Bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κO)-but-3-en-4(olato-κO)]cobalt(II) dihydrate (4). Yellow solid (99 %), \( \nu_{\text{max}} \) (KBr) / cm\(^{-1}\) 3383 (OH), 1608 (CO), 1574, 1535, 1490, 1460, 1433, 1288, 1252, 1186, 1163, 1132, 1077, 1026; \( \delta_{\text{F}} \) (CDCl\(_3\)/acetone, 377 MHz) +6.1. Found C, 45.97; H, 3.16. C\(_{20}\)H\(_{16}\)CoF\(_6\)O\(_6\) (525.26) requires C, 45.73; H, 3.07 %.

ESI-MS: Found: 511.94 \([\text{CoL}^2+\text{Na}^+]\), C\(_{20}\)H\(_{12}\)CoF\(_6\)NaO\(_4\) requires 511.99.

3.1.2 Bis-[1-(4-fluorophenyl)-3-(oxo-κO)-but-1-en-1(olato-κO)]cobalt(II) dihydrate (5). Yellow solid (84 %), \( \nu_{\text{max}} \) (KBr) / cm\(^{-1}\) 3391 (OH), 1603 (CO), 1572, 1523, 1499, 1417, 1388, 1297, 1233, 1157, 1163, 1110, 1011; \( \delta_{\text{F}} \) (CDCl\(_3\)/acetone, 377 MHz) –112.0. Found C, 53.33; H, 4.92. C\(_{20}\)H\(_{20}\)CoF\(_2\)O\(_6\) (453.30) requires C, 52.99; H, 4.45 %.

ESI-MS: Found: 439.99 \([\text{CoL}^2+\text{Na}^+]\), C\(_{20}\)H\(_{16}\)CoF\(_2\)NaO\(_4\) requires 440.02.

3.1.3 Bis-[1,1,1-trifluoro-4-(4-fluorophenyl)-2-(oxo-κO)-but-3-en-4(olato-κO)]-cobalt(II) \( \times \) 2 EtOH (6). Orange solid (89 %), \( \nu_{\text{max}} \) (KBr) / cm\(^{-1}\) 3399 (OH), 1616 (CO), 1584, 1535, 1546, 1504, 1458, 1312, 1288, 1239, 1184, 1137, 1061, 1013; \( \delta_{\text{F}} \) (CDCl\(_3\)/acetone, 377 MHz) +6.7, –107.0. Found C, 46.68; H, 3.78. C\(_{24}\)H\(_{22}\)CoF\(_8\)O\(_6\) (617.35) requires C, 46.69; H, 3.59 %.

ESI-MS: Found: 547.93 \([\text{CoL}^3+\text{Na}^+]\), C\(_{20}\)H\(_{10}\)CoF\(_8\)NaO\(_4\) requires 547.97.

3.1.4 Bis-[1,3-di(4-fluorophenyl)-3-(oxo-κO)-prop-1-en-1(olato-κO)]cobalt(II) \( \times \) 2 EtOH (7). Yellow solid (76 %), \( \nu_{\text{max}} \) (KBr) / cm\(^{-1}\) 3367 (OH), 1600 (CO), 1574, 1553, 1527, 1491, 1433, 1387, 1300, 1218, 1157, 1096, 1051, 1012; \( \delta_{\text{F}} \) (CDCl\(_3\)/acetone, 377 MHz) –110.9. Found C, 61.23; H, 4.60. C\(_{34}\)H\(_{30}\)CoF\(_4\)O\(_6\) (669.53) requires C, 60.99; H, 4.52 %.

ESI-MS: Found: 600.13 \([\text{CoL}^4+\text{Na}^+]\), C\(_{30}\)H\(_{18}\)CoF\(_4\)NaO\(_4\) requires 600.04.

3.2.1 rel-(1\(R,2R\))-1,2-Diphenylhex-5-en-1-ol (15)

A solution of \textit{trans} stilbene oxide (1.01 g, 5.10 mmol) in dry Et\(_2\)O (15 mL) was added in an atmosphere of nitrogen in a dropwise manner to a solution of but-4-en-1-yl magnesium bromide prepared from 4-bromo-1-butene (1.43 g [97 %], 10.3 mmol) and
magnesium (339 mg, 14.0 mmol) in dry Et₂O (15 mL). The reaction mixture was stirred for 17 h at 22 °C and successively treated with satd. aqueous NH₄Cl (20 mL) and aqueous 1 M HCl (10 mL). The organic layer was separated and the aqueous layer extracted with Et₂O (3 × 15 mL). Combined organic phases were dried (MgSO₄) and concentrated under reduced pressure. The oily residue was purified by column chromatography [SiO₂, acetone/pentane = 1/10, (v/v)]. Yield: 522 mg (2.07 mmol, 41 %), Rᶠ 0.41 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δ_H (600 MHz, CDCl₃) 1.46–1.53 (1 H, m), 1.57–1.65 (2 H, m), 2.13–2.21 (1 H, m), 2.26–2.33 (1 H, m), 3.89 (1 H, d, J 8.6), 4.37 (1 H, td, Jₓ 8.6, Jᵧ 2.6), 4.95 (1 H, d, J 10.3), 5.01 (1 H, dd, J 17.0, 1.8), 5.78 (1 H, ddt, Jₓ 17.0, 10.3, Jᵧ 6.8), 7.18–7.25 (3 H, m), 7.27–7.34 (5 H, m) 7.37–7.41 (2 H, m). δ_C (100 MHz, CDCl₃) 30.1, 34.1, 58.9, 73.1, 114.8, 126.5, 126.9, 128.2, 128.6, 128.7, 128.8, 129.0, 129.1, 138.4, 141.3, 142.2.
4 Oxidation – Radical Substitution Cascades

4.1 Oxidation of 1-phenylpent-4-en-1-ol (1a)

4.1.1 Trapping with methyl disulfide

A solution of alcohol 1a (163 mg, 1.01 mmol) and cobalt catalyst 5 (22.9 mg, 50.5 µmol) in methyl disulfide (9.5 mL) and CHD (1.0 mL) was stirred at 70 °C for 6 h, while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and concentrated under reduced pressure to afford a residue that was purified by column chromatography [SiO₂, Et₂O/pentane = 1:10 (v/v)].

trans-2-(methylsulfanyl)methyl-5-phenyltetrahydrofuran (3a). Yield: 151 mg (726 µmol, 72 %), Rf 0.50 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (600 MHz, CDCl₃) 1.84–1.94 (2 H, m), 2.20–2.25 (1 H, m), 2.22 (3 H, s, CH₃), 2.39–2.43 (1 H, m), 2.70 (1 H, dd, J 13.3, 6.7), 2.82 (1 H, dd, J 13.3, 5.4), 4.45 (1 H, quin, J 6.4), 5.07 (1 H, t, J 6.9), 7.25–7.27 (1 H, m), 7.33–7.36 (4 H, m). NOESY 2-H || 5-H. δC (100 MHz, CDCl₃) 16.5 (CH₃), 31.7, 35.2, 39.6, 79.2, 80.8, 125.5, 127.1, 128.3, 143.3. GC-MS (EI, 70 eV) m/z (%) 208 (39, M⁺), 147 (100), 129 (63), 117 (20), 105 (31), 91 (94), 77 (25). HRMS (EI⁺) m/z 208.0921 (M⁺); calculated mass for C₁₂H₁₆OS⁺: 208.0922.

trans-2-methyl-5-phenyltetrahydrofuran (8a). Yield: 16.2 mg (100 µmol, 10 %). Analytical data agree with published values.²

4.1.2 Trapping with ethyl disulfide

A solution of alcohol 1a (163 mg, 1.00 mmol) and cobalt catalyst 5 (22.7 mg, 50.1 µmol) in diethyl disulfide (2.49 g, 20.2 mmol) and CHD (0.5 mL) was stirred at 70 °C for 16 h, while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified by column chromatography [SiO₂, Et₂O/pentane = 1:10 (v/v)].

trans-2-(ethylsulfanyl)methyl-5-phenyltetrahydrofuran (11). Yield: 80.6 mg (363 µmol, 36 %), Rf 0.50 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (400 MHz, CDCl₃) 1.28 (3 H, t, J 7.4), 1.79–1.93 (2 H, m), 2.17–2.26 (1 H, m), 2.35–2.43 (1 H, m), 2.64 (2 H, q, J 7.4), 2.70 (1 H, dd, J 13.3, 7.0), 2.84 (1 H, dd, J 13.3, 5.3), 7.25–
4.41 (1 H, quin, J 6.4), 5.05 (1 H, t, J 7.0), 7.21–7.28 (1 H, m), 7.31–7.38 (4 H, m). \( \delta_C \) (100 MHz, CDCl\(_3\)) 14.9, 26.8, 31.8, 35.2, 37.1, 79.4, 80.8, 125.5, 127.1, 128.3, 143.3. GC-MS (EI, 70 eV) \( m/z \) (%) 222 (17, \( M^+ \)), 161 (5), 147 (100), 129 (53), 117 (24), 105 (41), 91 (87), 77 (40). HRMS (EI\(^+\)) \( m/z \) 222.1080 (\( M^+ \)); calculated mass for \( C_{13}H_{18}OS^+ \): 222.1078.

**trans-2-methyl-5-phenyltetrahydrofuran (8a).** Yield: 63.8 mg (393 \( \mu \)mol, 39 %). Analytical data agree with published values.\(^2\)

### 4.1.3 Trapping with allyl disulfide

A solution of alcohol 1a (163 mg, 1.00 mmol) and cobalt catalyst 5 (22.8 mg, 50.1 \( \mu \)mol) in diallyl disulfide (2.50 mL [80 %], 13.7 mmol) and CHD (0.5 mL) was stirred at 70 °C for 16 h, while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified by column chromatography [SiO\(_2\), Et\(_2\)O/pentane = 1:10 (\( v/v \))].

**trans-2-(but-1'-en-4'-yl)-5-phenyltetrahydrofuran (13).** Yield: 43.7 mg (216 \( \mu \)mol, 22 %), \( R_f \) 0.64 [SiO\(_2\), acetone/pentane = 1:5 (\( v/v \))], colorless oil. \( \delta_H \) (400 MHz, CDCl\(_3\)) 1.58–1.71 (2 H, m), 1.75–1.91 (2 H, m), 2.10–2.19 (2 H, m), 2.33–2.41 (1 H, m), 4.21 (1 H, ddt, \( J_d \) 7.5, 6.8, \( J_t \) 6.2), 4.95–5.02 (2 H, m), 5.06 (1 H, dq, \( J_d \) 17.1, \( J_q \) 1.7), 5.87 (1 H, ddt, \( J_d \) 17.1, 10.3, \( J_t \) 6.6), 7.21–7.35 (5 H, m). \( \delta_C \) (100 MHz, CDCl\(_3\)) 30.4, 32.3, 35.3, 35.4, 79.4, 80.1, 114.5, 125.5, 128.3, 138.5, 143.9. GC-MS (EI, 70 eV) \( m/z \) (%) 202 (19, \( M^+ \)), 187 (6), 173 (8), 160 (11), 147 (65), 129 (42), 117 (40), 105 (100), 91 (89), 77 (33). HRMS (EI\(^+\)) \( m/z \) 202.1358 (\( M^+ \)); calculated mass for \( C_{14}H_{18}O^+ \): 202.1358.

Another fraction of a colorless oil was obtained (106 mg \( R_f \) 0.52 [SiO\(_2\), acetone/pentane = 1:5 (\( v/v \))], which consisted of **trans-2-methyl-5-phenyltetrahydrofuran** (8a) (145 \( \mu \)mol, 14 %), **trans-2-(allylsulfanyl)-methyl-5-phenyltetrahydrofuran** (12) (241 \( \mu \)mol, 24 %), [\( \delta_H \) (400 MHz, CDCl\(_3\)) 2.64 (1 H, dd, \( J_d \) 13.4, 6.6), 2.77 (1 H, dd, \( J_d \) 13.4, 5.7), 3.18–3.28 (2 H, m), 4.40 (1 H, quin, \( J_d \) 6.4), 5.04 (1 H, t, \( J_t \) 7.0), 5.09–5.16 (1 H, m), 5.87 (1 H, ddt, \( J_d \) 17.0, 9.9, \( J_t \) 7.3), 5.82 (1 H, ddt, \( J_d \) 17.0, 9.9, \( J_t \) 7.2); GC-MS (EI, 70 eV) \( m/z \) (%) 234 (3, \( M^+ \)), 193 (18), 160 (15), 147 (96), 129 (56), 117 (21), 105 (52), 91 (100), 77 (27). HRMS (EI\(^+\)) \( m/z \) 234.1083 (\( M^+ \)); calculated mass for \( C_{14}H_{18}OS^+ \): 234.1078.\(^2\)] and **trans-(5'-phenyltetrahydrofuryl)-methyl allyl disulfide** (14) (96.4 \( \mu \)mol, 10 %), [\( \delta_H \) (400 MHz, CDCl\(_3\)) 2.86 (1 H, dd, \( J_d \) 13.3, 6.8), 3.06 (1 H, dd, \( J_d \) 13.3, 5.7), 3.38 (2 H, d, \( J_t \) 7.4), 4.49 (1 H, quin, \( J_d \) 6.5), 5.12–5.18 (1 H, m), 5.22 (1
H, dq, $J_d$ 17.0, $J_q$ 1.3), 5.87 (1 H, ddt, $J_d$ 17.0, 9.9, $J_t$ 7.3); GC-MS (EI, 70 eV) $m/z$ (%)
266 (3, $M^+$), 193 (21), 160 (9), 147 (77), 129 (54), 117 (29), 105 (85), 91 (100), 77 (39).
HRMS (EI$^+$) $m/z$ 266.0797 ($M^+$); calculated mass for C$_{14}$H$_{18}$OS$_2$: 266.0799.
Due to overlap in the high field area of the $^1$H-NMR spectrum (1.5–2.5 ppm), signals of 3-H and 4-H of the tetrahydrofuran rings could not be assigned unequivocally to either of the three compounds ($8a$, $12$, $14$).

4.2 Oxidation of cis-2-(prop-2-en-1-yl)cyclopentan-1-ol (1d)
A solution of alcohol 1d (84.5 mg, 669 µmol) and cobalt catalyst 5 (15.0 mg, 33.1 µmol) in dimethyl disulfide (6.35 mL [99%], 70.9 mmol) and CHD (0.65 mL) was stirred at 70 °C for 6 h, while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and concentrated under reduced pressure to afford a residue that was purified by column chromatography [SiO$_2$, methyl tert-butyl ether/pentane = 1:10 → 1:5 (v/v)].

rel-(1S,3R,5S)-3-(methylsulfanyl)methyl-2-oxabicyclo[3.3.0]octane (3d). Yield: 81.9 mg (475 µmol, 71 %), $R_f$ 0.60 [SiO$_2$, acetone/pentane = 1:5 (v/v)], colorless oil. $\delta_H$(400 MHz, CDCl$_3$) 1.36–1.44 (1 H, m), 1.46–1.80 (7 H, m), 1.85 (1 H, dd, $J$ 8.2, 7.6), 2.13 (3 H, s, CH$_3$), 2.47–2.55 (1 H, m), 2.60–2.71 (2 H, m), 4.14 (1 H, quint, $J$ 6.5), 4.51–4.56 (1 H, m). $\delta_C$ (100 MHz, CDCl$_3$) 16.3 (CH$_3$), 24.7, 32.8, 34.7, 38.8, 39.1, 42.7, 78.5, 84.8. GC-MS (EI, 70 eV) $m/z$ (%) 172 (6), 124 (1), 111 (51), 93 (7), 81 (6), 67 (100). HRMS (EI$^+$) $m/z$ 172.0912 ($M^+$); calculated mass for C$_{9}$H$_{16}$OS$: 172.0922.

rel-(1S,3S,5S)-3-methyl-2-oxabicyclo[3.3.0]octane (8d). Yield: 926 µg (7.35 µmol, 11 %), $R_f$ 0.53 [SiO$_2$, acetone/pentane = 1:5 (v/v)], colorless oil. $\delta_H$(400 MHz, CDCl$_3$) 1.17 (1 H, d, $J$ 6.1), 1.33–1.42 (1 H, m), 1.44–1.54 (1 H, m), 1.57–1.78 (6 H, m), 2.61–2.71 (1 H, m), 4.03–4.10 (1 H, m), 4.51–4.58 (1 H, m). $\delta_C$ (100 MHz, CDCl$_3$) 20.6, 25.1, 34.8, 41.5, 43.1, 74.8, 84.4. GC-MS (EI, 70 eV) $m/z$ (%) 126 (8, $M^+$), 111 (80), 97 (42), 83 (7), 67 (100). HRMS (EI$^+$) $m/z$ 126.1033 ($M^+$); calculated mass for C$_{8}$H$_{16}$O$: 126.1045.

4.3 Oxidation of cis-2-(prop-2-en-1-yl)cyclohexan-1-ol (1e)
A solution of alcohol 1e (140.7 mg, 1.00 mmol) and cobalt catalyst 5 (23.3 mg,
51.4 μmol) in dimethyl disulfide (9.5 mL [99%], 106 mmol) and CHD (1.0 mL) was stirred at 70 °C for 8 h, while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and concentrated under reduced pressure to afford a residue that was purified by column chromatography [SiO₂, Et₂O/pentane = 1:10 (v/v)].

rel-(1S,3R,5S)-3-(methylsulfanyl)-methyl-2-oxabicyclo[4.3.0]nonane (3e). Yield: 138.3 mg (742 μmol, 74 %), Rₚ 0.69 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (400 MHz, CDCl₃) 1.12–1.26 (2 H, m), 1.32–1.59 (5 H, m), 1.71–1.77 (1 H, m), 1.81–1.88 (2 H, m), 2.00–2.06 (1 H, m), 2.13 (3 H, s, Me), 2.56 (1 H, dd, J 13.2, 6.5), 2.67 (1 H, dd, J 13.2, 5.6), 3.97 (1 H, q, J 3.7), 4.30 (1 H, quin, J 6.7). δC (100 MHz, CDCl₃) 16.3 (CH₃), 20.5, 23.9, 27.5, 28.2, 38.1, 38.3, 40.5, 76.2, 76.8. GC-MS (EI, 70 eV) m/z (%) 186 (7, M⁺), 168 (3), 125 (40), 107 (31), 81 (100). HRMS (EI⁺) m/z 186.1073 (M⁺); calculated mass for C₁₀H₁₈O⁺: 186.1078.

rel-(1S,3S,5S)-3-methyl-2-oxabicyclo[4.3.0]nonane (8e). Yield: 13.9 mg (99.1 μmol, 10 %). Analytical data agree with published values.⁷

4.4 Oxidation of rel-(1S,2R)-1,2-diphenylpent-4-en-1,2-diol (1f)

A solution of alcohol 1f (127 mg, 500 μmol) and cobalt catalyst 5 (11.5 mg, 25.4 μmol) in methyl disulfide (5.0 mL) and CHD (0.5 mL) was stirred at 60 °C for 5 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and concentrated under reduced pressure to afford an oily residue that was purified by column chromatography [SiO₂, Et₂O/pentane = 1:10 (v/v)].

rel-(2S,3R,5R)-5-(methylsulfanyl)methyl-2,3-diphenyltetrahydrofuran-3-ol (3f). Yield: 100 mg (334 μmol, 67 %), Rₚ 0.37 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (600 MHz, CDCl₃) 1.78 (1 H, s, OH), 2.26 (3 H, s, CH₃), 2.56 (1 H, d, J 7.4), 2.88–2.99 (1 H, m), 4.86–4.94 (1 H, m), 5.45 (1 H, s), 7.05 (2 H, dd, J 6.3, 2.7 ), 7.23–7.32 (4 H, m), 7.38 (2 H, t, J 7.4), 7.42–7.46 (2 H, m). NOESY 2-H || 5-H. δC (150 MHz, CDCl₃) 16.9 (CH₃), 39.7, 47.9, 78.4, 83.2, 89.5, 125.3, 126.6, 127.2, 128.27, 128.34, 135.5, 141.7. GC-MS (EI, 70 eV) m/z (%) 300 (<1, M⁺), 234 (3), 221 (8), 192 (8), 147 (17), 115 (10), 105 (100), 91 (8), 77 (33). HRMS (EI⁺) m/z 282.1090 (M⁺–H₂O); calculated mass for C₁₈H₁₈O⁵⁺: 282.1078.

rel-(2S,3R,5S)-5-methyl-2,3-diphenyltetrahydrofuran-3-ol (8f). Yield: 12.9 mg (50.7 μmol, 10 %), Rₚ 0.42 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (600 MHz, CDCl₃) 1.49 (3 H, d, J 6.1), 1.74 (1 H, d, J 1.8, OH), 2.21–2.27 (1 H, m),
2.52 (1 H, dd, J 12.9, 5.5), 4.76–4.83 (1 H, m), 5.40 (1 H, s), 7.03–7.07 (2 H, m), 7.24–7.26 (3 H, m), 7.28–7.31 (1 H, m), 7.37 (2 H, t, J 7.7), 7.40–7.44 (2 H, m). δC (100 MHz, CDCl$_3$) 21.5, 50.9, 75.2, 83.5, 90.0, 125.3, 126.6, 127.1, 128.1, 128.26, 128.29, 136.0, 142.1. GC–MS (EI, 70 eV) m/z (%) 254 (<1, M$^+$), 236 (13), 193 (10), 178 (6), 165 (8), 148 (88), 133 (65), 115 (23), 105 (100), 91 (8), 77 (65). HRMS (EI$^+$) m/z 254.1312 (M$^+$); calculated mass for C$_{17}$H$_{18}$O$_2$ $^+$: 254.1307.

### 4.5 Oxidation of 2-phenylpent-4-en-1-ol (1g)

A solution of alcohol 1g (164 mg, 1.01 mmol) and cobalt catalyst 5 (22.9 mg, 50.5 µmol) in dimethyl disulfide (9.5 mL [99%], 106 mmol) and CHD (1.0 mL) was stirred at 70 °C for 6 h, while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and concentrated under reduced pressure to afford a residue that was purified by column chromatography [SiO$_2$, Et$_2$O/pentane = 1:10 (v/v)].

**cis-2-(methylsulfanyl)methyl-4-phenyltetrahydrofuran (3g).** Yield: 144 mg (692 µmol, 68 %, cis:trans 88:12), R$_f$ 0.48 [SiO$_2$, acetone/pentane = 1:5 (v/v)], colorless oil. δH (400 MHz, CDCl$_3$) 1.84 (1 H, dt, J$^d$ 12.3, J$^t$ 10.0), 2.20 (3 H, s, CH$_3$), 2.53 (1 H, ddd, J 12.3, 7.2, 5.8), 2.71–2.77 (1 H, m), 2.78–2.85 (1 H, m), 3.44–3.55 (1 H, m), 3.84 (1 H, t, J 8.3), 4.19 (1 H, t, J 8.3), 4.23–4.31 (1H, m), 7.19–7.36 (5 H, m). NOESY 2-H ↔ 4-H. δC (100 MHz, CDCl$_3$) 16.4 (CH$_3$, trans), 16.5 (CH$_3$, cis), 39.1 (trans), 39.4 (cis), 39.7 (trans), 40.3 (cis), 44.5 (trans), 45.6 (cis), 74.5 (cis), 74.8 (trans), 78.5 (trans), 79.6 (cis), 126.6, 127.2, 128.6, 141.8 (cis), 142.1 (trans). GC–MS (EI, 70 eV) m/z (%) 208 (15, M$^+$), 190 (4), 147 (52), 129 (39), 115 (14), 103 (10), 91 (100), 77 (14). HRMS (EI$^+$) m/z 208.0928 (M$^+$); calculated mass for C$_{12}$H$_{16}$OS$^+$: 208.0922.

**cis-2-methyl-4-phenyltetrahydrofuran (8g).** Yield: 27.3 mg (168 µmol, 17 %). Analytical data agree with published values.$^2$9

### 4.6 Oxidation of rel-(1S,2S)-1-phenylpent-4-en-1,2-diol (1h)

A solution of alcohol 1h (89.2 mg, 500 µmol) and cobalt catalyst 5 (11.6 mg, 25.6 µmol) in dimethyl disulfide (5.0 mL [99%], 55.8 mmol) and CHD (0.5 mL) was stirred at 70 °C for 6 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. A GC–MS-spectrum revealed that Benzaldehyde (70 %) was the major product.
4.7 Oxidation of rel-(1R,2R)-1,2-diphenylpent-4-en-1-ol (1i)

A solution of alcohol 1i (120 mg, 504 µmol) and cobalt catalyst 5 (11.6 mg, 25.6 µmol) in dimethyl disulfide (5.0 mL [99%], 55.8 mmol) and CHD (0.5 mL) was stirred at 70 °C for 8 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and concentrated under reduced pressure to afford a residue that was purified by column chromatography [SiO₂, Et₂O/pentane = 1:10 (v/v)].

rel-(2R,4R,5R)-2-(methylsulfanyl)methyl-4,5-diphenyltetrahydrofuran (3i). Yield: 103 mg (360 µmol, 72 %), Rf 0.42 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (400 MHz, CDCl₃) 2.26 (3 H, s, CH₃), 2.30–2.39 (1 H, m), 2.47–2.57 (1 H, m), 2.78–2.85 (1 H, m), 2.74–2.83 (1 H, m), 2.87–2.95 (1 H, m), 3.78 (1 H, q, J 6.7), 4.83 (1 H, quint, J 6.3), 5.37 (1 H, d, J 6.3), 6.85–6.97 (4 H, m), 7.02–7.12 (6 H, m). NOESY 2-H ← 3-H, 2-H || 5-H, 3-H || 5-H. δC (100 MHz, CDCl₃) 16.5 (CH₃), 37.2, 40.3, 50.2, 78.4, 84.1, 126.3, 126.6, 127.4, 127.7, 128.5, 139.3, 139.6. HRMS (EI⁺) m/z 284.1209 (M⁺); calculated mass for C₁₈H₂₀O₂⁺: 284.1235.

rel-(2R,3R,5S)-5-methyl-2,3-diphenyltetrahydrofuran (8i). Yield: 8.72 mg (36.6 µmol, 7 %), Rf 0.45 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (400 MHz, CDCl₃) 1.44 (3 H, d, J 6.3), 2.09 (1 H, ddd, J 12.7, 7.4, 5.3), 2.51 (1 H, ddd, J 13.0, 7.4, 6.3), 3.78 (1 H, q, J 6.6), 4.78–4.88 (1 H, m), 5.36 (1 H, d, J 6.3), 6.85–6.98 (4 H, m), 7.03–7.13 (6 H, m). δC (100 MHz, CDCl₃) 22.9, 39.3, 50.3, 74.9, 83.5, 126.1, 126.3, 126.5, 127.4, 127.7, 128.5, 139.7, 139.9. HRMS (EI⁺) m/z 238.1364 (M⁺); calculated mass for C₁₇H₁₈O⁺: 238.1358.

4.8 Oxidation of rel-(1R,2R)-1,2-diphenylhex-5-en-1-ol (15)

A solution of alcohol 15 (169 mg, 669 µmol) and cobalt catalyst 5 (15.1 mg, 33.3 µmol) in methyl disulfide (6.6 mL) and CHD (0.65 mL) was stirred at 70 °C for 16 h while being exposed to laboratory atmosphere. Another batch of cobalt catalyst 5 (15.2 mg, 33.5 µmol) and CHD (0.65 mL) were added and the reaction mixture was stirred another 6 h at 70 °C. The reaction mixture was cooled to 20 °C and concentrated under reduced pressure to afford a residue that was purified by column chromatography [SiO₂, Et₂O/pentane = 1:10 (v/v)].

rel-(2R,3R,6R)-6-(methylsulfanyl)-methyl-2,3-diphenyltetrahydropyran (16). Yield: 134 mg (450 µmol, 67 %), Rf 0.51 [SiO₂, acetone/pentane = 1:5 (v/v)], colorless oil. δH (400 MHz, CDCl₃) 1.57–1.72 (2 H, m), 1.84–1.93 (1 H, m), 1.95–2.04 (1 H, m), 2.09 (3
H, s, (CH\(_3\)), 2.55 (1 H, dd, J 13.3, 7.2), 2.69 (1 H, dd, J 13.3, 5.1), 3.92 (1 H, d, J 8.1), 4.16 (1 H, quin, J 6.6), 4.75 (1 H, dt, J\(_d\) 8.1, J, 6.0), 7.13–7.19 (2 H, m), 7.21–7.28 (6 H, m), 7.32–7.36 (2 H, m). NOESY 2-H ↔ 3-H, 2-H || 6-H, 3-H || 6-H. \(\delta\)C (100 MHz, CDCl\(_3\)) 16.4 (CH\(_3\)), 31.2, 31.3, 39.3, 56.8, 79.1, 81.1, 126.1, 126.3, 128.1, 128.3, 128.5, 128.7, 142.4, 142.9. GC-MS (EI, 70 eV) m/z (%) 298 (<1, M\(^+\)), 237 (1), 193 (5), 178 (5), 165 (21), 152 (12), 131 (100), 115 (8), 103 (20), 87 (20). HRMS (EI\(^+\)) m/z 298.1384 (M\(^+\)); calculated mass for C\(_{19}\)H\(_{22}\)O: 298.1391.

rel-(2R,3R,6S)-6-methyl-2,3-diphenyltetrahydropyran (17). Yield: 15.4 mg (61.0 \(\mu\)mol, 9 %), \(R_f\) 0.56 [SiO\(_2\), acetone/pentane = 1:5 (v/v)], colorless oil. \(\delta\)H (400 MHz, CDCl\(_3\)) 1.21 (3 H, d, J 6.1), 1.39–1.49 (1 H, m), 1.58–1.68 (1 H, m), 1.85–2.00 (1 H, m), 3.92 (1 H, d, J 8.4), 4.09 (1 H, quind, J\(_{qu}d\) 7.9, J\(_d\) 6.1), 4.76 (1 H, dt, J\(_d\) 8.4, J\(_t\) 6.2), 7.14–7.19 (2 H, m), 7.23–7.29 (6 H, m), 7.33–7.37 (1 H, m). \(\delta\)C (100 MHz, CDCl\(_3\)) 21.4, 31.6, 33.6, 57.0, 75.3, 80.4, 126.1, 126.3, 128.2, 128.4, 128.6, 128.7, 142.8, 143.1. GC-MS (EI, 70 eV) m/z (%) 252 (<1, M\(^+\)), 178 (3), 165 (17), 152 (7), 115 (5), 85 (100), 77 (3). HRMS (EI\(^+\)) m/z 252.1515 (M\(^+\)); calculated mass for C\(_{18}\)H\(_{20}\)O: 252.1514.
5 5-Phenyltetrahydrofuryl-2-methyl methyl sulfoxide (9)

A solution of tert-butyl hydroperoxide (0.25 mL, 0.5–0.6 M, in nonane/CHCl₃) was added under nitrogen atmosphere to a solution of 2-[(2-oxidophenyl)iminomethyl](ethanolato)oxidovanadium(V)⁴¹ (10.7 mg, 29.0 µmol) in CHCl₃ (2.0 mL). The mixture was briefly refluxed (5 min), a solution of trans-2-(methylsulfanyl)methyl-5-phenyltetrahydrofuran (3a) (59.7 mg, 289 µmol) in CHCl₃ (2.0 mL) was added to the warm solution and the reaction mixture was stirred at 22 °C for 48 h. The dark brown solution was filtrated through a short pad of neutral Al₂O₃ for removing the vanadium residues. The filtrate was concentrated under reduced pressure to leave an oil, which was purified by flash chromatography (SiO₂, acetone). Yield: 42.4 mg, 189 µmol, 66 %, Rᵣ 0.12 [SiO₂, acetone], colorless oil, 50/50 mixture of diastereomers with respect to configuration at sulfur. δₜ (400 MHz, CDCl₃) 1.76–2.03 (4 H, m), 2.26–2.35 (2 H, m), 2.37–2.46 (2 H, m), 2.66 (3 H, s, CH₃), 2.70 (3 H, s, CH₃), 2.92–3.09 (4 H, m), 4.61–4.74 (2 H, m), 5.06 (2 H, dt, Jₚ 8.1, Jₜ 6.1), 7.21–7.27 (2 H, m), 7.28–7.35 (8 H, m). δₜ (100 MHz, CDCl₃) 32.3, 32.7, 35.0, 38.9, 39.8, 58.8, 61.6, 73.2, 73.4, 80.8, 81.1, 125.4, 127.3, 128.31, 128.33, 142.6, 142.7. HRMS (EI⁺) m/z 224.0834 (M⁺) respectively 224.0821 (M⁺); calculated mass for C₁₂H₁₆O₂S⁺: 224.0871. The intensity of the molecular ion in HRMS spectra of the two diastereomeric sulfoxides was very weak.

Since the retention times (GC) of the sulfoxide diastereomers differ from derived thioether trans-3a, the fragments at m/z 208.0919 (diastereomer 1) and m/z 208.0916 (diastereomer 2), originating from a formal loss of oxygen (calculated mass for C₁₂H₁₆OS⁺: 208.0922) was used to characterize the sulfoxide stereoisomers of 9.
6 5-Phenyltetrahydrofuryl-2-methyl methyl sulfone (10)

A solution of tert-butyl hydroperoxide (0.1 mL, 5–6 M, in nonane) was added under nitrogen atmosphere to a solution of 2-[(2-oxidophenyl)iminomethyl]- (ethanolato)oxidovanadium(V)\textsuperscript{14} (18.2 mg, 49.3 µmol) in CHCl\textsubscript{3} (2.5 mL). The mixture was briefly refluxed (5 min), a solution of trans-2-(methylsulfanyl)methyl-5-phenyltetrahydrofuran (3a) (104 mg, 497 µmol) in CHCl\textsubscript{3} (2.5 mL) was added to the warm solution and the reaction mixture was stirred at 22 °C for 48 h. The dark brown solution was filtrated through a short pad of neutral Al\textsubscript{2}O\textsubscript{3} for removing the vanadium residues. The filtrate was concentrated under reduced pressure to leave an oil, which was purified by flash chromatography [SiO\textsubscript{2}, acetone/CH\textsubscript{2}Cl\textsubscript{2} = 1/40 (v/v)]. Yield: 89.5 mg, 372 µmol, 75 %, R\textsubscript{f} 0.43 [SiO\textsubscript{2}, acetone/CH\textsubscript{2}Cl\textsubscript{2} = 1:40 (v/v)], colorless oil. δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 1.79–1.96 (2 H, m), 2.29–2.36 (1 H, m), 2.39–2.47 (1 H, m), 3.06 (3 H, s, CH\textsubscript{3}), 3.33 (1 H, dd, J 14.7, 9.1), 4.73 (1 H, tdd, J \textsubscript{t} 8.6, J\textsubscript{d} 6.0, 2.5), 5.08 (1 H, dd, J 8.5, 6.1), 7.25–7.37 (5 H, m). δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 32.5, 34.9, 42.6, 60.3, 74.0, 81.2, 125.2, 127.4, 128.5, 142.5. HRMS (EI\textsuperscript{+}) m/z 240.0814 (M\textsuperscript{+}); calculated mass for C\textsubscript{12}H\textsubscript{16}O\textsubscript{3}S\textsuperscript{+}: 240.0820.
7. Library of carbon-13 NMR spectra of selected compounds

Figure S1: $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of trans-2-(methylsulfanyl)methyl-5-phenyltetrahydrofuran (3a).

Figure S2: $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of rel-(1S,3R,5S)-3-(methylsulfanyl)methyl-2-oxabicyclo[3.3.0]octane (3d).
Figure S3. $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of rel-(1S,3R,5S)-3-(methylsulfanyl)methyl-2-oxabicyclo[4.3.0]nonane (3e).

Figure S4. $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of rel-(2S,3R,5R)-5-(methylsulfanyl)methyl-2,3-diphenyltetrahydrofuran-3-ol (3f).
**Figure S5.** $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of cis-2-(methylsulfanyl)methyl-4-phenyltetrahydrofuran (3g).

**Figure S6.** $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of rel-(2R,4R,5R)-2-(methylsulfanyl)methyl-4,5-diphenyltetrahydrofuran (3i).
Figure S7. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of rel-(1S,3S,5S)-3-Methyl-2-oxabicyclo[3.3.0]octane (8d).

Figure S8. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of rel-(2S,3R,5S)-5-methyl-2,3-diphenyltetrahydrofuran-3-ol (8f).
**Figure S9.** $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of *rel-(2R,3R,5S)-5-methyl-2,3-diphenyltetrahydrofuran (8i)*.

**Figure S10.** $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of (5-Phenyltetrahydrofuryl)-2-methyl methyl sulfoxide (9) (50/50-mixture of stereoisomers at sulfur).
Figure S11: $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of (5-phenyltetrahydrofuryl)-2-methyl methyl sulfone (10).

Figure S12. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of trans-2-(ethylsulfanyl)methyl-5-phenyltetrahydrofuran (11).
**Figure S13.** $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of trans-2-(but-1-en-4-yl)-5-phenyltetrahydrofuran (13).

**Figure S14.** $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of rel-(2R,3R,6R)-6-(methylsulfanyl)-methyl-2,3-diphenyltetrahydropyran (16).
Figure S15. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of $rel$-(2R,3R,6S)-6-methyl-2,3-diphenyltetrahydropyran (17).
8 References


