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}H-, ^{13}C- and ^{19}F-NMR spectra were recorded with FT-NMR DPX 400 and DMX 600 instruments (*Bruker*). Chemical shifts refer to the δ-scale (coupling constants J are given in Hz). The resonances of residual protons and the corresponding carbons of deuterated solvents ($CDCl_3$: δ_H 7.26, δ_C 77.0) were used as internal standards for ^{1}H-, and ^{13}C-NMR. ^{19}F-NMR chemical shifts were referenced versus α,α,α-Trifluorotoluene (δ_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 × 0.25 mm, 0.25 µm). 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 µM were continuously infused into the ESI chamber at a flow rate of 2 µL/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**),[2,3] (*E*)-Methyl 6-hydroxy-6-phenylhex-2-enoate (**1b**),[4] 1-phenylhex-4-en-1-ol (**1c**),[5] *cis*-2-allylcyclopentanol (**1d**),[6] *cis*-2-allylcyclohexanol (**1e**),[7] *rel*-(1*S*,2*R*)-1,2-diphenylpent-4-en-1,2-diol (**1f**),[8] 2-phenylpent-4-en-1-ol (**1g**),[9] *rel*-(1*S*,2*S*)-1-phenylpent-4-en-1,2-diol (**1h**)[10], and *rel*-(1*R*,2*R*)-1,2-diphenylpent-4-en-1-ol (**1i**)[11] were prepared according to published procedures.

3 Cobalt Complexes and Alkenols

All cobalt complexes were prepared as reported previously.[12]

3.1.1 Bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4(olato-κ*O*)]cobalt(II) dihydrate (4). Yellow solid (99 %), ν_{max} (KBr) / cm^{-1} 3383 (OH), 1608 (CO), 1574, 1535, 1490, 1460, 1433, 1288, 1252, 1186, 1163, 1132, 1077, 1026; δ_F ($CDCl_3$/acetone, 377 MHz) +6.1. Found C, 45.97; H, 3.16. $C_{20}H_{16}CoF_6O_6$ (525.26) requires C, 45.73; H, 3.07 %. ESI-MS: Found: 511.94 [$CoL^1{}_2$+Na^+], $C_{20}H_{12}CoF_6NaO_4$ requires 511.99.

3.1.2 Bis-[1-(4-fluorophenyl)-3-(oxo-κ*O*)-but-1-en-1(olato-κ*O*)]cobalt(II) dihydrate (5). Yellow solid (84 %), ν_{max} (KBr) / cm^{-1} 3391 (OH), 1603 (CO), 1572, 1523, 1499, 1417, 1388, 1297, 1233, 1157, 1163, 1110, 1011; δ_F ($CDCl_3$/acetone, 377 MHz) –112.0. Found C, 53.33; H, 4.92. $C_{20}H_{20}CoF_2O_6$ (453.30) requires C, 52.99; H, 4.45 %. ESI-MS: Found: 439.99 [$CoL^2{}_2$+Na^+], $C_{20}H_{16}CoF_2NaO_4$ requires 440.02.

3.1.3 Bis-[1,1,1-trifluoro-4-(4-fluorophenyl)-2-(oxo-κ*O*)-but-3-en-4(olato-κ*O*)]-cobalt(II) × 2 EtOH (6). Orange solid (89 %), ν_{max} (KBr) / cm^{-1} 3399 (OH), 1616 (CO), 1584, 1535, 1546, 1504, 1458, 1312, 1288, 1239, 1184, 1137, 1061, 1013; δ_F ($CDCl_3$/acetone, 377 MHz) +6.7, –107.0. Found C, 46.68; H, 3.78. $C_{24}H_{22}CoF_8O_6$ (617.35) requires C, 46.69; H, 3.59 %. ESI-MS: Found: 547.93 [$CoL^3{}_2$+Na^+], $C_{20}H_{10}CoF_8NaO_4$ requires 547.97.

3.1.4 Bis-[1,3-di(4-fluorophenyl)-3-(oxo-κ*O*)-prop-1-en-1(olato-κ*O*)]cobalt(II) × 2 EtOH (7). Yellow solid (76 %), ν_{max} (KBr) / cm^{-1} 3367 (OH), 1600 (CO), 1574, 1553, 1527, 1491, 1433, 1387, 1300, 1218, 1157, 1096, 1051, 1012; δ_F ($CDCl_3$/acetone, 377 MHz) –110.9. Found C, 61.23; H, 4.60. $C_{34}H_{30}CoF_4O_6$ (669.53) requires C, 60.99; H, 4.52 %. ESI-MS: Found: 600.13 [$CoL^4{}_2$+Na^+], $C_{30}H_{18}CoF_4NaO_4$ requires 600.04.

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

A solution of *trans* stilbene oxide (1.01 g, 5.10 mmol) in dry Et_2O (15 mL) was added in an atmophere 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 Et_2O (15 mL). The reaction mixture was stirred for 17 h at 22 °C and successively treated with satd. aqueous NH_4Cl (20 mL) and aqueous 1 M HCl (10 mL). The organic layer was separated and the aqueous layer extracted with Et_2O (3 × 15 mL). Combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The oily residue was purified by column chromatography [SiO_2, acetone/pentane = 1/10, (*v*/*v*)]. Yield: 522 mg (2.07 mmol, 41 %), R_f 0.41 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (600 MHz, $CDCl_3$) 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, J_t 8.6, J_d 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, J_d 17.0, 10.3, J_t 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, $CDCl_3$) 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 [SiO_2, Et_2O/pentane = 1:10 (*v*/*v*)].

***trans*-2-(methylsulfanyl)methyl-5-phenyltetrahydrofuran (3a)**. Yield: 151 mg (726 µmol, 72 %), R_f 0.50 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (600 MHz, $CDCl_3$) 1.84–1.94 (2 H, m), 2.20–2.25 (1 H, m), 2.22 (3 H, s, CH_3), 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. δ_C (100 MHz, $CDCl_3$) 16.5 (CH_3), 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 $C_{12}H_{16}OS^+$: 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 [SiO_2, Et_2O/pentane = 1:10 (*v*/*v*)].

***trans*-2-(ethylsulfanyl)methyl-5-phenyltetrahydrofuran (11)**. Yield: 80.6 mg (363 µmol, 36 %), R_f 0.50 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (400 MHz, $CDCl_3$) 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),

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). δ_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 µmol, 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 µmol) 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_2O/pentane = 1:10 (*v*/*v*)].

***trans*-2-(but-1'-en-4'-yl)-5-phenyltetrahydrofuran (13).** Yield: 43.7 mg (216 µmol, 22 %), R_f 0.64 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_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). δ_C (100 MHz, $CDCl_3$) 30.4, 32.3, 35.3, 35.4, 79.4, 80.1, 114.5, 125.5, 127.0, 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 µmol, 14 %)**, *trans*-2-(allylsulfanyl)-methyl-5-phenyltetrahydrofuran** (**12**) (241 µmol, 24 %), [δ_H (400 MHz, $CDCl_3$) 2.64 (1 H, dd, *J* 13.4, 6.6), 2.77 (1 H, dd, *J* 13.4, 5.7), 3.18–3.28 (2 H, m), 4.40 (1 H, quin, *J* 6.4), 5.04 (1 H, t, *J* 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.] and ***trans*-(5'-phenyltetra-hydrofuryl)-methyl allyl disulfide** (**14**) (96.4 µmol, 10 %), [δ_H (400 MHz, $CDCl_3$) 2.86 (1 H, dd, *J* 13.3, 6.8), 3.06 (1 H, dd, *J* 13.3, 5.7), 3.38 (2 H, d, *J* 7.4), 4.49 (1 H, quin, *J* 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*-(1*S*,3*R*,5*S*)-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. δ_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). δ_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 $C_9H_{16}OS^+$: 172.0922.

***rel*-(1*S*,3*S*,5*S*)-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. δ_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). δ_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 $C_8H_{14}O^+$: 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 [SiO_2, Et_2O/pentane = 1:10 (*v*/*v*)].

***rel*-(1*S*,3*R*,5*S*)-3-(methylsulfanyl)-methyl-2-oxabicyclo[4.3.0]nonane (3e)**. Yield: 138.3 mg (742 µmol, 74 %), R_f 0.69 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (400 MHz, $CDCl_3$) 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). δ_C (100 MHz, $CDCl_3$) 16.3 (CH_3), 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 $C_{10}H_{18}OS^+$: 186.1078.

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

4.4 Oxidation of *rel*-(1*S*,2*R*)-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 [SiO_2, Et_2O/pentane = 1:10 (*v*/*v*)].

***rel*-(2*S*,3*R*,5*R*)-5-(methylsulfanyl)methyl-2,3-diphenyltetrahydrofuran-3-ol (3f).** Yield: 100 mg (334 µmol, 67 %), R_f 0.37 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (600 MHz, $CDCl_3$) 1.78 (1 H, s, OH), 2.26 (3 H, s, CH_3), 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. δ_C (150 MHz, $CDCl_3$) 16.9 (CH_3), 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^+–H_2O); calculated mass for $C_{18}H_{18}OS^+$: 282.1078.

***rel*-(2*S*,3*R*,5*S*)-5-methyl-2,3-diphenyltetrahydrofuran-3-ol (8f)**. Yield: 12.9 mg (50.7 µmol, 10 %), R_f 0.42 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (600 MHz, $CDCl_3$) 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). δ_C (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_2O/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. δ_H (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. δ_C (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*-(1*S*,2*S*)-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*-(1*R*,2*R*)-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 [SiO_2, Et_2O/pentane = 1:10 (*v*/*v*)].

***rel*-(2*R*,4*R*,5*R*)-2-(methylsulfanyl)methyl-4,5-diphenyltetrahydrofuran (3i)**. Yield: 103 mg (360 µmol, 72 %), R_f 0.42 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (400 MHz, $CDCl_3$) 2.26 (3 H, s, CH_3), 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, $CDCl_3$) 16.5 (CH_3), 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 $C_{18}H_{20}OS^+$: 284.1235.

***rel*-(2*R*,3*R*,5*S*)-5-methyl-2,3-diphenyltetrahydrofuran (8i).** Yield: 8.72 mg (36.6 µmol, 7 %), R_f 0.45 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (400 MHz, $CDCl_3$) 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). δ_C (100 MHz, $CDCl_3$) 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 $C_{17}H_{18}O^+$: 238.1358.

4.8 Oxidation of rel-(1*R*,2*R*)-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 [SiO_2, Et_2O/pentane = 1:10 (*v*/*v*)].

***rel*-(2*R*,3*R*,6*R*)-6-(methylsulfanyl)-methyl-2,3-diphenyltetrahydropyran (16).** Yield: 134 mg (450 µmol, 67 %), R_f 0.51 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (400 MHz, $CDCl_3$) 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_t 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. δ_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 $C_{19}H_{22}OS$: 298.1391.

***rel*-(2*R*,3*R*,6*S*)-6-methyl-2,3-diphenyltetrahydropyran (17)**. Yield: 15.4 mg (61.0 µmol, 9 %), R_f 0.56 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_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_{quint} 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). δ_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/$CHCl_3$) was added under nitrogen atmosphere to a solution of 2-[(2-oxidophenyl)-iminomethyl](ethanolato)oxidovanadium(V)[14] (10.7 mg, 29.0 µmol) in $CHCl_3$ (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 $CHCl_3$ (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 Al_2O_3 for removing the vanadium residues. The filtrate was concentrated under reduced pressure to leave an oil, which was purified by flash chromatography (SiO_2, acetone). Yield: 42.4 mg, 189 µmol, 66 %, R_f 0.12 [SiO_2, acetone], colorless oil, 50/50 mixture of diastereomers with respect to configuration at sulfur. δ_H (400 MHz, $CDCl_3$) 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, CH_3), 2.70 (3 H, s, CH_3), 2.92–3.09 (4 H, m), 4.61–4.74 (2 H, m), 5.06 (2 H, dt, J_d 8.1, J_t 6.1), 7.21–7.27 (2 H, m), 7.28–7.35 (8 H, m). δ_C (100 MHz, $CDCl_3$) 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 $C_{12}H_{16}O_2S^+$: 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 $C_{12}H_{16}OS^+$: 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)[14] (18.2 mg, 49.3 µmol) in $CHCl_3$ (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 $CHCl_3$ (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_2O_3 for removing the vanadium residues. The filtrate was concentrated under reduced pressure to leave an oil, which was purified by flash chromatography [SiO_2, acetone/CH_2Cl_2 = 1/40 (*v*/*v*)]. Yield: 89.5 mg, 372 µmol, 75 %, R_f 0.43 [SiO_2, acetone/CH_2Cl_2 = 1:40 (*v*/*v*)], colorless oil. δ_H (400 MHz, $CDCl_3$) 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_3), 3.33 (1 H, dd, *J* 14.7, 9.1), 4.73 (1 H, tdd, J_t 8.6, J_d 6.0, 2.5), 5.08 (1 H, dd, *J* 8.5, 6.1), 7.25–7.37 (5 H, m). δ_C (100 MHz, $CDCl_3$) 32.5, 34.9, 42.6, 60.3, 74.0, 81.2, 125.2, 127.4, 128.5, 142.5. HRMS (EI^+) *m/z* 240.0814 (M^+); calculated mass for $C_{12}H_{16}O_3S^+$: 240.0820.

7. Library of carbon-13 NMR spectra of selected compounds

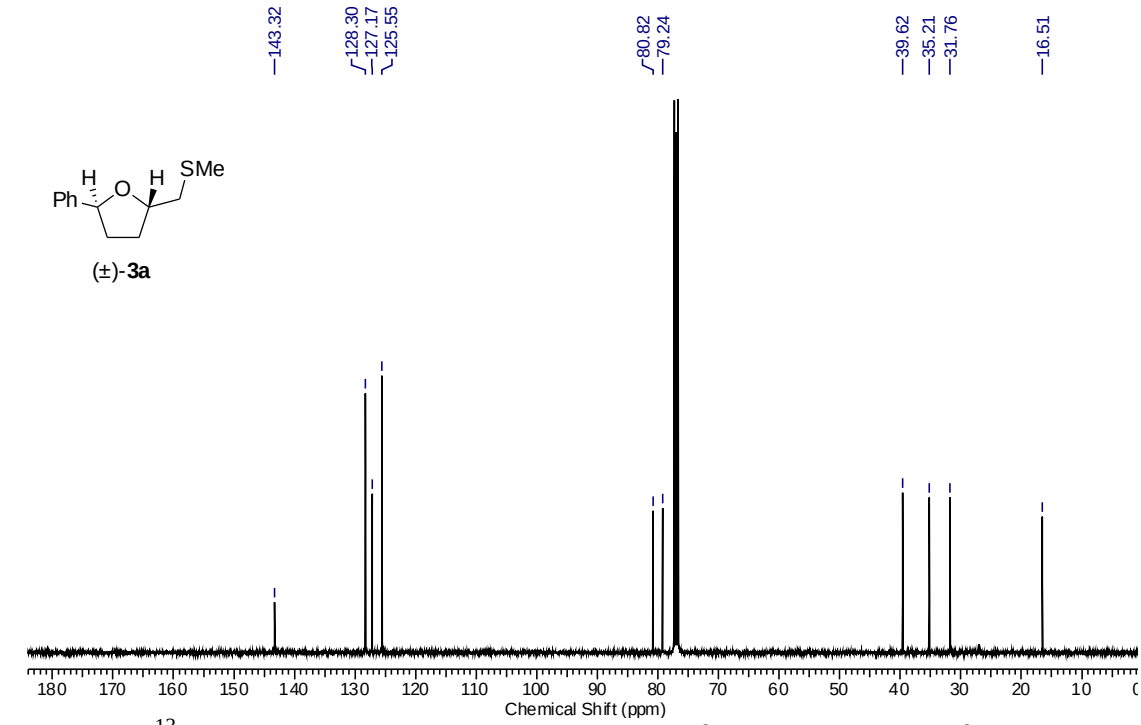

Figure S1: ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of *trans*-2-(methylsulfanyl)methyl-5-phenyltetrahydrofuran (**3a**).

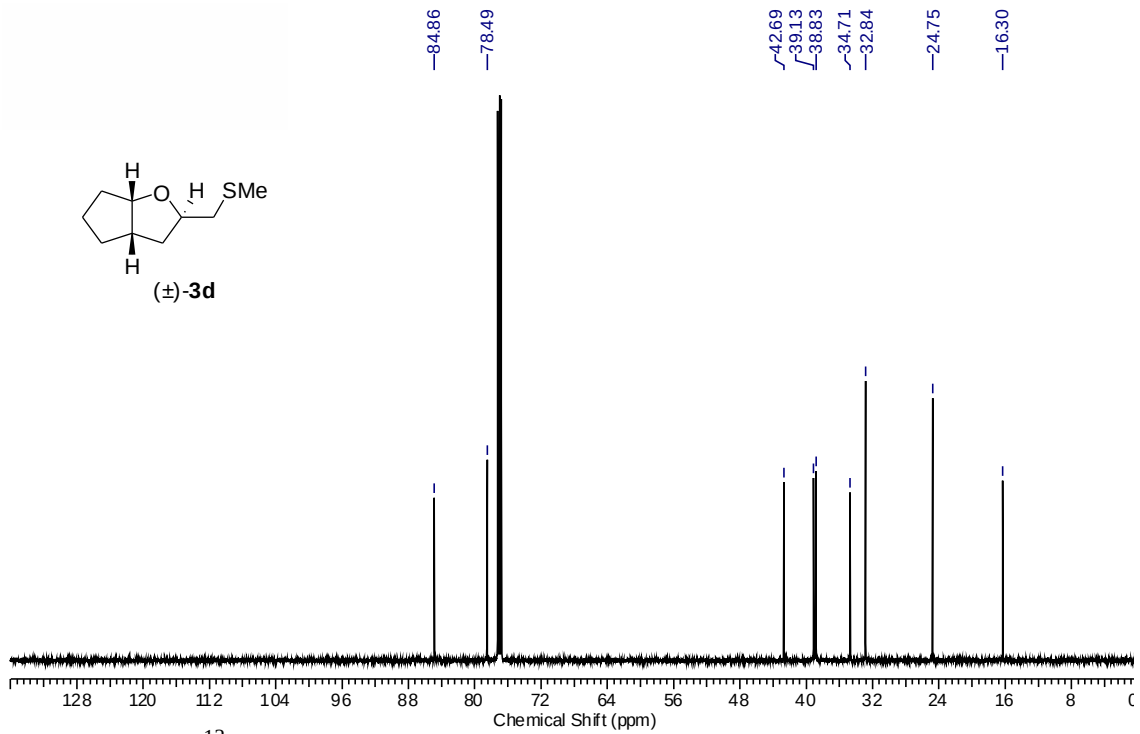

Figure S2: ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of *rel*-(1*S*,3*R*,5*S*)-3-(methylsulfanyl)methyl-2-oxabicyclo[3.3.0]octane (**3d**).

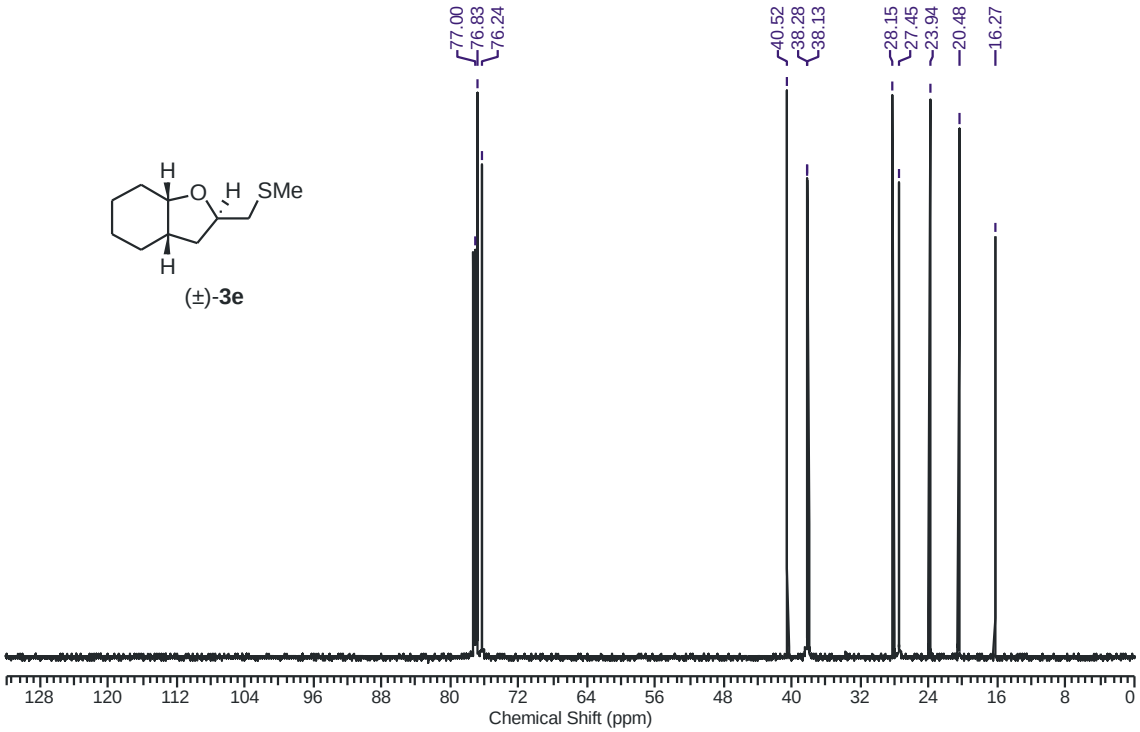

Figure S3. ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of *rel*-(1*S*,3*R*,5*S*)-3-(methylsulfanyl)methyl-2-oxabicyclo[4.3.0]nonane (**3e**).

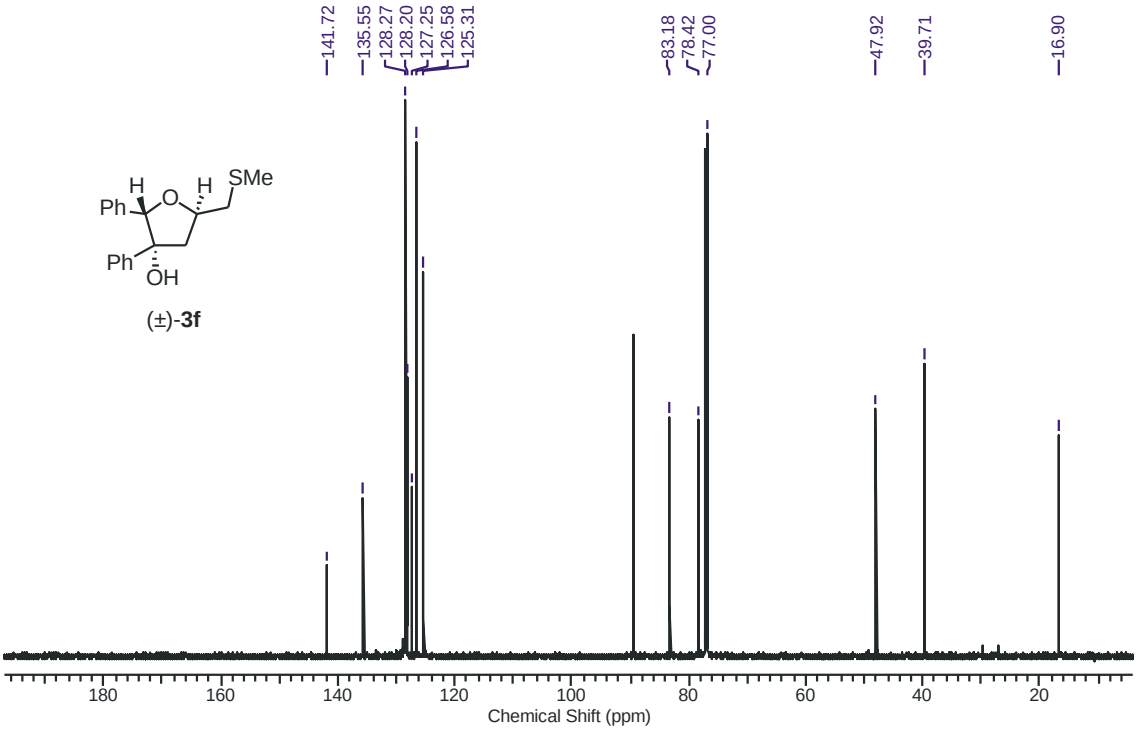

Figure S4. ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of *rel*-(2*S*,3*R*,5*R*)-5-(methylsulfanyl)methyl-2,3-diphenyltetrahydrofuran-3-ol (**3f**).

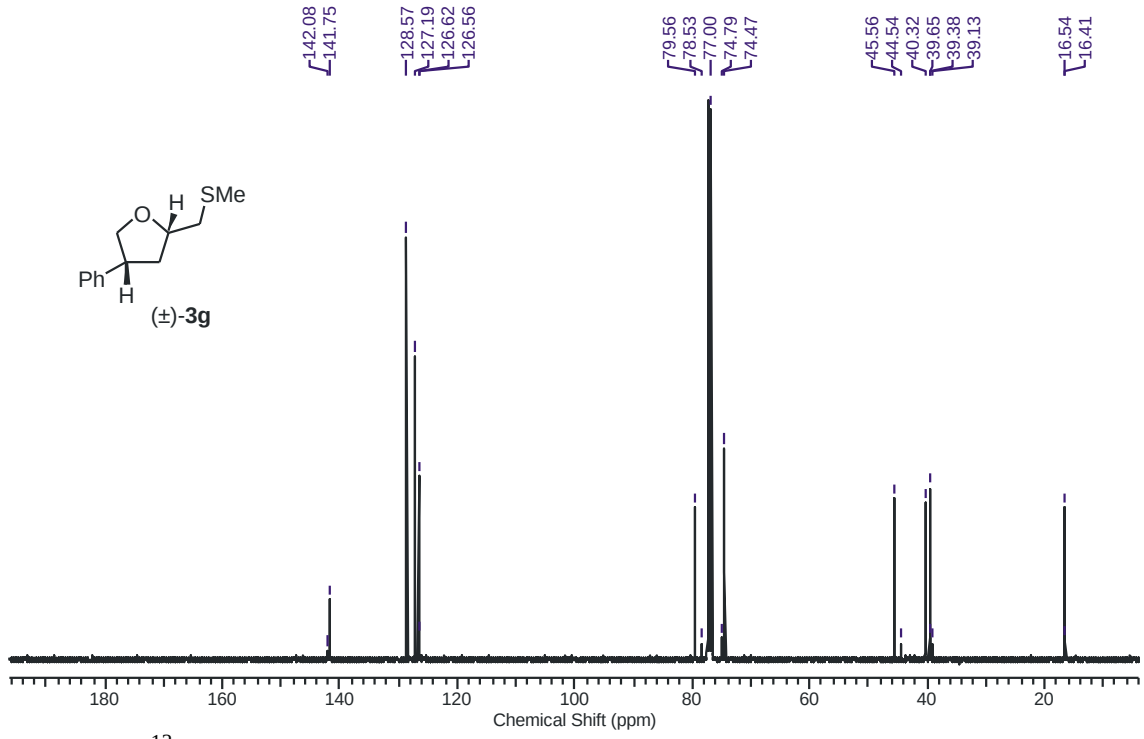

Figure S5. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of *cis*-2-(methylsulfanyl)methyl-4-phenyltetrahydrofuran (**3g**).

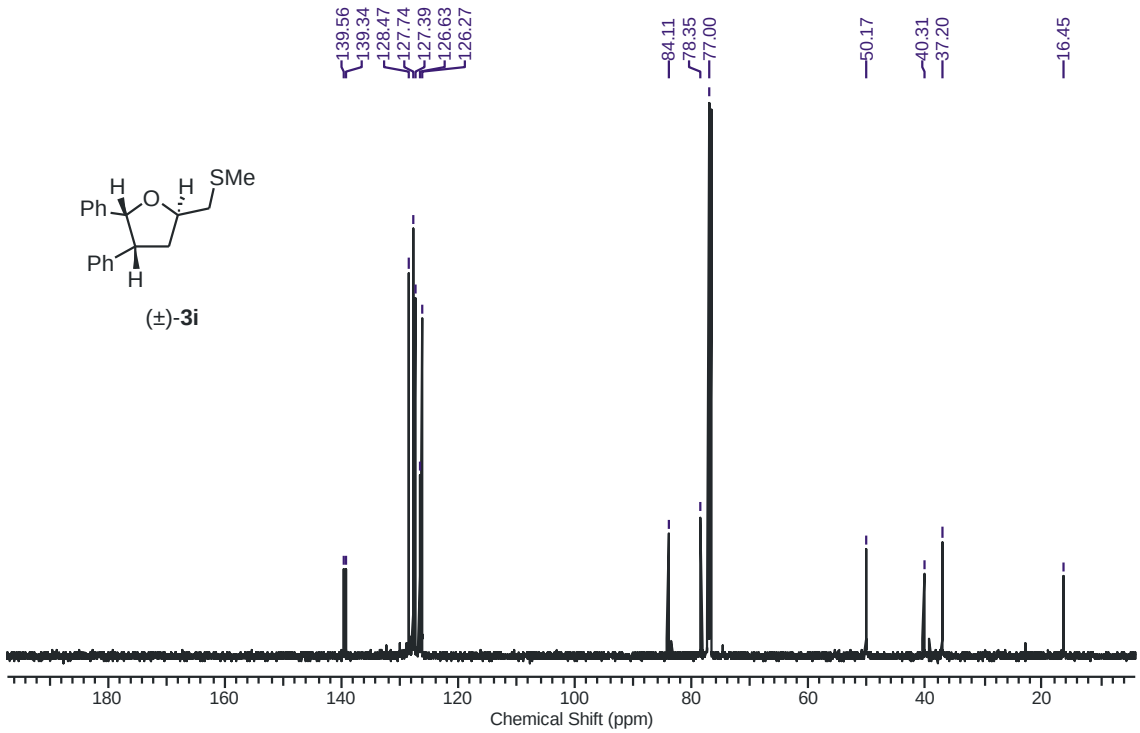

Figure S6. ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of *rel*-(2*R*,4*R*,5*R*)-2-(methylsulfanyl)methyl-4,5-diphenyltetrahydrofuran (**3i**).

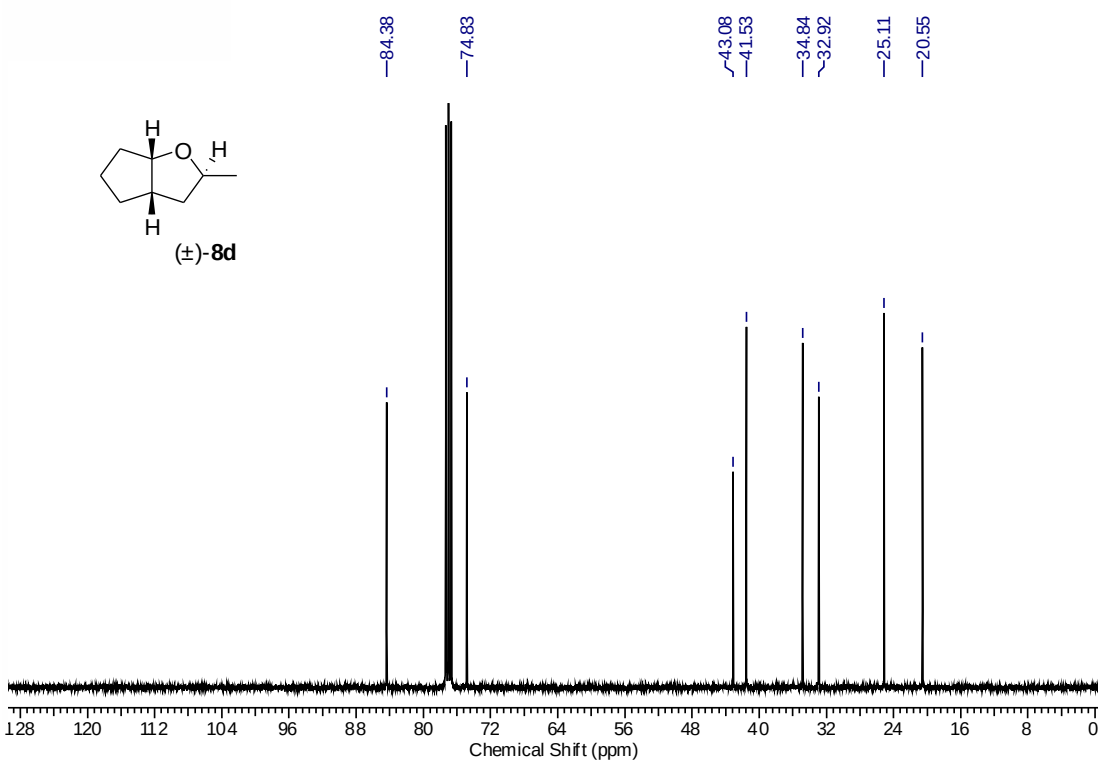

Figure S7. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of *rel*-(1*S*,3*S*,5*S*)-3-Methyl-2-oxabicyclo[3.3.0]octane (**8d**) .

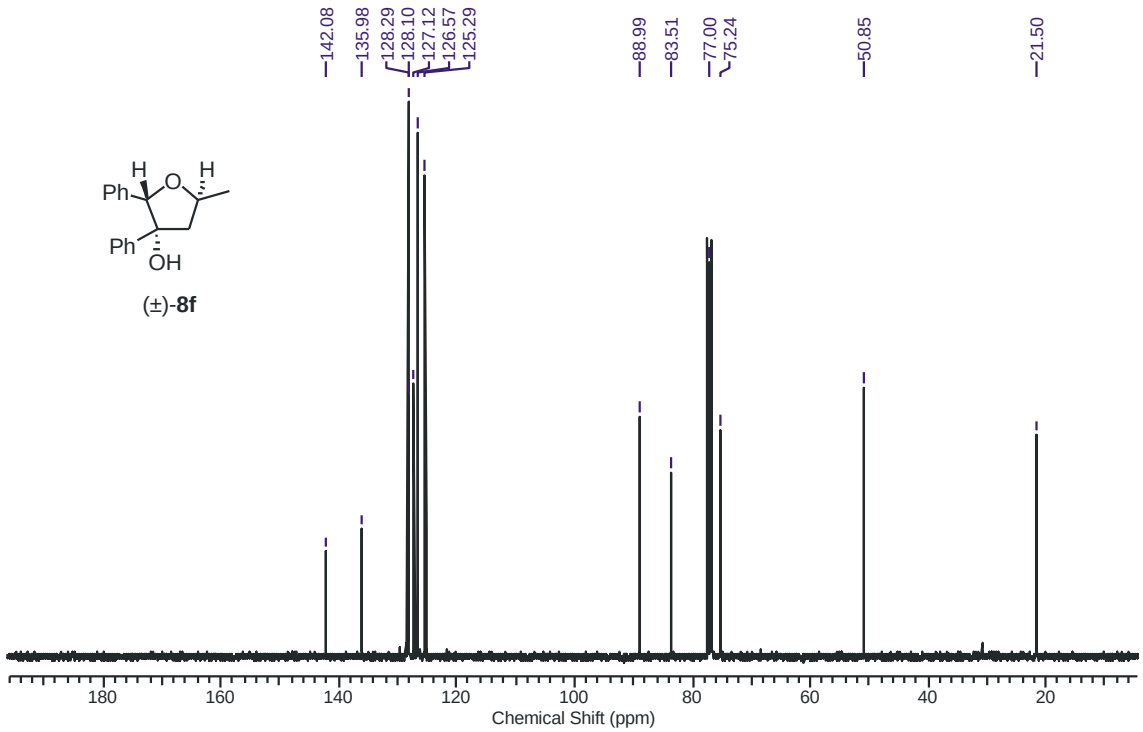

Figure S8. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of *rel*-(2*S*,3*R*,5*S*)-5-methyl-2,3-diphenyltetrahydrofuran-3-ol (**8f**).

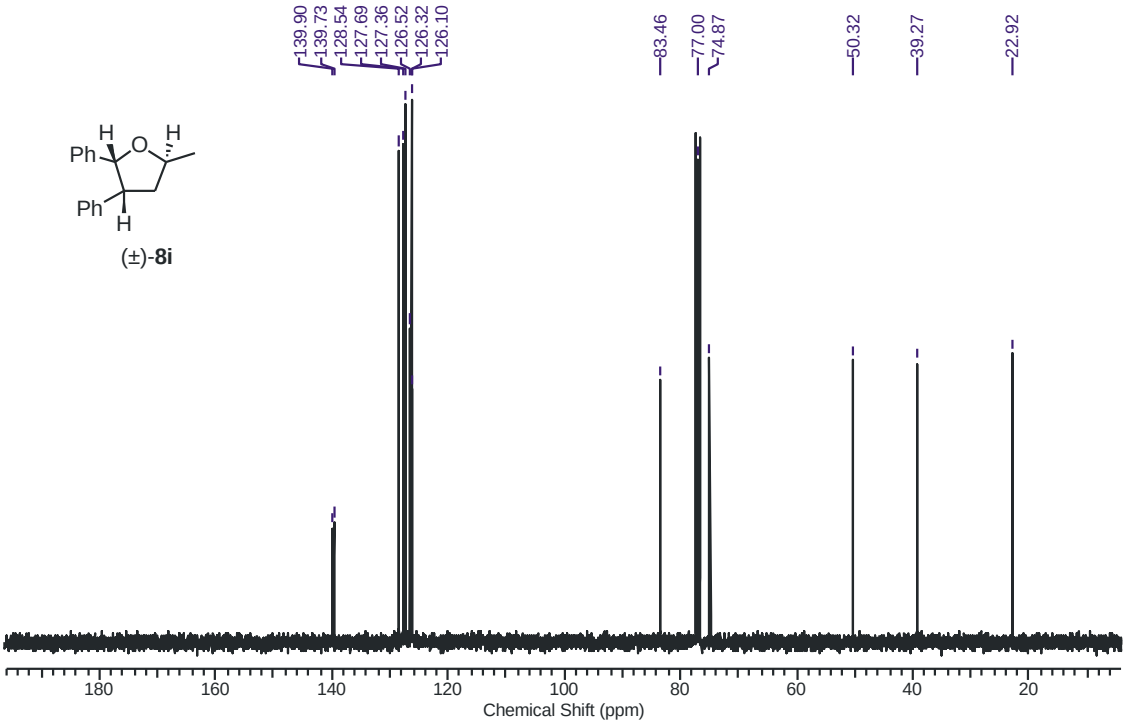

Figure S9. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of *rel*-(2*R*,3*R*,5*S*)-5-methyl-2,3-diphenyltetrahydrofuran (**8i**).

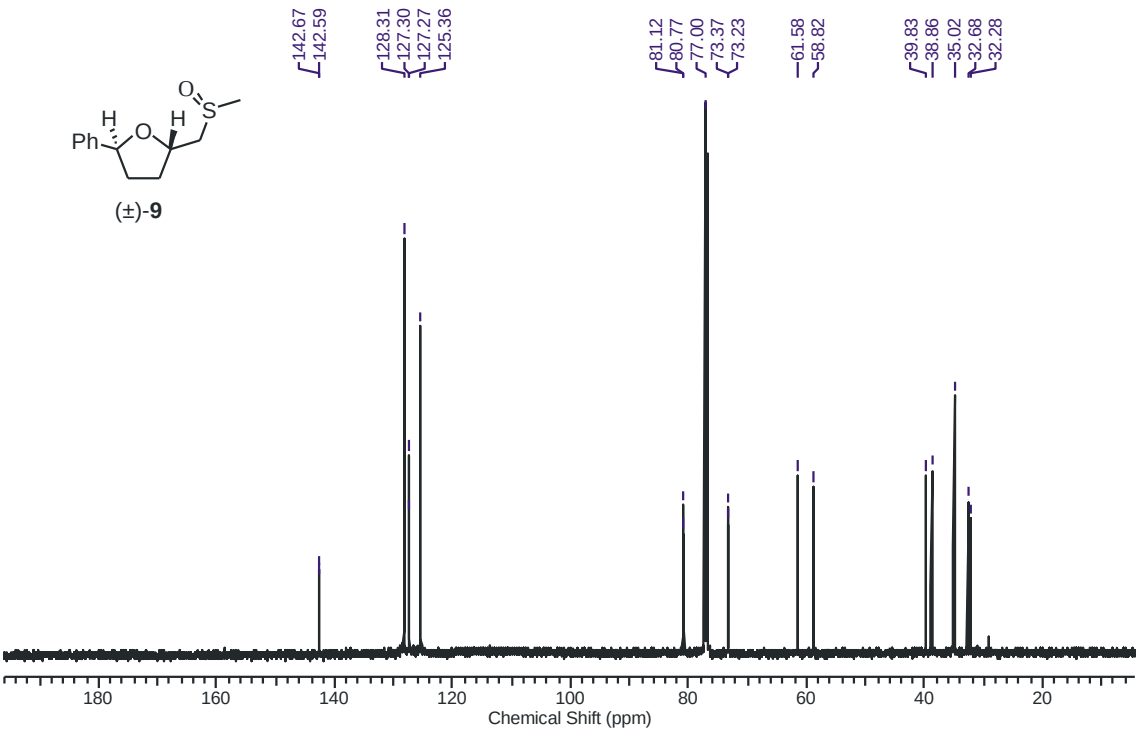

Figure S10. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of (5-Phenyltetrahydrofuryl)-2-methyl methyl sulfoxide (**9**) (50/50-mixture of stereoisomers at sulfur).

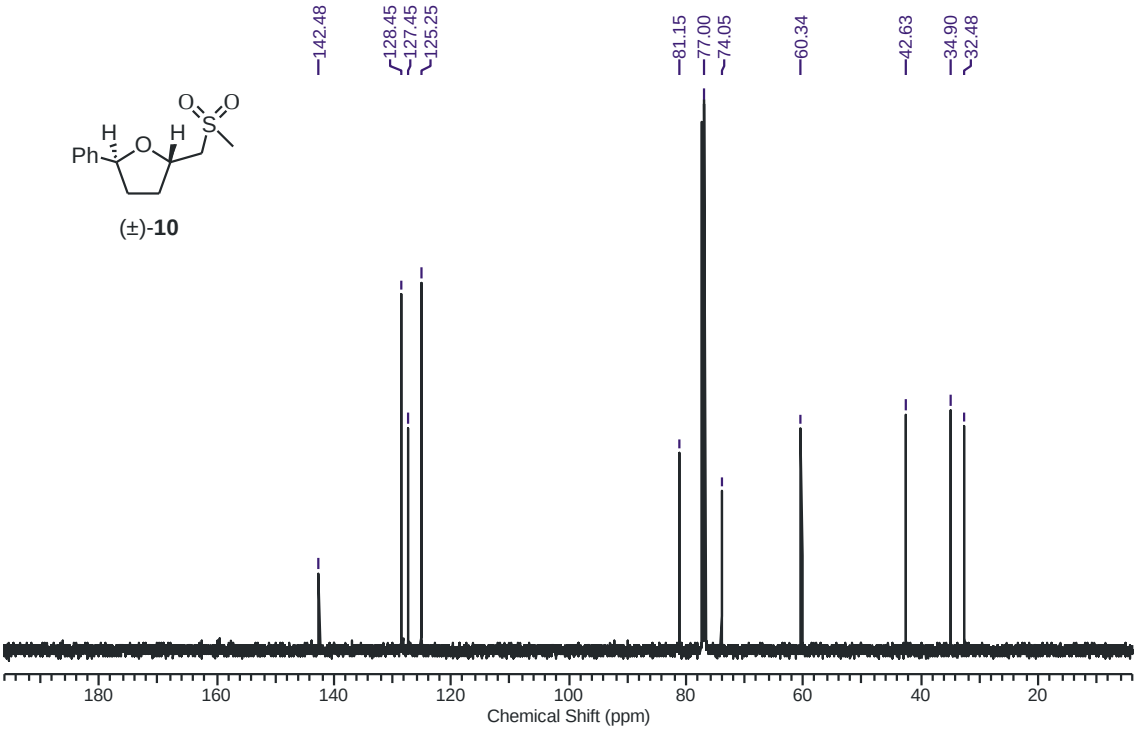

Figure S11: ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of (5-phenyltetrahydrofuryl)-2-methyl methyl sulfone (**10**).

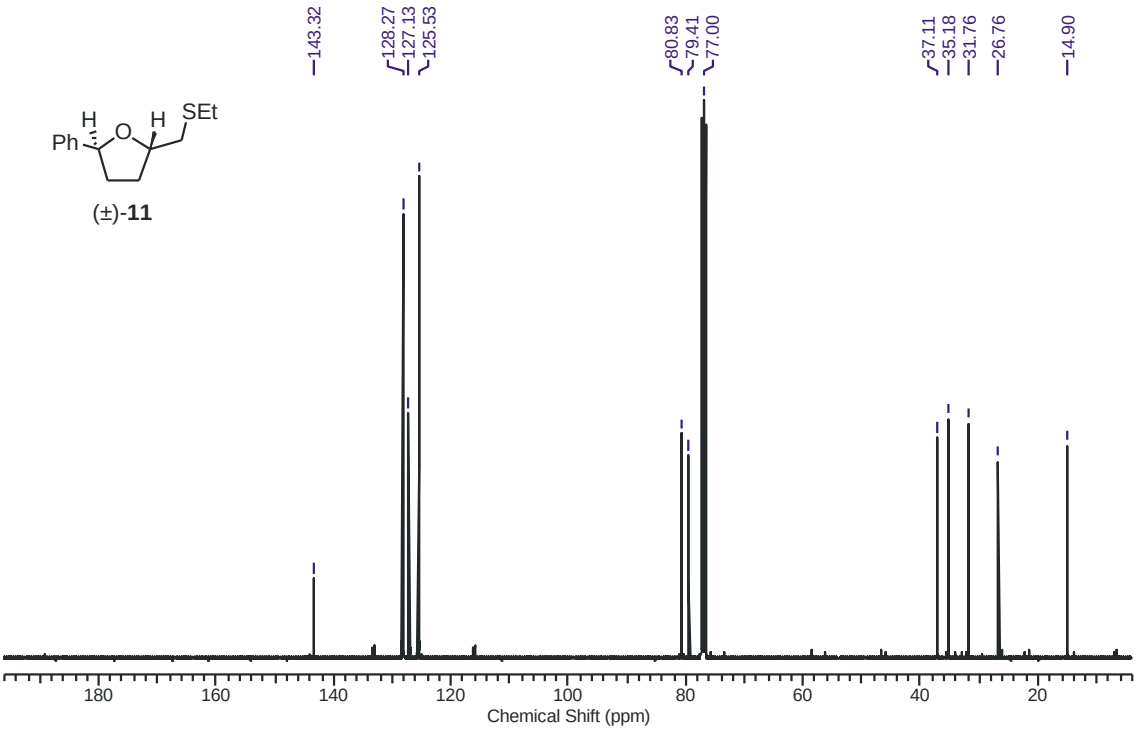

Figure S12. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of *trans*-2-(ethylsulfanyl)methyl-5-phenyltetrahydrofuran (**11**).

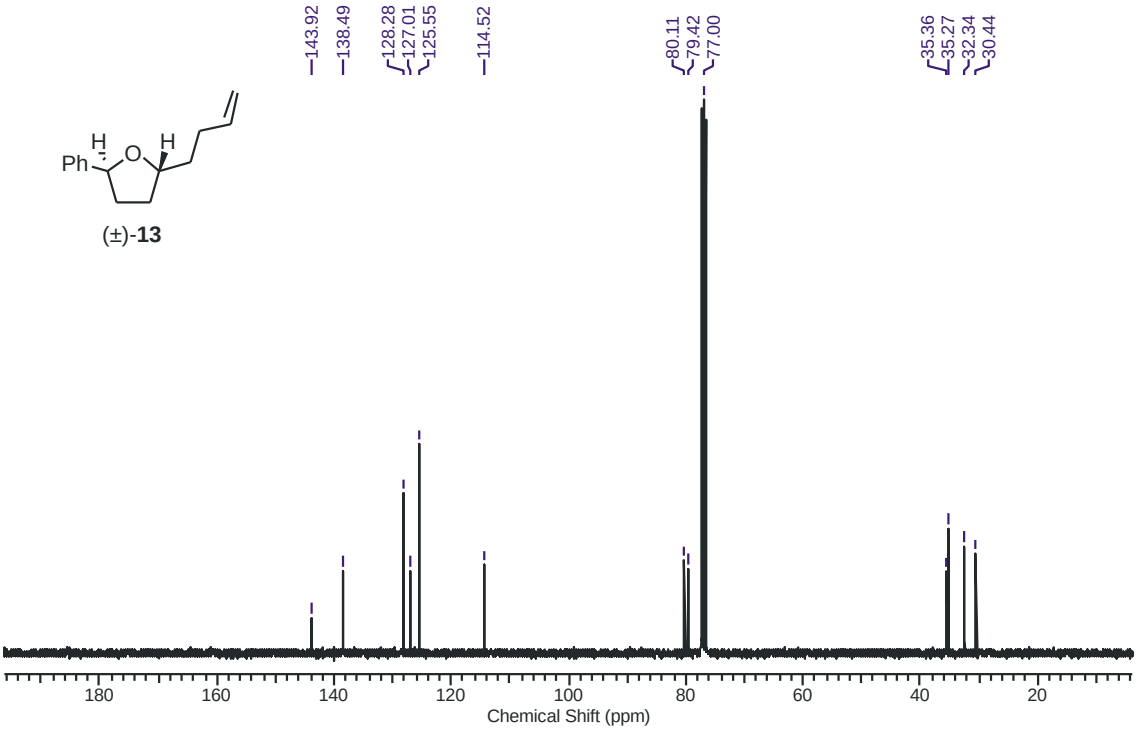

Figure S13. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of *trans*-2-(but-1-en-4-yl)-5-phenyltetrahydrofuran (**13**).

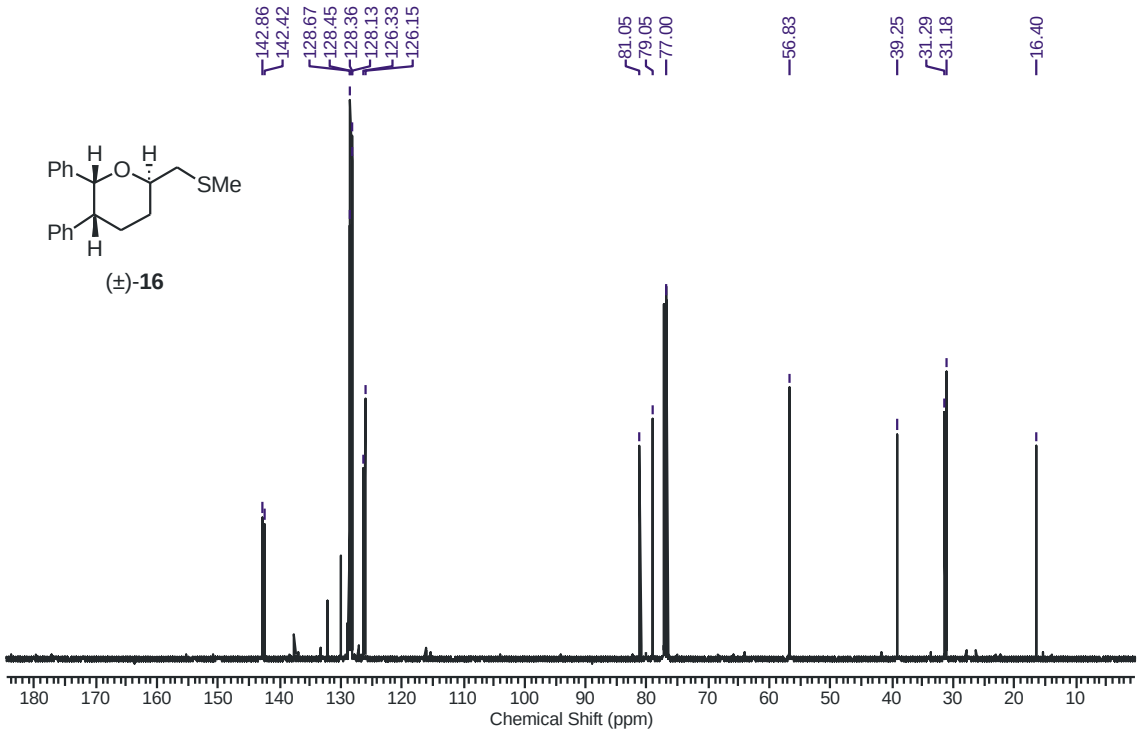

Figure S14. ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of *rel*-(2*R*,3*R*,6*R*)-6-(methylsulfanyl)-methyl-2,3-diphenyltetrahydropyran (**16**).

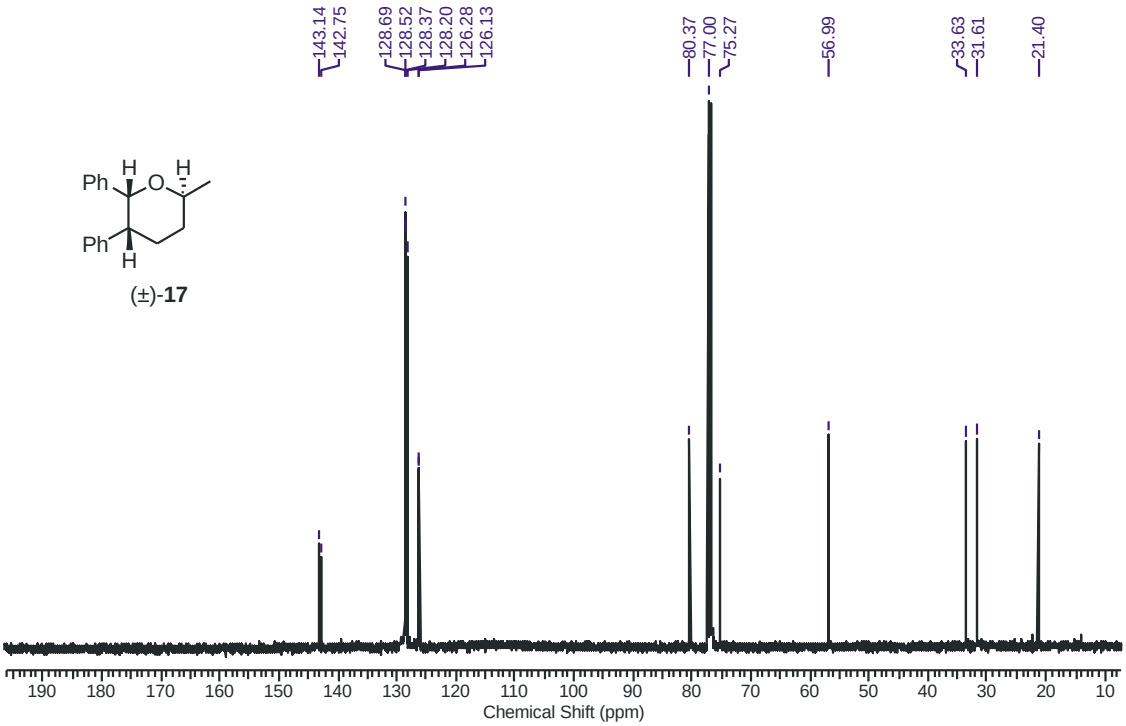

Figure S15. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of *rel*-(2*R*,3*R*,6*S*)-6-methyl-2,3-diphenyltetrahydropyran (**17**).

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