Electronic Supporting Information for

Annulated and Bridged Tetrahydrofurans from Alkenoxyl Radical Cyclization

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Contents

1 General Remarks

(*i*) Numbering of compounds in the *Electronic Supporting Information* and the accompanying publication are consistent. (*ii*) References refer exclusively to the *Electronic Supporting Information*.

2 Instrumentation

2.1 NMR-spectroscopy

Proton- and carbon-13-NMR spectra were measured with FT-NMR DPX 200, DPX 400 and DMX 600 instruments (*Bruker*). Chemical shifts refer to the δ-scale. Proton resonances of residual non-deuterated solvent molecules (δ_H 7.26 for $CDCl_3$; δ_H 7.16 for benzene; δ_H 2.50 for DMSO), and carbon-13 chemical shifts of $CDCl_3$ (δ_C 77.0), C_6D_6 (δ_C 128.06), and DMSO-d_6 (δ_C 39.52) served as internal standards.

2.2 Electron impact mass spectrometry

Mass spectra (EI, 70 eV) were recorded with a Mass Selective Detector HP 6890 (*Hewlett Packard*).

2.3 High resolution mass spectrometry

High resolution mass spectra were measured with a GCT Premier Micromass instrument (*Waters*).

2.4 Optical rotation

Optical rotations of chiral compounds at λ = 589 nm were recorded with a Krüss P3001/RS-polarimeter and a Perkin-Elmer polarimeter type 241 (λ_1 = 546 nm und λ_2 = 579 nm), and extrapolated using the Drude equation.[1]

2.5 UV/Vis-spectra

UV/Vis-spectra were recorded in 1-cm quartz cuvettes with a Cary 100 Conc UV/Vis spectrophotometer (Varian).

2.6 Combustion analysis

Combustion analyses were performed with a Carlo Erba 1106 instrument (analytical laboratory, Universität Würzburg) and a vario Micro cube (analytical laboratory, Technische Universität Kaiserslautern).

2.7 Melting points

Melting points [°C] were determined on a Koffler hot-plate melting point microscope (*Reichert*) and are not corrected.

3 Reagents and Chromatography

3.1 Reagents

Benzene, dimethyl formamide, dichloromethane, tetrahydrofuran and diethyl ether were purified and dried according to standard procedures.[2] All other reagents were used as received from commercial suppliers (Sigma Aldrich, Acros Organics, Fisher Scientific, Merck), unless otherwise indicated.

3-Hydroxy-4-methylthiazole-2(3*H*)-thione,[3] 3-hydroxy-4-methylthiazole-2(3*H*)-thione tetraethylammonium salt,[4] isopropyltriphenylphosphonium bromide,[5] diethyl azodicarboxylate (DEAD),[6] *trans*-hexahydrophthalic acid anhydride[7,8,9] were prepared according to published procedures.

3.2 Thin layer chromatography

Reaction progress was monitored via thin layer chromatography (tlc) on aluminum sheets coated with silica gel (60 F_{254}, *Merck*). Compounds on developed tlc-sheets were detected with the aid of the UV-VIS indicator commercially disposed on the sheets, showing colored or darker spots by illuminating devloped sheets with a hand lamp emitting 254 nm light. Alternatively, developed tlc-sheets were stained by Ekkert´s reagent and subsequently heated, leading to blue-green spots for organobromines, blue spots for alcohols and yellow spots for 3-alkenoxy-4-methylthiazole-2(3*H*)-thiones (e.g. **1**).

3.3 Column chromatography

Geduran Si60-silica gel (40–63 μm) served as stationary phase for column chromatography (flash chromatography).

3.4 Gas chromatography coupled to mass spectrometry

Mass spectra (EI, 70 eV) were recorded with a Mass Selective Detector HP 6890 (*Hewlett Packard*) connected to an Agilent-gaschromatograph.

4 Alkenols

4.1 ***trans*-2-(Prop-2-en-1-yl)-cyclopentan-1-ol** was prepared from cyclopentene oxide and 2-propen-1-yl magnesium bromide.[10,11,12] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.15–1.29 (m, 1 H), 1.49–1.64 (m, 2 H), 1.66–1.84 (m, 2 H), 1.85–1.97 (m, 2 H), 2.03 (dt, J_d = 13.9 Hz, J_t =7.1 Hz, 1 H), 2.18 (dt, J_d = 14.0 Hz, J_t = 6.9 Hz, 1 H), 3.86 (q, J = 5.5 Hz, 1 H), 4.95–5.13 (m, 2 H), 5.77–5.93 (m, 1 H). The spectrum showed no resonance for the hydroxyl proton. ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.6, 29.7, 34.3, 38.1, 47.6, 78.7, 115.6, 137.6.

4.2 ***cis*-2-(Prop-2-en-1-yl)-cyclopentan-1-ol**. A solution of *p*-nitrobenzoic acid (7.35 g, 44.0 mmol), *trans*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (2.06 g, 16.3 mmol), and triphenylphosphine (12.9 g, 49.0 mmol) in benzene (80 mL) was treated in a dropwise manner with diethyl azodicarboxylate (DEAD, 8.83 g, 49.0 mmol). The reaction mixture was stirred for four hours at 21 °C. The solvent was removed under reduced pressure to leave an oil, which was purified by column chromatography [diethyl ether/pentane = 1:20 (*v*/*v*)]. *cis-2-(Prop-2-en-1-yl)cyclopent-1-yl 4-nitrobenzoate* (3.58 g, 13.0 mmol, 80 %), yellowish liquid. R_f = 0.22 for diethyl ether/pentane = 1:20 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.53–1.61 (m, 1 H), 1.64–1.73 (m, 1 H), 1.83–1.90 (m, 2 H), 1.91–1.98 (m, 1 H), 2.02–2.12 (m, 2 H), 2.16 (dt, J_d = 14.2, J_t = 7.3 Hz, 1 H), 2.31 (dt, J_d = 13.9, J_t = 7.0 Hz, 1 H), 4.92–5.01 (m, 2 H), 5.45 (t, J = 4.8 Hz, 1 H), 5.80 (ddt, J_d = 17.0, 10.1, J_t = 7.0 Hz, 1 H), 8.17–8.20 (m, 2 H), 8.27–8.31 (m, 2 H). ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 22.0, 29.6, 32.5, 33.9, 44.3, 79.5, 115.6, 123.5, 130.5, 136.2, 137.1, 150.4, 164.2. Anal. Calcd. for $C_{15}H_{17}NO_4$ (275.31): C, 65.44; H, 6.22; N, 5.09; Found: C, 65.21; H, 6.30; N, 5.01. *cis*-2-(Prop-2-en-1-yl)cyclopent-1-yl 4-nitrobenzoate (3.44 g, 12.5 mmol) was dissolved in a solution of tetrahydrofuran/methanol [1:1 (*v*/*v*) (10 mL)] and cooled to 0 °C (ice bath). A solution of potassium hydroxide in methanol/water [1:1 (*v*/*v*) (1 M, 14 mL)] was added in one portion to the solution of the benzoate, while beeing cooled with an ice bath to 0 °C. The resulting mixture was stirred for ninety minutes at 22 °C. Dichloromethane (50 mL) was added and the resulting mixture was washed with a saturated aqueous solution sodium hydrogen carbonate (25 mL) and subsequently with brine (25 mL). The organic solvent was removed under reduced pressure (600 mbar/40 °C) to leave an oil, which was purified by chromatography [diethyl ether/pentane = 1:2 (*v*/*v*)]. Yield 1.19 g (9.43 mmol, 75%), colorless liquid. R_f = 0.32 for diethyl ether/pentane = 1:2 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.30–1.46 (m, 2 H), 1.51–1.69 (m, 2 H), 1.69–1.90 (m, 4 H), 2.10–2.20 (m, 1 H), 2.21–2.32 (m, 1 H), 4.12–4.21 (m, 1 H), 4.95–5.11 (m, 2 H), 5.87 (ddt, J_d = 17.1, 10.2, J_t = 6.9Hz, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.9, 28.7, 33.7, 34.6, 45.2, 74.5, 115.0, 138.2. Anal. Calcd. for $C_8H_{14}O_4$ (126.20): C, 76.14; H, 11.28; Found: C, 75.72; H, 11.23.

4.3 ***trans*-2-(3-Methylbut-2-en-1-yl)-cyclopentan-1-ol** was prepared from cyclopentanone, following the procedure of Streinz and Romaňuk.[13] Separation of *cis*- and *trans*-cyclopentanols was achieved by column chromatography, using diethyl ether/pentane = 1:3 (*v*/*v*) as eluent. *cis-2-(3-methylbut-2-en-1-yl)-cyclopentan-1-ol*. R_f = 0.31. *trans-2-(3-methylbut-2-en-1-yl)-cyclopentan-1-ol*. R_f = 0.19. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.20 (dq, J_d = 12.6, J_q = 7.9 Hz, 1 H), 1.48–1.64 (m, 5 H), 1.65–1.78 (m, 5 H), 1.82–1.99 (m, 3 H), 2.04–2.16 (m, 1 H), 3.83 (q, *J* = 5.8 Hz, 1 H), 5.18 (t, *J* = 7.2 Hz, 1 H). The spectrum showed no resonance for the hydroxyl proton. ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.8, 21.6, 25.8, 29.7, 31.9, 34.2, 48.6, 78.8, 123.0, 132.5.

4.4 ***trans*-2-(Prop-2-en-1-yl)-cyclohexan-1-ol** was prepared from cyclohexene oxide and 2-propen-1-yl magnesium bromide, according to the method described by Chandrasekaran and co-workers.[10,14,15] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.85–1.02 (m, 1 H), 1.09–1.40 (m, 4 H), 1.57–1.82 (m, 4 H), 1.88–2.04 (m, 2 H), 2.37–2.52 (m, 1 H), 3.26 (td, J_t = 9.8, J_d = 4.5 Hz, 1 H), 4.97–5.11 (m, 2 H), 5.85 (ddt, J_d = 17.2, 10.0, J_t = 7.3 Hz, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 24.9, 25.5, 30.4, 35.5, 37.5, 44.9, 74.6, 116.0, 137.5.

4.5 ***cis*-2-(Prop-2-en-1-yl)-cyclohexan-1-ol** was prepared from *trans*-2-(prop-2-en-1-yl)-cyclohexan-1-ol[15] (317 mg, 2.26 mmol) by inverting the configuration at the hydroxyl carbon, according to the procedure described in section 4.2. Reaction time: one hour. Eluent for column chromatography [diethyl ether/pentane = 1:10 (*v*/*v*), R_f = 0.47]. *cis-2-(Prop-2-en-1-yl)-cyclohexan-1-yl 4-nitrobenzoate*: 410 mg (1.42 mmol, 63 %), colorless crystals. M.p. 62–64 °C. ^{1}H-NMR (CDCl$_3$, 600 MHz) δ 1.32–1.41 (m, 1 H), 1.49–1.61 (m, 4 H), 1.66–1.76 (m, 2 H), 1.77–1.83 (m, 1 H), 1.99–2.09 (m, 2 H), 2.09–2.16 (m, 1 H), 4.94 (d, J = 17.1 Hz, 1 H), 4.98 (d, J = 10.1 Hz, 1 H), 5.28–5.33 (m, 1 H), 5.76 (ddt, J_d = 17.1, 10.1, J_t = 7.0, Hz, 1 H), 8.22 (d, J = 9.2 Hz, 2 H), 8.31 (d, J = 9.2 Hz, 2 H). ^{13}C-NMR (CDCl$_3$, 63 MHz) δ 21.0, 25.0, 27.4, 30.1, 36.9, 40.2, 74.0, 116.4, 123.6, 130.6, 136.2, 136.3, 150.4, 164.0. Anal. Calcd. for $C_{16}H_{19}NO_4$ (289.33): C, 66.42; H, 6.62; N, 4.84; Found: C, 66.55; H, 6.73; N, 4.86. *cis-2-(Prop-2-en-1-yl)-cyclohexan-1-ol* ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 1.15–1.27 (m, 1 H), 1.28–1.69 (m, 8 H), 1.70–1.79 (m, 1 H), 1.98 (dt, J = 14.1, 7.2 Hz, 1 H), 2.14 (dt, J = 14.0, 7.0 Hz, 1 H), 3.80–3.90 (m, 1 H), 4.92–5.06 (m, 2 H), 5.78 (ddt, J = 17.1, 10.0, 7.2, 7.2 Hz, 1 H). ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 20.4, 25.0, 26.3, 32.9, 36.5, 41.2, 69.0, 115.6, 137.4. Anal. Calcd. for $C_9H_{16}O_4$ (140.22): C, 77.09; H, 11.50; Found: C, 76.90; H, 11.59.

4.6 ***cis*-[2-(Ethenyl)-cyclohex-1-yl]-methanol**[16] was prepared from *cis*-8-oxabicyclo[4.3.0]nonan-7-ol, obtained by the method of Lambert and co-workers as single diastereomer, and subsequent Wittig-alkenylation. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 1.27–1.81 (m, 10 H), 2.48 (dq, J_d = 8.6, J_q = 4.1 Hz, 1 H), 3.36–3.58 (m, 2 H), 4.97–5.15 (m, 2 H), 6.05 (ddd, J=17.1, 10.2, 8.9 Hz, 1 H). ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 22.3, 25.0, 25.2, 30.9, 41.0, 42.5, 65.5, 115.1, 139.3.

4.7 ***trans*-[2-(Ethenyl)-cyclohex-1-yl]-methanol**. A solution of *trans*-1,2-cyclohexane-dicarboxylic acid anhydride (5.00 g, 32.4 mmol) in tetrahydrofuran (15 mL) was added in a dropwise manner to a suspension of sodium borohydride (2.49 g, 65.8 mmol) in tetrahydrofuran (75 mL) at 0 °C. The reaction mixture was stirred for three hours in an ice bath, which was allowed to thaw (temperature of the ice bath after 3 hours: 15 °C). This mixture was cooled to 0 °C and *slowly* treated with methanol (10 mL). The rate of methanol addition thereby is crucial to prevent extensive gas evolution. The likewise obtained mixture was concentrated under reduced pressure (300 mbar/ 40 °C) to leave a residue, which was taken up in a mixture of brine (100 mL) and ethyl acetate (65 mL), and cooled to 0 °C. An aqueous 2 M solution of hydrochloric acid (32 mL, 64 mmol) was added to this mixture at 0 °C. The phases were separated. The cold aqueous layer was extracted rapidly with ethyl acetate (3 × 50 mL). Combined organic layers were washed with brine (70 mL) and concentrated under reduced pressure (200 mbar/ 40 °C) to leave a colorless solid (4.31 g, 27.2 mmol, 84 %), which was recrystallized from ethyl acetate (20 mL). *trans-2-(Hydroxymethyl)-cyclohexanecarboxylic acid.*[17,18] Yield 3.33 g (21.0 mmol, 65 %), colorless crystals. M.p. 99–100 °C. ^{1}H-NMR (DMSO-d_6, 600 MHz) δ 0.94–1.04 (m, 1 H), 1.11–1.23 (m, 2 H), 1.28–1.37 (m, 1 H), 1.56 (tdt, J_t = 11.0, 3.8, J_d = 7.2 Hz, 1 H), 1.66 (d, J = 9.2 Hz, 2 H), 1.81 (d, J = 12.1 Hz, 2 H), 1.97 (td, J_t = 11.4, J_d = 3.7 Hz, 1 H), 3.16 (dd, J = 10.3, 7.0 Hz, 1 H), 3.34 (dd, J = 10.3, 4.0 Hz, 1 H), 4.34 (br. s., 1 H), 11.95 (br. s., 1 H). ^{13}C-NMR (DMSO-d_6, 150 MHz) δ 25.0, 25.1, 28.1, 29.5, 41.0, 45.3, 64.1, 176.8. Anal. Calcd. for $C_8H_{14}O_3$ (158.20): C, 60.74; H, 8.92; Found: C, 60.44; H, 9.22. *trans*-2-(Hydroxymethyl)-cyclohexanecarboxylic acid was treated with a catalytic amount of *p*-toluenesulfonic acid monohydrate to afford *trans*-8-oxabicyclo[4.3.0]nonan-7-one,[8,19] which was reduced with DIBAL-H to furnish *trans*-8-oxabicyclo[4.3.0]nonan-7-ol[16] as mixture of the hydroxyaldehyde and stereoisomeric lactols. *Lactol – major stereoisomer*. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 0.95–2.04 (m, 9 H), 3.31 (dd, J = 10.8, 7.8 Hz, 1 H), 3.43–3.45 (m, 1 H), 4.09 (t, J = 7.3 Hz, 1 H), 5.30 (t, J = 4.0 Hz, 1 H). The spectrum displayed no resonance for the hydroxyl proton. ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 24.8, 25.5, 25.6, 28.1, 40.4, 49.5, 72.5, 98.3. *Lactol – minor stereoisomer*. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 0.95–2.04 (m, 9 H), 3.58 (dd, J = 11.0, 7.6 Hz, 1 H), 3.90 (t, J = 7.0 Hz, 1 H), 4.04–4.07 (m, 1 H), 5.07 (dd, J = 7.1, 5.9 Hz, 1 H). The spectrum displayed no resonance for the hydroxyl proton.^{13}C-NMR (CDCl$_3$, 100 MHz) δ 25.5, 25.6, 26.5, 27.4, 44.4, 52.3, 71.4, 102.5. *Hydroxyaldehyde*. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 0.95–2.04 (m, 10 H), 3.42–3.49 (m, 1 H), 3.55–3.60 (m, 1 H), 9.58 (d, J = 7.1, 5.9 Hz, 1 H). The spectrum displayed no resonance for the hydroxyl proton.

^{13}C-NMR ($CDCl_3$, 100 MHz) δ 24.8, 24.9, 25.8, 27.7, 39.9, 53.6, 66.6, 205.4. Wittig-alkenylation of *trans*-8-oxabicyclo[4.3.0]nonan-7-ol[16] in extension to the method described for the cis-isomer[16] in section 4.6 furnished *trans-[2-(ethenyl)-cyclohex-1-yl]-methanol.* ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.98–1.37 (m, 5 H), 1.52–1.87 (m, 6 H), 3.43 (dd, J = 11.0, 5.8 Hz, 1 H), 3.60 (dd, J = 10.9, 4.7 Hz, 1 H), 4.95 (dd, J = 10.1, 2.0 Hz, 1 H), 5.03 (dd, J = 17.2, 2.0 Hz, 1 H), 5.70 (dt, J_d = 17.2, J_t = 9.6 Hz, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 25.7, 25.8, 29.1, 33.4, 44.3, 45.9, 67.1, 114.0, 143.8. Anal. Calcd. for $C_9H_{16}O$ (140.22): C, 77.09; H, 11.50; Found: C, 76.54; H, 11.56.

4.8 ***cis*-[2-(Methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol** was prepared in extension to the method described by Lambert[16] for *cis*-[2-(ethenyl)-cyclohex-1-yl]-methanol. In an atmosphere of nitrogen, isopropyltriphenylphosphonium bromide (2.90 g, 7.53 mmol) was suspended in dry tetrahydrofuran (30 mL) and cooled to 0 °C. *n*-Butyl lithium (4.7 mL, 7.52 mmol, 1.6 M in hexane) was added to this mixture in one portion at 0 °C. The resulting deep red-colored suspension was stirred for two and a half hours at 21 °C. Meanwhile *cis*-8-oxabicyclo[4.3.0]nonan-7-ol, was dissolved in dry tetrahydrofuran (20 mL) and treated at –78 °C with a solution of *n*-butyl lithium (3.0 mL, 4.8 mmol) in hexane (1.6 M). The reaction mixture was afterwards allowed to warm for three minutes to 0 °C, and was then cooled to –78 °C again. To this mixture was added in a dropwise manner the solution of 2-propylidene triphenylphosphine in tetrahydrofuran within twenty-five minutes. The cooling bath was removed after complete addition of the phosphorous reagent, and the reaction mixture is allowed to warm to 21 °C. The reaction mixture was stirred for additional 5 hours at room temperature and then treated with a saturated aqueous ammonium chloride solution (40 mL) and water (40 mL). Phases were separated. The aqueous layer was extracted with diethyl ether (2 × 20 mL). Combined organic layers were washed with brine (60 mL) and concentrated under reduced pressure (800 mbar/ 40 °C) to afford an oily residue, which was purified by chromatography [diethyl ether/pentane = 1:1 (*v*/*v*)]. Yield: 679 mg (4.03 mmol, 80 %) colorless oil. R_f = 0.39 for diethyl ether/pentane = 1:1 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.26–1.38 (m, 2 H), 1.40–1.57 (m, 6 H), 1.64 (d, J = 1.2 Hz, 3 H), 1.67–1.75 (m, 2 H), 1.71 (d, J = 0.9

Hz, 3 H), 2.65–2.73 (m, 1 H), 3.38–3.48 (m, 2 H), 5.35 (dt, J_d = 10.1, J_t = 1.2 Hz, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.8, 22.1, 24.7, 25.3, 26.2, 31.7, 34.4, 43.0, 66.1, 124.1, 132.2. Anal. Calcd. for $C_{11}H_{20}O$ (168.28): C, 78.51; H, 11.98; Found: C, 78.26; H, 11.88.

4.9 ***trans*-[2-(Methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol** was prepared according to the procedure outlined in section 4.7 for the cis-isomer. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.00–1.12 (m, 2 H), 1.19–1.32 (m, 3 H), 1.49–1.60 (m, 2 H), 1.63 (d, J = 1.6 Hz, 3 H), 1.67–1.83 (m, 3 H), 1.63 (d, J = 1.6 Hz, 3 H), 1.98 (qd, J_q = 10.5, J_d = 3.8 Hz, 1 H), 3.32–3.41 (m, 1 H), 3.56 (dd, J = 10.8, 5.0 Hz, 1 H), 4.96–5.02 (m, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 18.1, 25.8 (2C/ HMQC), 25.9, 29.3, 33.4, 40.1, 45.2, 67.8, 130.0, 131.2. Anal. Calcd. for $C_{11}H_{20}O$ (168.28): C, 78.51; H, 11.98; Found: C, 78.15; H, 12.07.

4.10 **2-(1-Methylenecyclohex-2-yl)-ethan-1-ol** was prepared from cyclohexanone according to the method reported by Segre[20] and Gream[21], and respective co-workers. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.24–1.35 (m, 1 H), 1.40–1.58 (m, 4 H), 1.60–1.78 (m, 3 H), 1.85–1.97 (m, 1 H), 1.98–2.09 (m, 1 H), 2.17–2.29 (m, 2 H), 3.66 (t, J = 6.6 Hz, 2 H), 4.60 (s, 1 H), 4.66 (s, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 23.9, 28.7, 33.9, 34.4, 35.0, 39.8, 61.4, 105.9, 152.6.

4.11 **(1-Methylcyclohex-1-en-4-yl)-methanol** was prepared from 2-methylbuta-1,3-diene (isoprene) and methyl acrylate in a Diels-Alder-reaction as described by Inukai and Kasai[22], and reduction of *O*-methyl-(1-methylcyclohex-1-en-4-yl)-carboxylate by $LiAlH_4$ according to Monti and co-workers.[23] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.15–1.35 (m, 1 H), 1.39 (s, 1 H), 1.61–1.90 (m, 3 H), 1.65 (s, 3 H), 1.91–2.20 (m, 3 H), 3.41–3.63 (m, 2 H), 5.38 (br. s., 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 23.6, 25.6, 28.2, 29.5, 36.2, 67.9, 119.8, 134.1.

4.12 2-{(1*S*,4*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethanol (verbenylethanol) was prepared by converting (*S*)-*cis*-verbenol into 2-{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethenyl ether[24,25] {$[\alpha]_D^{25}$ = 98.0 (*c* = 1.02/ethanol)}, followed by [1.3] sigmatropic rearrangement of the vinyl ether into 2-{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethanal[26,27] {$[\alpha]_D^{25}$ = –74.6 (*c* = 1.03/ethanol)}, and reduction of this aldehyde as follows. A suspension of 2-{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethanal (650 mg, 3.63 mmol), lithium aluminium hydride (207 mg, 5.50 mmol) and diethyl ether (20 mL) was stirred for one hour at 20 °C, and carefully hydrolyzed by an aqueous solution of 2 M hydrochloric acid (10 mL). After phase separation, the aqueous layer was extracted with diethyl ether (3 × 20 mL). The organic phases from the reaction mixture and combined organic washings were combined and concentrated under reduced pressure to leave a residue, which was purified by chromatography [diethyl ether/pentane = 1:1 (*v*/*v*), (R_f = 0.40)]. Yield: 480 mg (2.66 mmol, 73 %) colorless oil. $[\alpha]_D^{25}$ = –85.8 (*c* = 1.03/ethanol). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.85 (s, 3 H), 1.13 (d, *J* = 8.9 Hz, 1 H), 1.28 (s, 3 H), 1.33–1.45 (m, 1 H), 1.49–1.61 (m, 1 H), 1.63–1.69 (m, 4 H), 1.89–1.99 (m, 2 H), 2.18 (dt, J_d = 8.7, J_t = 5.7 Hz, 1 H), 2.31–2.42 (m, 1 H), 3.71 (t, *J* = 6.8 Hz, 2 H), 5.14 (br. s., 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 20.4, 22.9, 26.5, 27.9, 36.3, 36.6, 40.6, 45.1, 47.6, 61.3, 112.0, 144.8. Anal. Calcd. for $C_{12}H_{20}O$ (180.29): C, 79.94; H, 11.18; Found: C, 79.95; H, 11.08.

5 4-Toluenesulfonic Acid *O*-Esters from Alkenols

5.1 **General method.** A solution of an alkenol (1 mmol), 1.4-diazabicyclo[2.2.2]octane (DABCO, 2 mmol) in dichloromethane (2 mL) was cooled in an ice-bath to 0 °C and treated with 4-toluenesulfonyl chloride (1.5 mmol) in portions over a period of 5 min. The slurry was stirred for 2 hours at 20 °C and diluted with dichloromethane (8 mL) to afford a suspension which was washed with aqueous 2 M aqueous hydrochloric acid (10 mL) and a saturated aqueous solution of $NaHCO_3$ (10 mL). The organic layer was separated, dried ($MgSO_4$), and concentrated under reduced pressure. The remaining oil was purified by chromatography (SiO_2).

5.2 ***trans*-[2-(Prop-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate**[28] was prepared from *trans*-2-(prop-2-en-1-yl)cyclopentan-1-ol (545 mg, 4.32 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*). Yield: 1.16 g (4.14 mmol, 96 %), colorless liquid. R_f = 0.53 for diethyl ether/pentane = 1:3 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.13–1.23 (m, 1 H), 1.52–1.64 (m, 1 H), 1.64–1.73 (m, 1 H), 1.74–1.81 (m, 2 H), 1.81–1.92 (m, 2 H), 1.99–2.14 (m, 2 H), 2.44 (s, 3 H), 4.48–4.57 (m, 1 H), 4.84–4.94 (m, 2 H), 5.48–5.67 (m, 1 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.78 (d, *J* = 8.3 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 21.6, 22.2, 28.9, 31.9, 36.8, 45.1, 88.4, 116.3, 127.8, 129.7, 134.3, 135.9, 144.4. Anal. Calcd. for $C_{15}H_{20}O_3S$ (280.38): C, 64.26; H, 7.19; S, 11.43; Found: C, 64.42; H, 7.02; S, 11.36.

5.3 ***cis*-[2-(Prop-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate** was prepared from *cis*-2-(prop-2-en-1-yl)cyclopentan-1-ol (1.05 g, 8.32 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*). Yield: 1.87 g (6.69 mmol, 80 %), colorless liquid. R_f = 0.49 for diethyl ether/pentane = 1:3 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.34–1.47 (m, 1 H), 1.51–1.61 (m, 1 H), 1.69–1.91 (m, 5 H), 1.98–2.09 (m, 1 H), 2.11–2.20 (m, 1 H), 2.44 (s, 3 H), 4.86–4.97 (m, 3 H), 5.59–5.72 (m, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.78 (d, *J* = 8.4 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.4, 21.6, 28.6, 32.5, 33.3, 45.0, 86.8, 115.6, 127.7, 129.7, 134.5, 136.8, 144.4. Anal.

Calcd. for $C_{15}H_{20}O_3S$ (280.38): C, 64.26; H, 7.19; S, 11.43; Found: C, 64.37; H, 7.03; S, 11.49.

5.4 ***trans*-[2-(3-Methylbut-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate** was prepared from 2-(3-methylbut-2-en-1-yl)-cyclopentan-1-ol (2.00 g, 13.0 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:5 (*v*/*v*). Yield: 2.76 g (8.95 mmol, 69 %), colorless liquid. R_f = 0.36 for diethyl ether/pentane = 1:5 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.13–1.20 (m, 1 H), 1.50 (s, 3 H), 1.55–1.64 (m, 1 H), 1.63 (s, 3 H), 1.65–1.72 (m, 1 H), 1.72–1.77 (m, 1 H), 1.77–1.81 (m, 2 H), 1.82–1.89 (m, 1 H), 1.93 (dt, J_d = 14.3, J_t = 7.1 Hz, 1 H), 1.98–2.05 (m, 1 H), 2.44 (s, 3 H), 4.49–4.53 (m, 1 H), 4.89 (s, 1 H), 7.33 (d, *J* = 8.5 Hz, 2 H), 7.78 (d, *J* = 8.5 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.7, 21.6, 22.2, 25.7, 29.0, 30.9, 32.0, 46.0, 88.8, 121.7, 127.8, 129.7, 133.0, 134.4, 144.3. Anal. Calcd. for $C_{17}H_{24}O_3S$ (308.43): C, 66.20; H, 7.48; S, 10.39; Found: C, 66.35; H, 7.96; S, 10.03.

5.5 ***trans*-[2-(Prop-2-en-1-yl)-cyclohex-1-yl 4-toluenesulfonate**[28] was prepared from *trans*-2-(prop-2-en-1-yl)-cyclohexan-1-ol (3.82 g, 27.2 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*). Yield: 6.72 g (22.8 mmol, 84 %), colorless liquid. R_f = 0.52 for diethyl ether/pentane = 1:3 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.91–1.00 (m, 1 H), 1.14 (qt, J_q = 12.4, J_t = 3.5 Hz, 1 H), 1.24 (qt, J_q = 12.6, J_t = 3.4 Hz, 1 H), 1.40–1.48 (m, 1 H), 1.51–1.61 (m, 2 H), 1.66–1.75 (m, 2 H), 1.81–1.87 (m, 1 H), 1.95–2.01 (m, 1 H), 2.26–2.32 (m, 1 H), 2.44 (s, 3 H), 4.26 (td, J_t = 10.0, J_d = 4.4 Hz, 1 H), 4.90–4.99 (m, 2 H), 5.61 (dddd, *J* = 17.0, 10.3, 7.9, 6.5 Hz, 1 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 7.80 (d, *J* = 8.2 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.6, 24.3, 24.4, 29.7, 32.5, 36.1, 41.8, 85.6, 116.7, 127.6, 129.7, 134.7, 135.7, 144.4. Anal. Calcd. for $C_{16}H_{22}O_3S$ (294.41): C, 65.27; H, 7.53; S, 10.89; Found: C, 65.23; H, 7.52; S, 10.95.

5.6 ***cis*-[2-(Prop-2-en-1-yl)-cyclohexyl-1-yl 4-toluenesulfonate** was prepared from *cis*-2-(prop-2-en-1-yl)-cyclohexan-1-ol (990 mg, 7.06 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*). Yield: 1.81 g (6.15 mmol, 87 %), colorless liquid. R_f = 0.46 for diethyl ether/pentane = 1:3 (*v*/*v*). Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*), R_f = 0.46. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.16–1.27 (m, 1 H), 1.30–1.44 (m, 3 H), 1.46–1.55 (m, 3 H), 1.61–1.68 (m, 1 H), 1.84–2.02 (m, 3 H), 2.44 (s, 3 H), 4.77 (br. s., 1 H), 4.89–4.96 (m, 2 H), 5.62 (ddt, J_d = 17.2, 10.1, J_t = 7.1 Hz, 1 H), 7.32 (d, J = 8.2 Hz, 2 H), 7.80 (d, J = 8.2 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 20.3, 21.6, 24.4, 26.3, 30.6, 30.0, 40.9, 82.5, 116.4, 127.6, 129.6, 134.8, 136.2, 144.3. Anal. Calcd. for $C_{16}H_{22}O_3S$ (294.41): C, 65.27; H, 7.53; S, 10.89; Found: C, 65.48; H, 7.38; S, 10.95.

5.7 ***trans*-[2-(Ethenyl)-cyclohex-1-yl]-methyl 4-toluenesulfonate**[29] was prepared from *trans*-[2-(ethenyl)-cyclohex-1-yl]-methanol (365 mg, 2.60 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*). Yield: 682 mg (2.32 mmol, 89 %), colorless liquid. R_f = 0.52 for diethyl ether/pentane = 1:3 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.04–1.25 (m, 4 H), 1.42 (tdt, J_t = 11.1, 3.4, J_d = 7.1, 1 H), 1.64–1.75 (m, 3 H), 1.77–1.85 (m, 2 H), 2.46 (s, 3 H), 3.82 (dd, J = 9.4, 6.7 Hz, 1 H), 4.05 (dd, J = 9.4, 3.2 Hz, 1 H), 4.86–4.93 (m, 2 H), 5.49 (ddd, J = 17.0, 10.3, 9.1 Hz, 1 H), 7.35 (d, J = 8.2 Hz, 2 H), 7.78 (d, J = 8.2 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.6, 25.4 (2C/ HMQC), 28.8, 33.2, 41.0, 44.1, 73.6, 115.1, 127.9, 129.7, 133.1, 141.5, 144.5. Anal. Calcd. for $C_{16}H_{22}O_3S$ (294.41): C, 65.27; H, 7.53; S, 10.89; Found: C, 65.38; H, 7.47; S, 10.82.

5.8 ***cis*-[2-(Ethenyl)-cyclohex-1-yl]-methyl 4-toluenesulfonate** was prepared from *cis*-[2-(ethenyl)-cyclohexan-1-yl]-methanol (365 mg, 2.60 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*). Yield: 682 mg (2.32 mmol, 89 %), colorless liquid. R_f = 0.52 for diethyl ether/pentane = 1:3 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.15–1.34 (m, 2 H), 1.36–1.55 (m, 5 H), 1.57–1.66

(m, 1 H), 1.90 (dtt, J_d = 10.5, J_t = 7.2, 3.8 Hz, 1 H), 2.37–2.46 (m, 4 H), 3.75–3.88 (m, 2 H), 4.89–4.99 (m, 2 H), 5.75–5.90 (m, 1 H), 7.32 (d, J = 7.8 Hz, 2 H), 7.76 (d, J = 8.3 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.6, 21.8, 24.4, 24.6, 30.4, 39.0, 40.2, 72.5, 116.3, 127.8, 129.7, 133.1, 137.1, 144.5. Anal. Calcd. for $C_{16}H_{22}O_3S$ (294.41): C, 65.27; H, 7.53; S, 10.89; Found: C, 65.24; H, 7.52; S, 10.92.

5.9 ***trans*-[2-(Methylprop-1-en-1-yl)-cyclohex-1-yl]-methyl 4-toluenesulfonate** was prepared from *trans*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol (1.54 g, 9.15 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:5 (*v*/*v*). Yield: 2.73 g (8.46 mmol, 92 %), colorless liquid. R_f = 0.41 for Eluent used for chromatographic purification: diethyl ether/pentane = 1:5 (*v*/*v*), R_f = 0.41 diethyl ether/pentane = 1:5 (*v*/*v*) . ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.97–1.12 (m, 2 H), 1.13–1.23 (m, 2 H), 1.26–1.37 (m, 1 H), 1.51 (d, J = 1.5 Hz, 3 H), 1.54–1.62 (m, 1 H), 1.60 (d, J = 1.5 Hz, 3 H), 1.63–1.73 (m, 2 H), 1.74–1.80 (m, 1 H), 1.90–2.00 (m, 1 H), 2.44 (s, 3 H), 3.75 (dd, J = 9.3, 6.8 Hz, 1 H), 3.97 (dd, J = 9.2, 3.1 Hz, 1 H), 4.71–4.76 (m, 1 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.75 (d, J = 8.3 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 18.0, 21.6, 25.5, 25.6, 25.7, 29.0, 33.2, 38.2, 42.1, 73.9, 127.9, 128.2, 129.6, 132.0, 133.1, 144.4. Anal. Calcd. for $C_{18}H_{26}O_3S$ (322.46): C, 67.05; H, 8.13; S, 9.94; Found: C, 66.79; H, 8.10; S, 9.96.

5.10 ***cis*-[2-(Methylprop-1-en-1-yl)-cyclohex-1-yl]-methyl 4-toluenesulfonate** was prepared from *cis*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol (631 mg, 3.75 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:1 (*v*/*v*). Yield: 1.10 g (3.40 mmol, 91 %), colorless liquid. R_f = 0.59 for diethyl ether/pentane = 1:1 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.17–1.31 (m, 2 H), 1.35–1.48 (m, 5 H), 1.55 (s, 3 H), 1.59–1.69 (m, 1 H), 1.63 (s, 3 H), 1.87 (ddt, J_d = 10.8, 7.2, J_t = 3.5 Hz, 1 H), 2.44 (s, 3 H), 2.56–2.69 (m, 1 H), 3.79 (d, J = 7.3 Hz, 2 H), 5.16 (d, J = 10.0 Hz, 1 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.75 (d, J = 8.1 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 17.9, 21.59, 21.62, 24.1, 24.8, 26.1, 31.4, 33.8, 39.7, 73.2, 122.4, 127.8, 129.7, 133.22, 133.23, 144.4. Anal. Calcd. for $C_{18}H_{26}O_3S$ (322.46): C, 67.05; H, 8.13; S, 9.94; Found: C, 67.10; H, 8.00; S, 9.87.

5.11 2-(1-Methylenecyclohex-2-yl)-eth-1-yl 4-toluenesulfonate[30] was prepared from 2-(1-methylenecyclohex-2-yl)-ethan-1-ol (1.89 g, 13.5 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:3 (*v*/*v*). Yield: 3.80 g (12.9 mmol, 95 %), colorless liquid. R_f = 0.48 for diethyl ether/pentane = 1:3 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.16–1.24 (m, 1 H), 1.37–1.50 (m, 2 H), 1.52–1.67 (m, 4 H), 1.92–2.00 (m, 2 H), 2.10–2.17 (m, 2 H), 2.45 (s, 3 H), 4.00–4.10 (m, 2 H), 4.42 (s, 1 H), 4.61 (s, 1 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 150.9 MHz) δ 21.6, 23.8, 28.5, 31.1, 33.4, 34.3, 38.9, 69.0, 106.4, 127.9, 129.8, 133.1, 144.7, 150.9. Anal. Calcd. for $C_{16}H_{22}O_3S$ (294.41): C, 65.27; H, 7.53; S, 10.89; Found: C, 65.52; H, 7.43; S, 10.76.

5.12 (1-Methylcyclohex-1-en-4-yl)-methyl 4-toluenesulfonate was prepared from 1-(methylcyclohex-1-en-4-yl)-methanol (257 mg, 2.03 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:7 (*v*/*v*). Yield: 493 mg (1.76 mmol, 86 %), colorless liquid. R_f = 0.25 for diethyl ether/pentane = 1:7 (*v*/*v*). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.21–1.33 (m, 1 H), 1.54–1.77 (m, 2 H), 1.60 (s, 3 H), 1.81–2.09 (m, 4 H), 2.45 (s, 3 H), 3.89 (d, *J* = 6.7 Hz, 2 H), 5.22–5.33 (m, 1 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 21.6, 23.4, 25.0, 27.7, 28.8, 32.9, 74.4, 118.9, 127.8, 129.8, 133.0, 134.0, 144.6. Anal. Calcd. for $C_{15}H_{20}O_3S$ (280.38): C, 64.26; H, 7.19; S, 11.43; Found: C, 64.33; H, 6.85; S, 11.13.

5.13 2-{(1*S*,4*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethyl 4-toluenesulfonate was prepared from 2-[{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl]}-ethan-1-ol (440 mg, 2.44 mmol) according to procedure 5.1. Eluent used for chromatographic purification: diethyl ether/pentane = 1:1 (*v*/*v*). Yield: 690 mg (2.06 mmol, 85 %), yellowish liquid. R_f = 0.71 for diethyl ether/pentane = 1:1 (*v*/*v*). $[\alpha]_D^{25}$ = –38.9 (*c* = 1.01/ethanol). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.78 (s, 3 H), 0.99–1.06 (m, 1 H), 1.23 (s, 3 H), 1.53–1.64 (m, 1 H), 1.61 (s, 3 H), 1.64–1.79 (m, 2 H), 1.92 (t, J = 5.1 Hz, 1 H), 2.12 (dt, J_d = 8.9, J_t = 5.6 Hz, 1 H), 2.23–2.31 (m, 1 H), 2.45 (s, 3 H), 4.03–4.14 (m, 2 H), 4.94 (br. s., 1 H), 7.35 (d, J = 8.2 Hz, 2 H), 7.80 (d, J = 8.2 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 150.9 MHz) δ 20.4, 21.6, 22.9, 26.4, 27.7, 32.4, 35.9, 40.7, 44.6, 47.5, 69.1, 118.8, 127.9, 129.8, 133.2, 144.6, 145.6.

6 Bromocyclization with *N*-Bromosuccinimide

6.1 Bromocyclization of *trans*-2-(prop-2-en-1-yl)-cyclopentan-1-ol. A solution of *trans*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (126 mg, 1.00 mmol) in dichloromethane (5 ml) was treated at room temperature in small portions with *N*-bromosuccinimide (267 mg, 1.50 mmol). The resulting suspension was stirred for 14 days at room temperature (~20 °C). Solids were filtrated off and the filtrate washed with an aqueous saturated solution of sodium thiosulfate (10 mL). The aqueous washing was extracted with petroleum ether (4 × 20 mL). Combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to furnish a residue, which was purified by column chromatography on SiO_2 as stationary phase and a 9/1-mixture (*v*/*v*) of petroleum ether/diethyl ether as eluent. *1,4-trans-4,6-cis-4-Brom-2-oxabicyclo[4.3.0]nonane*. Yield 40 mg (20 %), yellow oil, R_f = 0.59 [petroleum ether /diethyl ether = 9/1 (*v*/*v*)]. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.07–1.31 (m, 1 H), 1.36–1.81 (m, 6 H), 1.83–2.00 (m, 1 H), 2.49– 2.68 (m, 1 H), 3.14–3.29 (m, 1 H), 3.55 (t, ^3J = 10.5 Hz, 1 H,), 3.99–4.20 (m, 2 H). ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 19.6, 26.3, 28.0, 41.0, 45.5, 46.1, 73.6, 83.9. MS (70 eV, EI) *m*/*z* (%) 205.1 (1) [M^+], 124.1 (3), 111.1 (56), 67.0 (100). Anal. Calcd. for $C_8H_{13}BrO$ (205.09): C, 46.85; H, 6.39; Found: C, 46.78; H, 6.25. *1,3-cis-1,5-trans-3-Bromomethyl-2-oxabicyclo[3.3.0]-octane*. *trans*-**3b**. Yield 17.9 mg (9 %), yellow oil, R_f = 0.49 [petroleum ether/diethyl ether = 9/1 (*v*/*v*)]. ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.12–1.27 (m, 1 H), 1.42–1.54 (m, 1 H), 1.61–1.86 (m, 4 H), 1.90–2.24 (m, 3 H), 3.38–3.53 (m, 2 H), 3.68 (dt, ^3J_d = 10.8 Hz, ^3J_t = 6.3 Hz, 1 H), 4.65–4.81 (m, 1 H). ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 21.2, 25.0, 27.3, 31.8, 36.0, 49.8, 86.7, 90.9. MS (70 eV, EI) *m*/*z* (%)205.1 (1) [M^+], 124.1 (3), 111.1 (62), 67.0 (100), 41.1 (19). Anal. Calcd. for $C_8H_{13}BrO$ (205.09): C, 46.85; H, 6.39; Found: C, 46.71; H, 6.29. *1,3-trans-1,5-trans-3-Brommethyl-2-oxabicyclo[3.3.0]-octane* *trans*-**3b**. Yield 42.1 mg (21 %), yellow oil, R_f = 0.43 [petroleum ether/diethyl ether = 9/1 (*v*/*v*)]. ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.11–1.31 (m, 1 H), 1.33–1.55 (m, 2 H), 1.60–1.75 (m, 1 H), 1.74–1.84 (m, 1 H), 1.97–2.25 (m, 4 H), 3.41–3.61 (m, 2 H), 3.81 (dt, ^3J_d = 17.2 Hz, ^3J_t = 6.4 Hz, 1 H,), 4.72-4.83 (m, 1 H). ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 21.1, 25.3, 27.1, 33.7, 36.4, 51.8, 87.5, 89.9.

7 NMR-Spectra of Alkenols, Tosylates and Bromocyclization Products

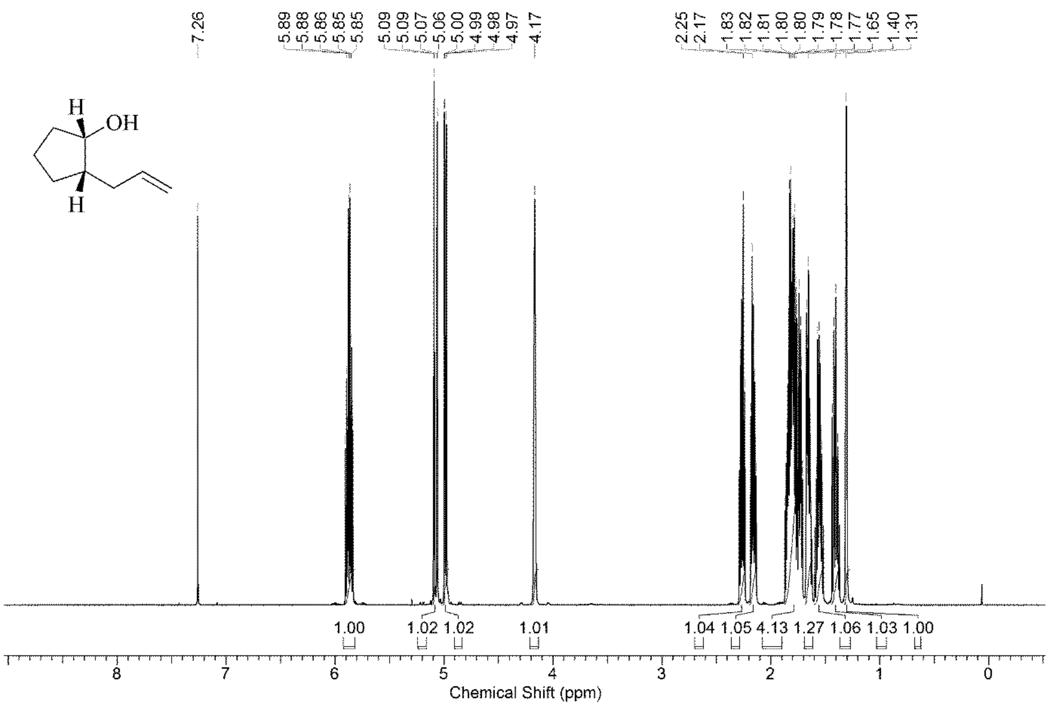


Figure S1. Proton-1 NMR-spectrum of *trans*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (600MHz, $CDCl_3$, 23 °C).

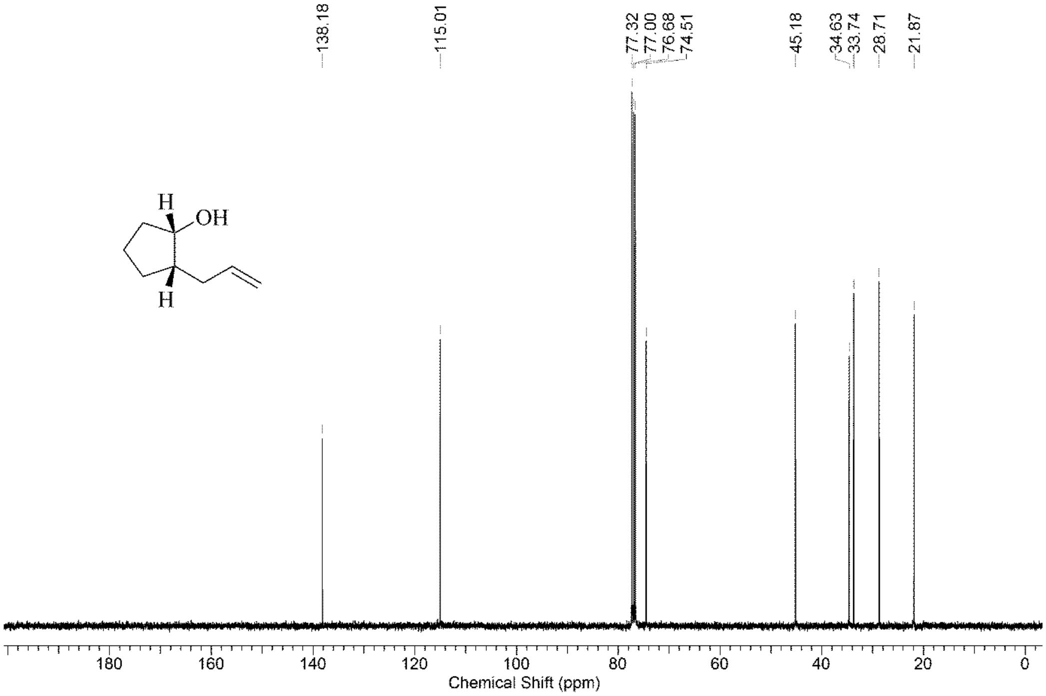


Figure S2. Carbon-13 NMR-spectrum of *trans*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (100MHz, $CDCl_3$, 23 °C).

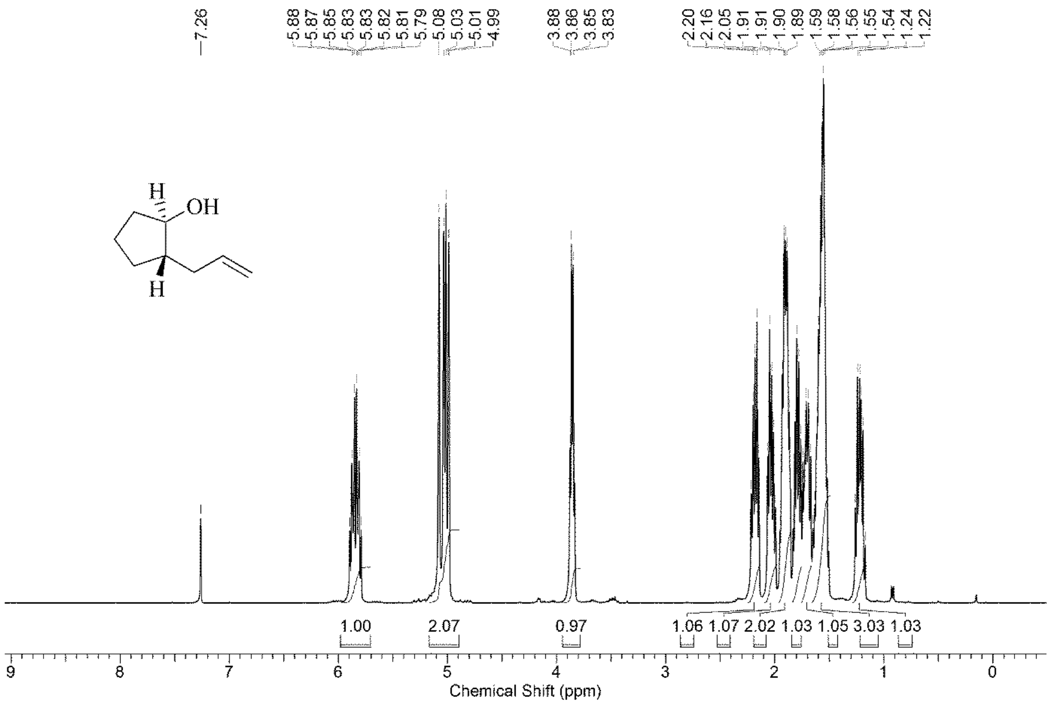


Figure S3. Proton-1 NMR-spectrum of *cis*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (400MHz, $CDCl_3$, 23 °C).

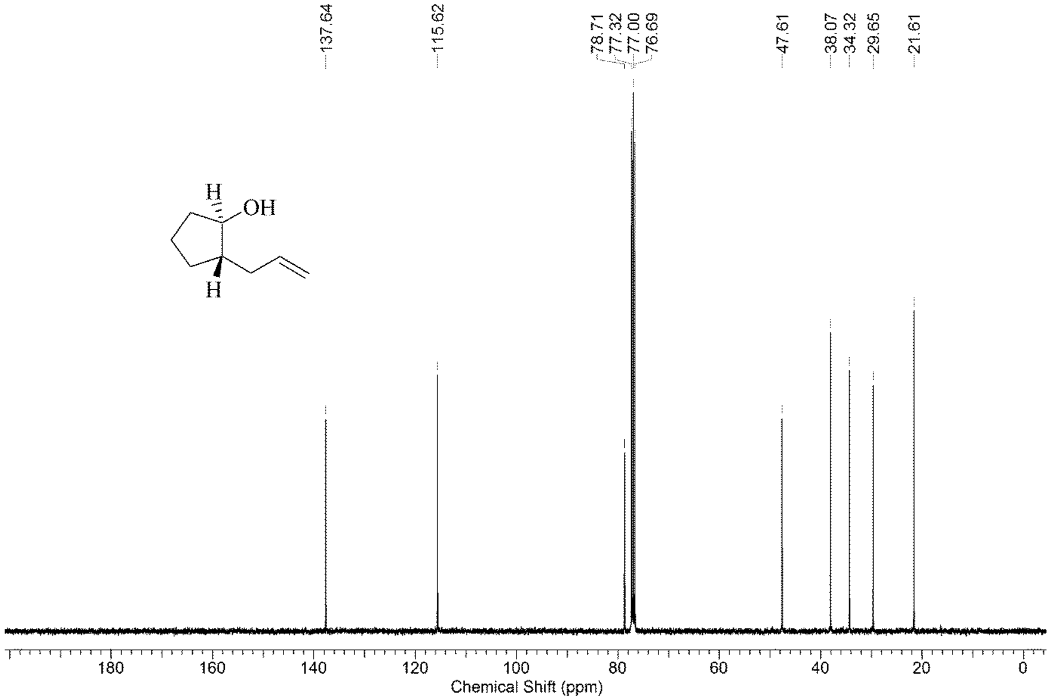


Figure S4. Carbon-13 NMR-spectrum of *cis*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (100MHz, $CDCl_3$, 23 °C).

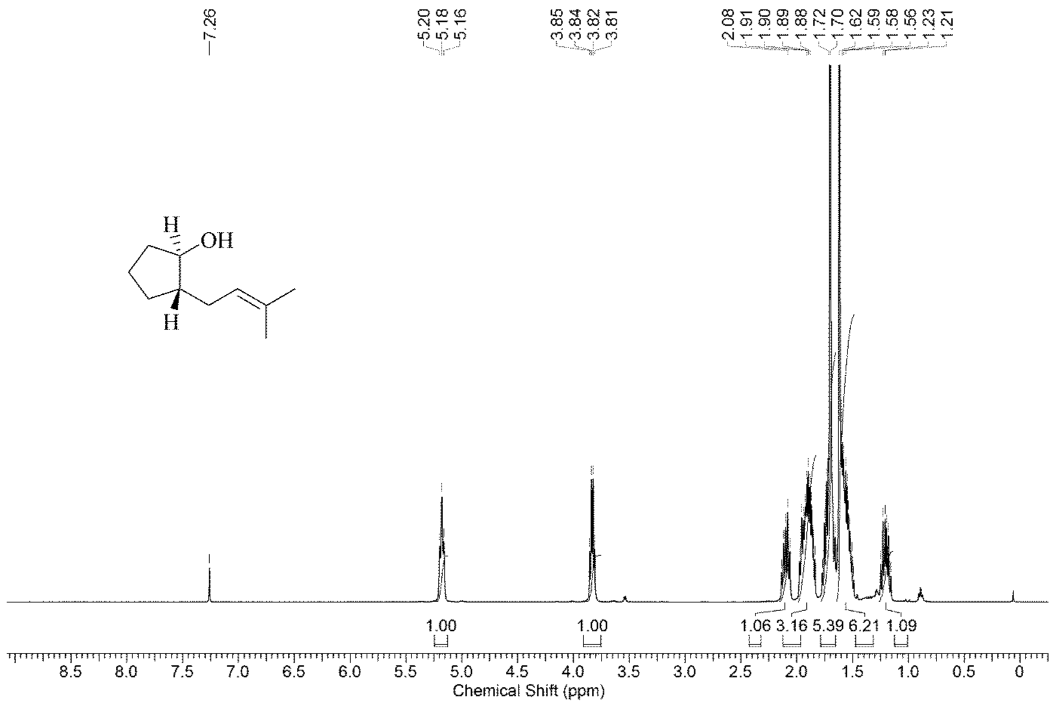


Figure S5. Proton-1 NMR-spectrum of *trans*-2-(3-methylbut-2-en-1-yl)-cyclopentan-1-ol (400MHz, $CDCl_3$, 23 °C).

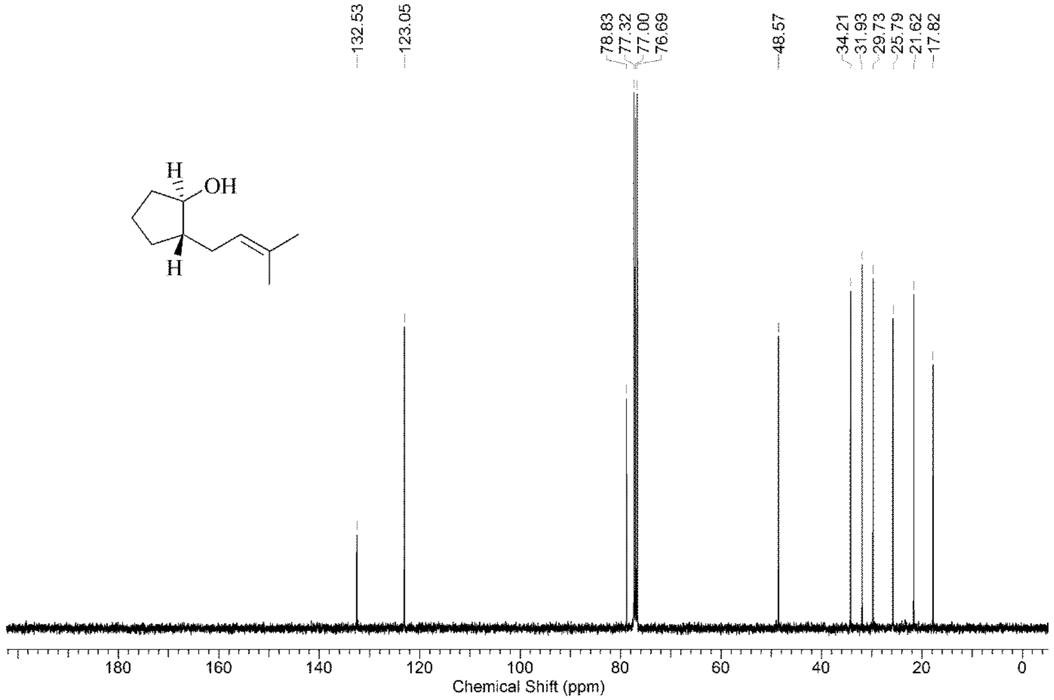


Figure S6. Carbon-13 NMR-spectrum of *trans*-2-(3-methylbut-2-en-1-yl)-cyclopentan-1-ol (100MHz, $CDCl_3$, 23 °C).

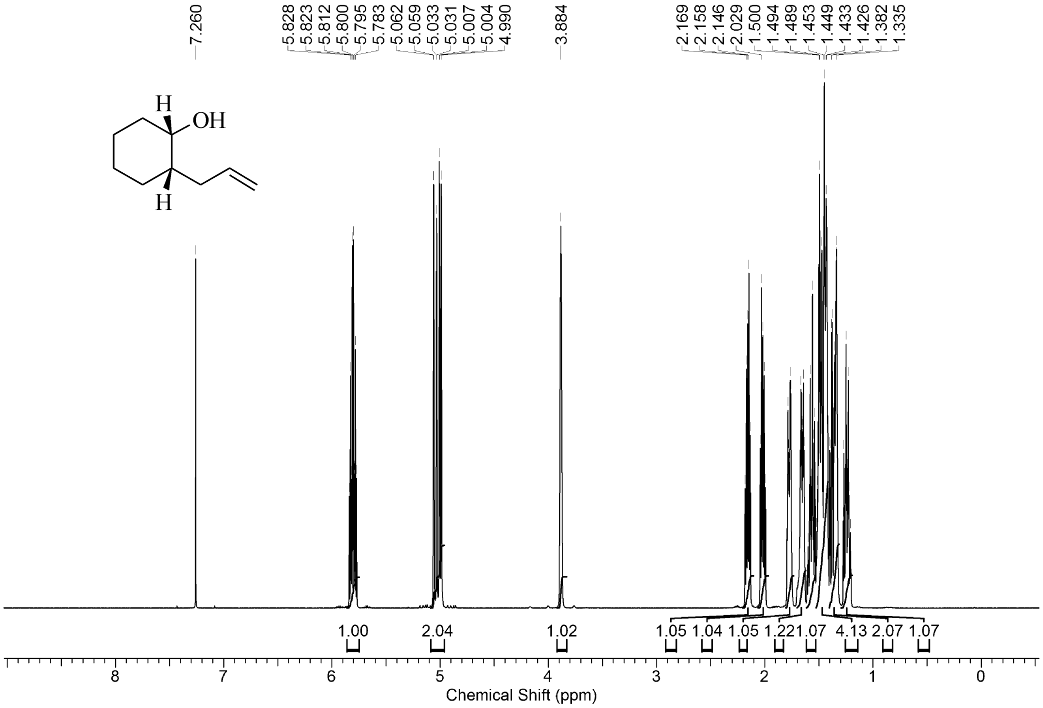


Figure S7. Proton-1 NMR-spectrum of *cis*-2-(prop-2-en-1-yl)-cyclohexan-1-ol (600MHz, $CDCl_3$, 23 °C).

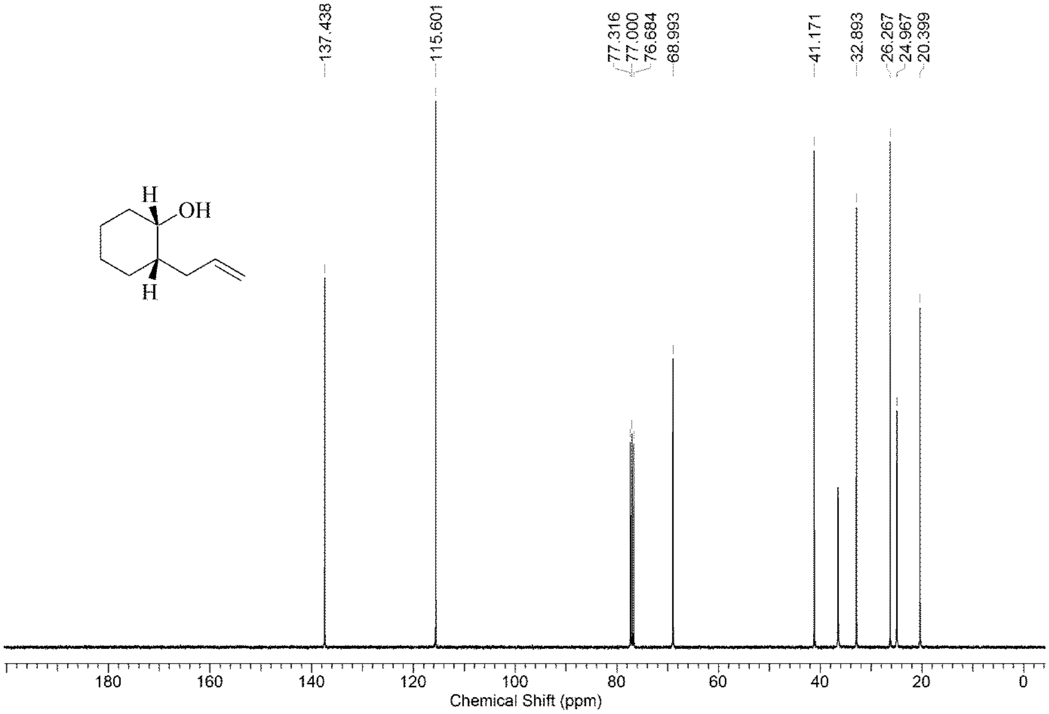


Figure S8. Carbon-13 NMR-spectrum of *cis*-2-(prop-2-en-1-yl)-cyclohexan-1-ol (100MHz, $CDCl_3$, 23 °C).

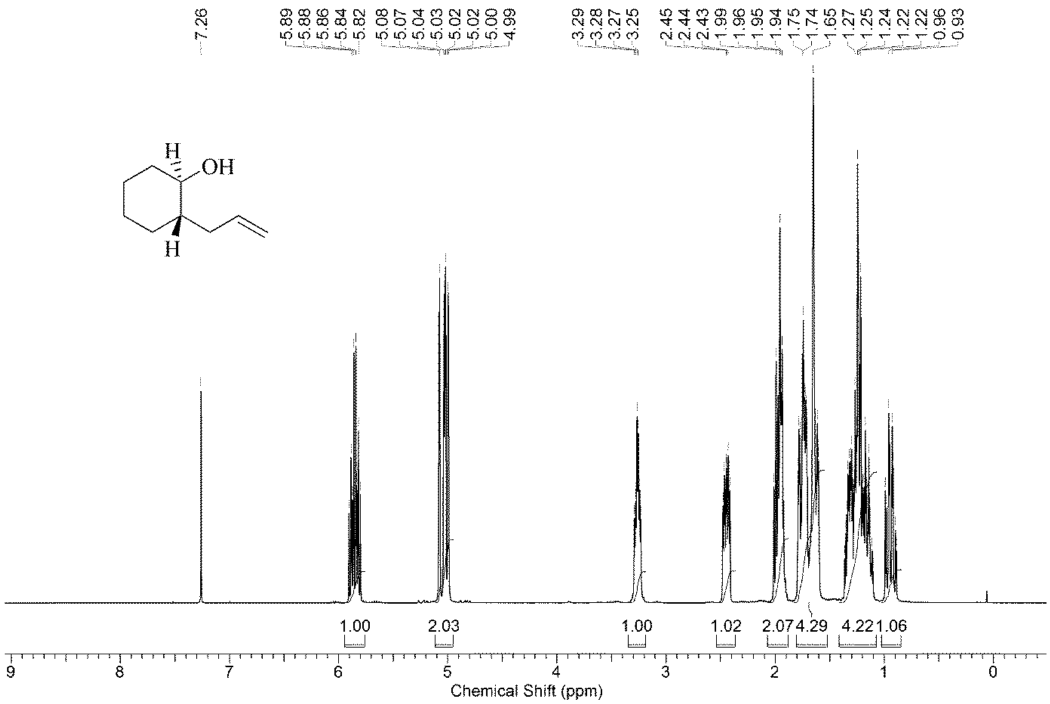


Figure S9. Proton-1 NMR-spectrum of *trans*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (400MHz, $CDCl_3$, 23 °C).

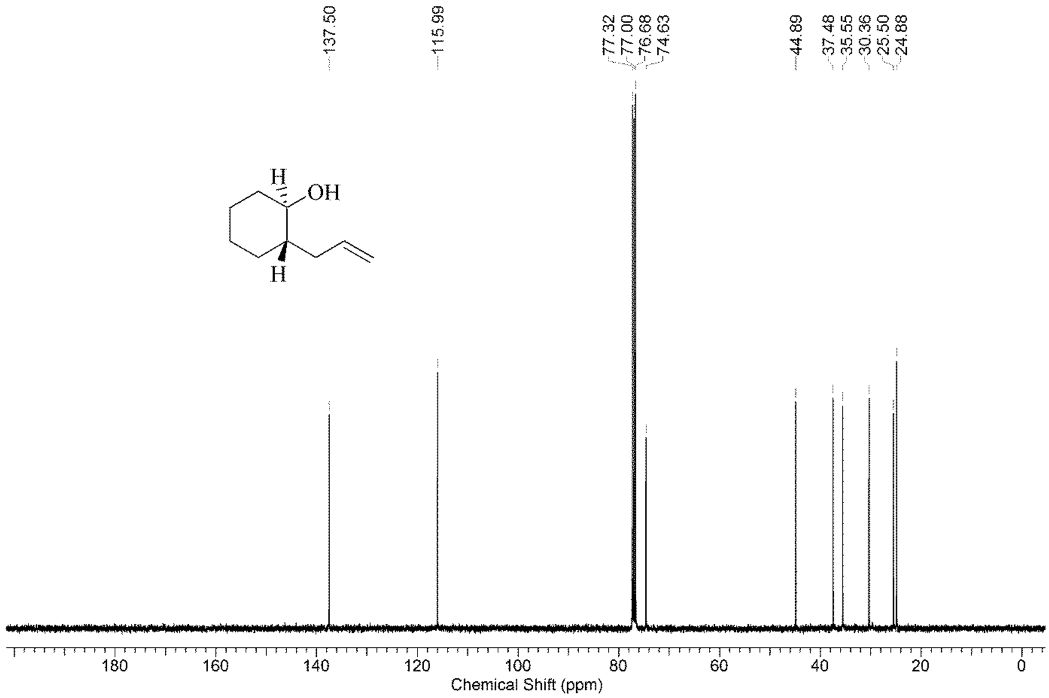


Figure S10. Carbon-13 NMR-spectrum of *trans*-2-(prop-2-en-1-yl)-cyclopentan-1-ol (100MHz, $CDCl_3$, 23 °C).

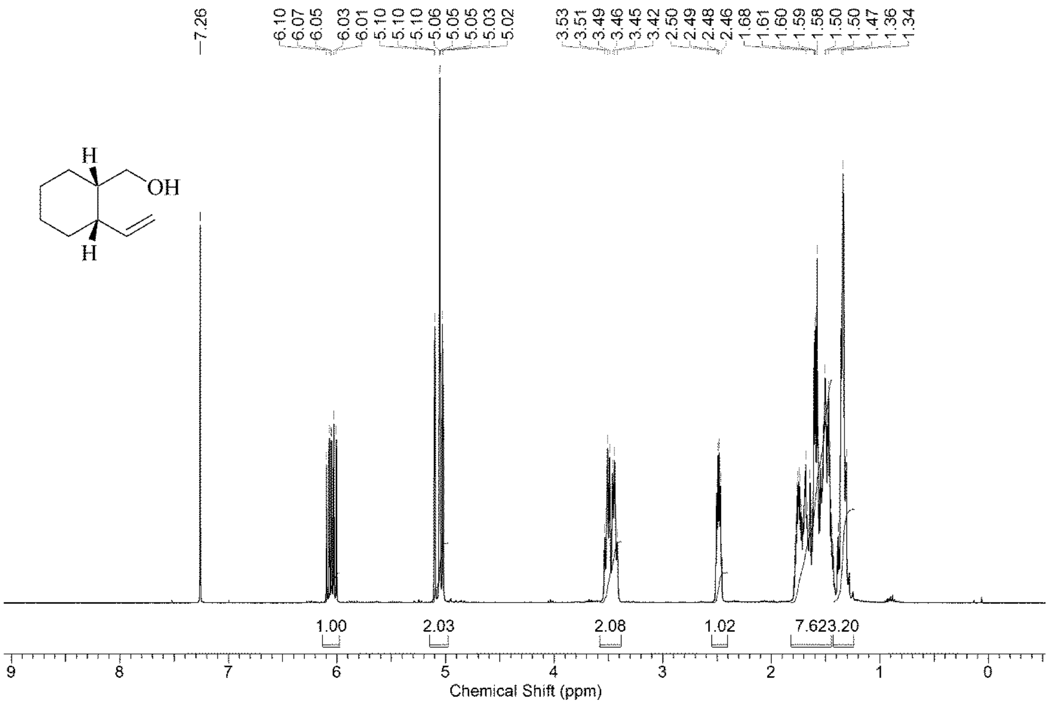


Figure S11. Proton-1 NMR-spectrum of *cis*-[2-(ethenyl)-cyclohex-1-yl]-methanol (400MHz, $CDCl_3$, 23 °C).

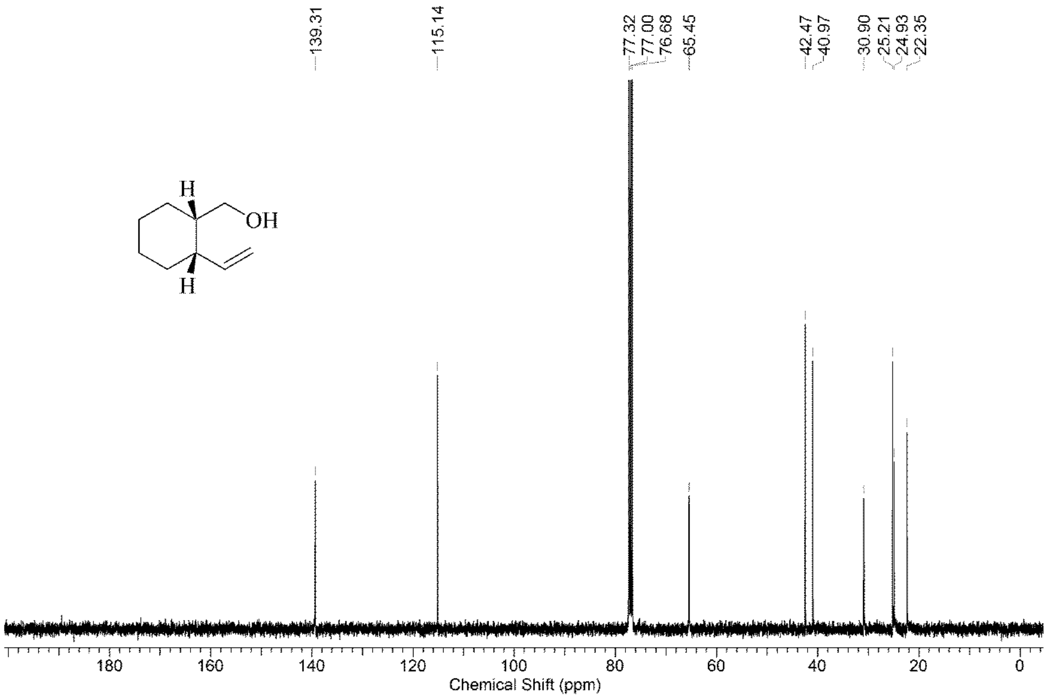


Figure S12. Carbon-13 NMR-spectrum of *cis*-[2-(ethenyl)-cyclohex-1-yl]-methanol (100MHz, $CDCl_3$, 23 °C).

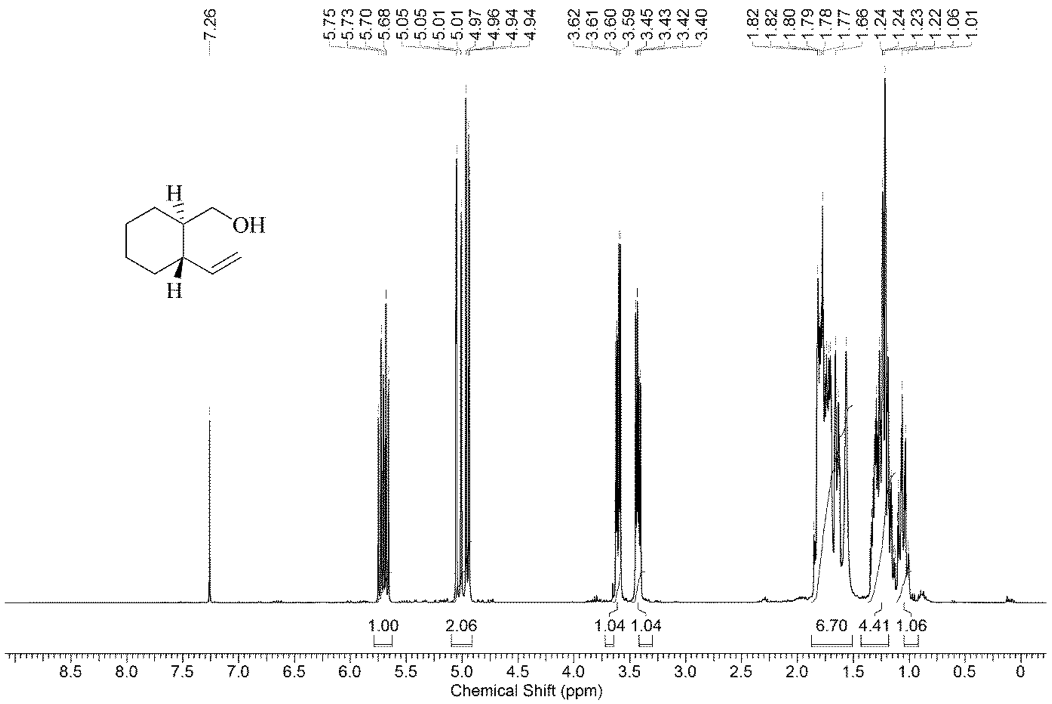


Figure S13. Proton-1 NMR-spectrum of *trans*-[2-(ethenyl)-cyclohex-1-yl]-methanol (400MHz, $CDCl_3$, 23 °C).

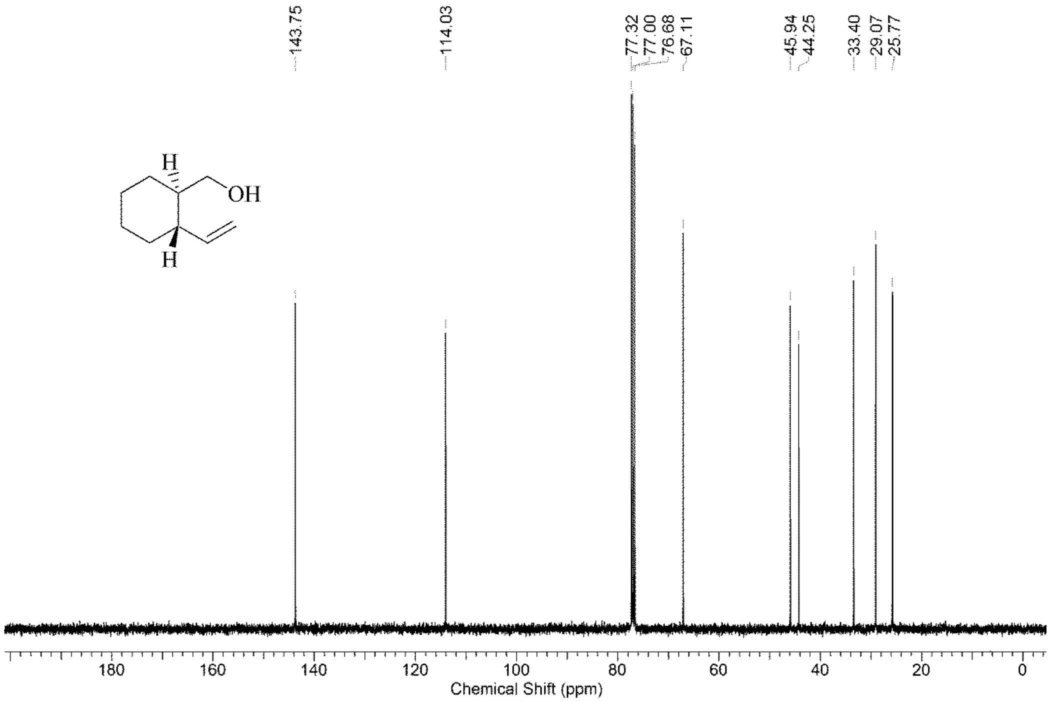


Figure S14. Carbon-13 NMR-spectrum of *trans*-[2-(ethenyl)-cyclohex-1-yl]-methanol (100MHz, $CDCl_3$, 23 °C).

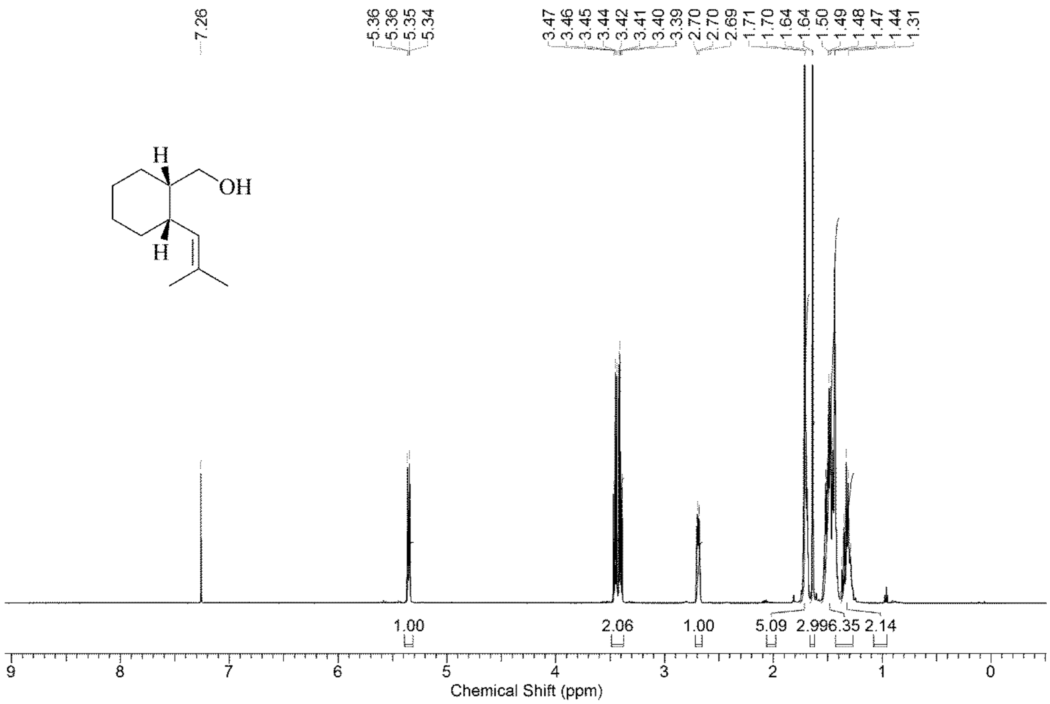


Figure S15. Proton-1 NMR-spectrum of *cis*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol (600MHz, $CDCl_3$, 23 °C).

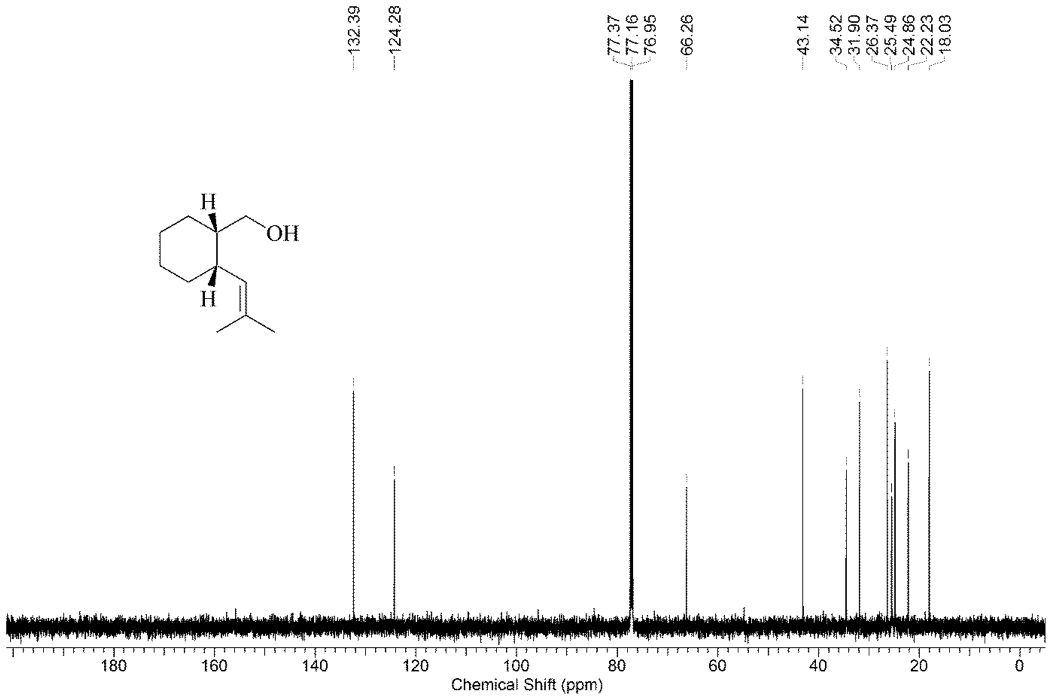


Figure S16. Carbon-13 NMR-spectrum of *cis*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol (150MHz, $CDCl_3$, 23 °C).

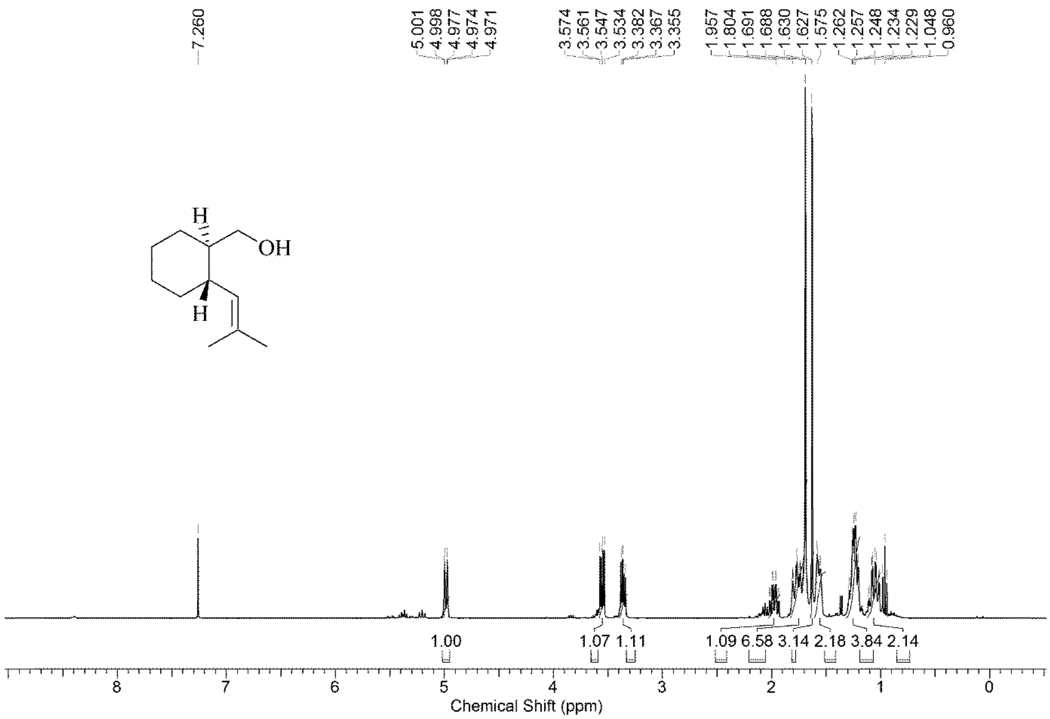


Figure S17. Proton-1 NMR-spectrum of *trans*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol (400MHz, $CDCl_3$, 23 °C).

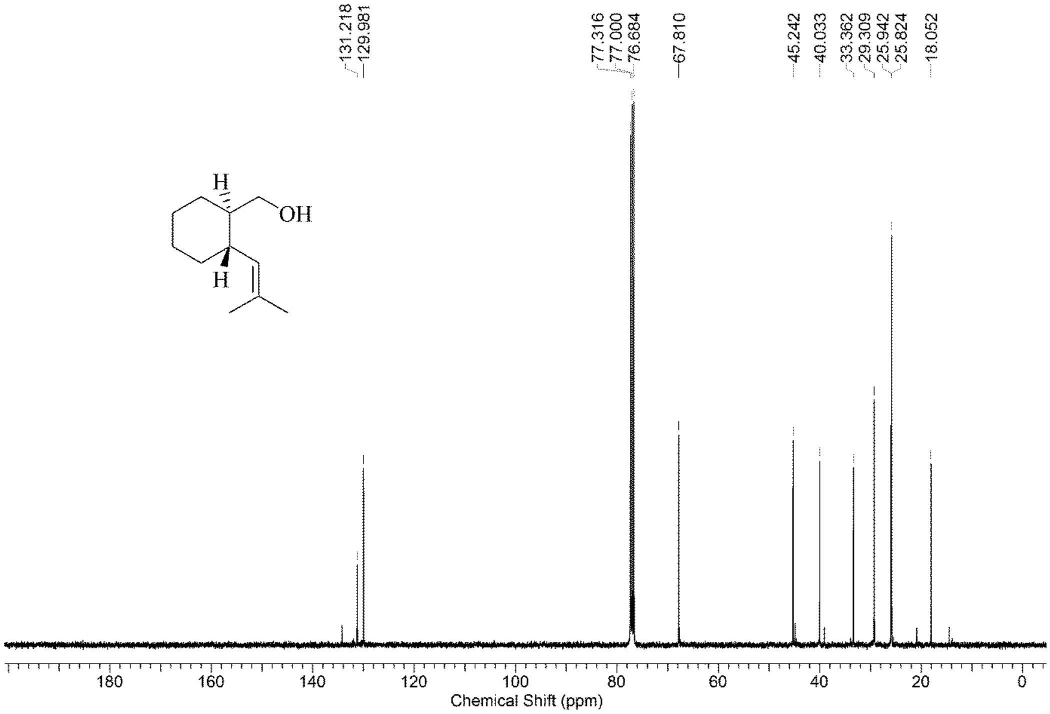


Figure S18. Carbon-13 NMR-spectrum of *trans*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methanol (100MHz, $CDCl_3$, 23 °C).

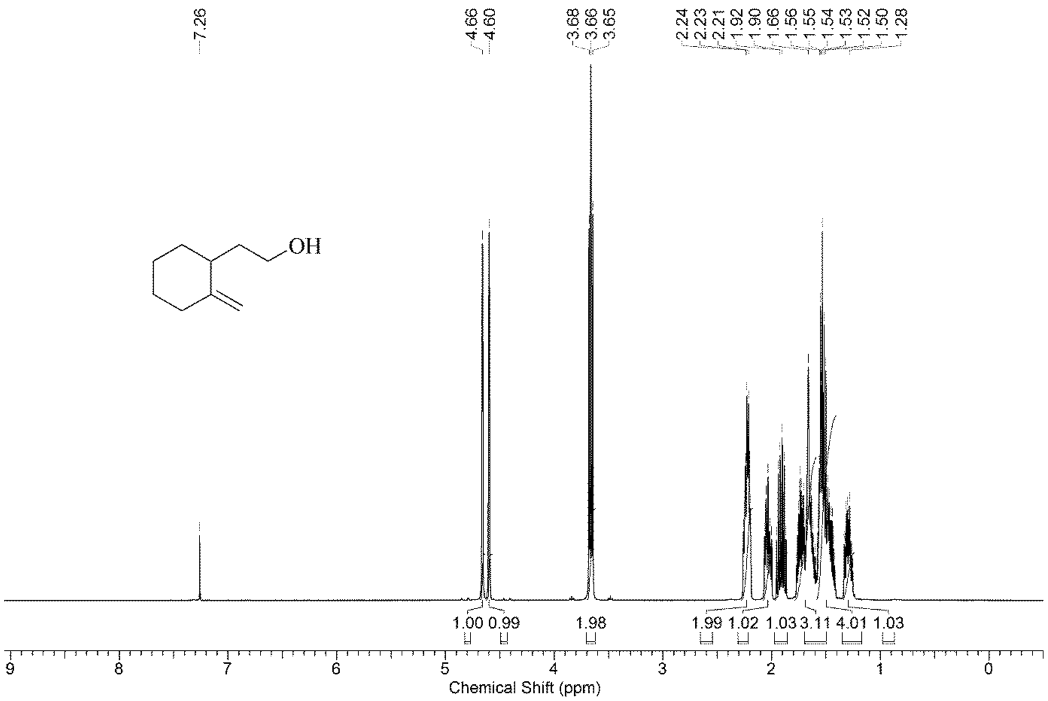


Figure S19. Proton-1 NMR-spectrum of 2-(1-methylenecyclohex-2-yl)-ethan-1-ol (400MHz, $CDCl_3$, 23 °C).

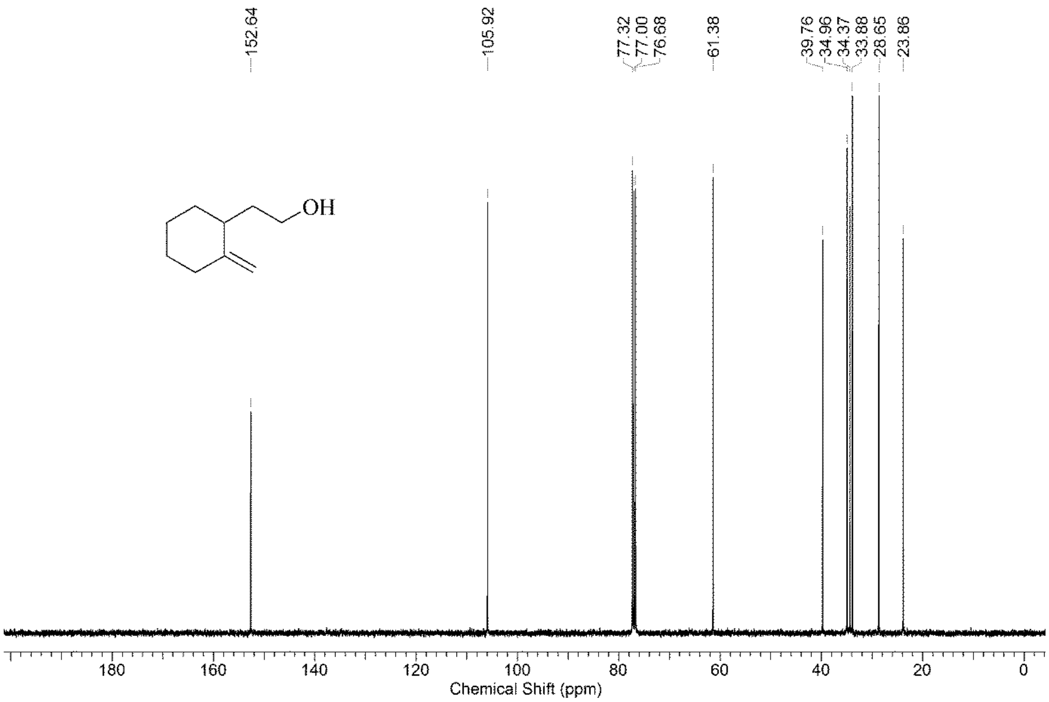


Figure S20. Carbon-13 NMR-spectrum of 2-(1-methylenecyclohex-2-yl)-ethan-1-ol (100MHz, $CDCl_3$, 23 °C).

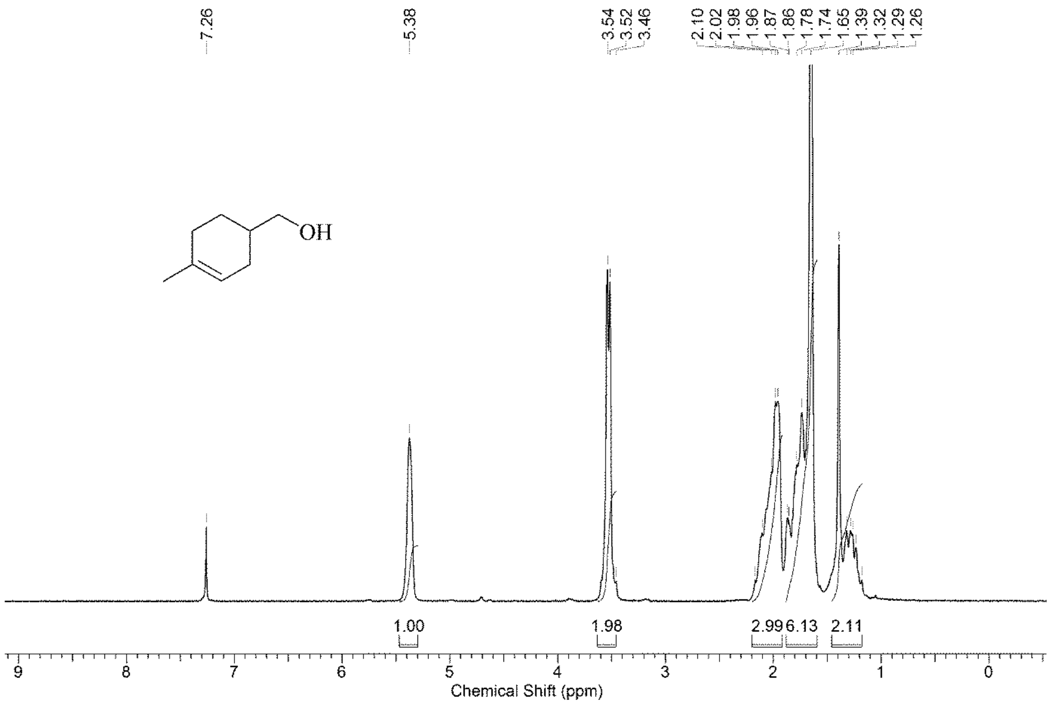


Figure S21. Proton-1 NMR-spectrum of (1-methylcyclohex-1-en-4-yl)-methanol (200MHz, $CDCl_3$, 23 °C).

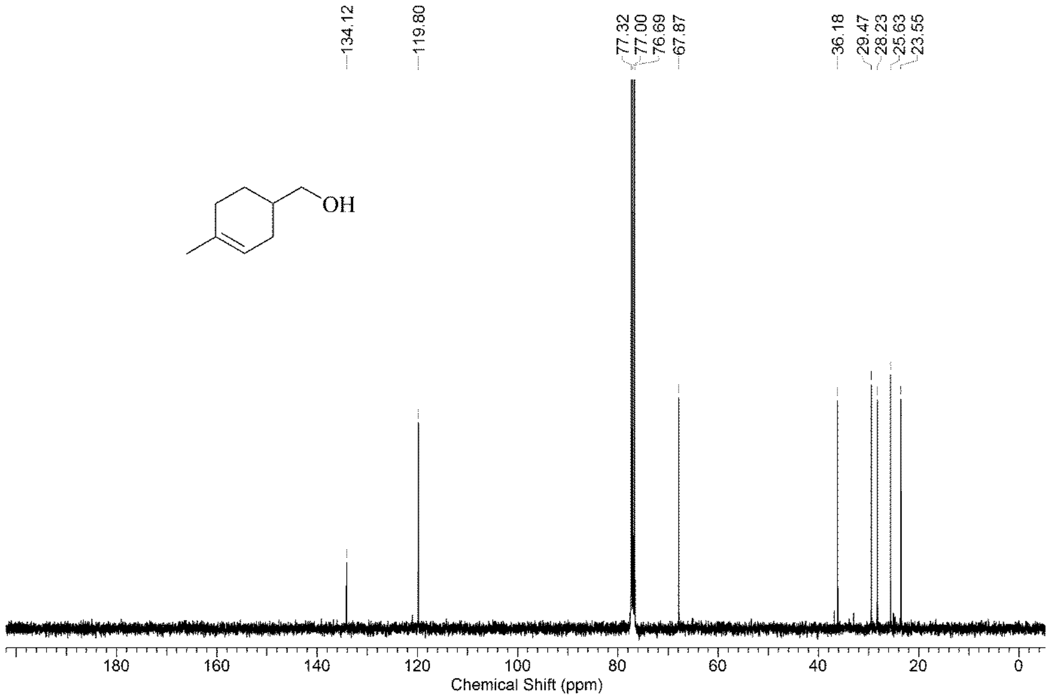


Figure S22. Carbon-13 NMR-spectrum of (1-methylcyclohex-1-en-4-yl)-methanol (100MHz, $CDCl_3$, 23 °C).

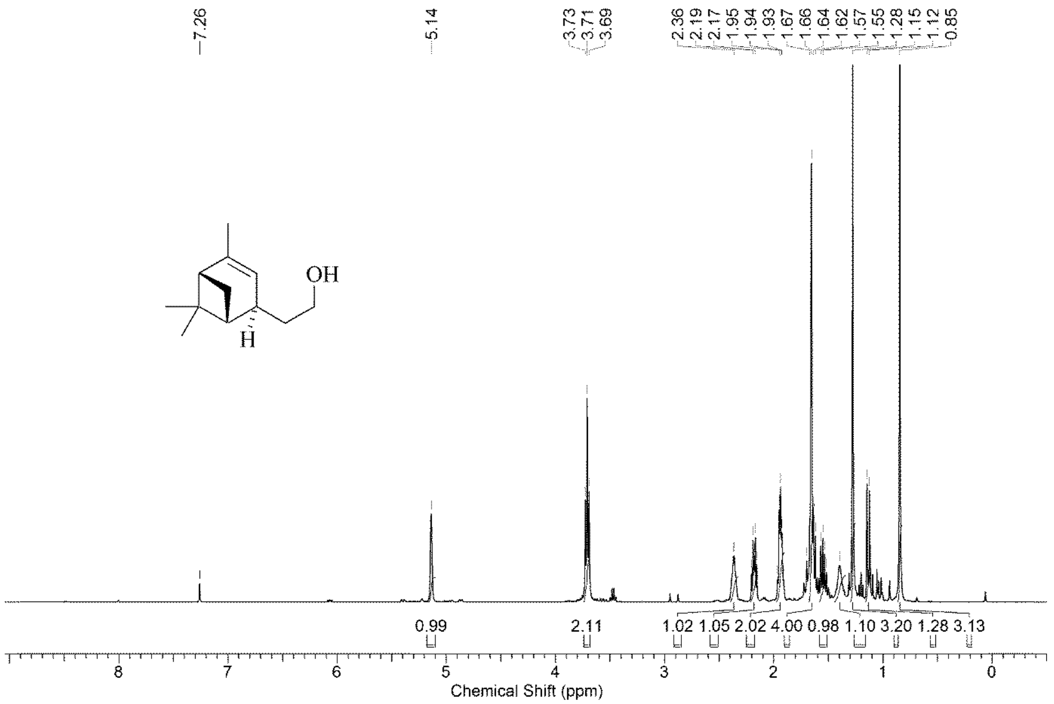


Figure S23. Proton-1 NMR-spectrum of 2-{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethanol (400MHz, $CDCl_3$, 23 °C).

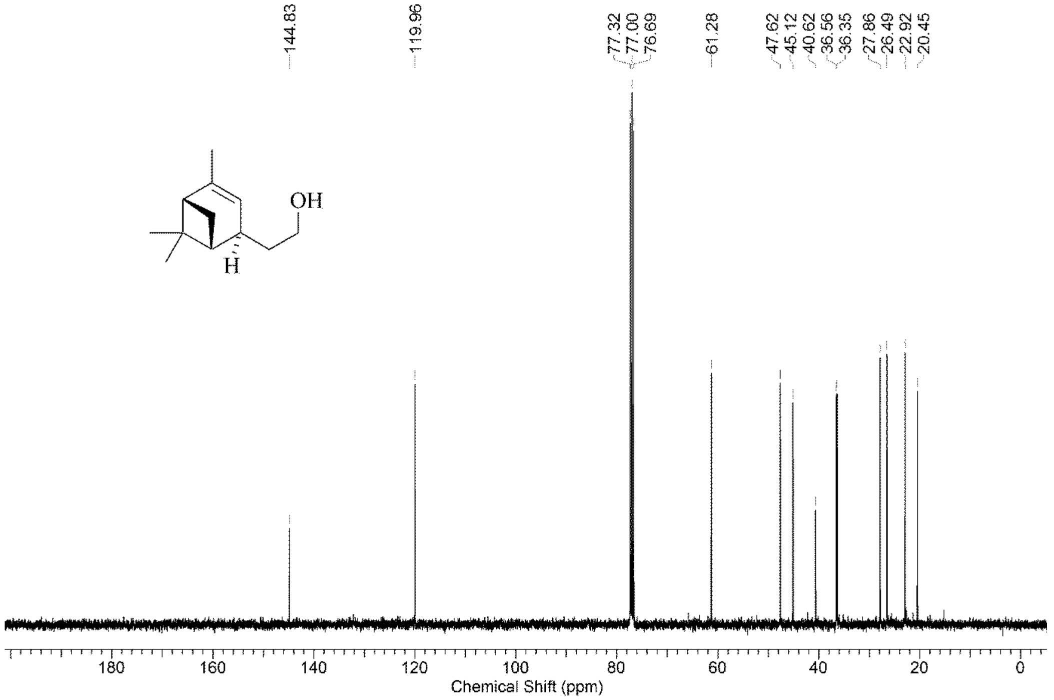


Figure S24. Carbon-13 NMR-spectrum of 2-{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethanol (100MHz, $CDCl_3$, 23 °C).

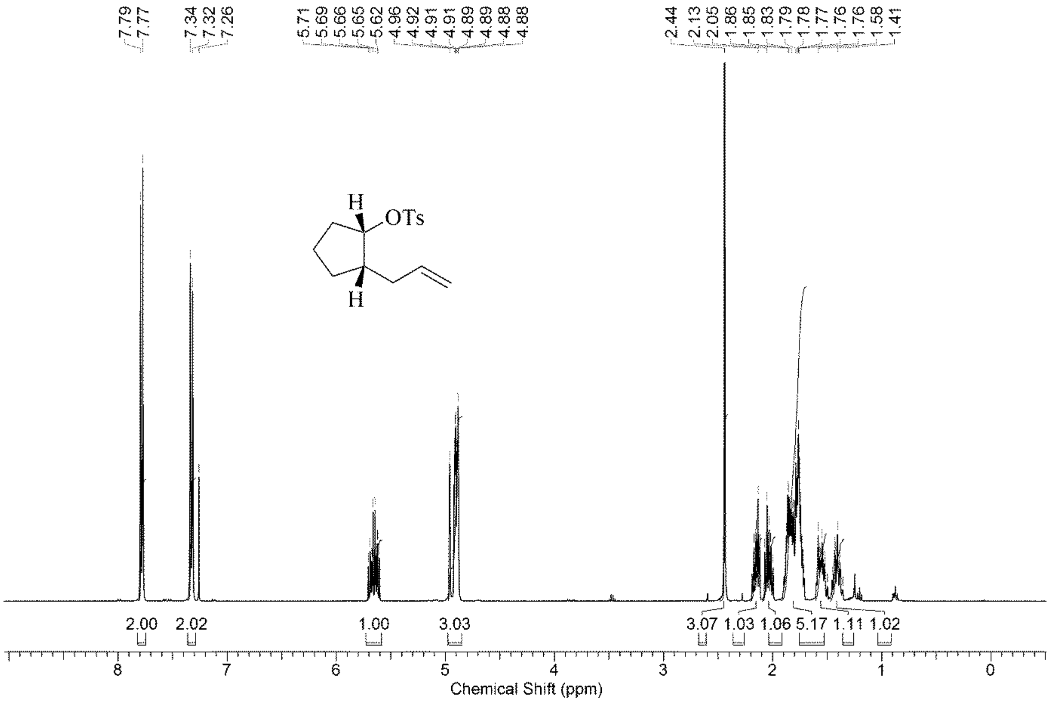


Figure S25. Proton-1 NMR-spectrum of *cis*-[2-(Prop-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate (400MHz, $CDCl_3$, 23 °C).

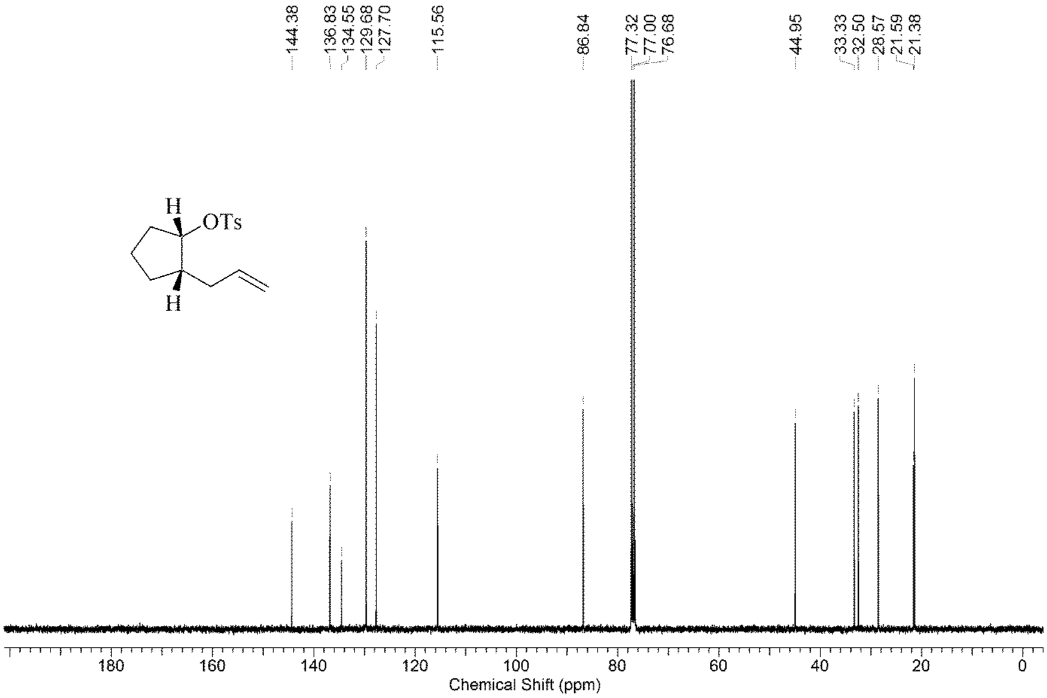


Figure S26. Carbon-13 NMR-spectrum of *cis*-[2-(Prop-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

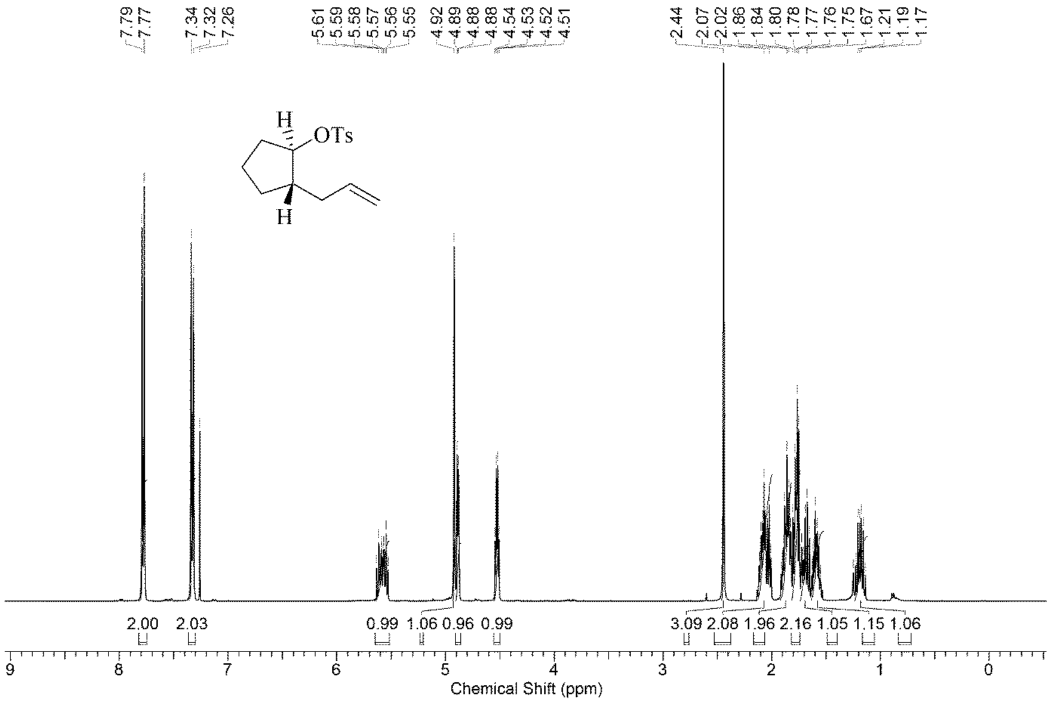


Figure S27. Proton-1 NMR-spectrum of *trans*-[2-(Prop-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate (400MHz, $CDCl_3$, 23 °C).

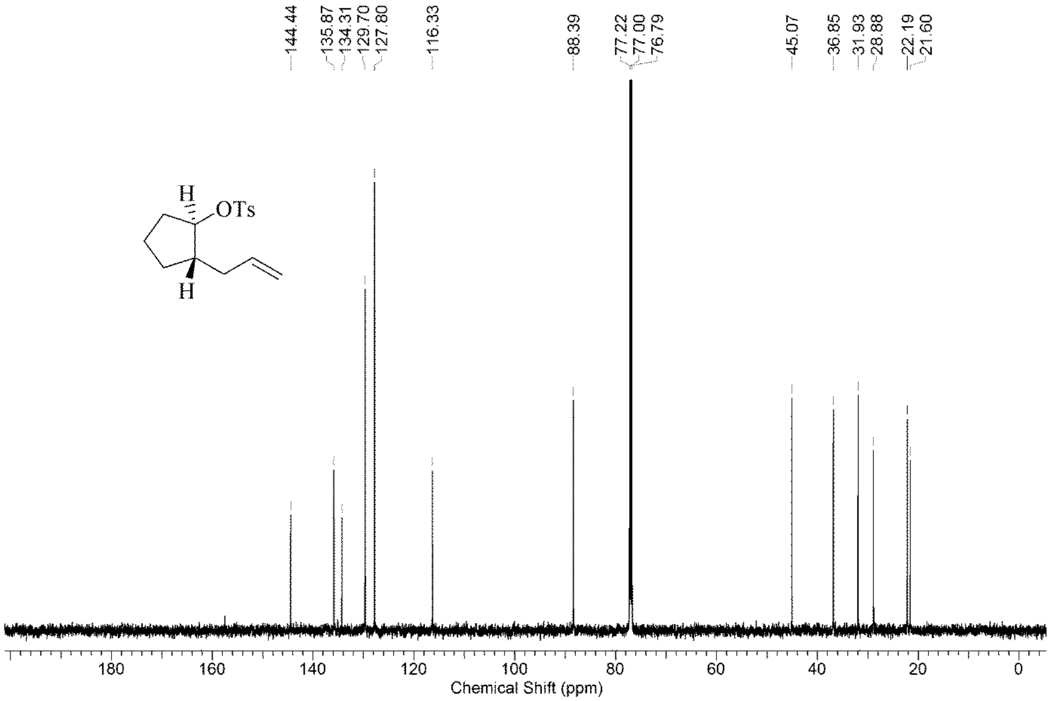


Figure S28. Carbon-13 NMR-spectrum of *trans*-[2-(Prop-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate (150MHz, $CDCl_3$, 23 °C).

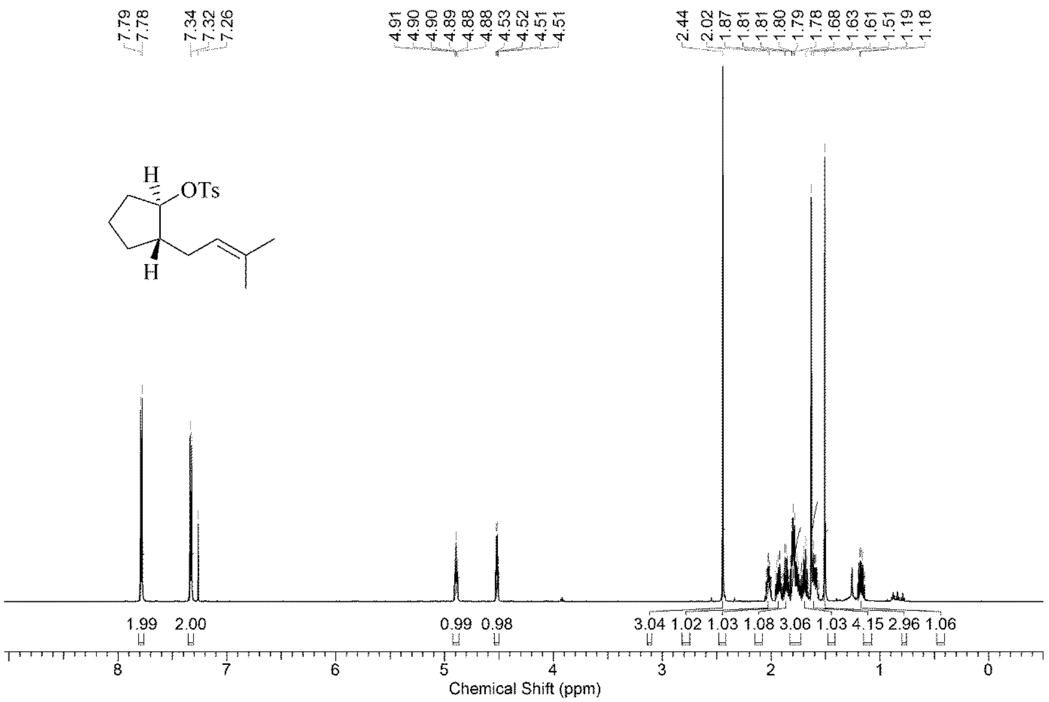


Figure S29. Proton-1 NMR-spectrum of *trans*-[2-(3-methylbut-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate (600MHz, $CDCl_3$, 23 °C).

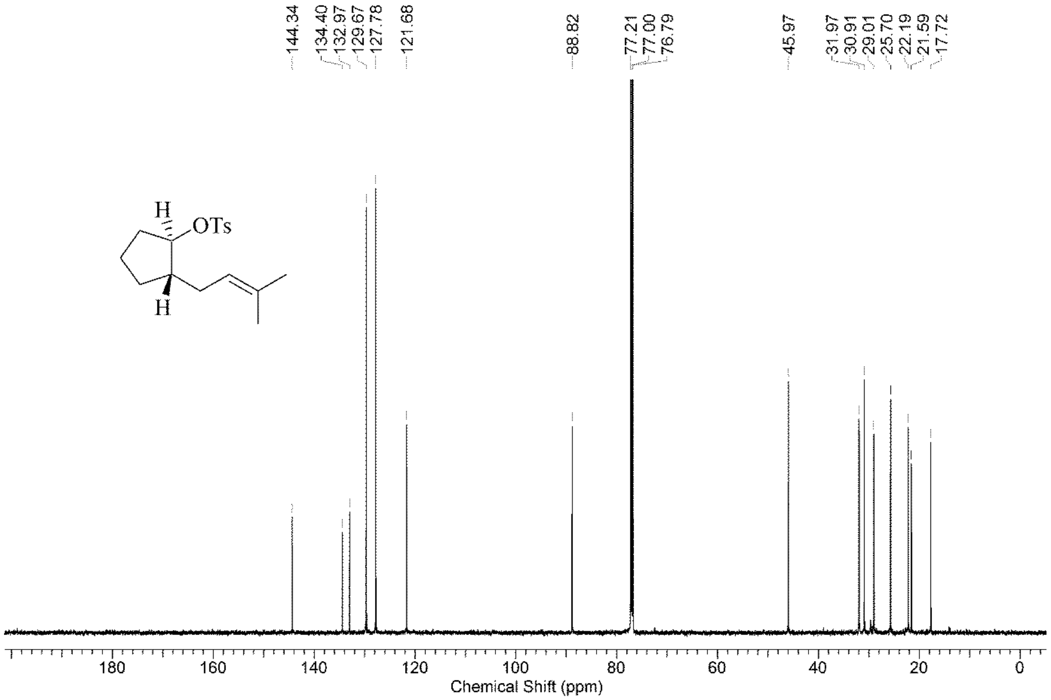


Figure S30. Proton-1 NMR-spectrum of *trans*-[2-(3-methylbut-2-en-1-yl)-cyclopent-1-yl] 4-toluenesulfonate (150MHz, $CDCl_3$, 23 °C).

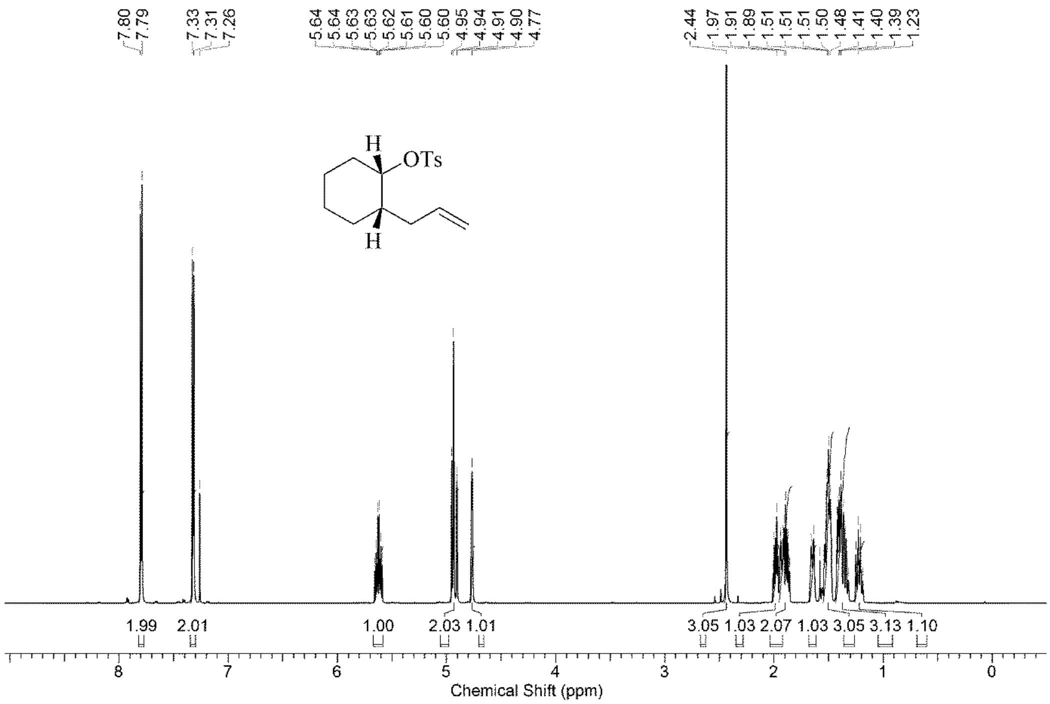


Figure S31. Proton-1 NMR-spectrum of *cis*-[2-(prop-2-en-1-yl)-cyclohexyl-1-yl 4-toluenesulfonate (600MHz, $CDCl_3$, 23 °C).

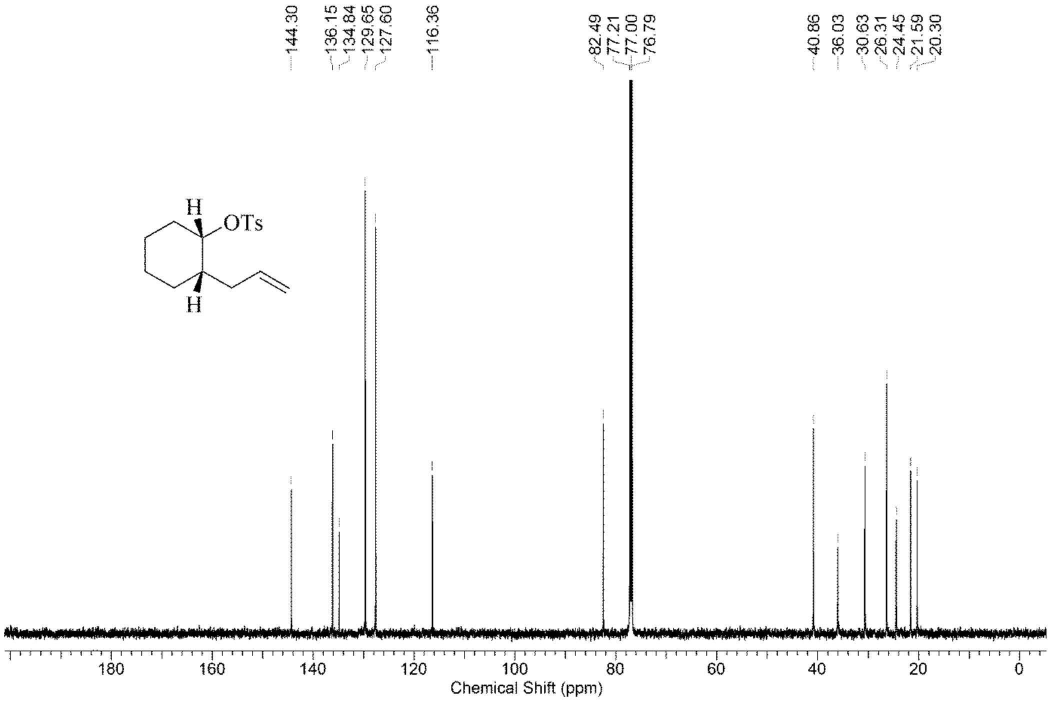


Figure S32. Carbon-13 NMR-spectrum of *cis*-[2-(prop-2-en-1-yl)-cyclohexyl-1-yl 4-toluenesulfonate (150MHz, $CDCl_3$, 23 °C).

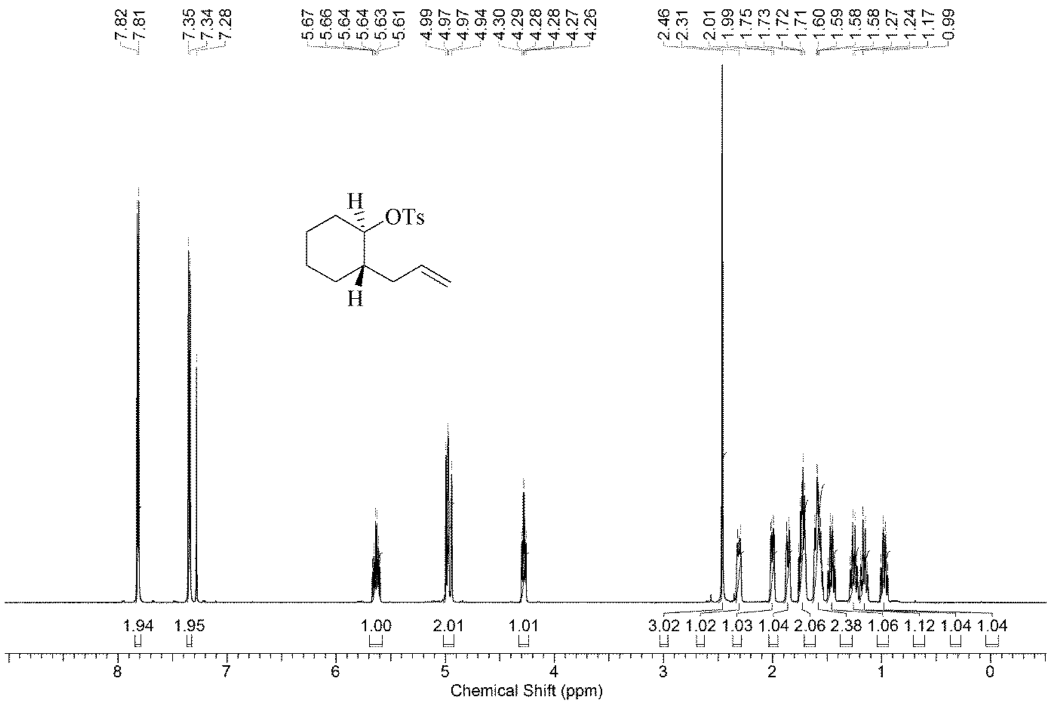


Figure S33. Proton-1 NMR-spectrum of *trans*-[2-(prop-2-en-1-yl)-cyclohexyl-1-yl 4-toluenesulfonate (600MHz, $CDCl_3$, 23 °C).

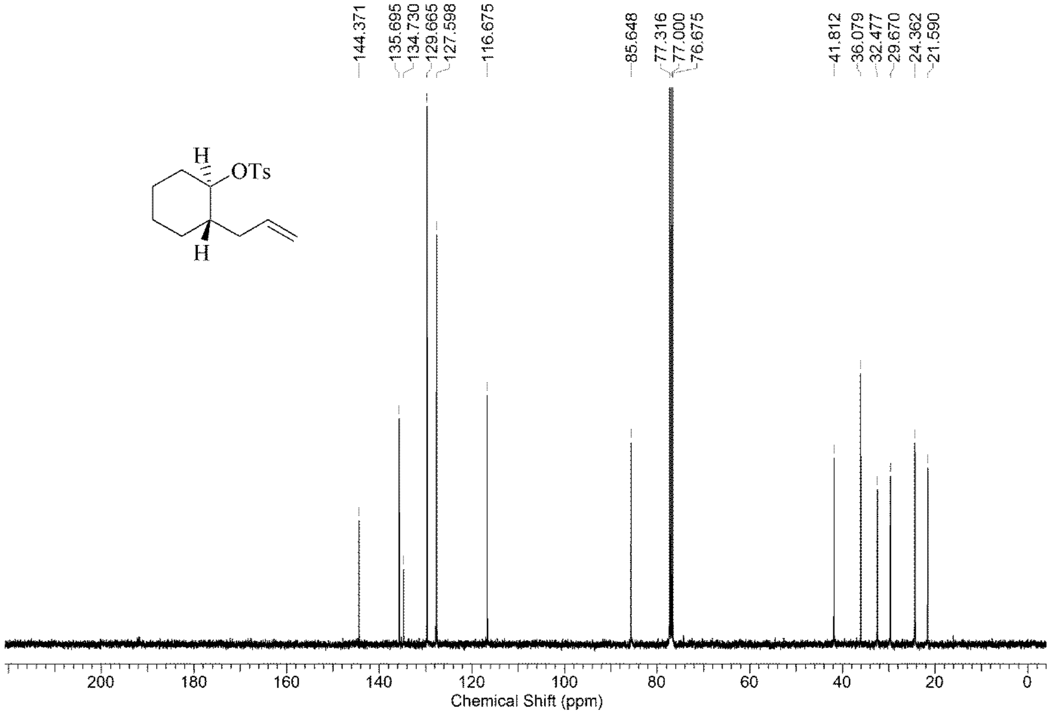


Figure S34. Carbon-13 NMR-spectrum of *trans*-[2-(prop-2-en-1-yl)-cyclohexyl-1-yl 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

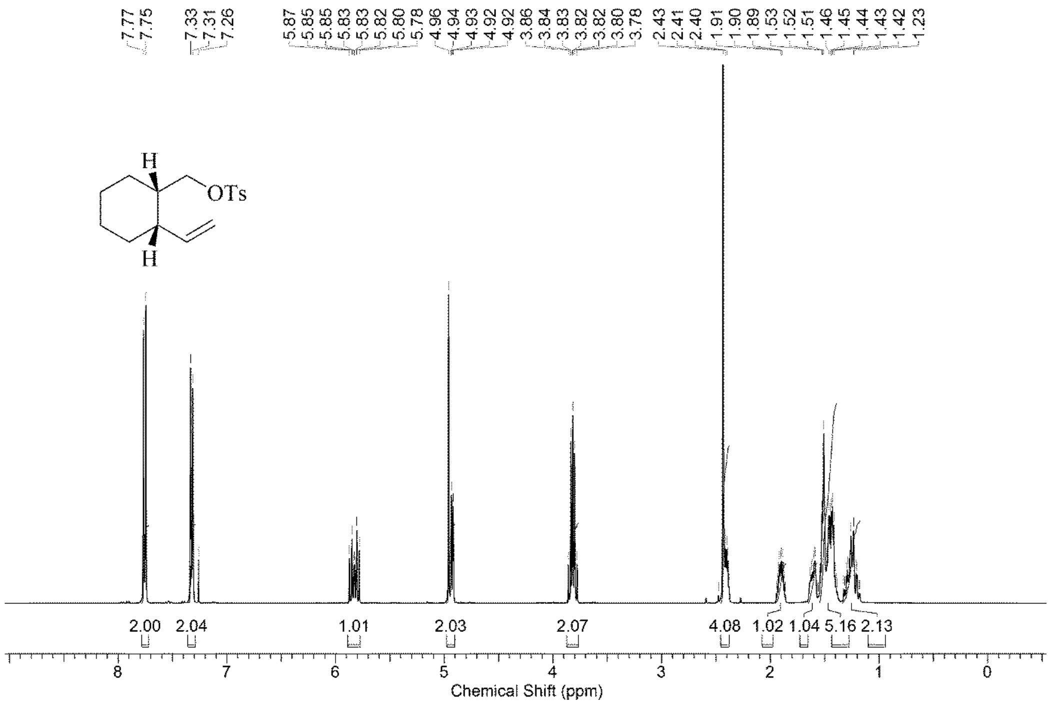


Figure S35. Proton-1 NMR-spectrum of *cis*-[2-(ethenyl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (400MHz, $CDCl_3$, 23 °C).

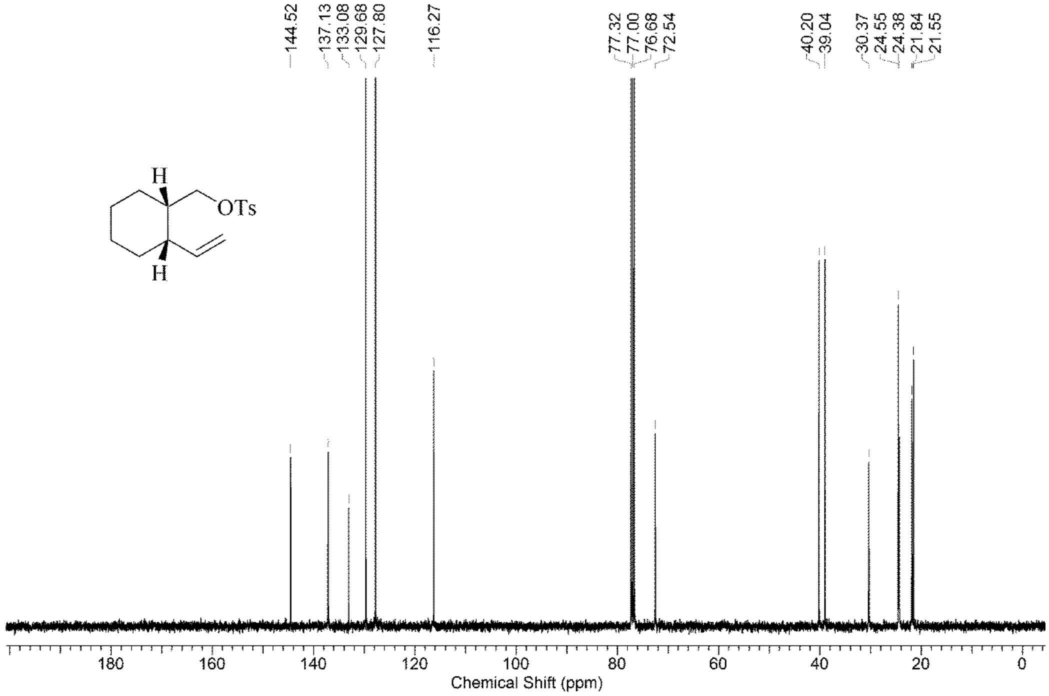


Figure S36. Carbon-13 NMR-spectrum of *cis*-[2-(ethenyl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

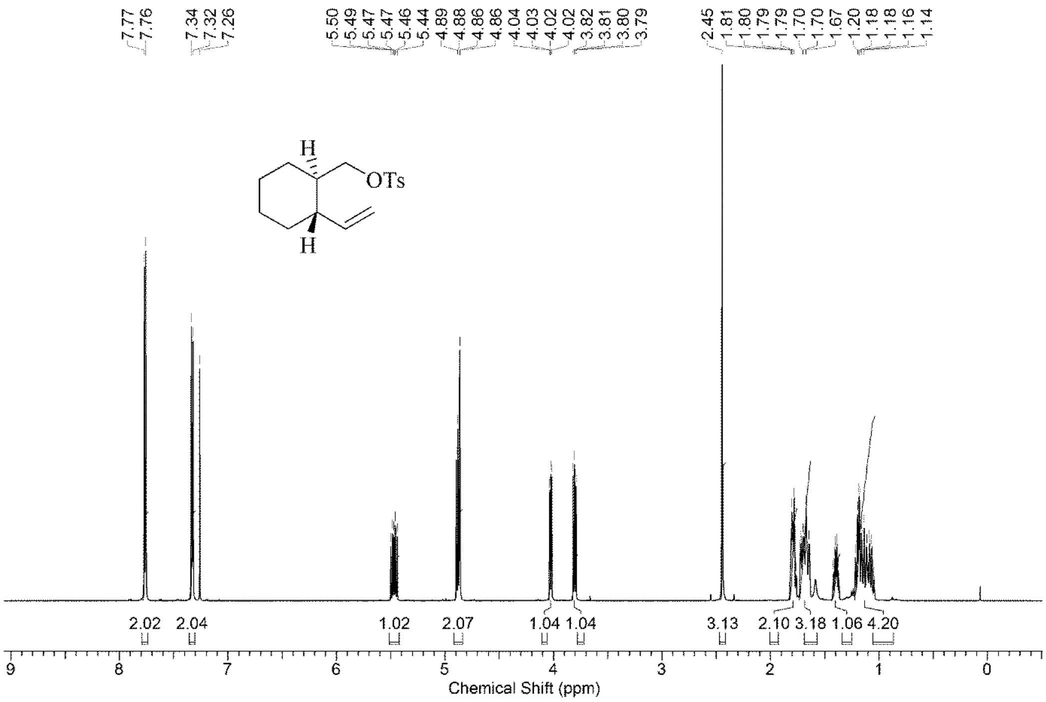


Figure S37. Proton-1 NMR-spectrum of *trans*-[2-(ethenyl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (600MHz, $CDCl_3$, 23 °C).

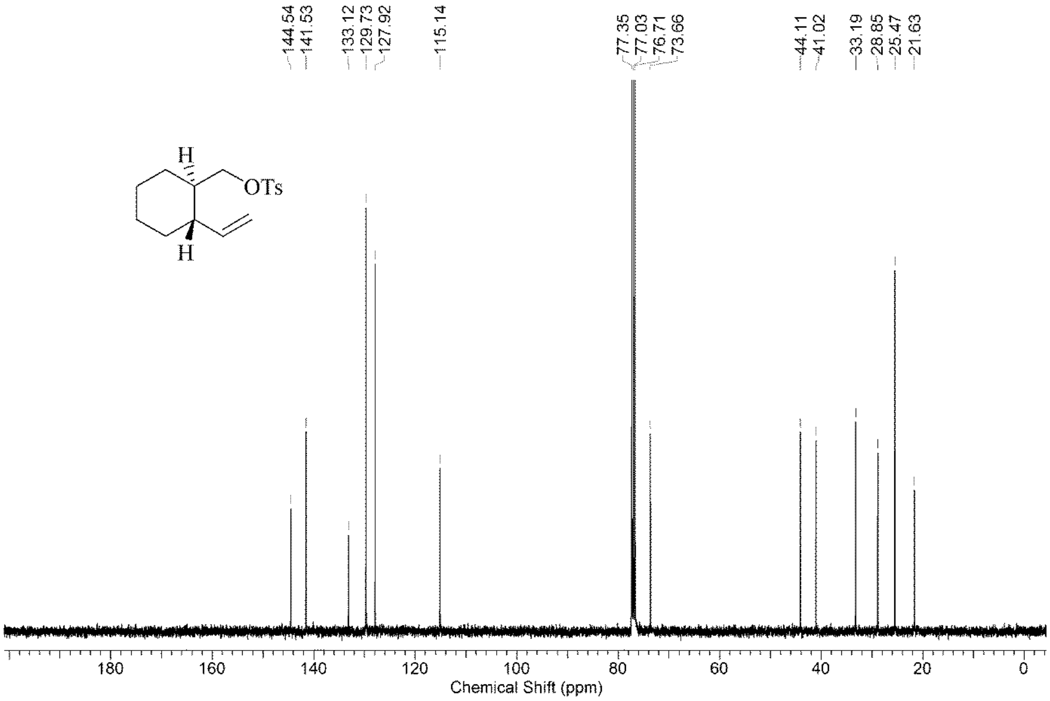


Figure S38. Carbon-13 NMR-spectrum of *trans*-[2-(ethenyl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

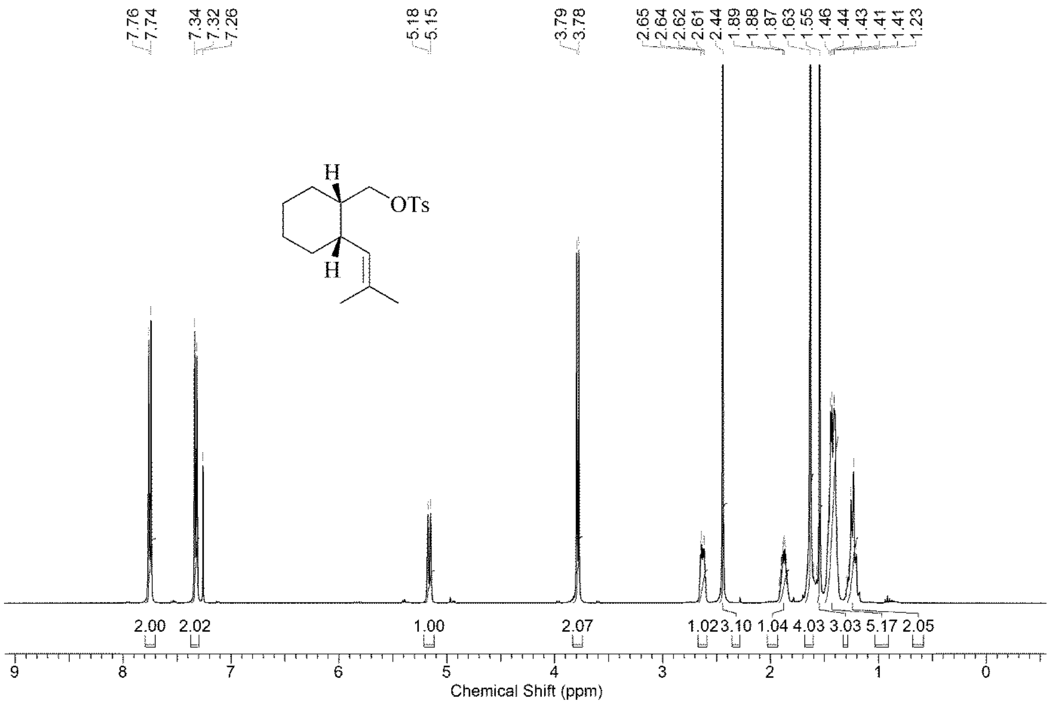


Figure S39. Proton-1 NMR-spectrum of *cis*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (400MHz, $CDCl_3$, 23 °C).

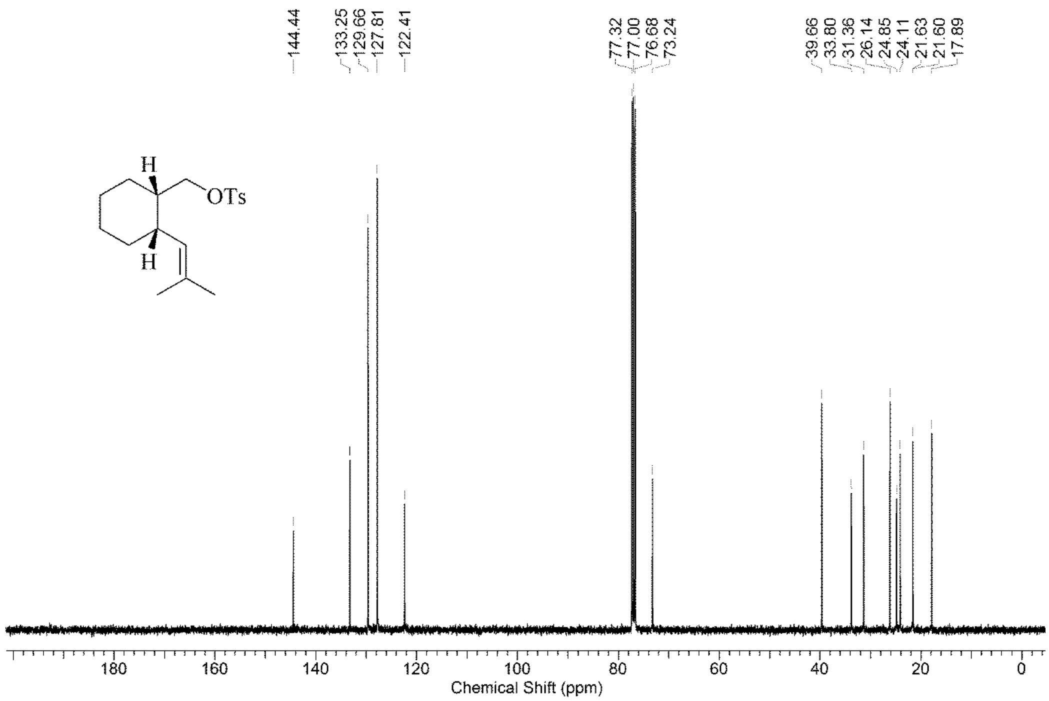


Figure S40. Carbon-13 NMR-spectrum of *cis*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

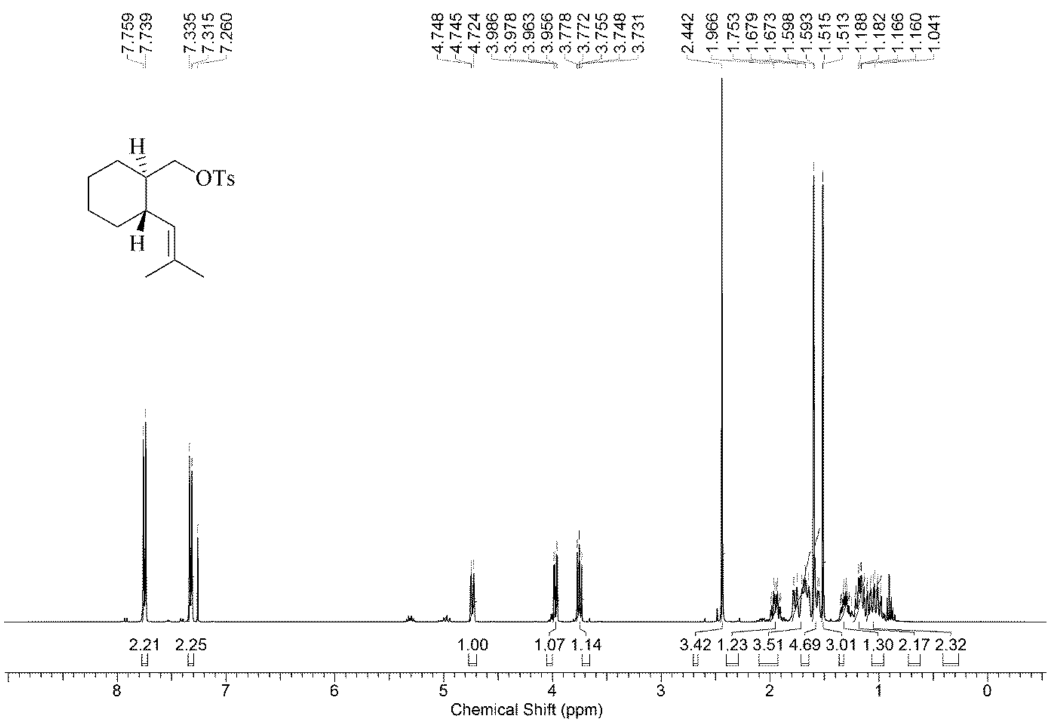


Figure S41. Proton-1 NMR-spectrum of *trans*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (400MHz, $CDCl_3$, 23 °C).

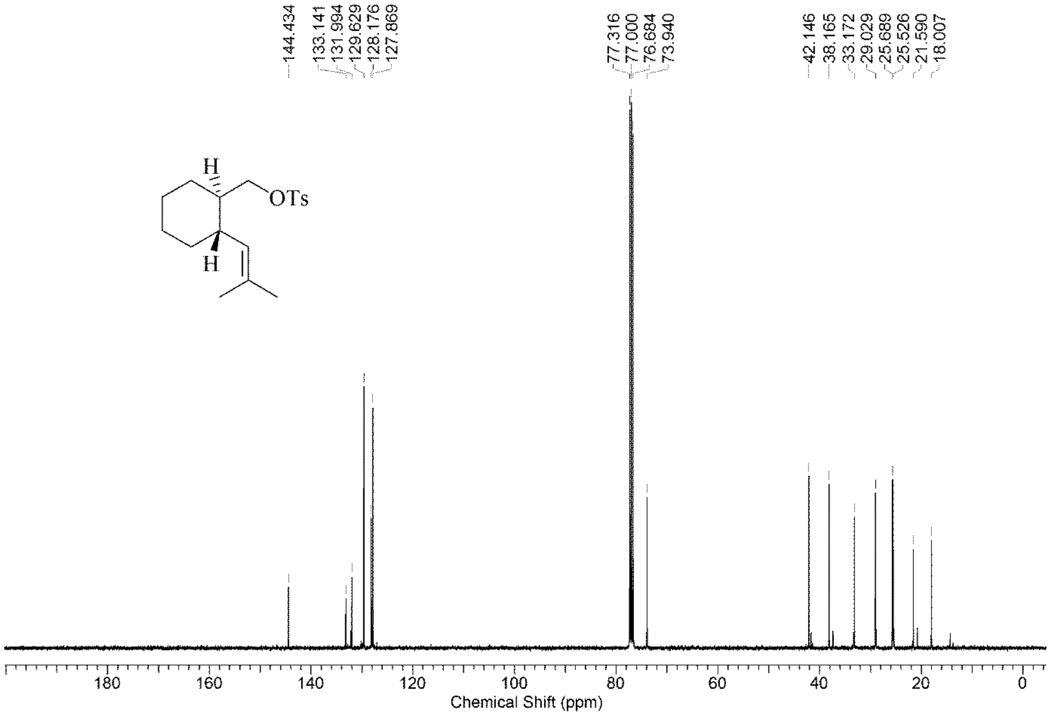


Figure S42. Carbon-13 NMR-spectrum of *trans*-[2-(methylprop-1-en-1-yl)-cyclohex-1-yl]-methyl 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

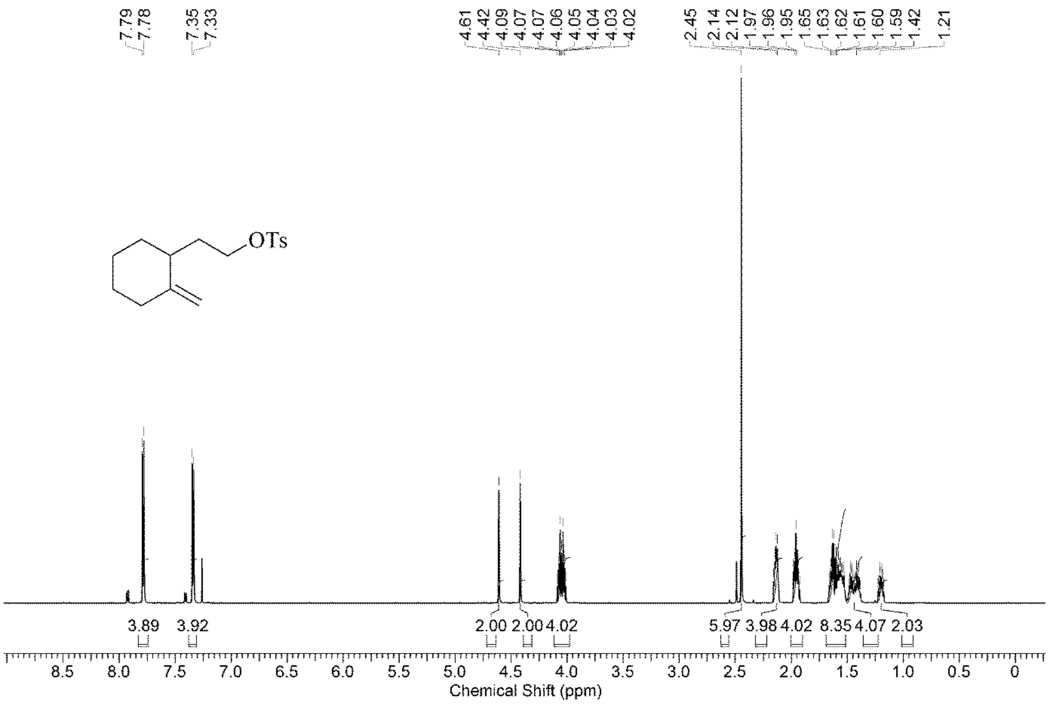


Figure S43. Proton-1 NMR-spectrum of 2-(1-methylenecyclohex-2-yl)-eth-1-yl 4-toluenesulfonate (600MHz, $CDCl_3$, 23 °C).

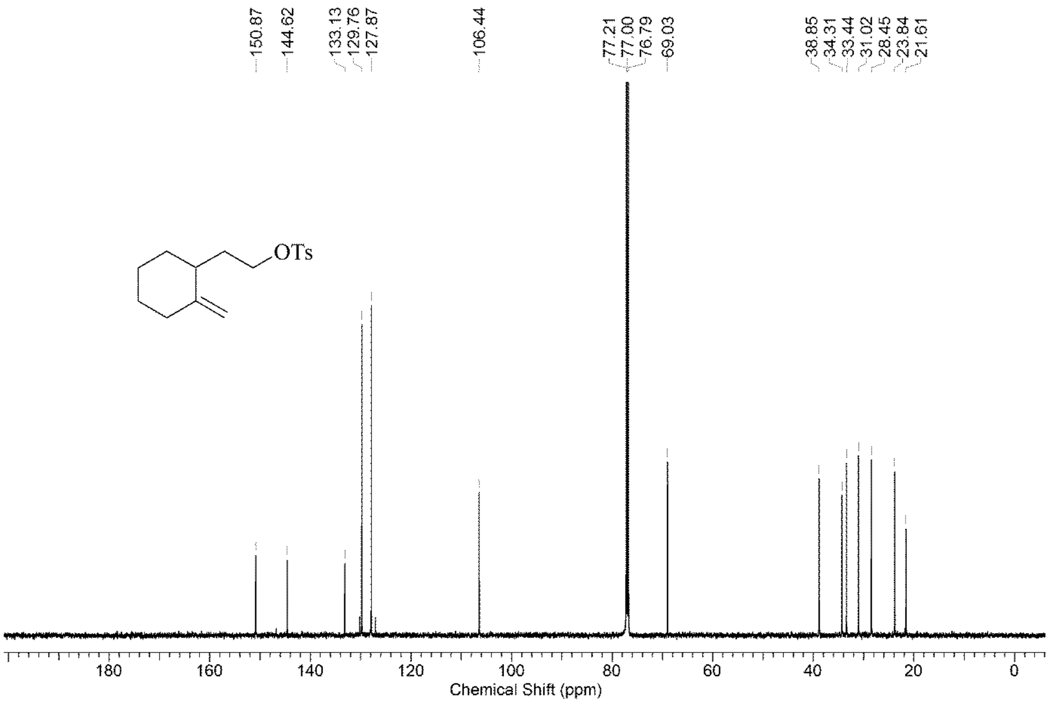


Figure S44. Carbon-13 NMR-spectrum of 2-(1-methylenecyclohex-2-yl)-eth-1-yl 4-toluenesulfonate (150MHz, $CDCl_3$, 23 °C).

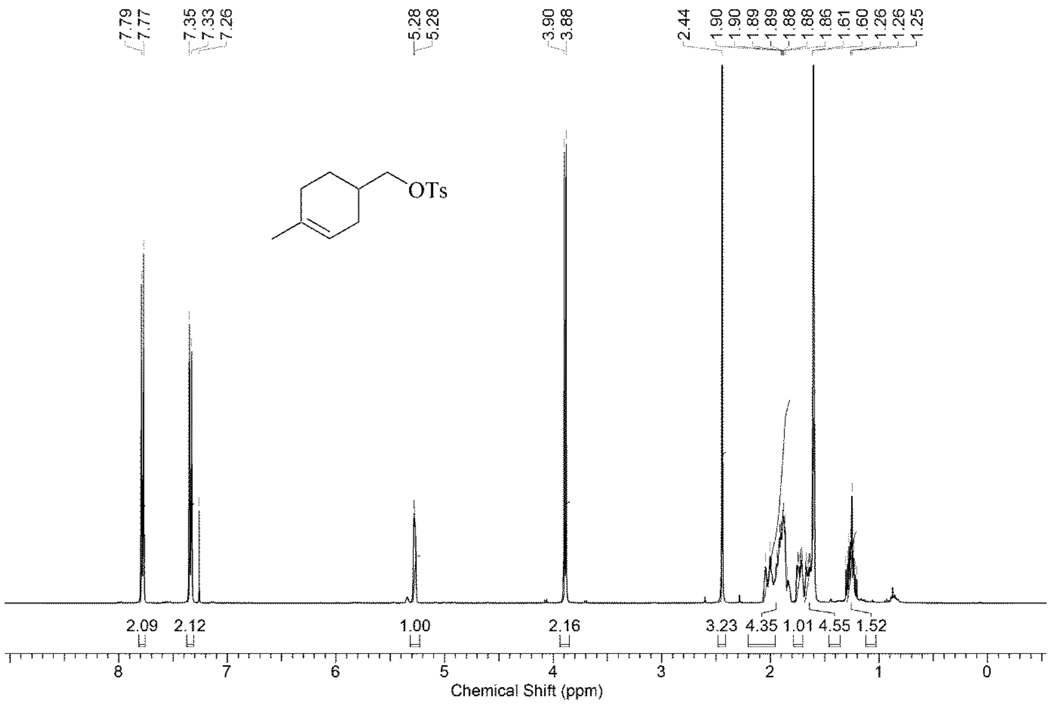


Figure S45. Proton-1 NMR-spectrum of (1-methylcyclohex-1-en-4-yl)-methyl 4-toluenesulfonate (400MHz, $CDCl_3$, 23 °C).

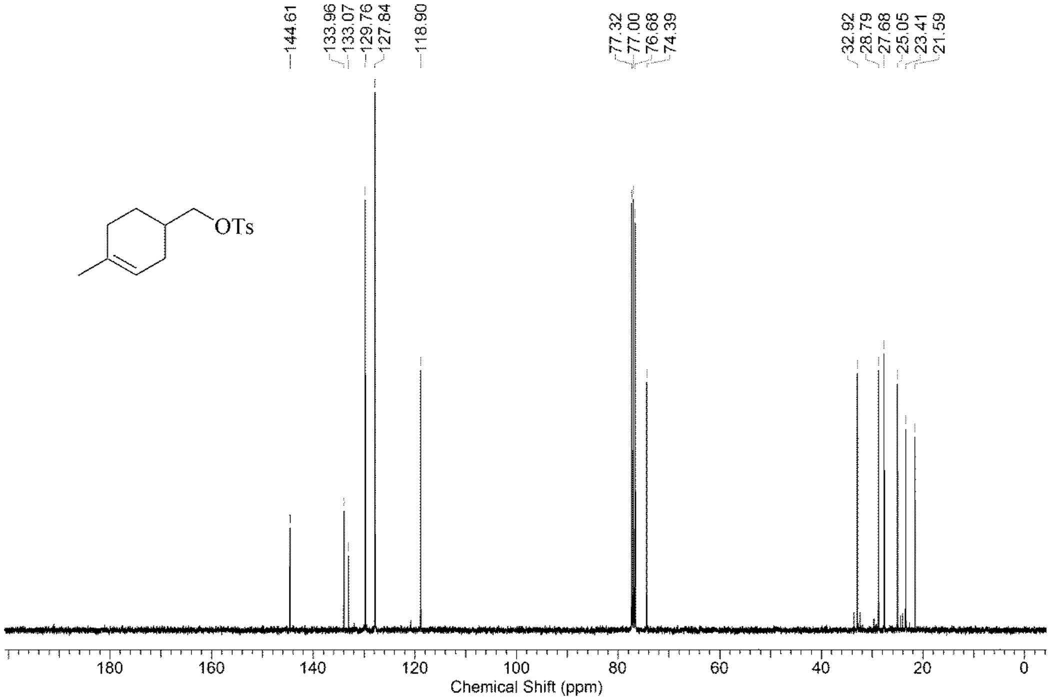


Figure S46. Carbon-13 NMR-spectrum of (1-methylcyclohex-1-en-4-yl)-methyl 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

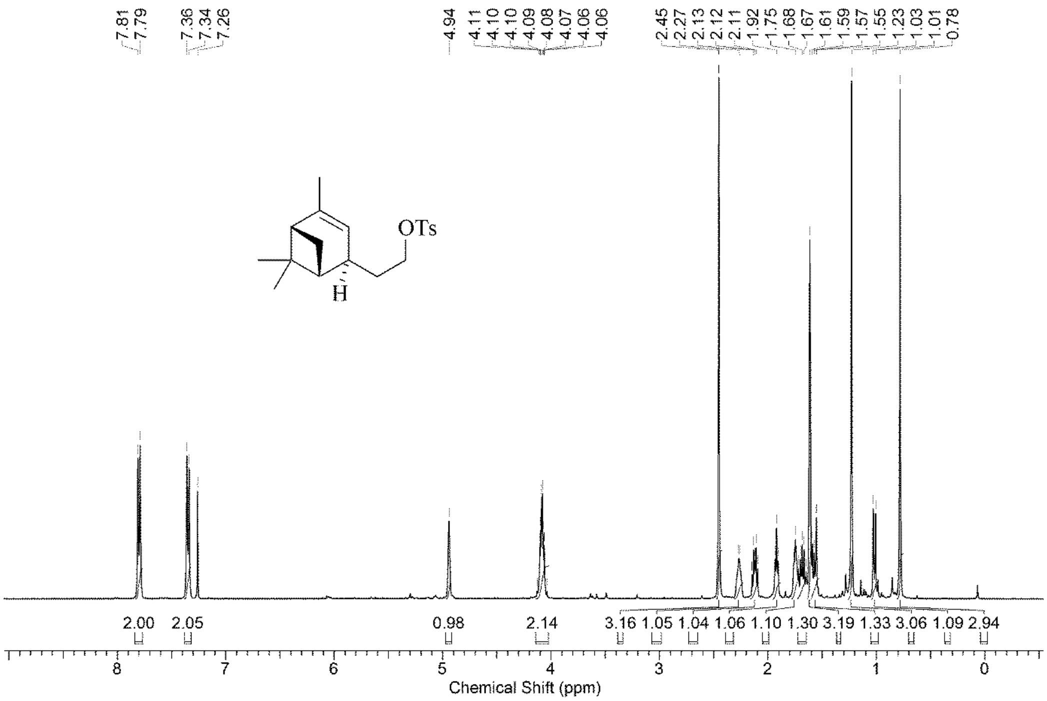


Figure S47. Proton-1 NMR-spectrum of 2-{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethyl 4-toluenesulfonate (400MHz, $CDCl_3$, 23 °C).

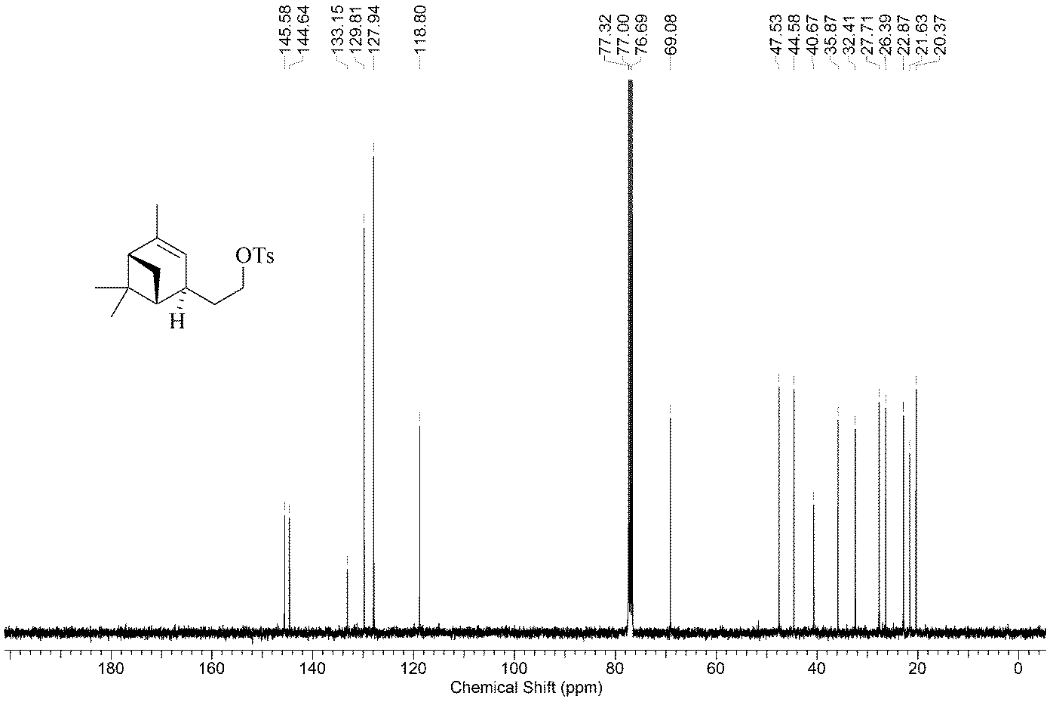


Figure S48. Carbon-1 NMR-spectrum of 2-{(1*S*,4*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-en-4-yl}-ethyl 4-toluenesulfonate (100MHz, $CDCl_3$, 23 °C).

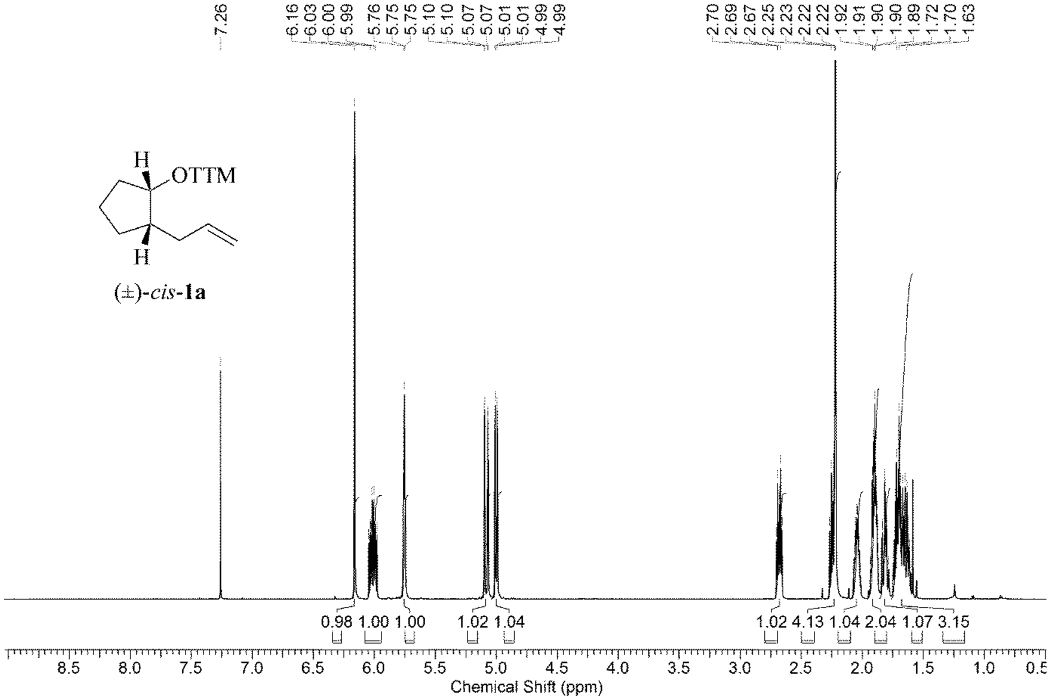


Figure S49. Proton-1 NMR-spectrum of 3-[*cis*-2-(prop-2-en-1-yl)-cyclopent-1-yloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1a**) (600MHz, $CDCl_3$, 23 °C).

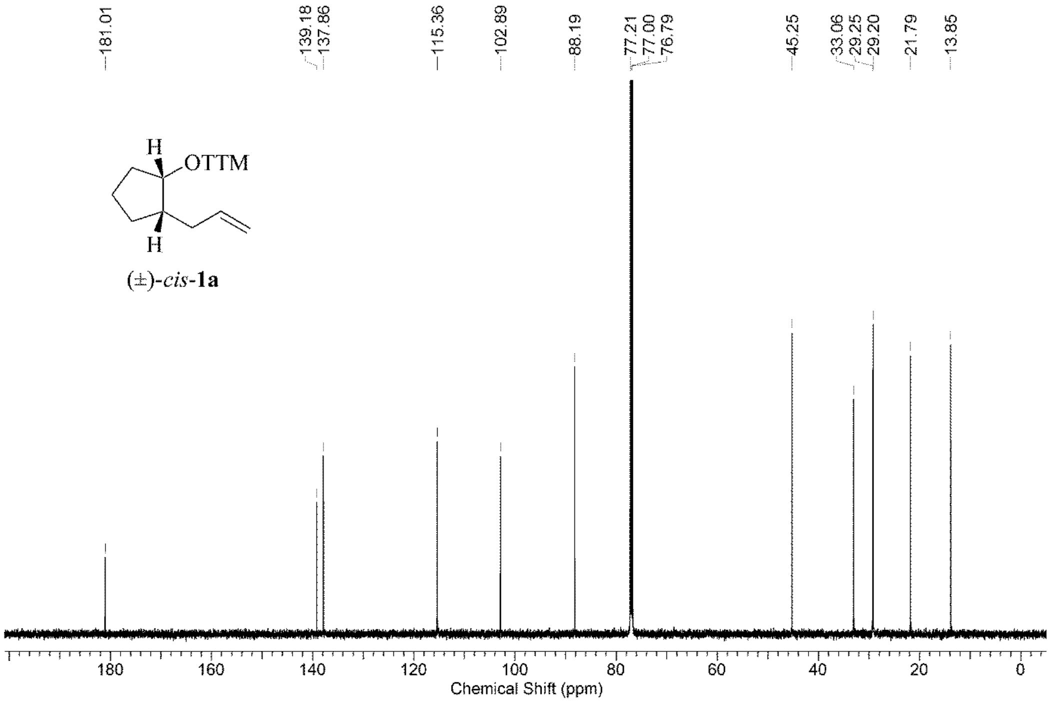


Figure S50. Carbon-1 NMR-spectrum of 3-[*cis*-2-(prop-2-en-1-yl)-cyclopent-1-yloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1a**) (150MHz, $CDCl_3$, 23 °C).

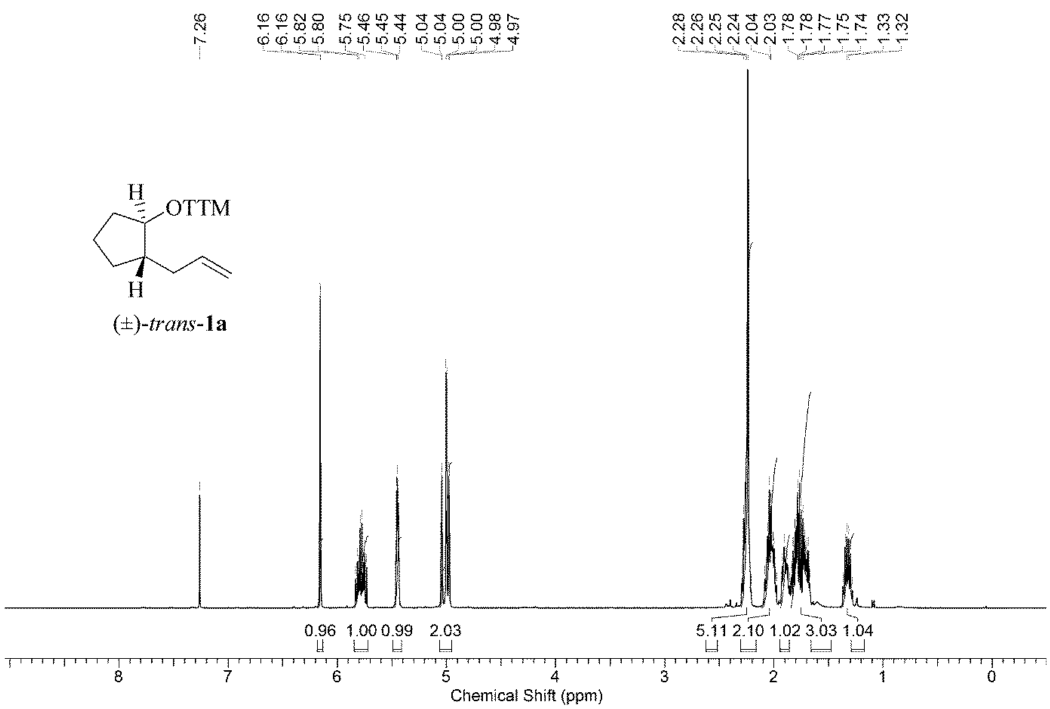


Figure S51. Proton-1 NMR-spectrum of 3-[*trans*-2-(prop-2-en-1-yl)-cyclopent-1-yloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1a**) (400MHz, $CDCl_3$, 23 °C).

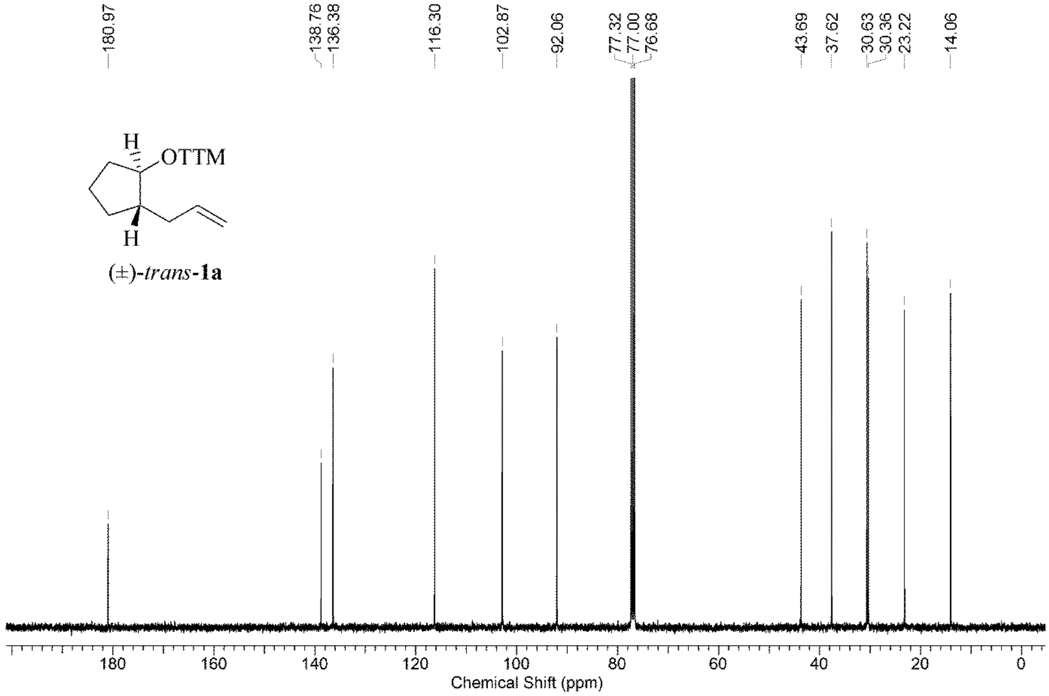


Figure S52. Carbon-13 NMR-spectrum of 3-[*trans*-2-(prop-2-en-1-yl)-cyclopent-1-yloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1a**) (100MHz, $CDCl_3$, 23 °C).

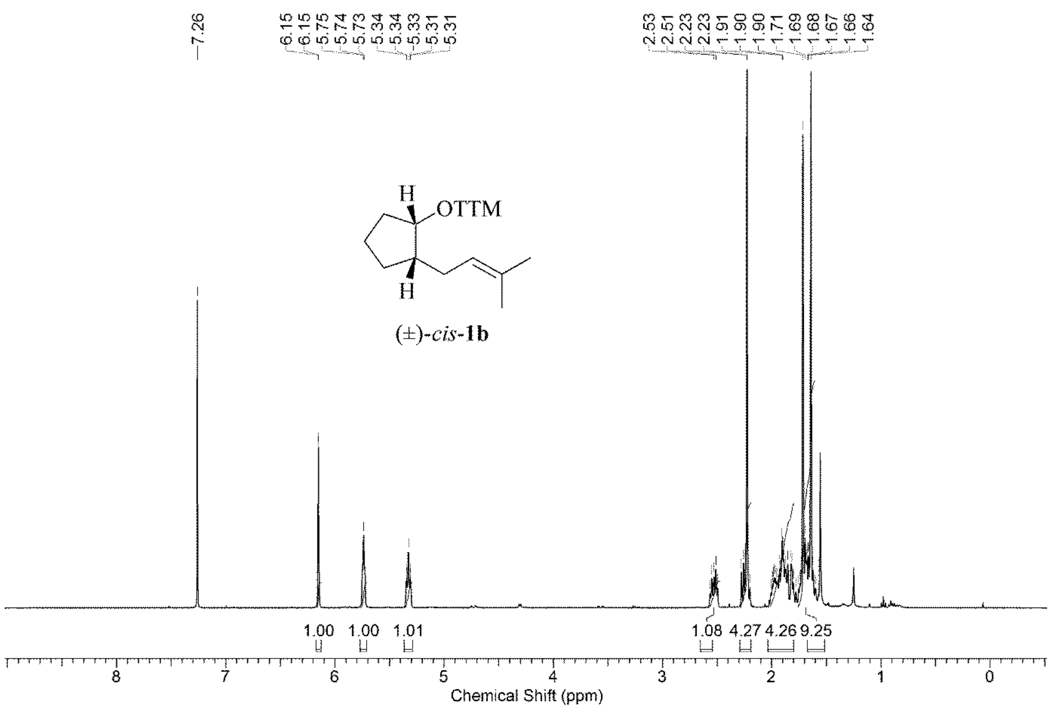


Figure S53. Proton-1 NMR-spectrum of 3-[*cis*-2-(3-methylbut-2-en-1-yl)-cyclopent-1-yloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1b**) (400MHz, $CDCl_3$, 23 °C).

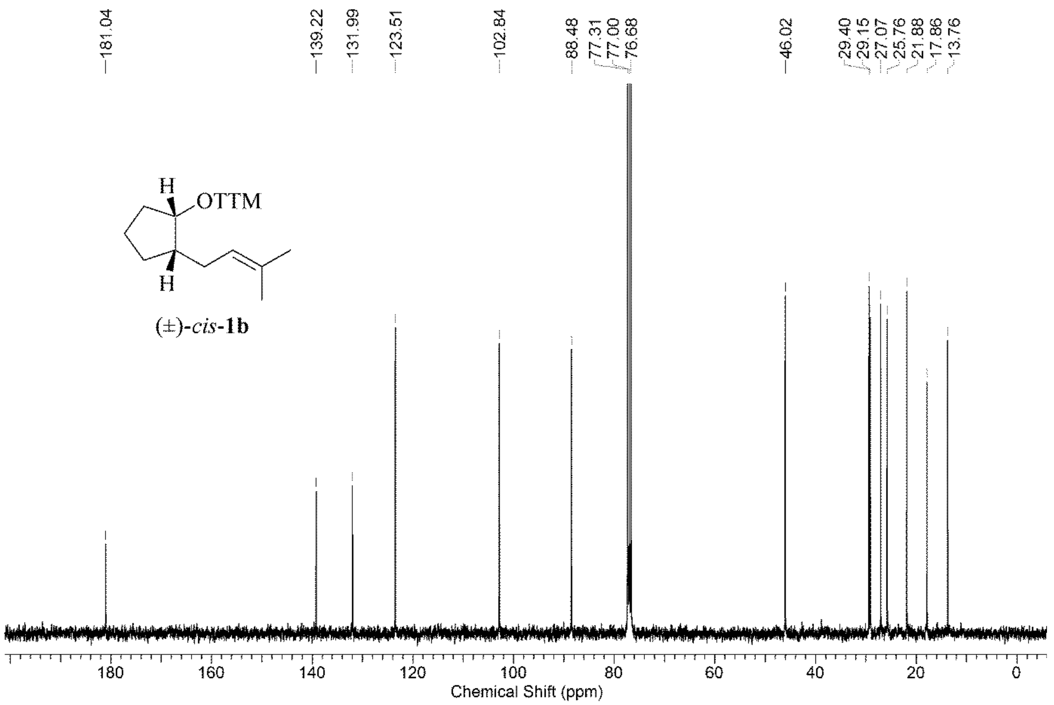


Figure S54. Carbon-13 NMR-spectrum of 3-[*cis*-2-(3-methylbut-2-en-1-yl)-cyclopent-1-yloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1b**) (100MHz, $CDCl_3$, 23 °C).

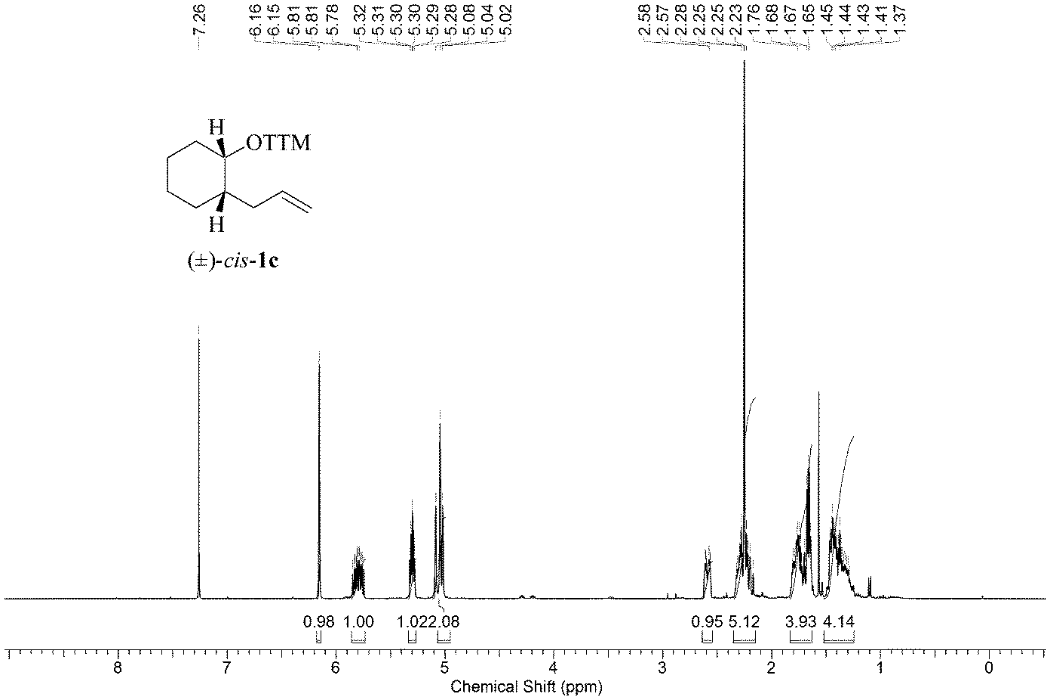


Figure S55. Proton-1 NMR-spectrum of 3-[*cis*-2-(prop-2-en-1-yl)-cyclohex-1-yloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1c**) (400MHz, $CDCl_3$, 23 °C).

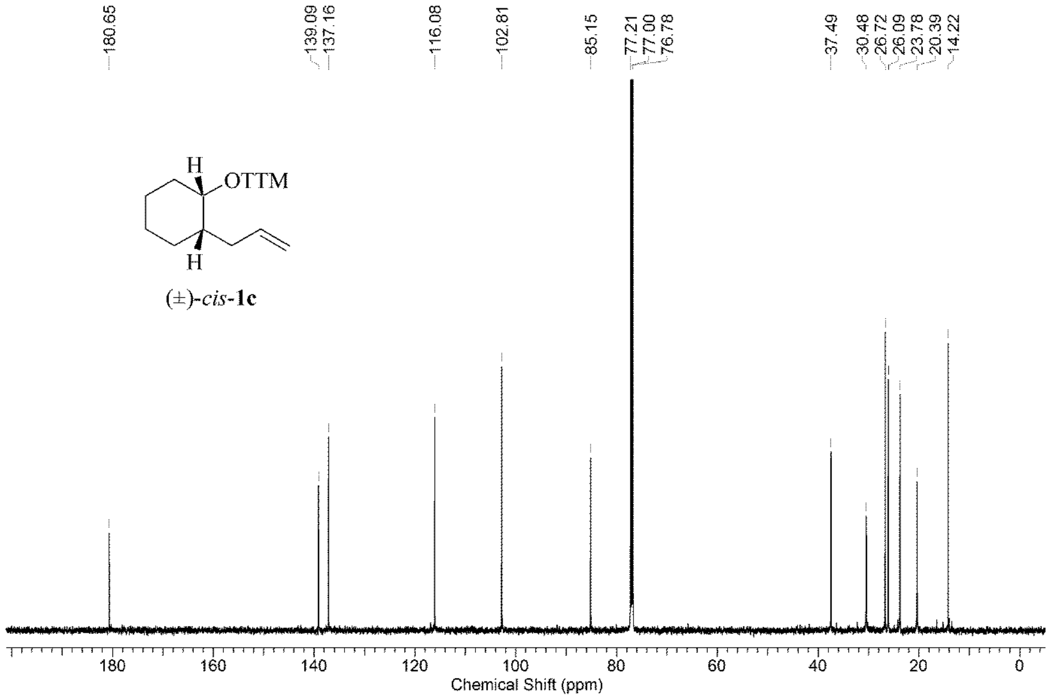


Figure S56. Carbon-13 NMR-spectrum of 3-[*cis*-2-(prop-2-en-1-yl)-cyclohex-1-yloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1c**) (150MHz, $CDCl_3$, 23 °C).

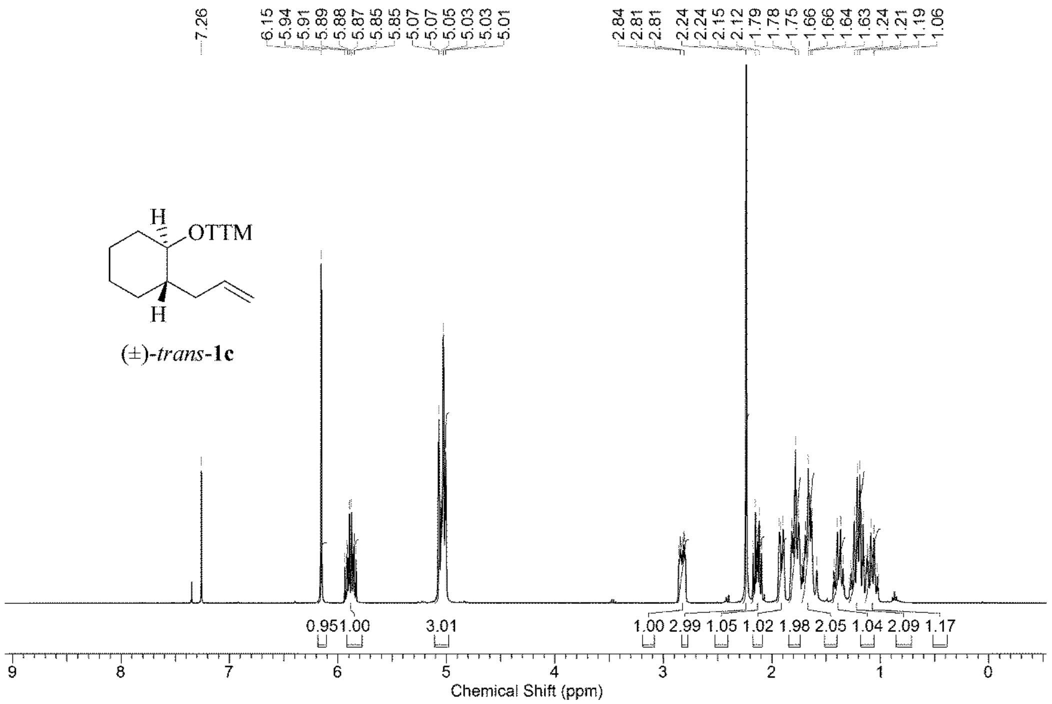


Figure S57. Proton-1 NMR-spectrum of 3-[*trans*-2-(prop-2-en-1-yl)-cyclohex-1-yloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1c**) (400MHz, $CDCl_3$, 23 °C).

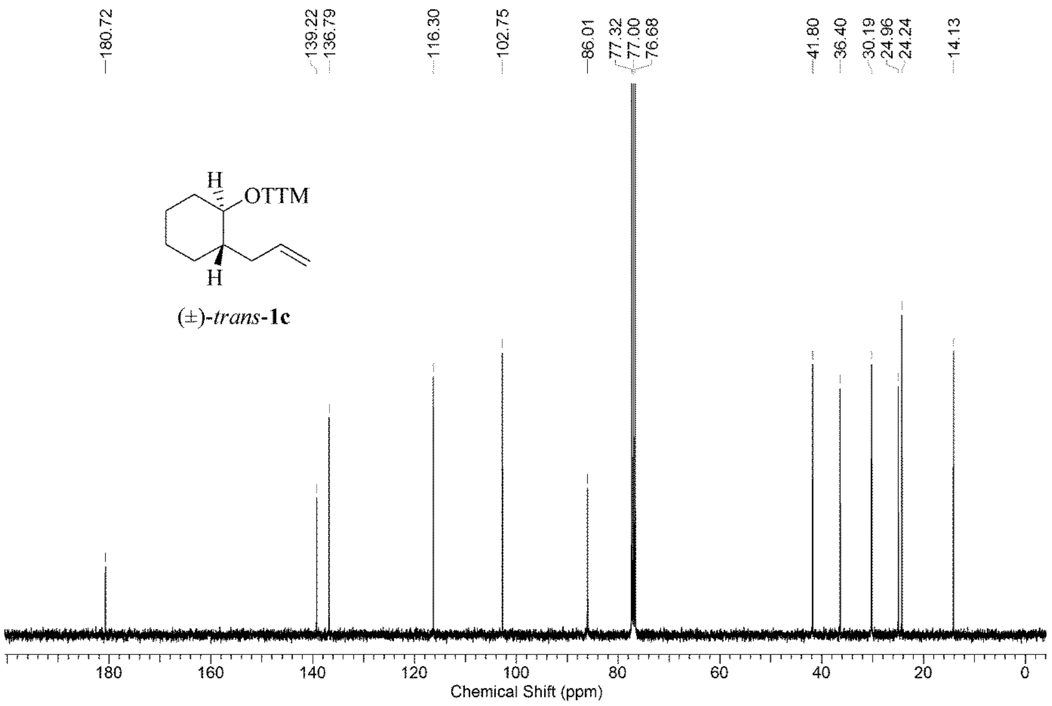


Figure S58. Carbon-13 NMR-spectrum of 3-[*trans*-2-(prop-2-en-1-yl)-cyclohex-1-yloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1c**) (100MHz, $CDCl_3$, 23 °C).

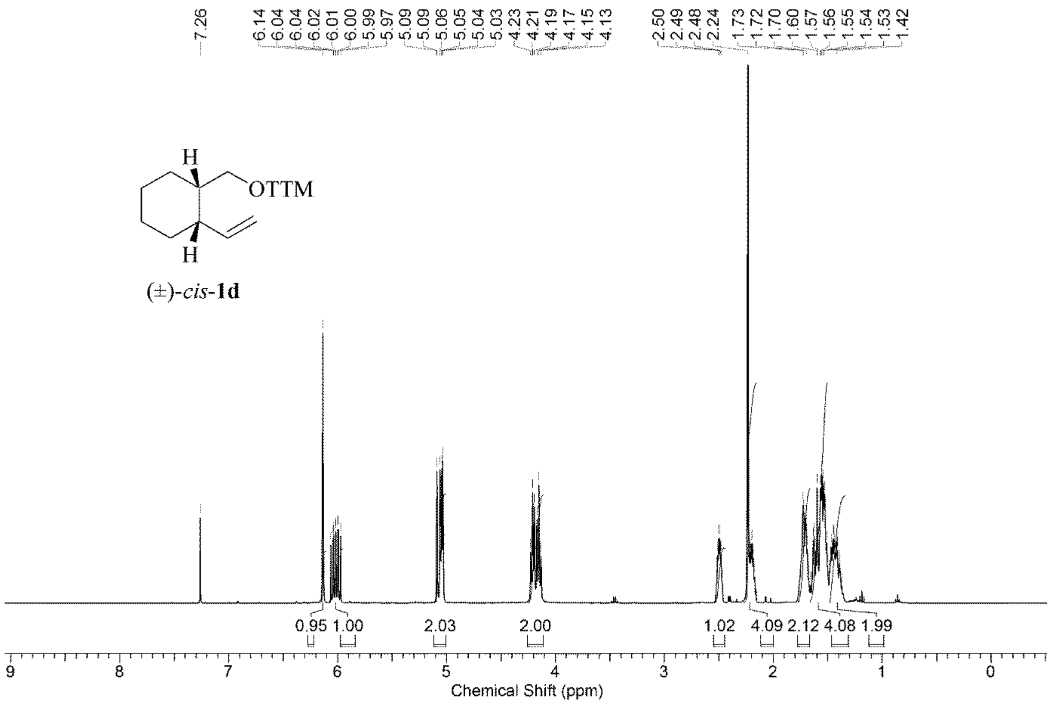


Figure S59. Proton-1 NMR-spectrum of 3-[*cis*-2-(eth-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1d**) (400MHz, $CDCl_3$, 23 °C).

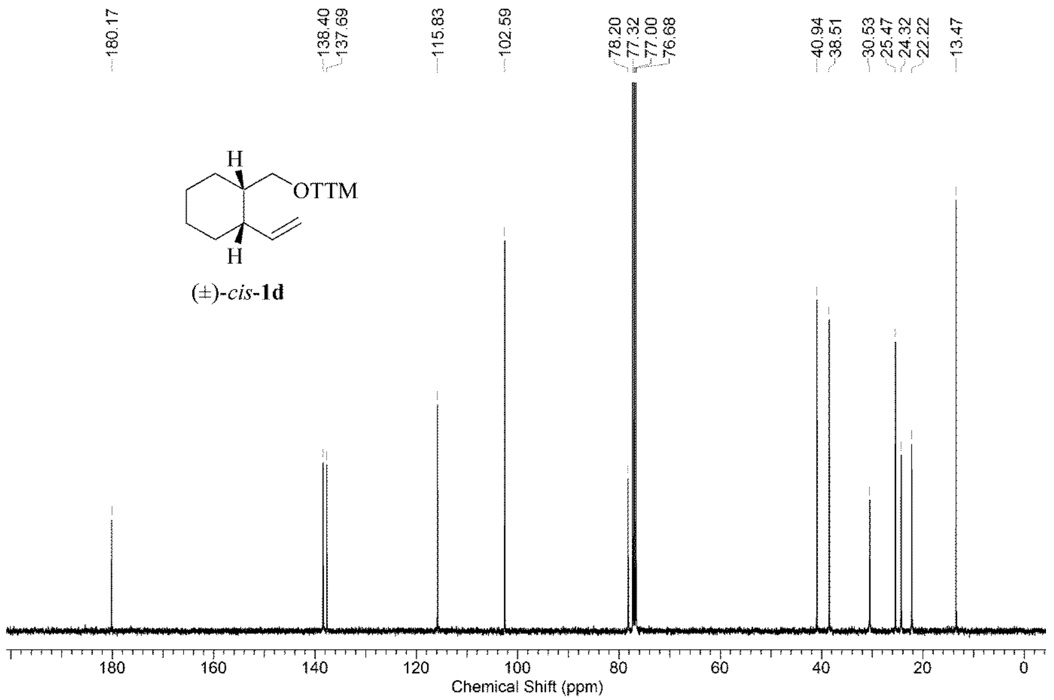


Figure S60. Carbon-13 NMR-spectrum of 3-[*cis*-2-(eth-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1d**) (100MHz, $CDCl_3$, 23 °C).

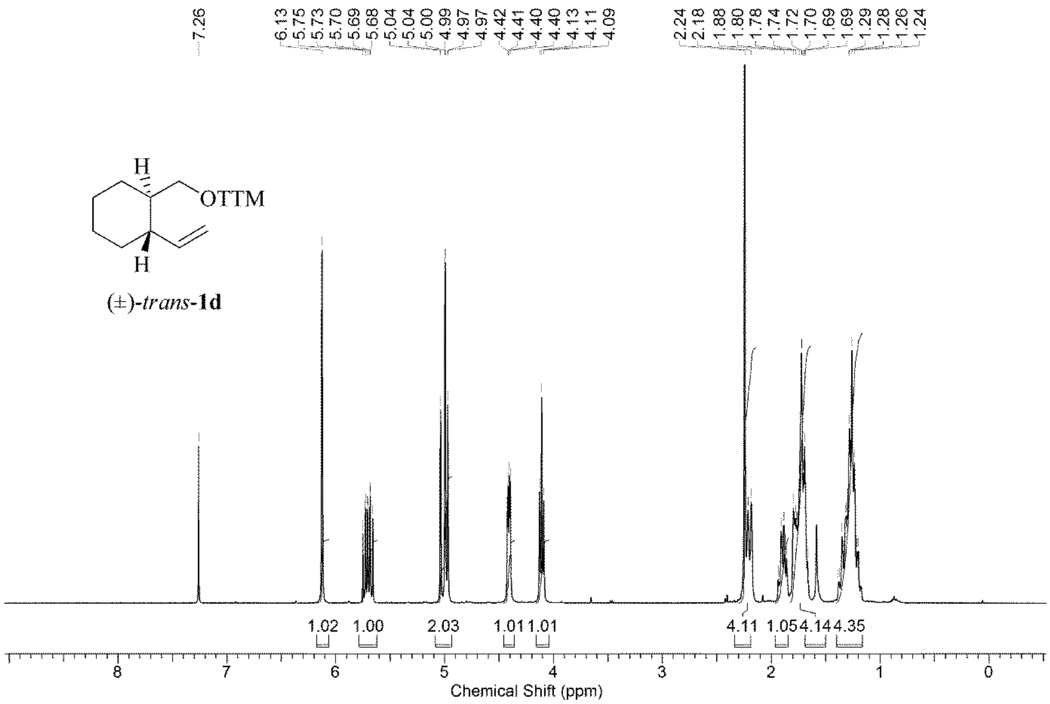


Figure S61. Proton-1 NMR-spectrum of 3-[*trans*-2-(eth-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1d**) (400MHz, $CDCl_3$, 23 °C).

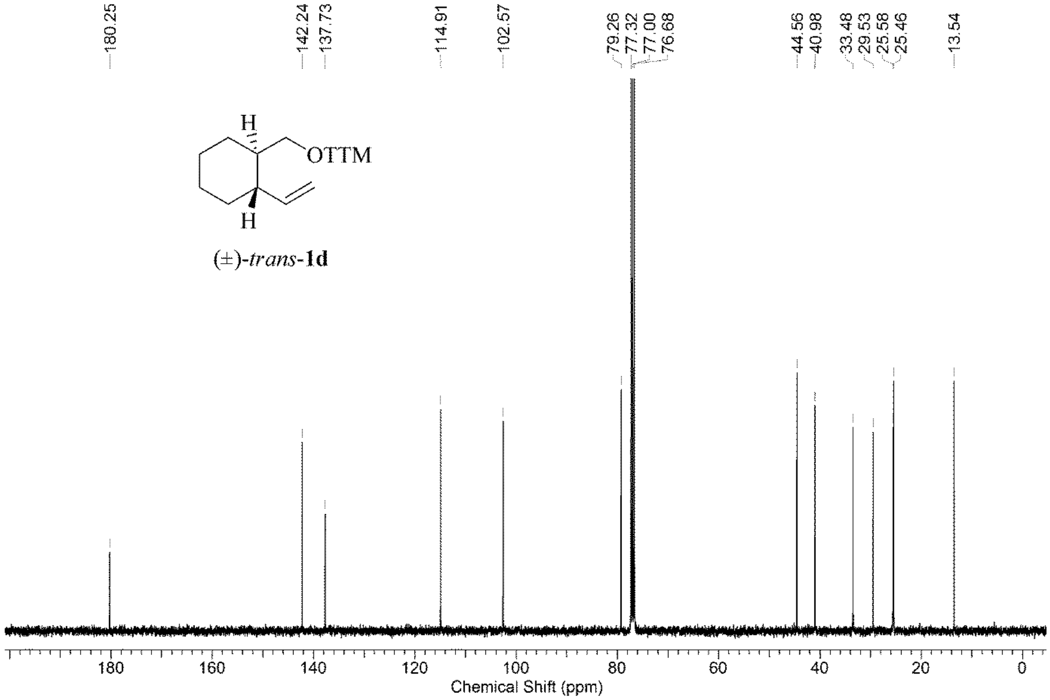


Figure S62. Carbon-13 NMR-spectrum of 3-[*trans*-2-(eth-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1d**) (100MHz, $CDCl_3$, 23 °C).

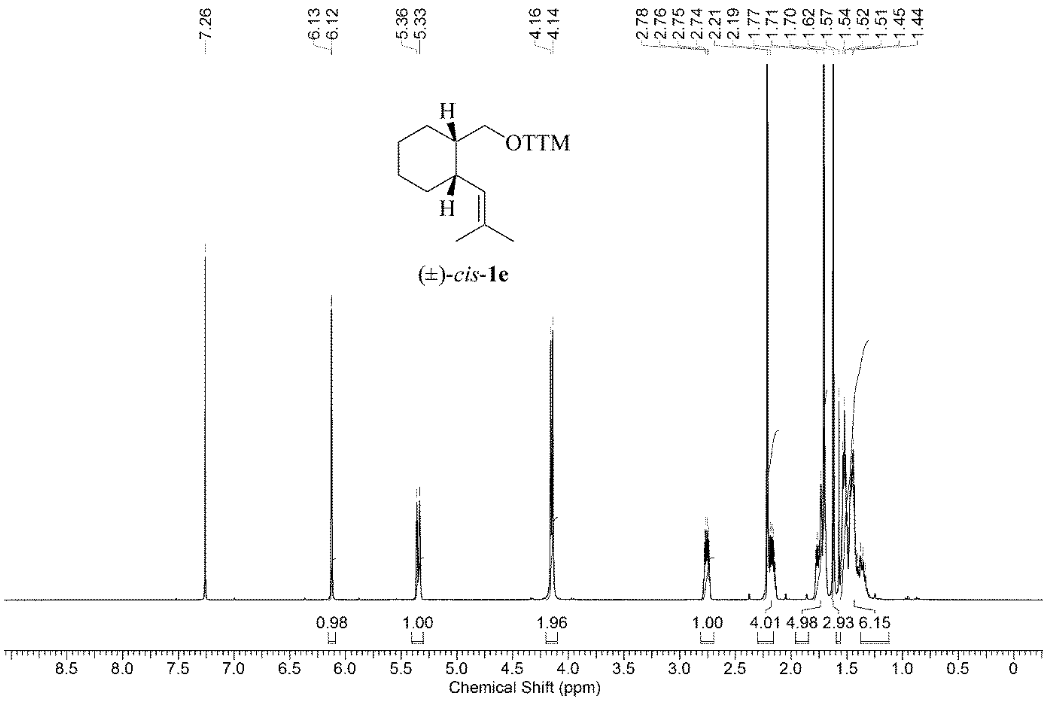


Figure S63. Proton-1 NMR-spectrum of 3-[*cis*-2-(2-methylprop-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1e**) (400MHz, $CDCl_3$, 23 °C).

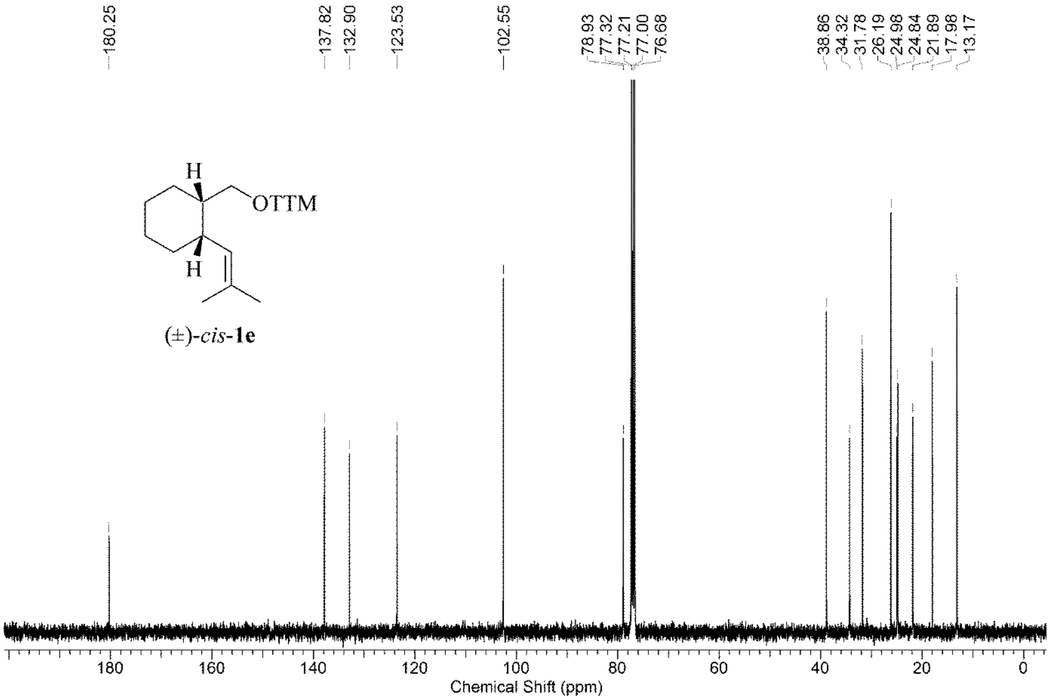


Figure S64. Carbon-13 NMR-spectrum of 3-[*cis*-2-(2-methylprop-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *cis*-(**1e**) (100MHz, $CDCl_3$, 23 °C).

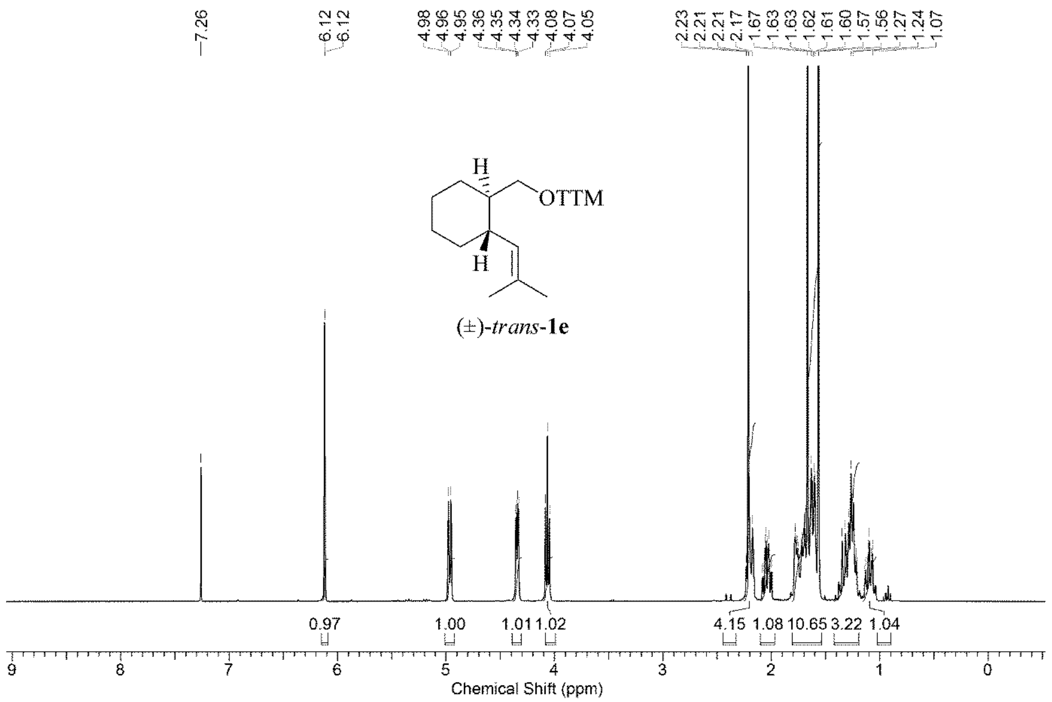


Figure S65. Proton-1 NMR-spectrum of 3-[*trans*-2-(2-methylprop-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1e**) (400MHz, $CDCl_3$, 23 °C).

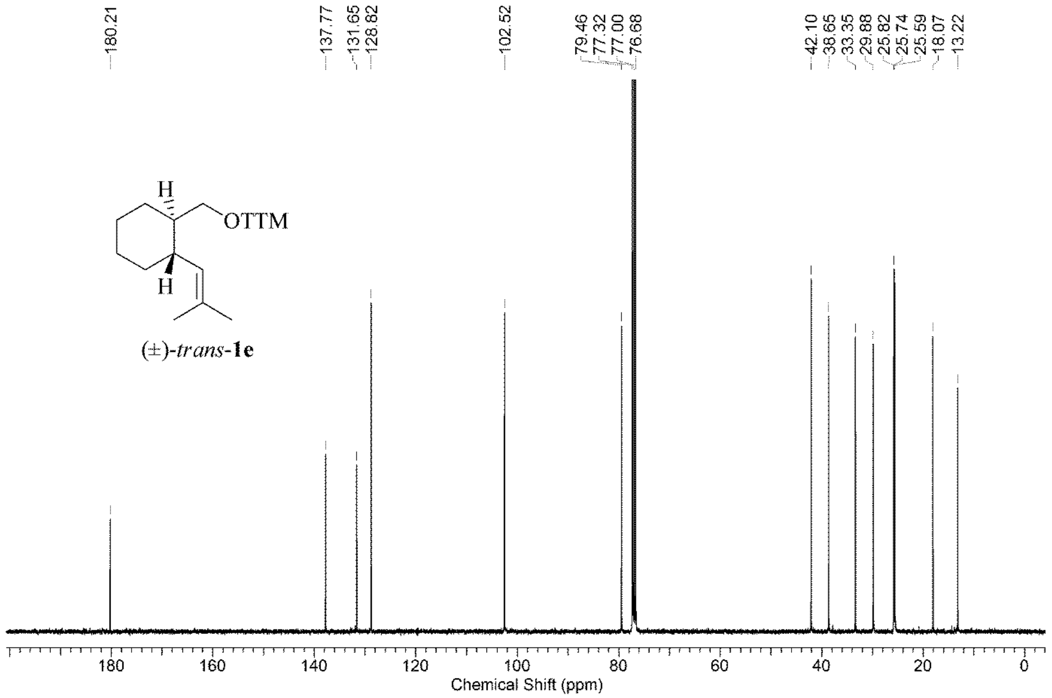


Figure S66. Carbon-13 NMR-spectrum of 3-[*trans*-2-(2-methylprop-1-en-1-yl)-cyclohex-1-ylmethyloxy]-4-methylthiazole-2(3*H*)-thione *trans*-(**1e**) (100MHz, $CDCl_3$, 23 °C).

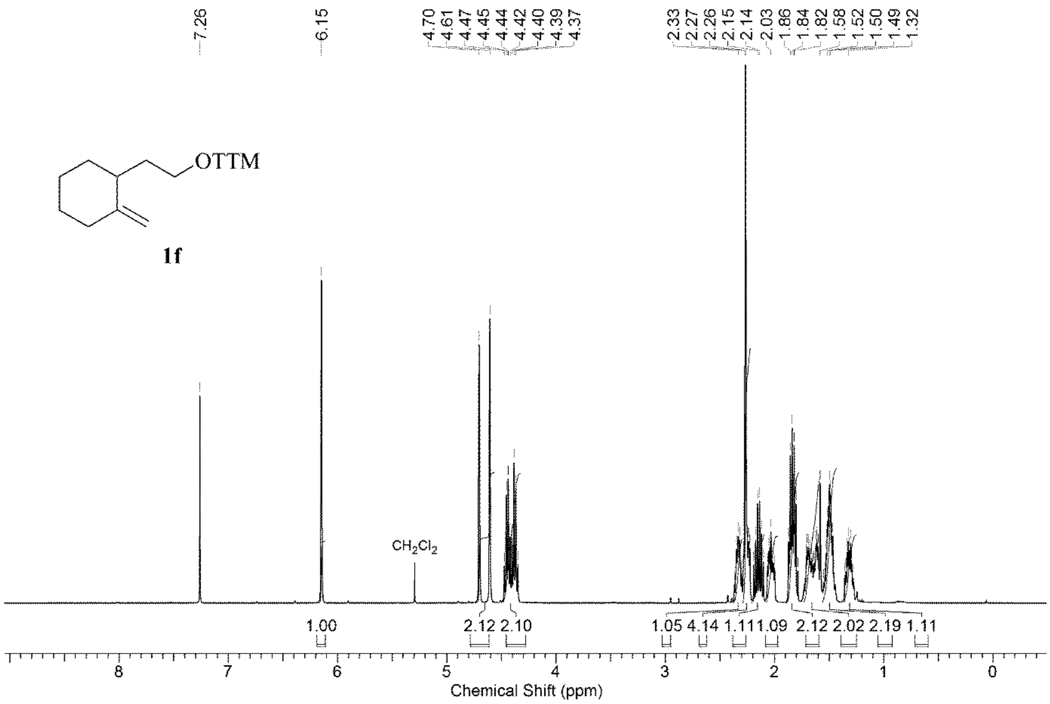


Figure S67. Proton-1 NMR-spectrum of 3-[2-(1-methylenecyclohex-2-yl)-eth-1-yl-2-oxy]-4-methylthiazole-2(3*H*)-thione (**1f**) (400MHz, $CDCl_3$, 23 °C).

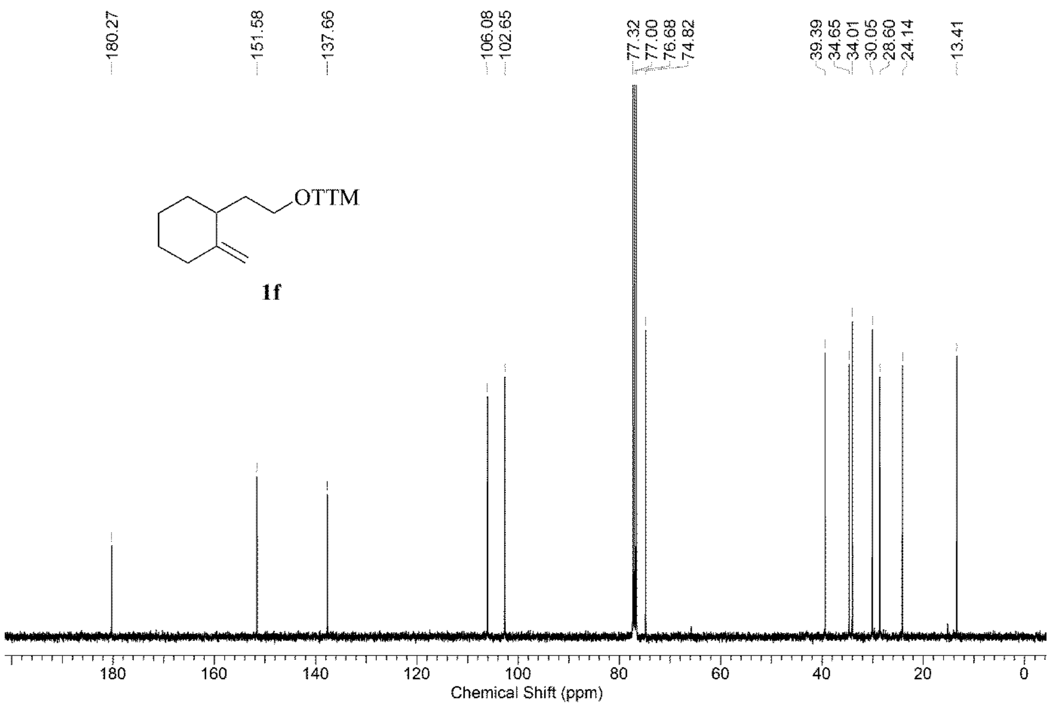


Figure S68. Carbon-13 NMR-spectrum of 3-[2-(1-methylenecyclohex-2-yl)-eth-1-yl-2-oxy]-4-methylthiazole-2(3*H*)-thione (**1f**) (100MHz, $CDCl_3$, 23 °C).

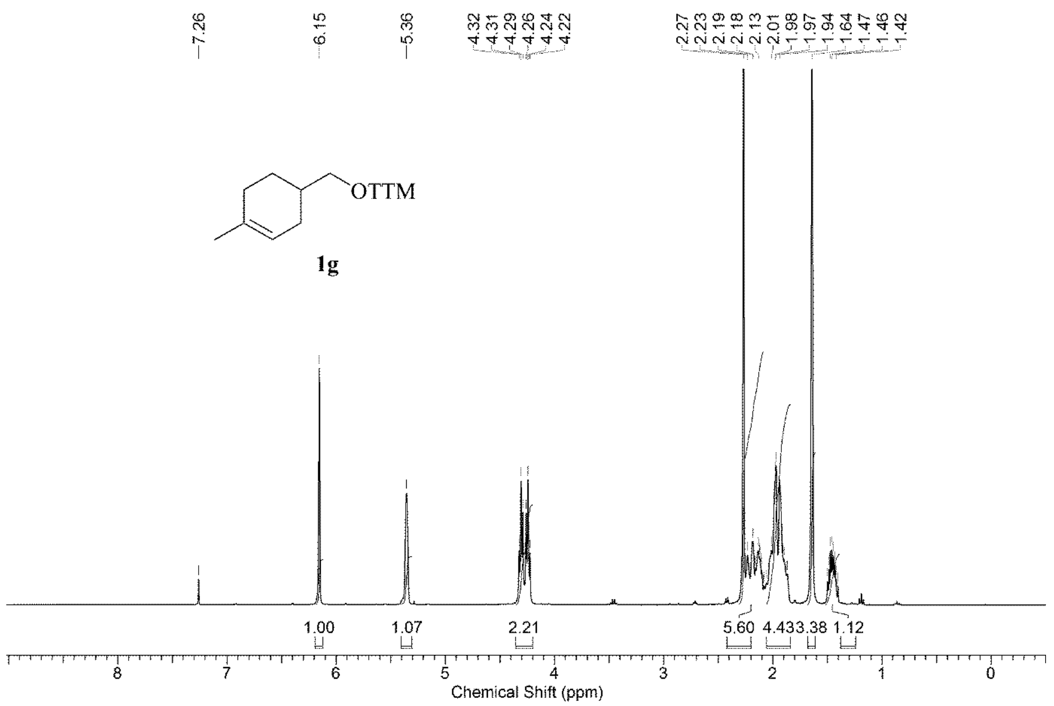


Figure S69. Proton-1 NMR-spectrum of 3-[(1-methylcyclohex-1-en-4-yl)-methyloxy]-4-methylthiazole-2(3*H*)thione (**1g**) (400MHz, $CDCl_3$, 23 °C).

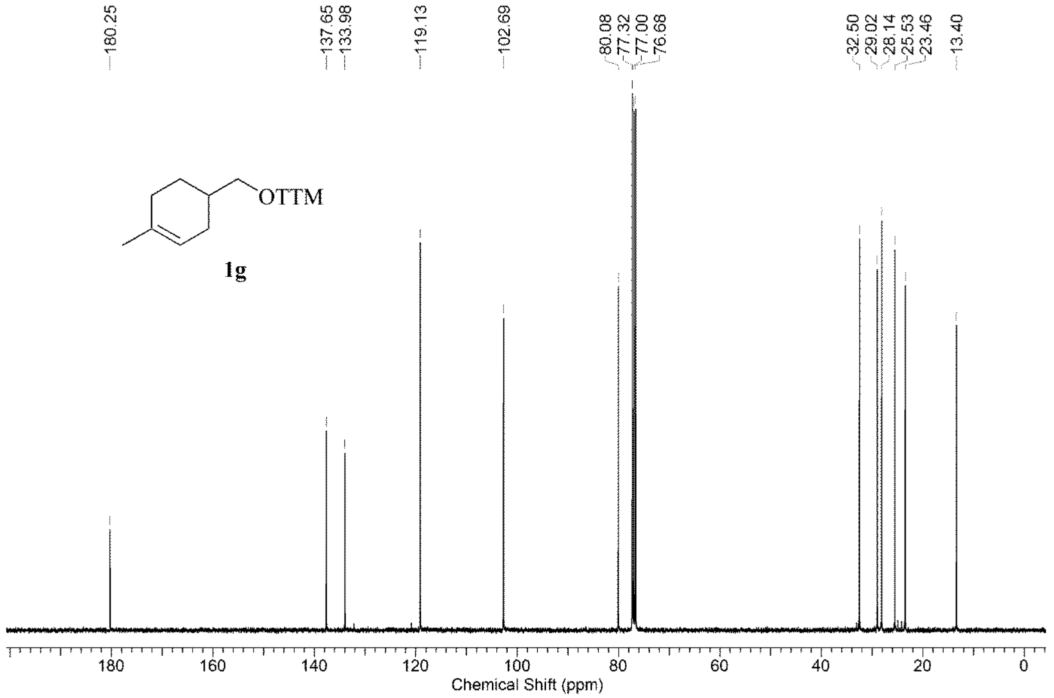


Figure S70. Carbon-13 NMR-spectrum of 3-[(1-methylcyclohex-1-en-4-yl)-methyloxy]-4-methylthiazole-2(3*H*)thione (**1g**) (100MHz, $CDCl_3$, 23 °C).

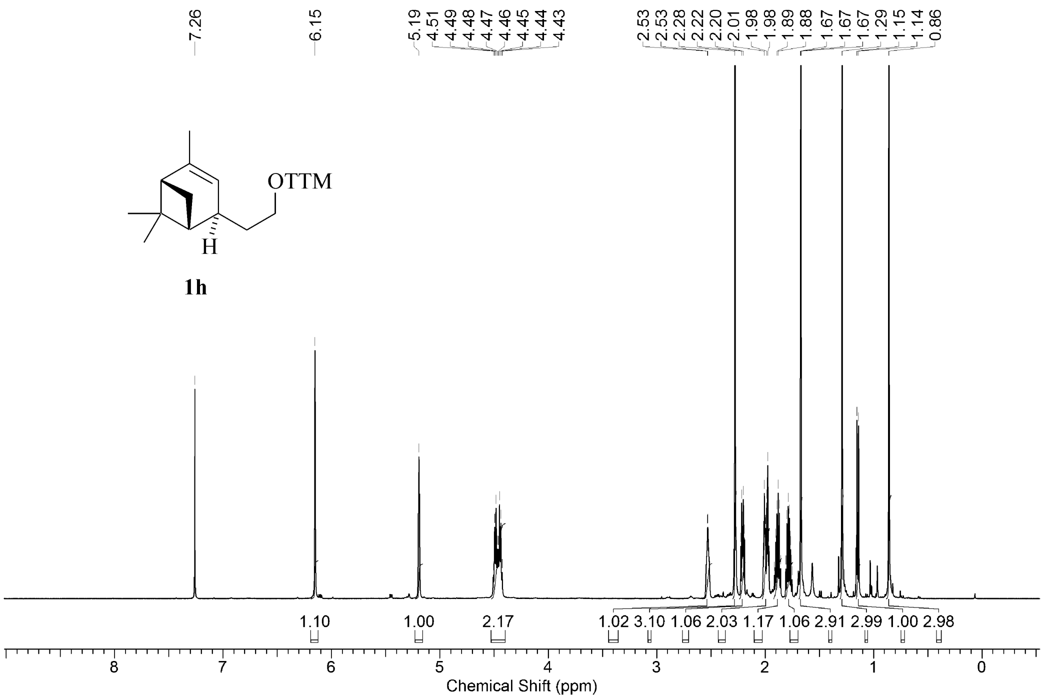


Figure S71. Proton-1 NMR-spectrum of 3-[{(1*S*,4*S*,5*R*)-2,6,6-trimethyl-bicyclo[3.1.1]-hept-2-en-4-yl}eth-1-yl-2-oxy]-4-methylthiazole-2(3*H*)-thione (**1h**) (600MHz, $CDCl_3$, 23 °C).

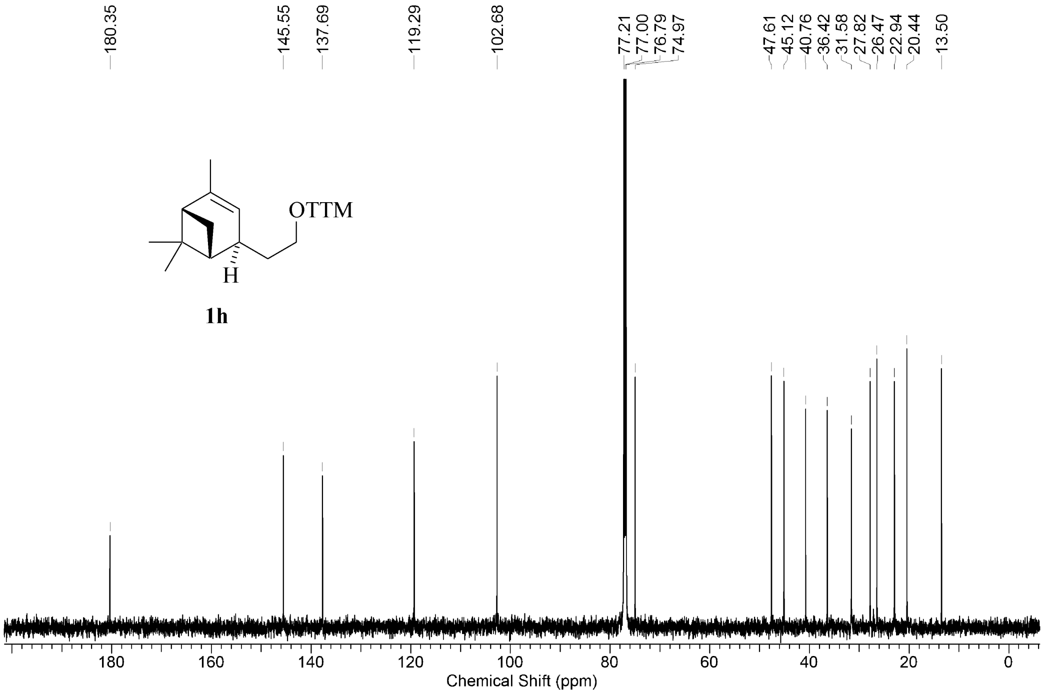


Figure S72. Carbon-13 NMR-spectrum of 3-[{(1*S*,4*S*,5*R*)-2,6,6-trimethyl-bicyclo[3.1.1]-hept-2-en-4-yl}eth-1-yl-2-oxy]-4-methylthiazole-2(3*H*)-thione (**1h**) (150MHz, $CDCl_3$, 23 °C).

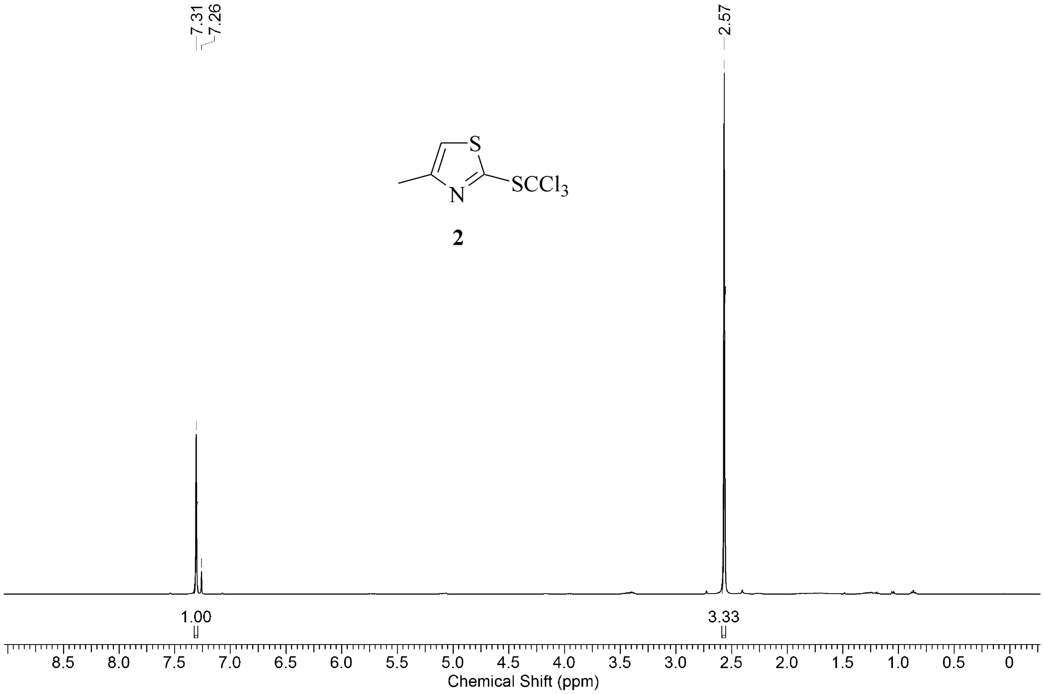


Figure S73. Proton-1 NMR-spectrum of 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (400MHz, $CDCl_3$, 23 °C).

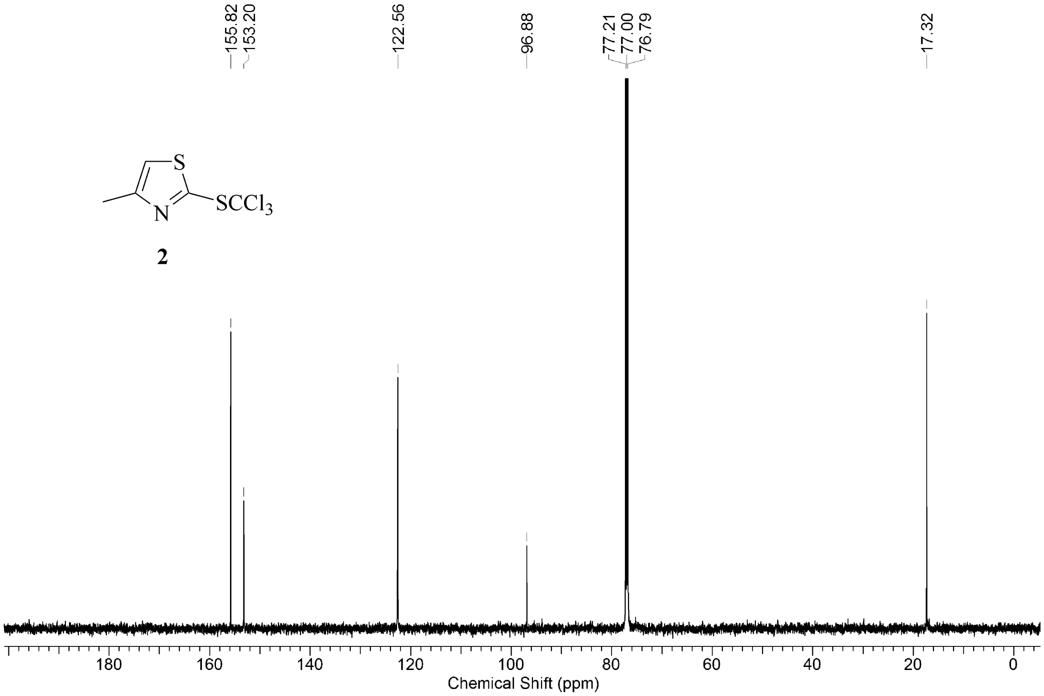


Figure S74. Carbon-13 NMR-spectrum of 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (150MHz, $CDCl_3$, 23 °C).

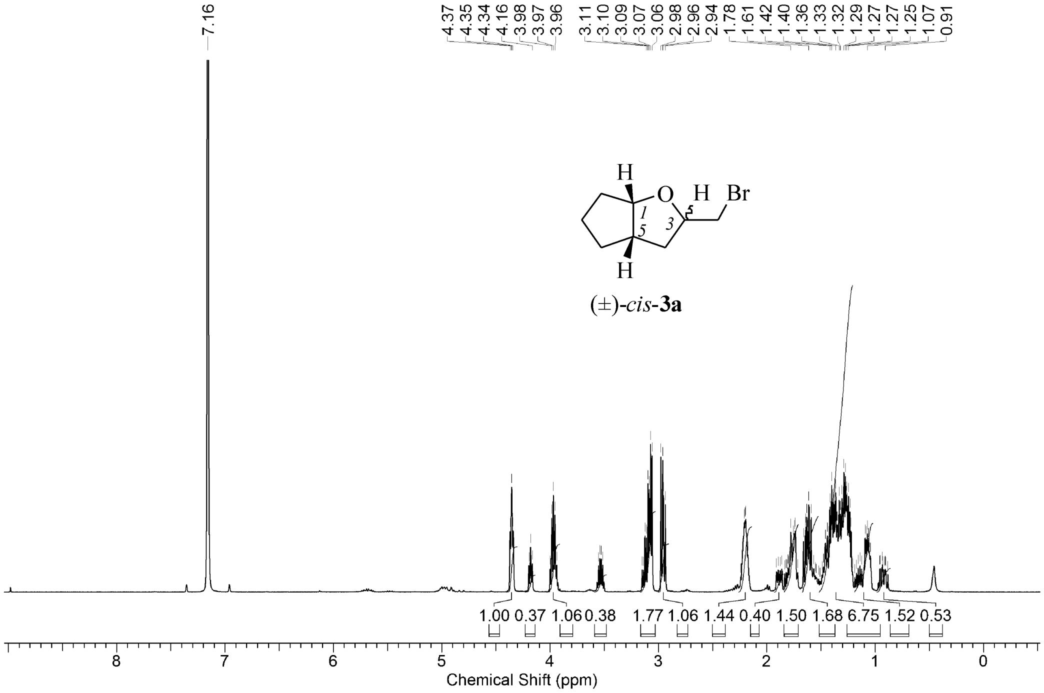


Figure S75. Proton-1 NMR-spectrum of 1,3-cis/trans-isomers, i.e *rel*-(1*S*,3*S*,5*S*)-**3a**/ *rel*-(1*S*,3*R*,5*S*)-**3a**, of 3-bromomethyl-2-oxabicyclo[3.3.0]octane *cis*-(**3a**) (400MHz, C_6D_6, 23 °C).

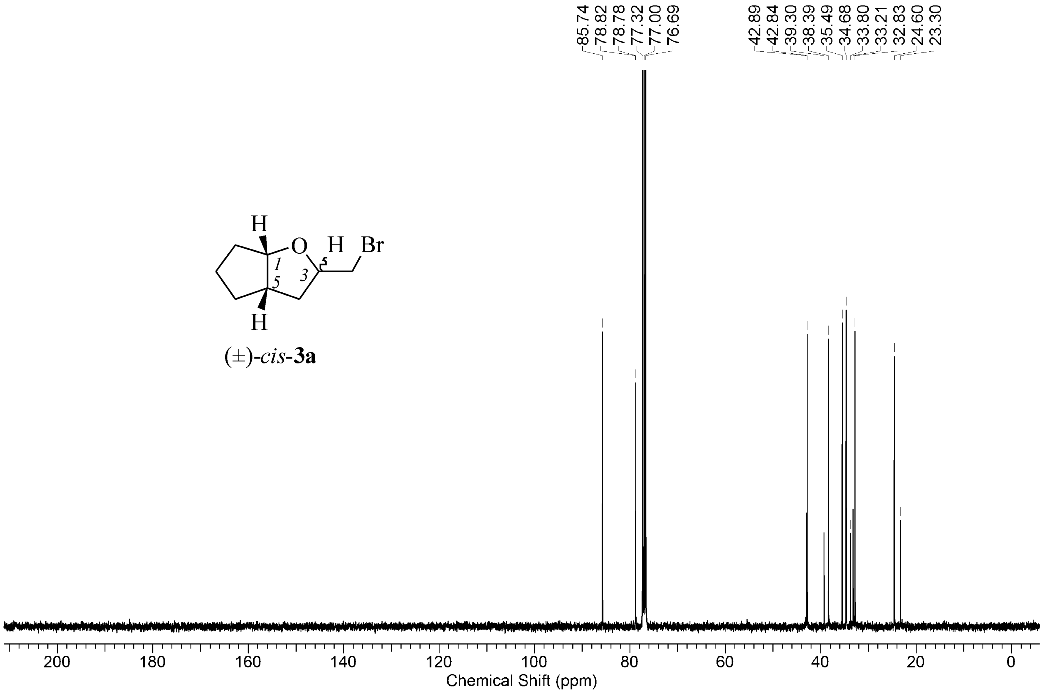


Figure S76. Carbon-13 NMR-spectrum of 1,3-cis/trans-isomers, i.e *rel*-(1*S*,3*S*,5*S*)-**3a**/ *rel*-(1*S*,3*R*,5*S*)-**3**, of 3-bromomethyl-2-oxabicyclo[3.3.0]octane *cis*-(**3a**) (100MHz, $CDCl_3$, 23 °C).

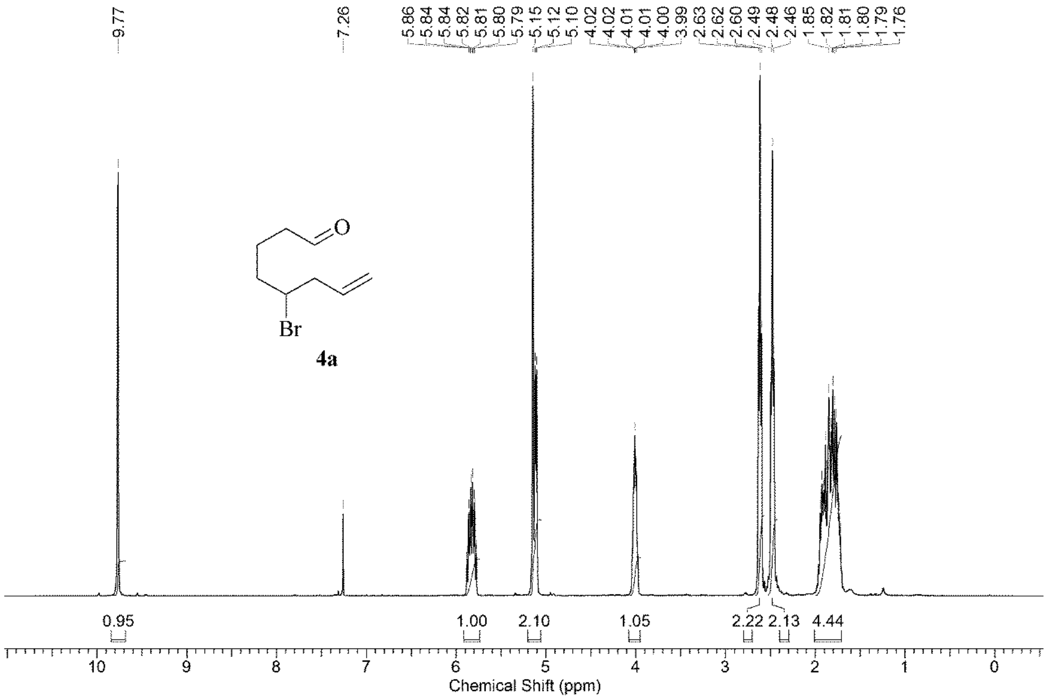


Figure S77. Proton-1 NMR-spectrum of 5-bromoct-7-enal (**4a**) (400MHz, $CDCl_3$, 23 °C).

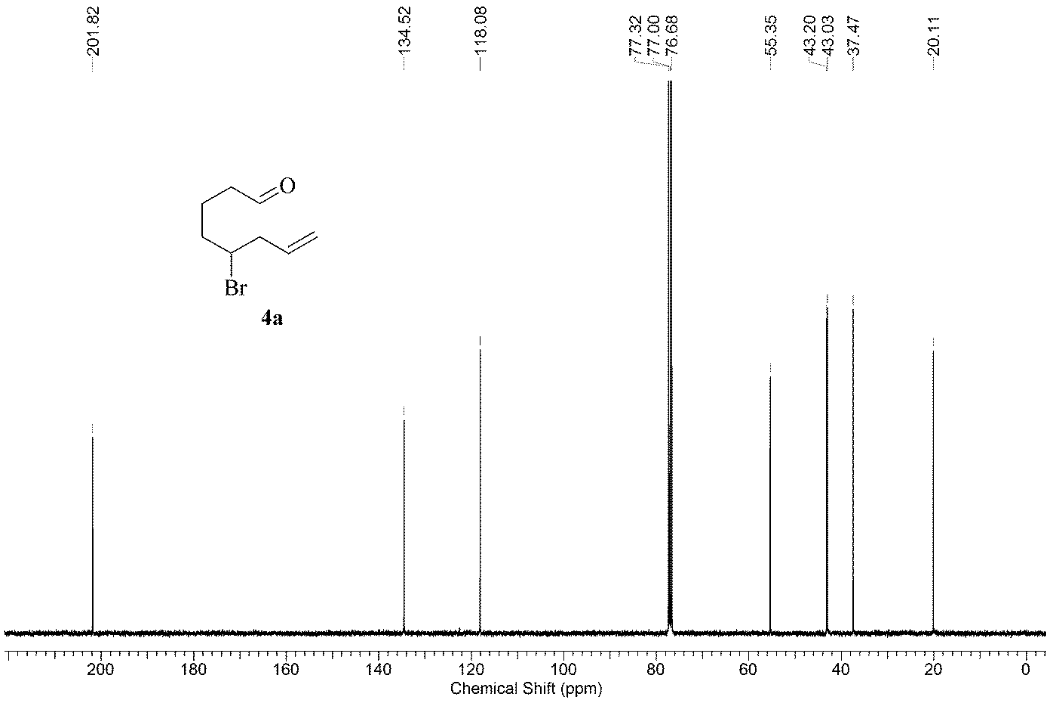


Figure S78. Carbon-13 NMR-spectrum of 5-bromoct-7-enal (**4a**) (100MHz, $CDCl_3$, 23 °C).

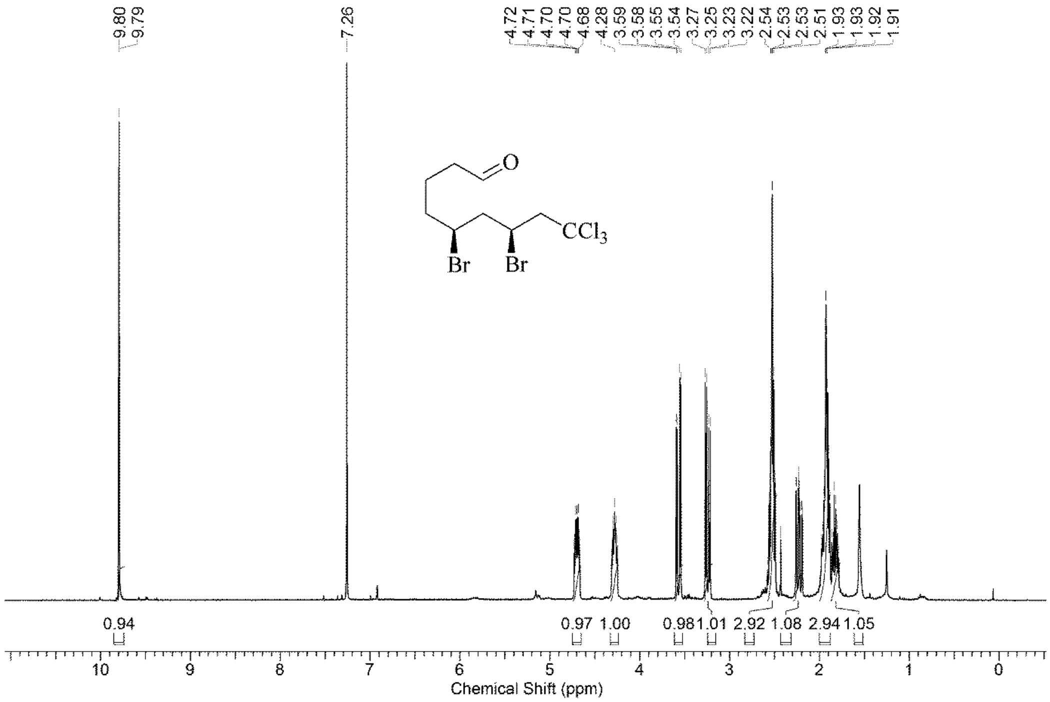


Figure S79. Proton-1 NMR-spectrum of like-5,7-dibromo-9,9,9-trichlorononanal (400MHz, $CDCl_3$, 23 °C).

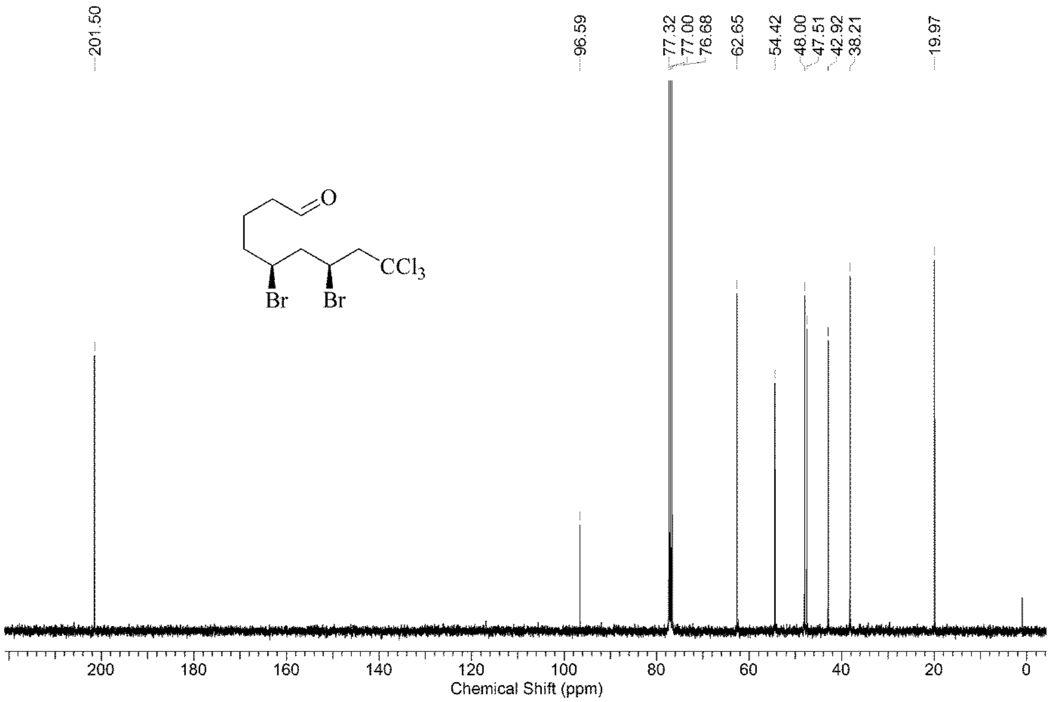


Figure S80. Carbon-13 NMR-spectrum of like-5,7-dibromo-9,9,9-trichlorononanal (100MHz, $CDCl_3$, 23 °C).

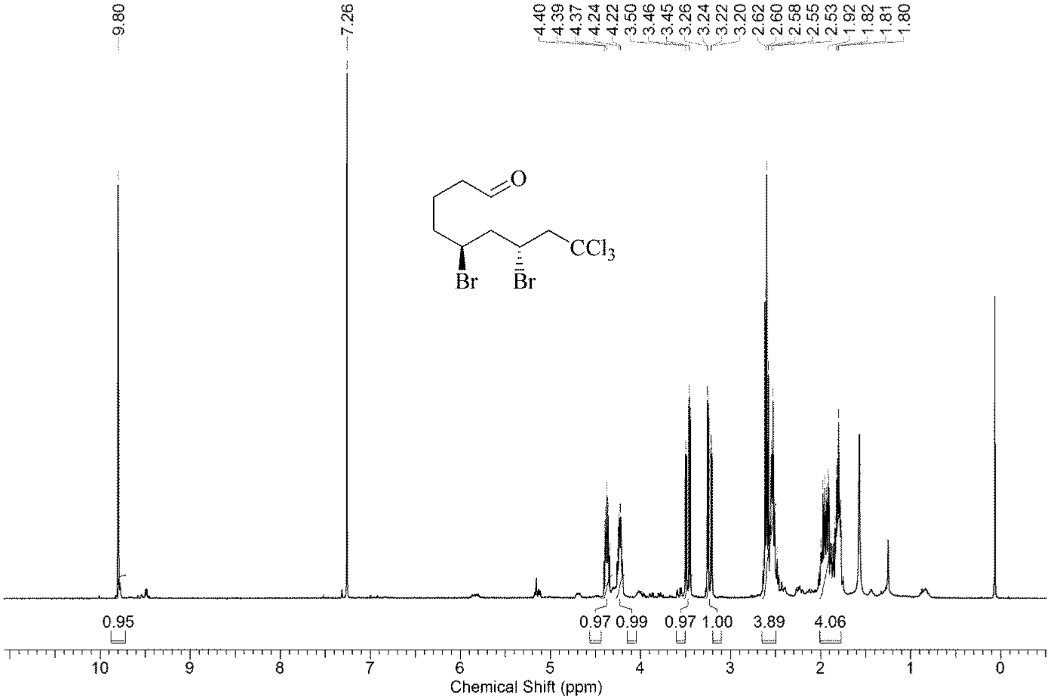


Figure S81. Proton-1 NMR-spectrum of unlike-5,7-dibromo-9,9,9-trichlorononanal (400MHz, $CDCl_3$, 23 °C).

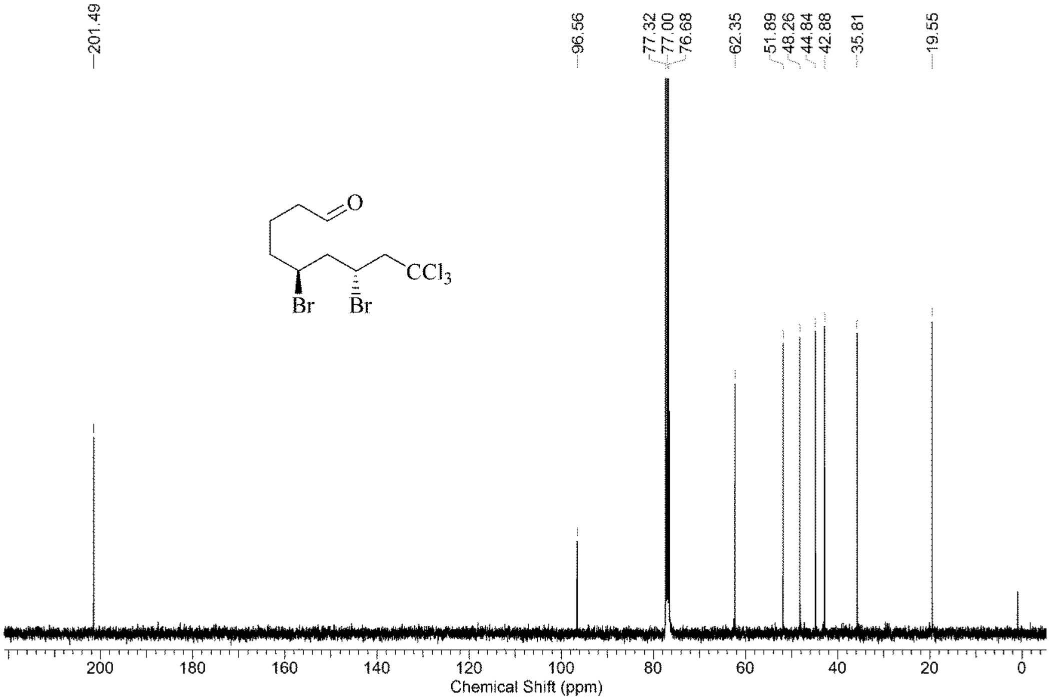


Figure S82. Carbon-13 NMR-spectrum of like-5,7-dibromo-9,9,9-trichlorononanal (100MHz, $CDCl_3$, 23 °C).

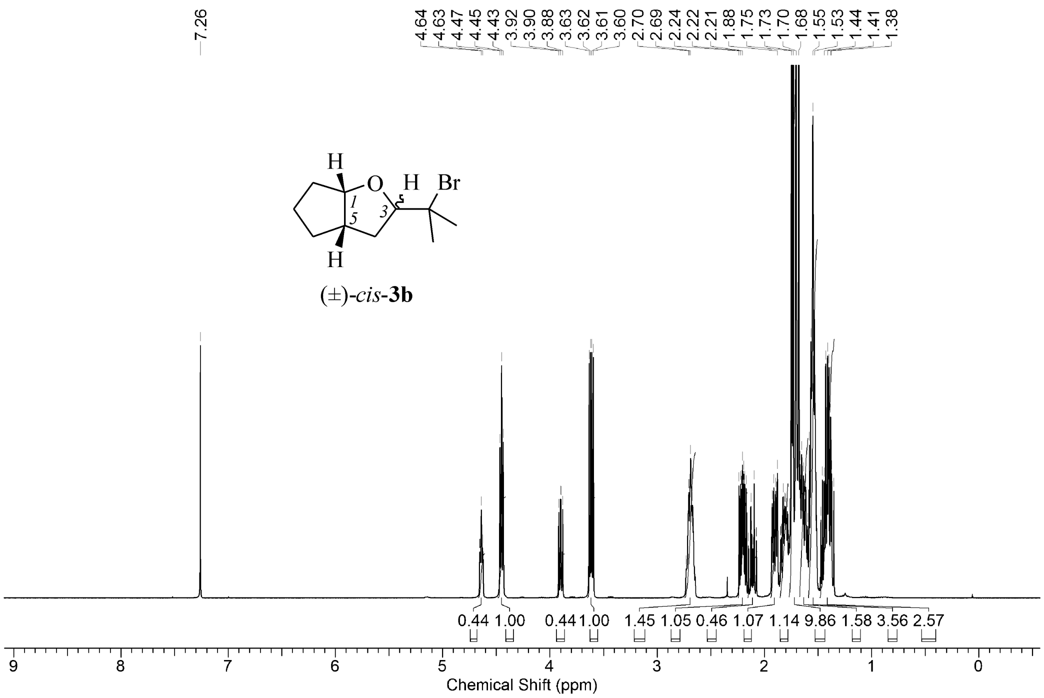


Figure S83. Proton-1 NMR-spectrum of 1,3-cis/trans-isomers, i.e. *rel*-(1*S*,3*S*,5*S*)-**3b**/ *rel*-(1*S*,3*R*,5*S*)-**3b**, of 3-(2-Bromoprop-2-yl)-2-oxabicyclo[3.3.0]octane *cis*-(**3b**) (400MHz, $CDCl_3$, 23 °C).

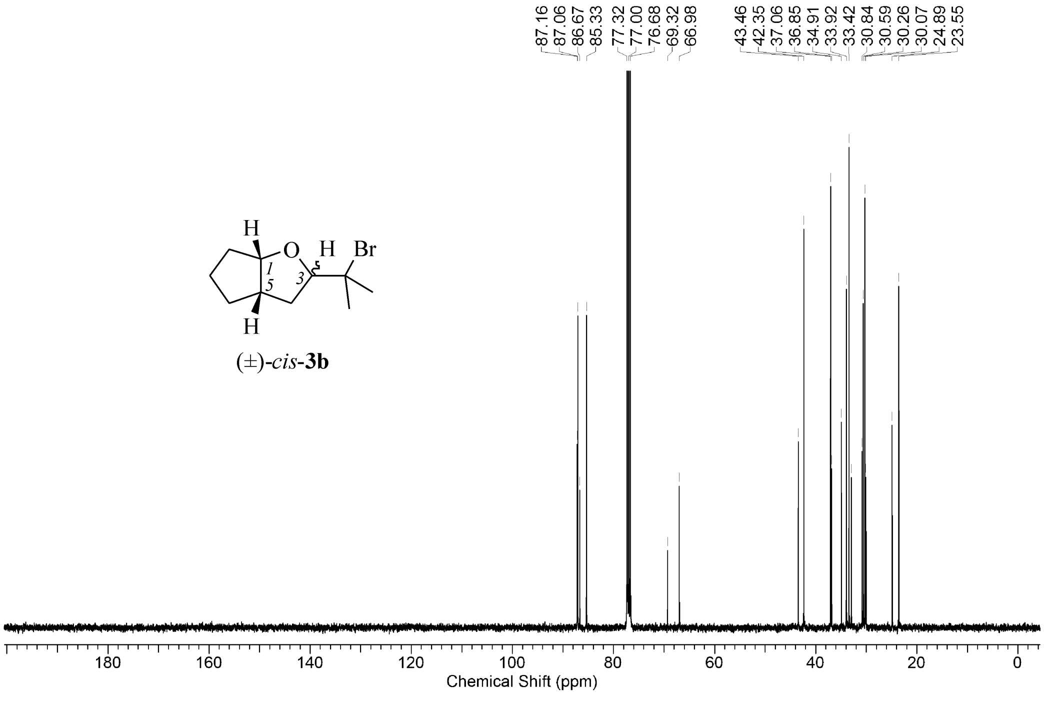


Figure S84. Carbon-13 NMR-spectrum of 1,3-cis/trans-isomers, i.e *rel*-(1*S*,3*S*,5*S*)-**3b**/ *rel*-(1*S*,3*R*,5*S*)-**3b**, of 3-(2-Bromoprop-2-yl)-2-oxabicyclo[3.3.0]octane *cis*-(**3b**) (100MHz, $CDCl_3$, 23 °C).

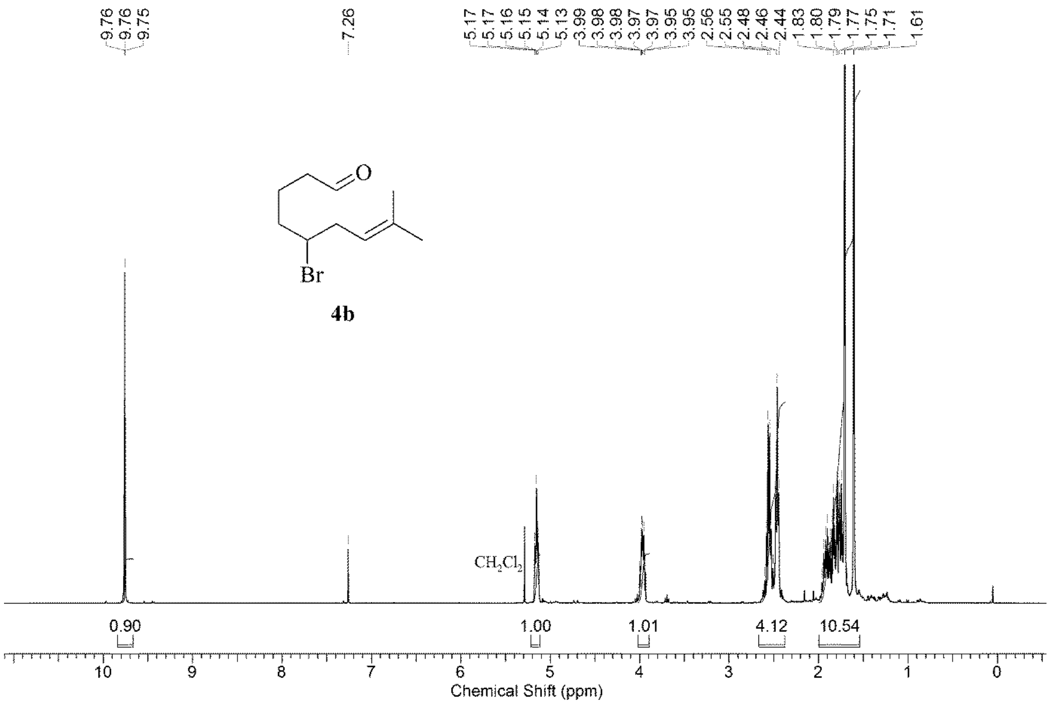


Figure S85. Proton-1 NMR-spectrum of 5-brom-8-methylnon-7-enal (**4b**) (400MHz, CDCl$_3$, 23 °C).

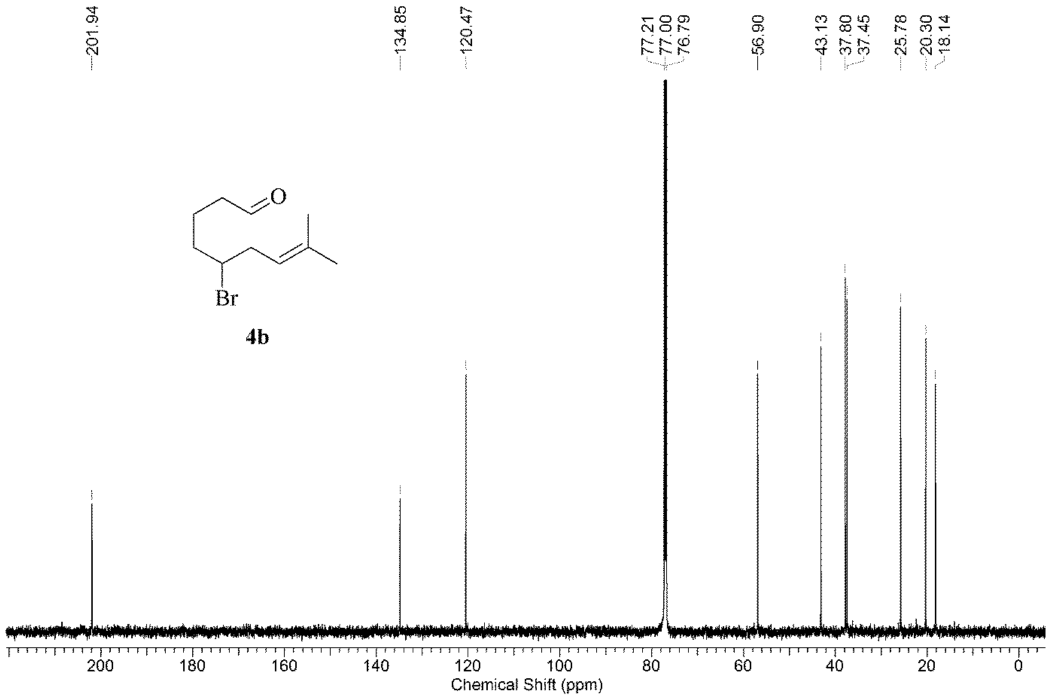


Figure S86. Carbon-13 NMR-spectrum of 5-brom-8-methylnon-7-enal (**4b**) (150MHz, CDCl$_3$, 23 °C).

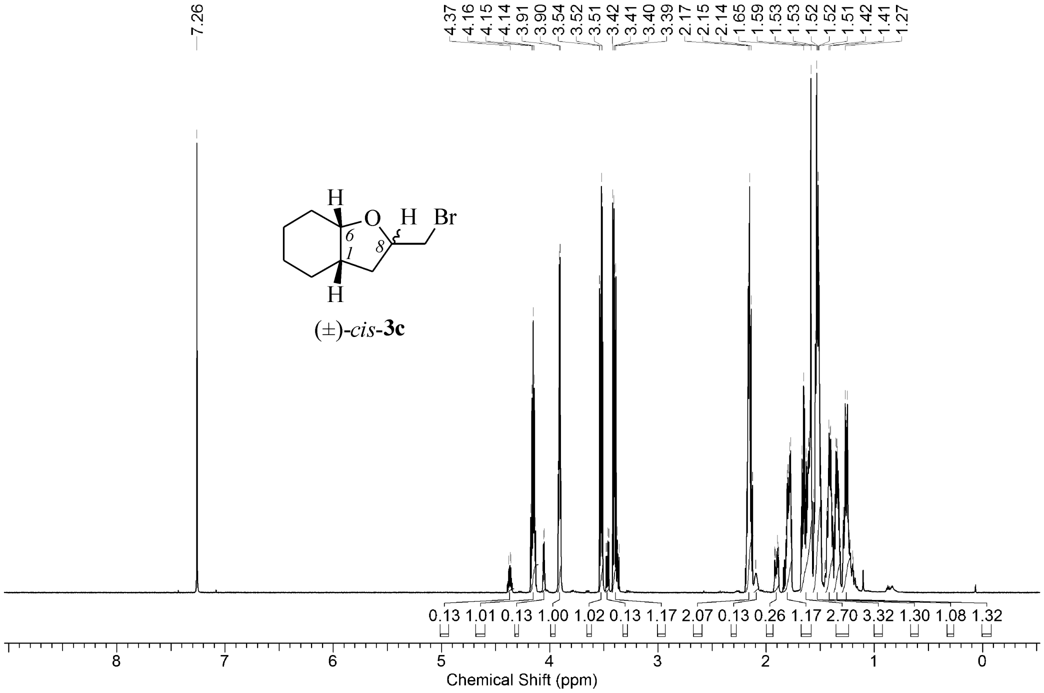


Figure S87. Proton-1 NMR-spectrum of 6,8-cis/trans-isomers, i.e *rel*-(1*S*,6*S*,8*S*)-**3c**/ *rel*-(1*S*,6*S*,8*R*)-**3c**, of 8-(bromomethyl)-7-oxabicyclo[4.3.0]nonane *cis*-(**3c**) (600MHz, $CDCl_3$, 23 °C).

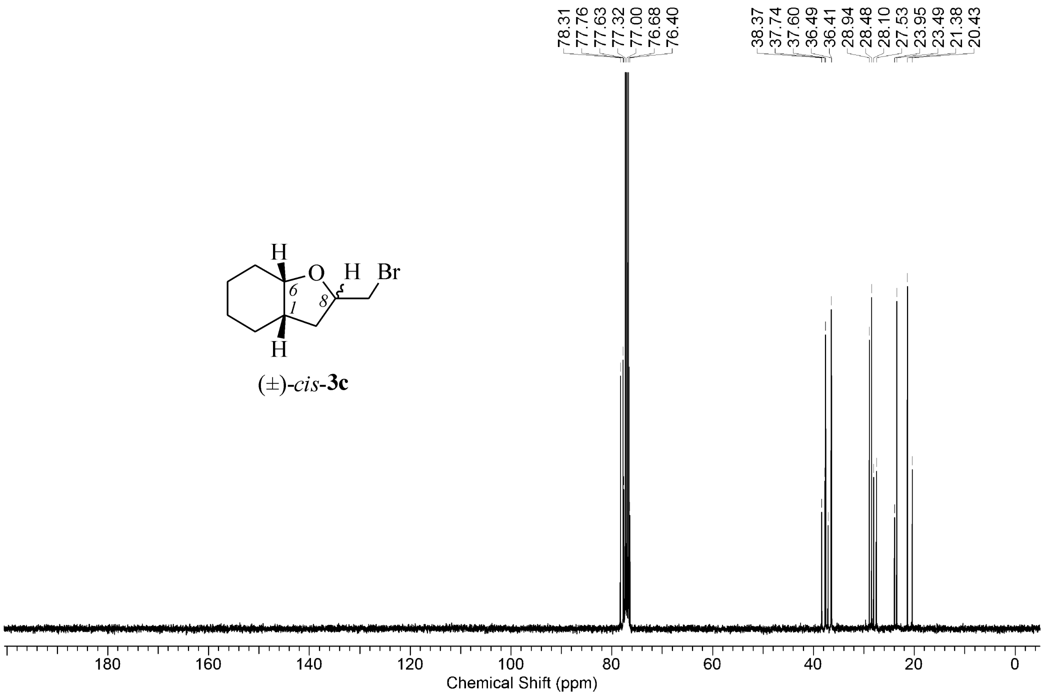


Figure S88. Carbon-13 NMR-spectrum of 6,8-cis/trans-isomers, i.e *rel*-(1*S*,6*S*,8*S*)-**3c**/ *rel*-(1*S*,6*S*,8*R*)-**3c**, of 8-(bromomethyl)-7-oxabicyclo[4.3.0]nonane *cis*-(**3c**) (100MHz, $CDCl_3$, 23 °C).

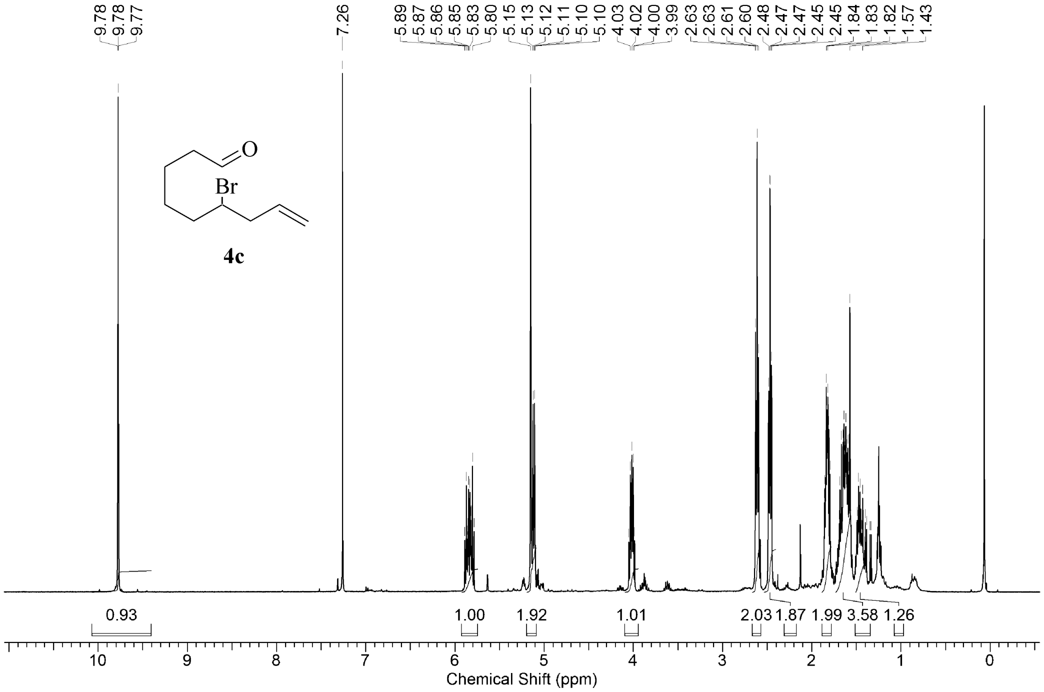


Figure S89. Proton-1 NMR-spectrum of 6-bromo-8-nonenal (**4c**) (400MHz, $CDCl_3$, 23 °C).

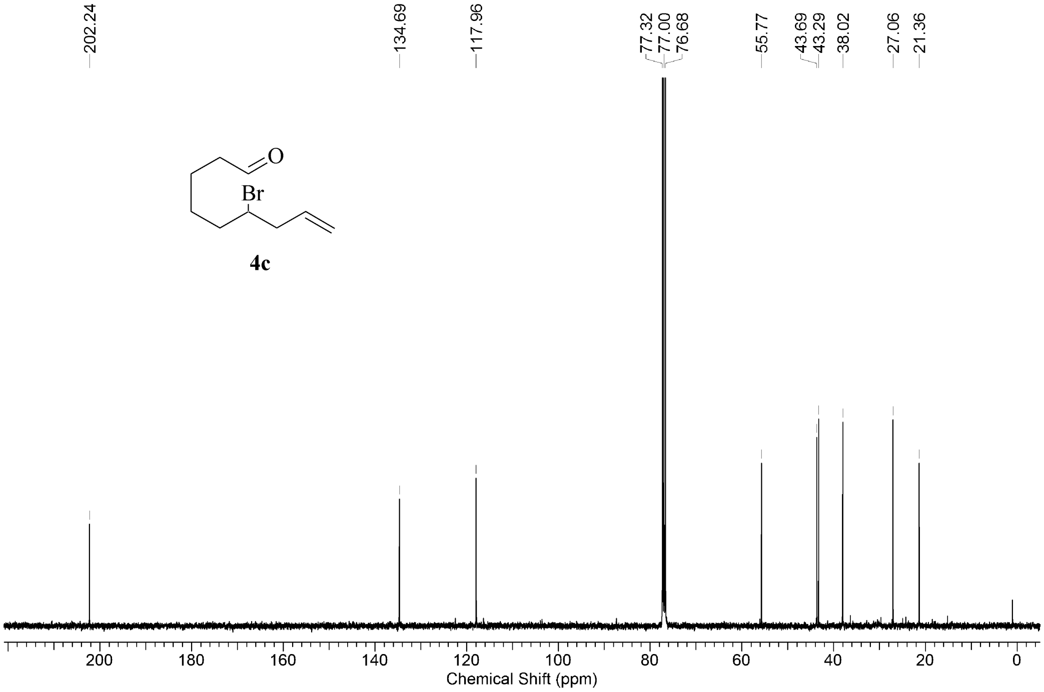


Figure S90. Carbon-13 NMR-spectrum of 6-bromo-8-nonenal (**4c**) (100MHz, $CDCl_3$, 23 °C).

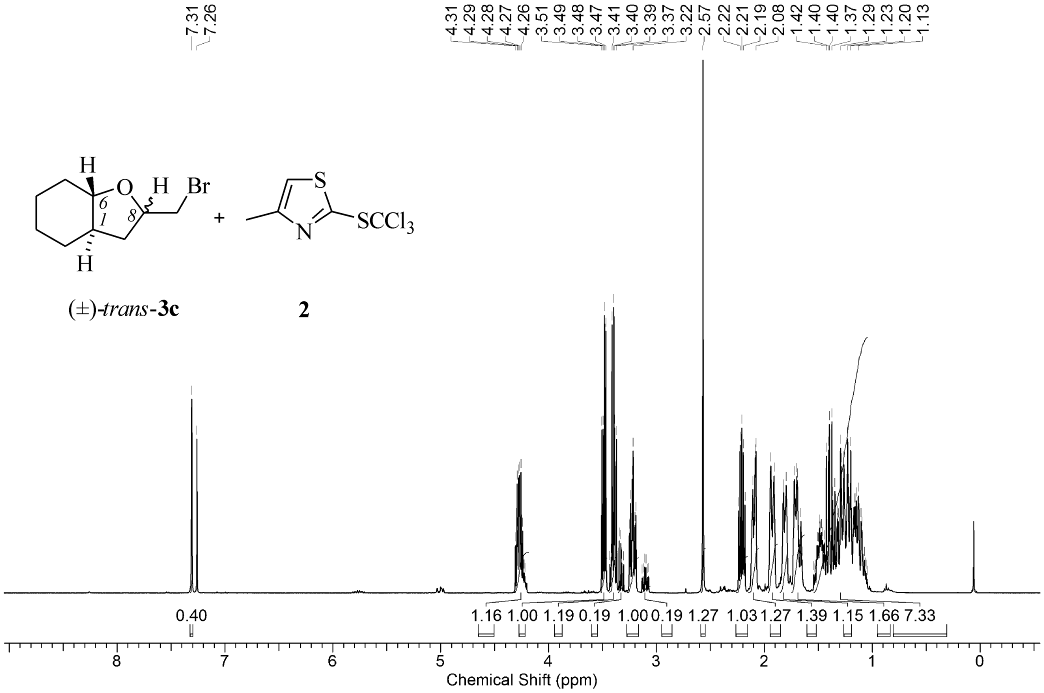


Figure S91. Proton-1 NMR-spectrum of 6,8-cis/trans-isomers, i.e *rel*-(1*R*,6*S*,8*S*)-**3c**/ *rel*-(1*R*,6*S*,8*R*)-**3c**, of 8-(bromomethyl)-7-oxabicyclo[4.3.0]nonane *trans*-(**3c**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (400MHz, $CDCl_3$, 23 °C).

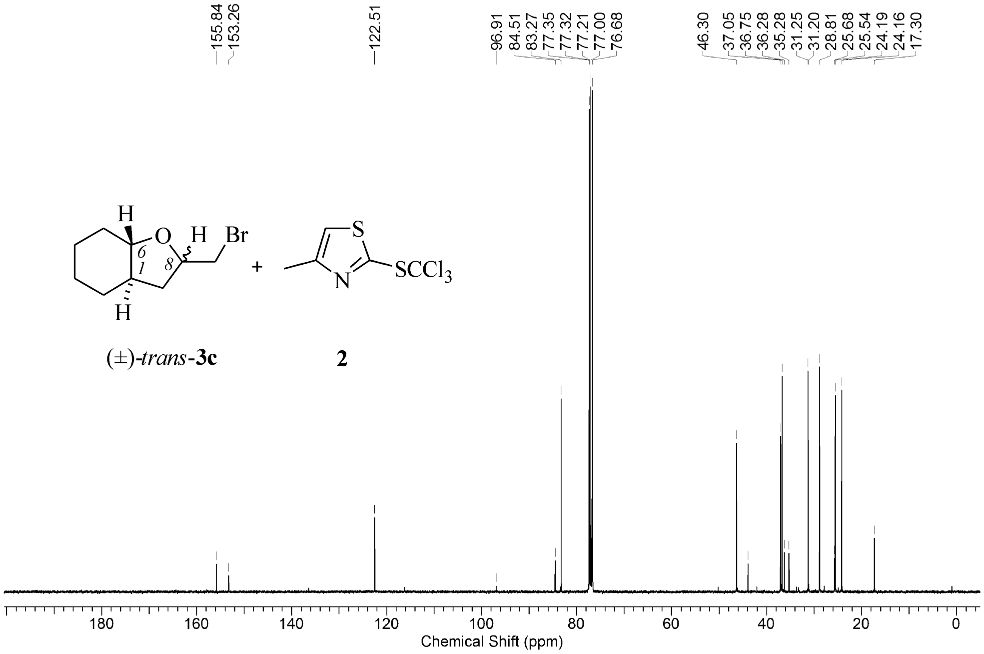


Figure S92. Carbon-13 NMR-spectrum of 6,8-cis/trans-isomers, i.e *rel*-(1*R*,6*S*,8*S*)-**3c**/ *rel*-(1*R*,6*S*,8*R*)-**3c**,of 8-(bromomethyl)-7-oxabicyclo[4.3.0]nonane *trans*-(**3c**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (100MHz, $CDCl_3$, 23 °C).

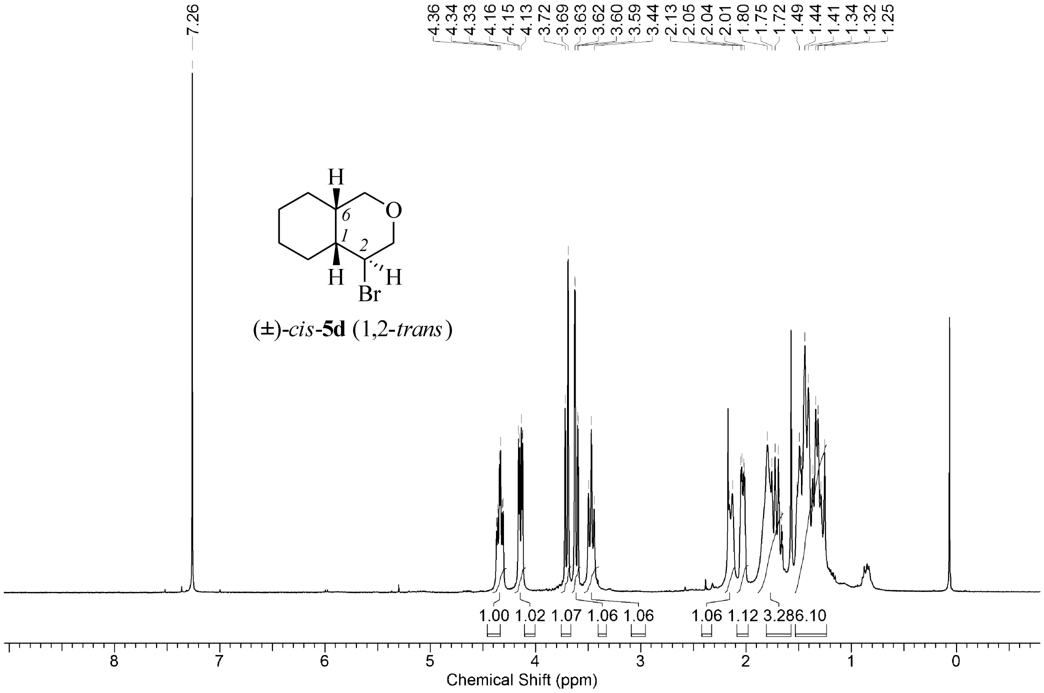


Figure S93. Proton-1 NMR-spectrum of, i.e *rel*-(1*S*,2*S*,6*S*)-**5d**, 2-bromo-4-oxabicyclo-[4.4.0]decane *cis*-(**5d**) (400MHz, $CDCl_3$, 23 °C).

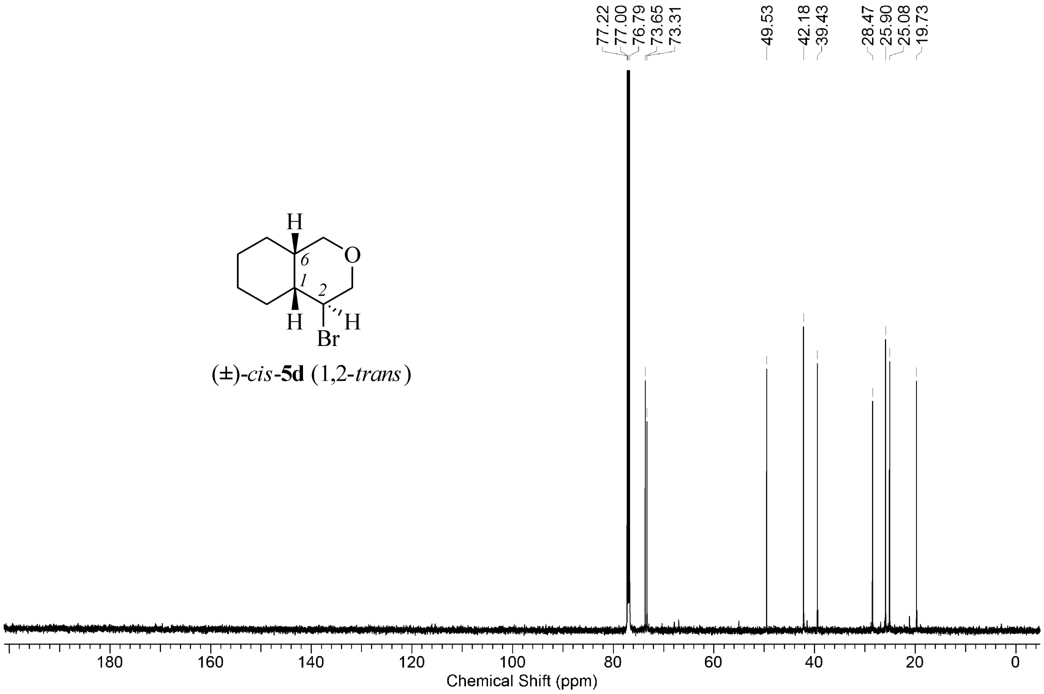


Figure S94. Carbon-13 NMR-spectrum of, i.e *rel*-(1*S*,2*S*,6*S*)-**5d**, 2-bromo-4-oxabicyclo-[4.4.0]decane *cis*-(**5d**) (150MHz, $CDCl_3$, −37 °C).

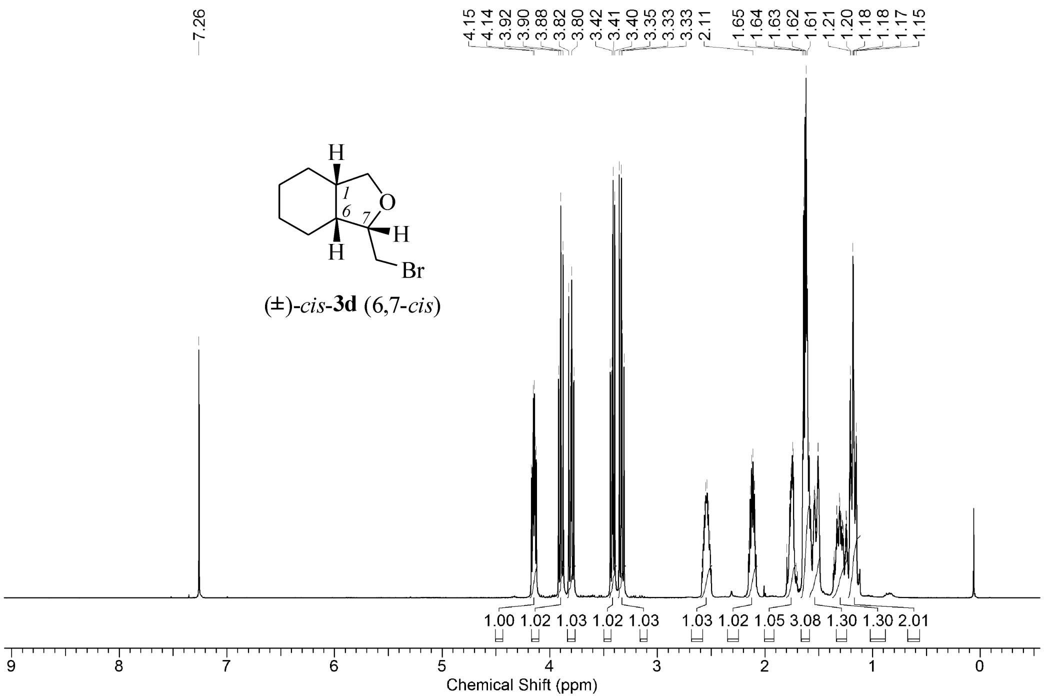


Figure S95. Proton-1 NMR-spectrum of, i.e *rel*-(1*S*,6*R*,7*S*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]nonane *cis*-(**3d**) (400MHz, $CDCl_3$, 23 °C).

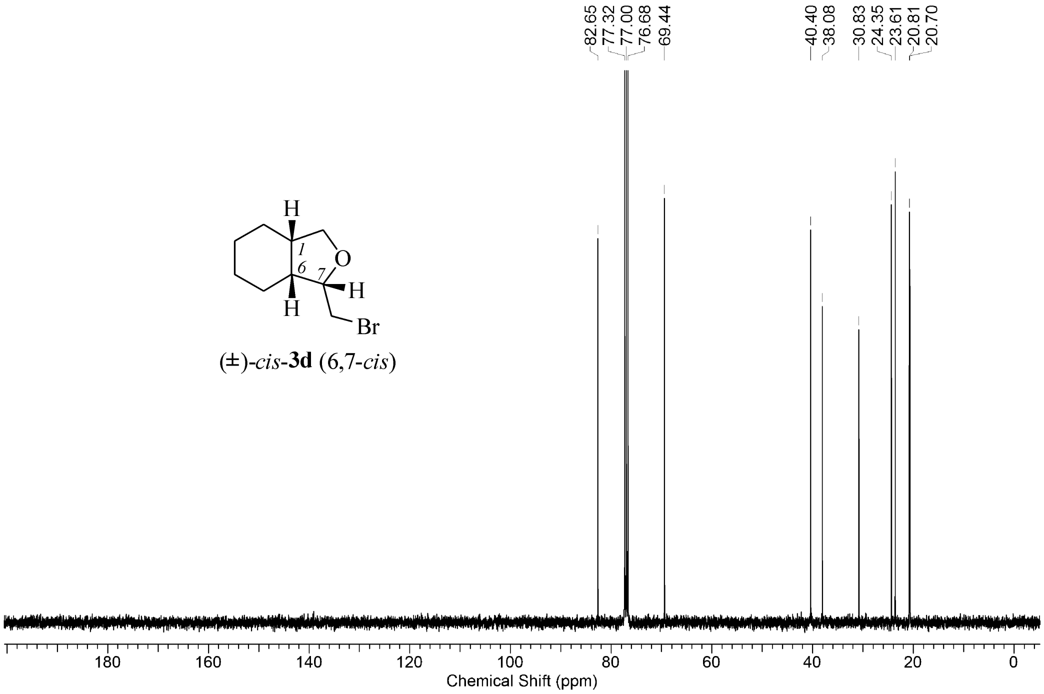


Figure S96. Carbon-13 NMR-spectrum of, i.e *rel*-(1*S*,6*R*,7*S*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]nonane *cis*-(**3d**) (100MHz, $CDCl_3$, 23 °C).

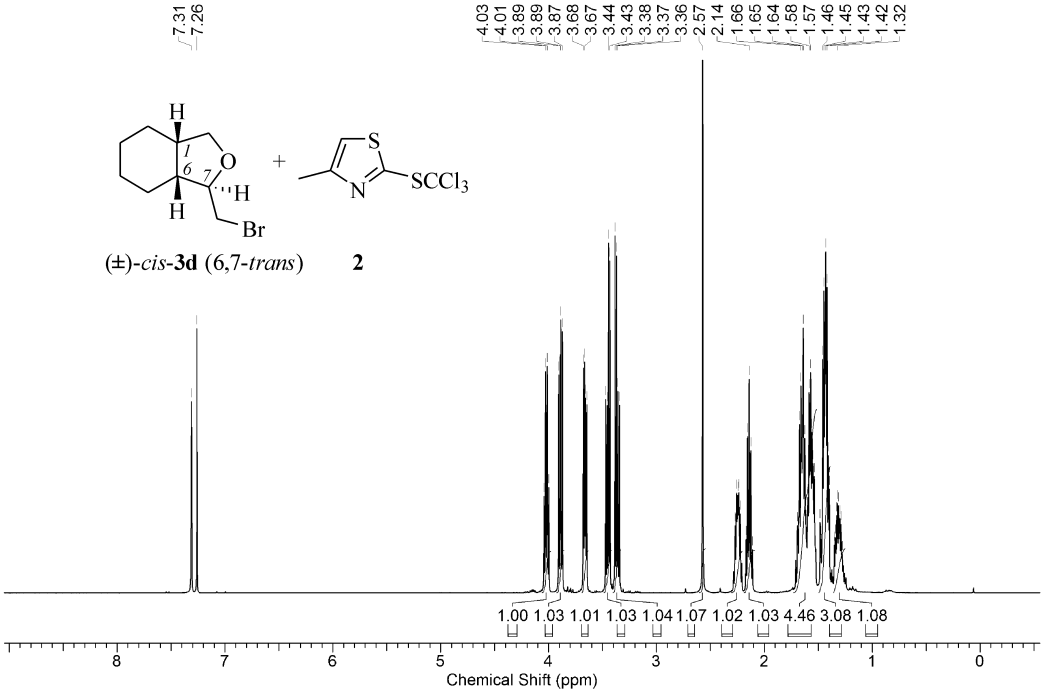


Figure S97. Proton-1 NMR-spectrum of, i.e *rel*-(1*S*,6*R*,7*R*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]nonane *cis*-(**3d**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (400MHz, $CDCl_3$, 23 °C).

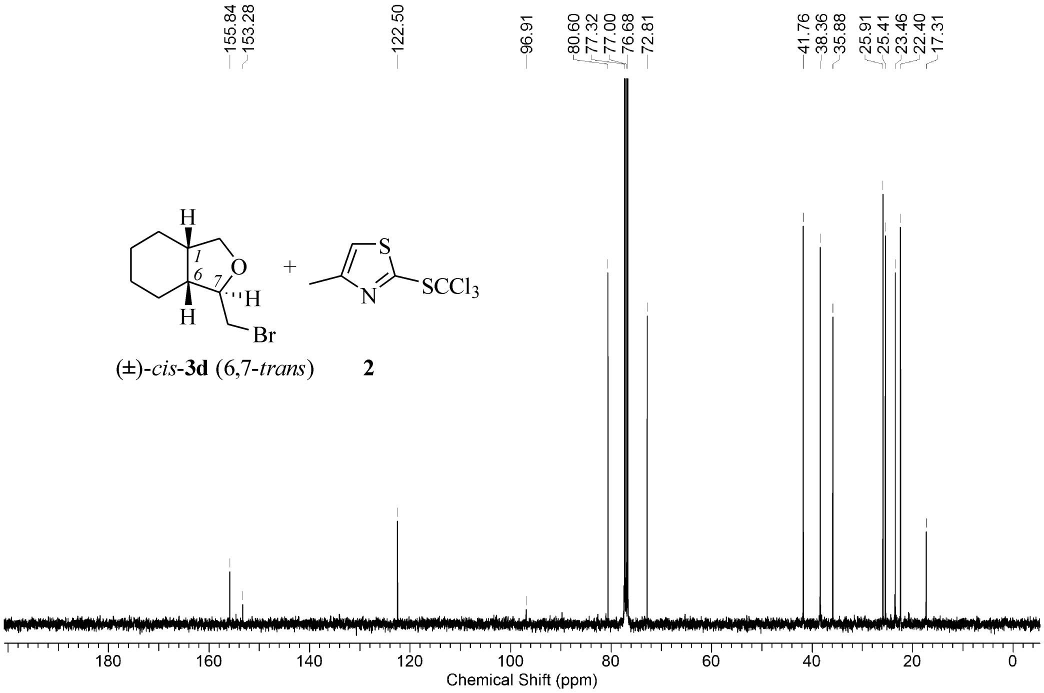


Figure S98. Carbon-13 NMR-spectrum of, i.e *rel*-(1*S*,6*R*,7*R*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]nonane *cis*-(**3d**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (100MHz, $CDCl_3$, 23 °C).

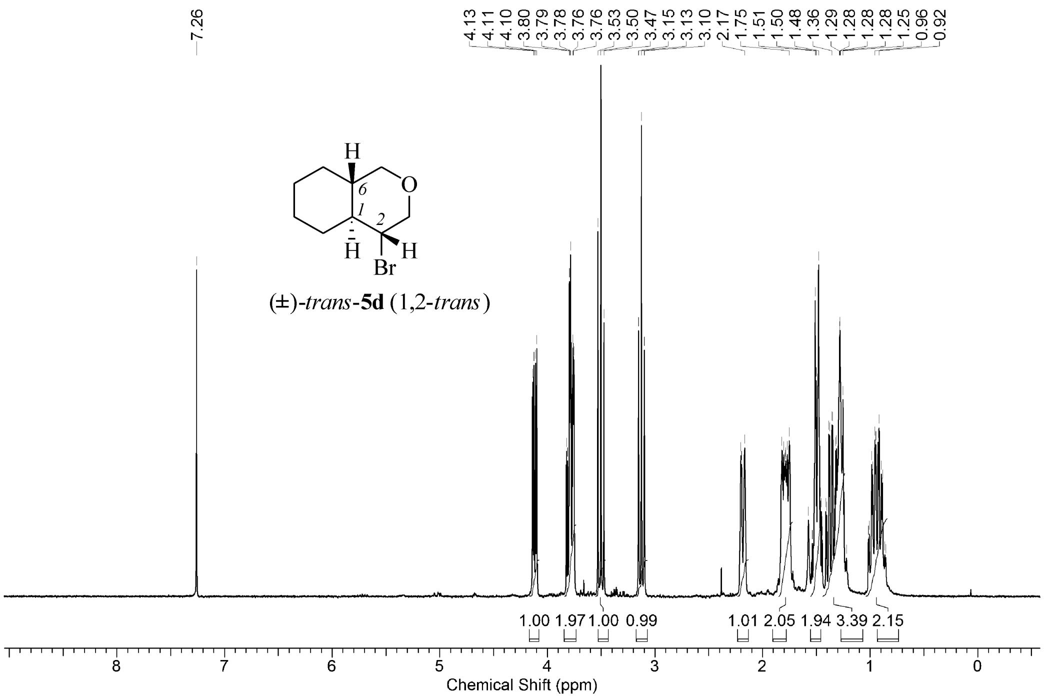


Figure S99. Proton-1 NMR-spectrum of, i.e *rel*-(1*R*,2*R*,6*S*)-**5d**, 2-bromo-4-oxabicyclo-[4.4.0]decane *trans*-(**5d**) (400MHz, $CDCl_3$, 23 °C).

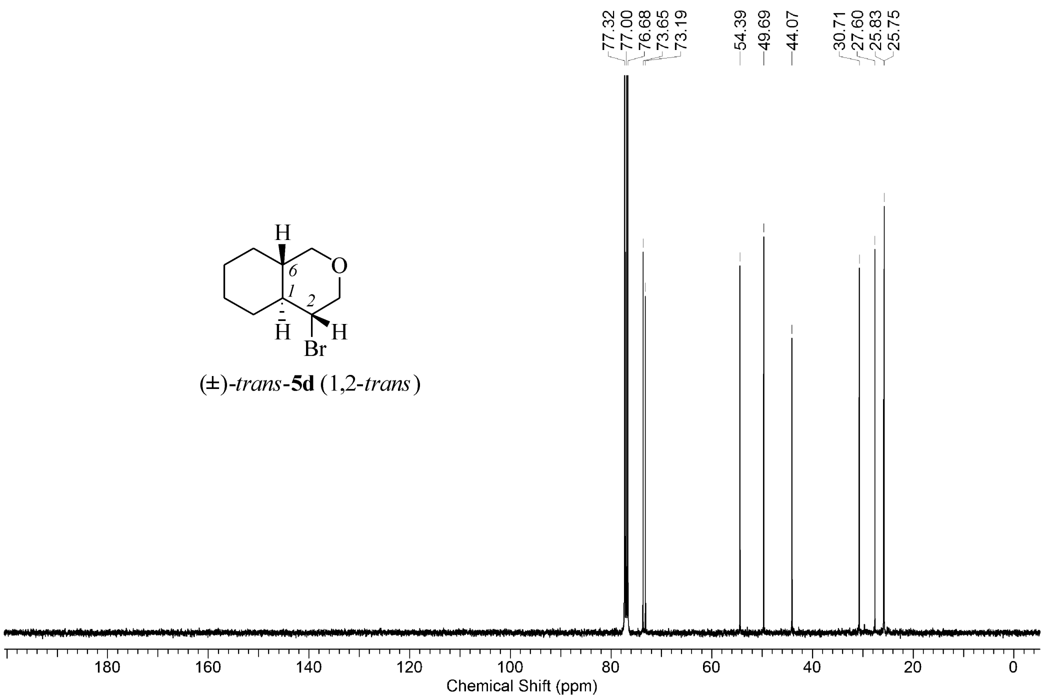


Figure S100. Carbon-13 NMR-spectrum of, i.e *rel*-(1*R*,2*R*,6*S*)-**5d**, 2-bromo-4-oxabicyclo-[4.4.0]decane *trans*-(**5d**) (100MHz, $CDCl_3$, 23 °C).

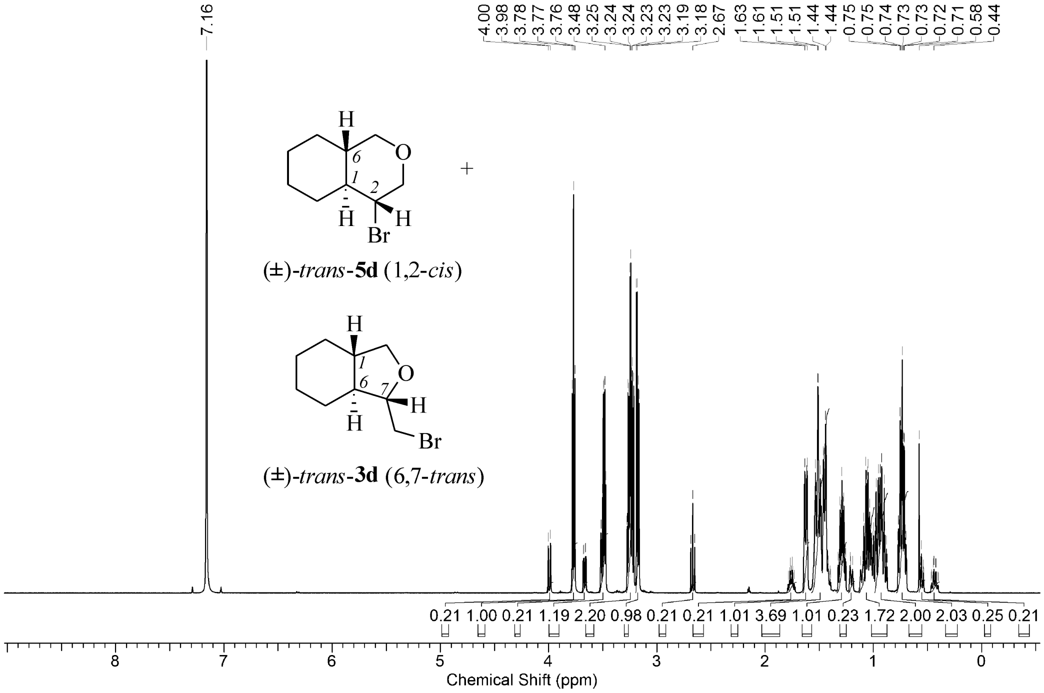


Figure S101. Proton-1 NMR-spectrum of, i.e *rel*-(1*R*,2*R*,6*S*)-**5d**, 2-bromo-4-oxabicycle-[4.4.0]decane *trans*-(**5d**) and of, i.e *rel*-(1*S*,6*S*,7*S*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]-nonane *trans*-(**3d**) (600MHz, C_6D_6, 23 °C).

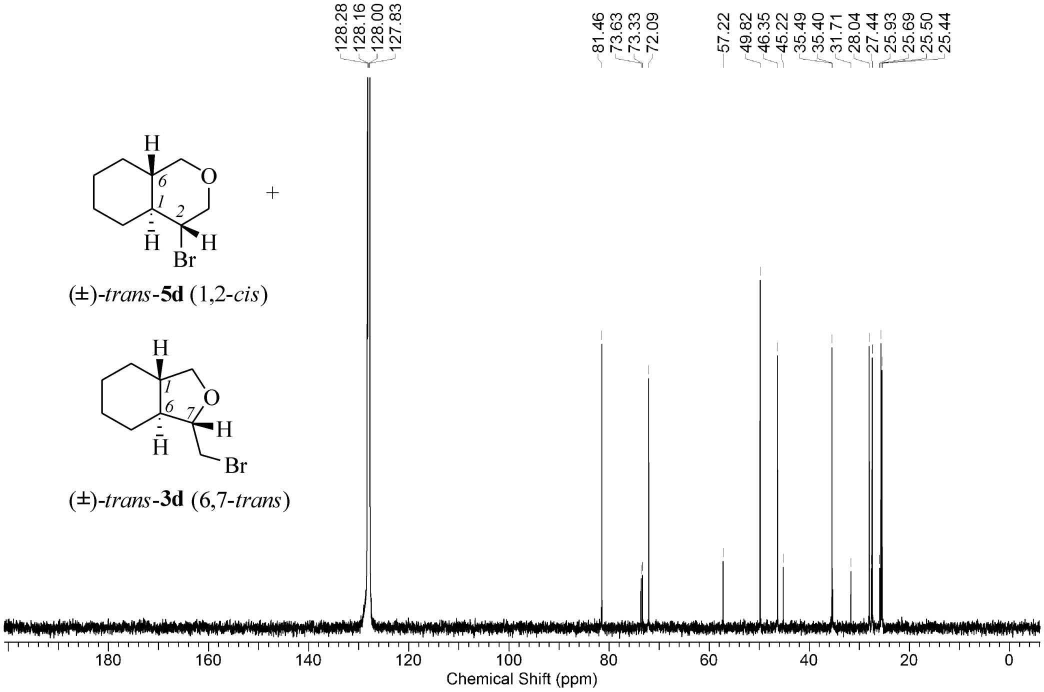


Figure S102. Carbon-13 NMR-spectrum of, i.e *rel*-(1*R*,2*R*,6*S*)-**5d**, 2-bromo-4-oxabicycle-[4.4.0]decane *trans*-(**5d**) and of, i.e *rel*-(1*S*,6*S*,7*S*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]-nonane *trans*-(**3d**) (150MHz, C_6D_6, 23 °C).

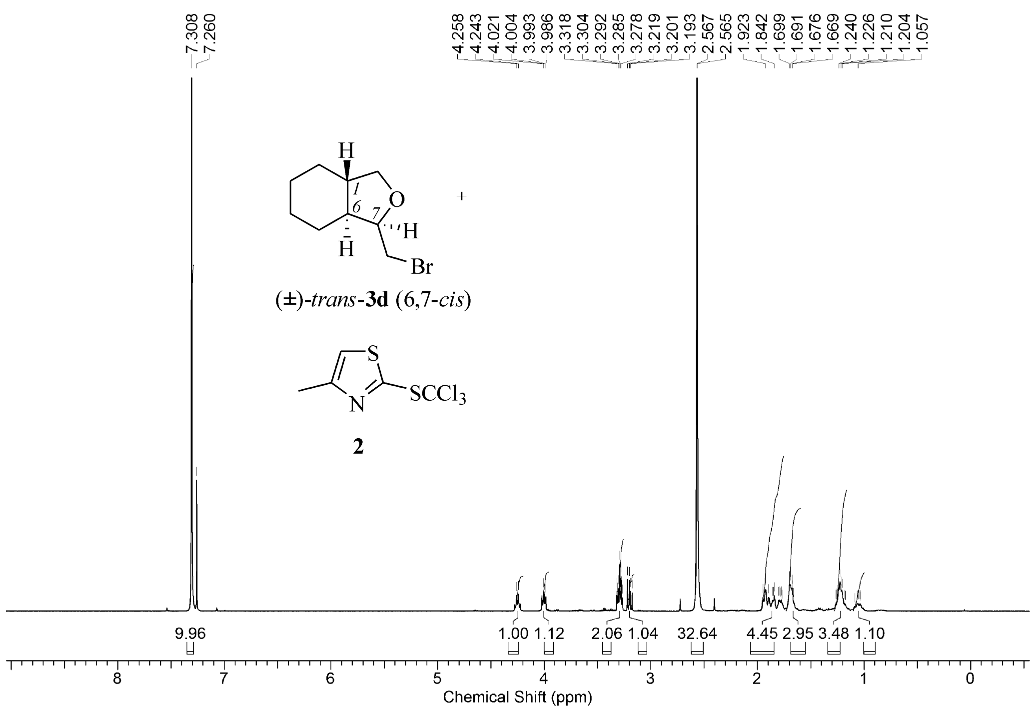


Figure S103. Proton-1 NMR-spectrum of, i.e *rel*-(1*S*,6*S*,7*R*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]nonane *trans*-(**3d**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (400MHz, $CDCl_3$, 23 °C).

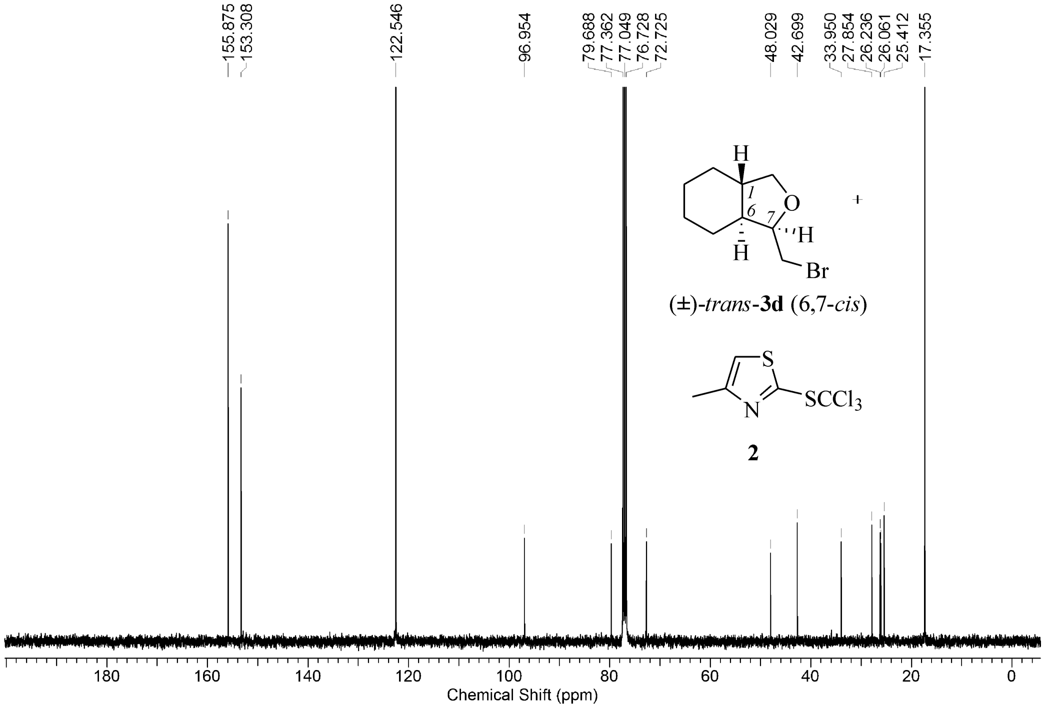


Figure S104. Carbon-13 NMR-spectrum of, i.e *rel*-(1*S*,6*S*,7*R*)-**3d**, 7-bromomethyl-8-oxabicyclo[4.3.0]nonane *trans*-(**3d**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (100MHz, $CDCl_3$, 23 °C).

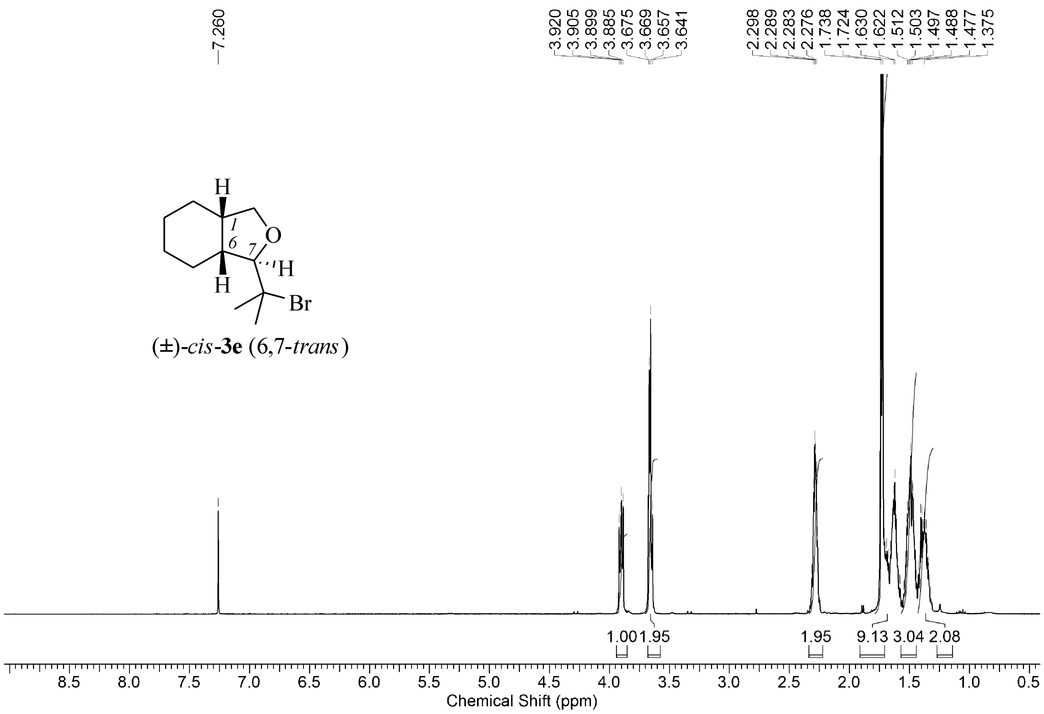


Figure S105. Proton-1 NMR-spectrum of, i.e *rel*-(1*R*,6*S*,7*R*)-**3e**, 7-(2-bromoprop-2-yl)-8-oxabicyclo[4.3.0]nonane *cis*-(**3e**) (400MHz, $CDCl_3$, 23 °C).

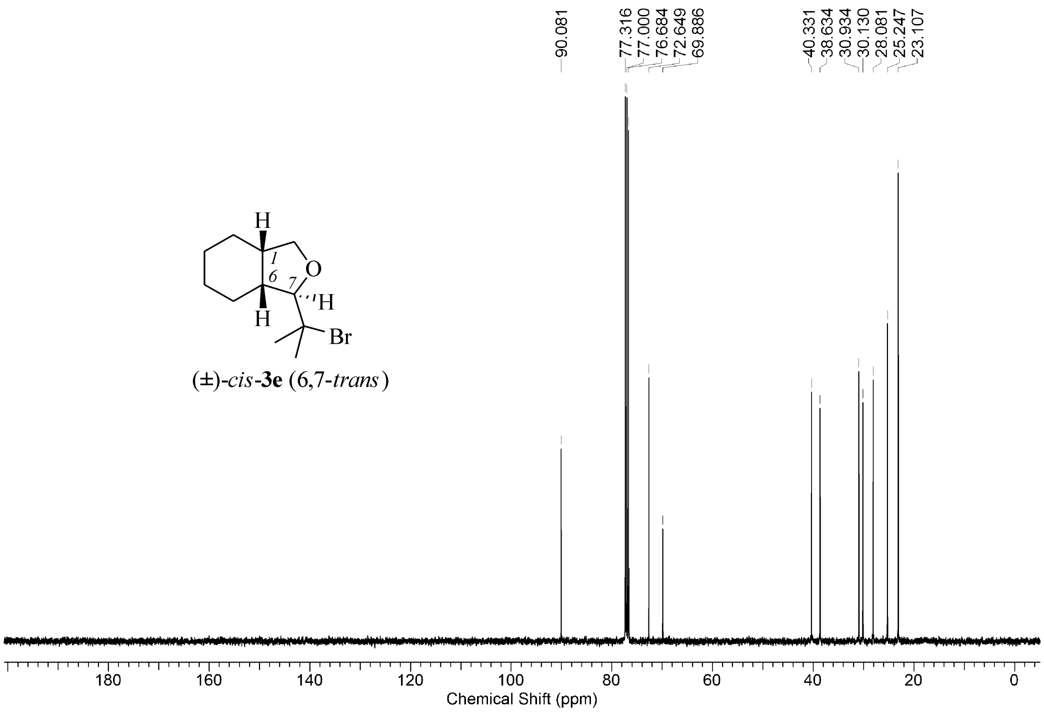


Figure S106. Carbon-13 NMR-spectrum of, i.e *rel*-(1*R*,6*S*,7*R*)-**3e**, 7-(2-bromoprop-2-yl)-8-oxabicyclo[4.3.0]nonane *cis*-(**3e**) (100MHz, $CDCl_3$, 23 °C).

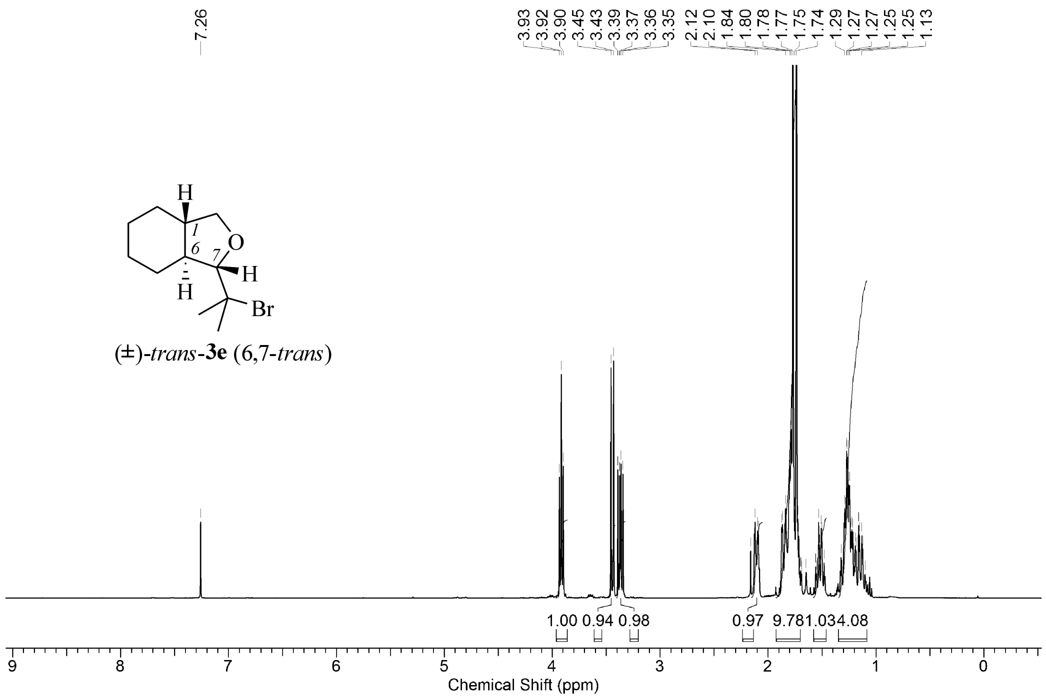


Figure S107. Proton-1 NMR-spectrum of, i.e *rel*-(1*S*,6*S*,7*S*)-**3e**, 7-(2-bromoprop-2-yl)-8-oxabicyclo[4.3.0]nonane *trans*-(**3e**) (400MHz, $CDCl_3$, 23 °C).

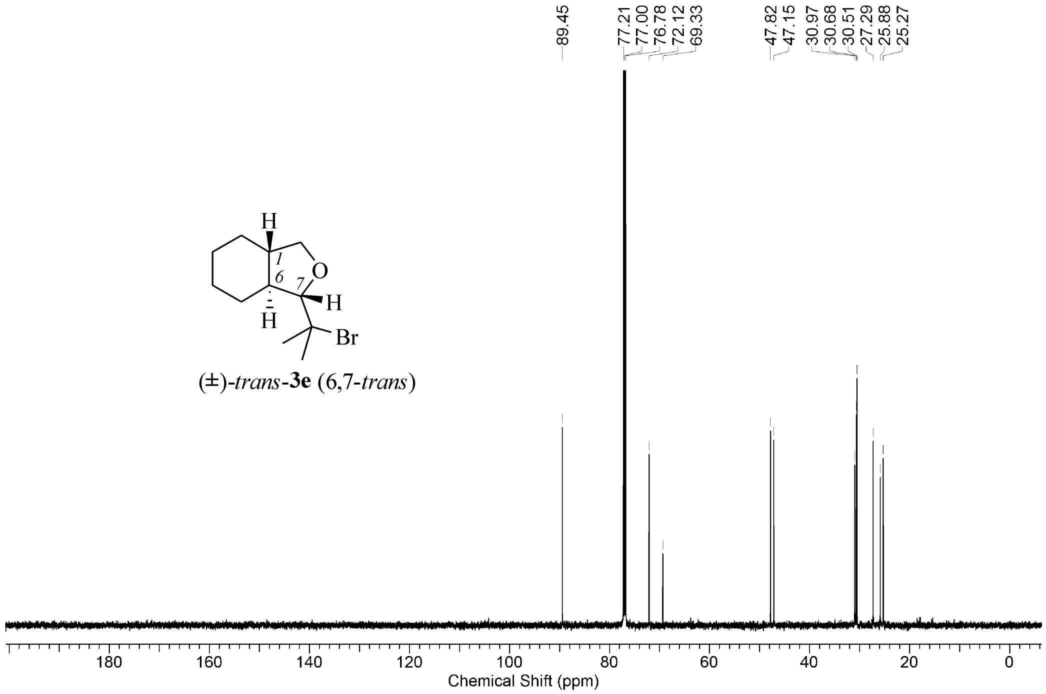


Figure S108. Carbon-13 NMR-spectrum of, i.e *rel*-(1*S*,6*S*,7*S*)-**3e**, 7-(2-bromoprop-2-yl)-8-oxabicyclo[4.3.0]nonane *trans*-(**3e**) (150MHz, $CDCl_3$, 23 °C).

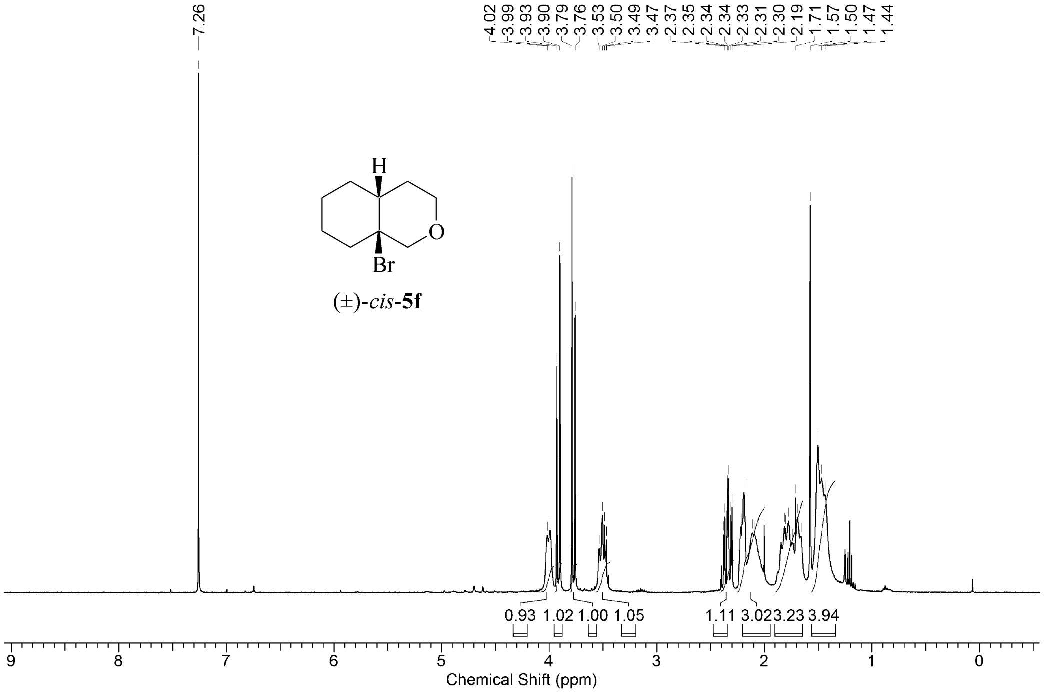


Figure S109. Proton-1 NMR-spectrum of *cis*-(1-bromo)-3-oxabicyclo[4.4.0]decane *cis*-(**5f**) (400MHz, $CDCl_3$, 23 °C).

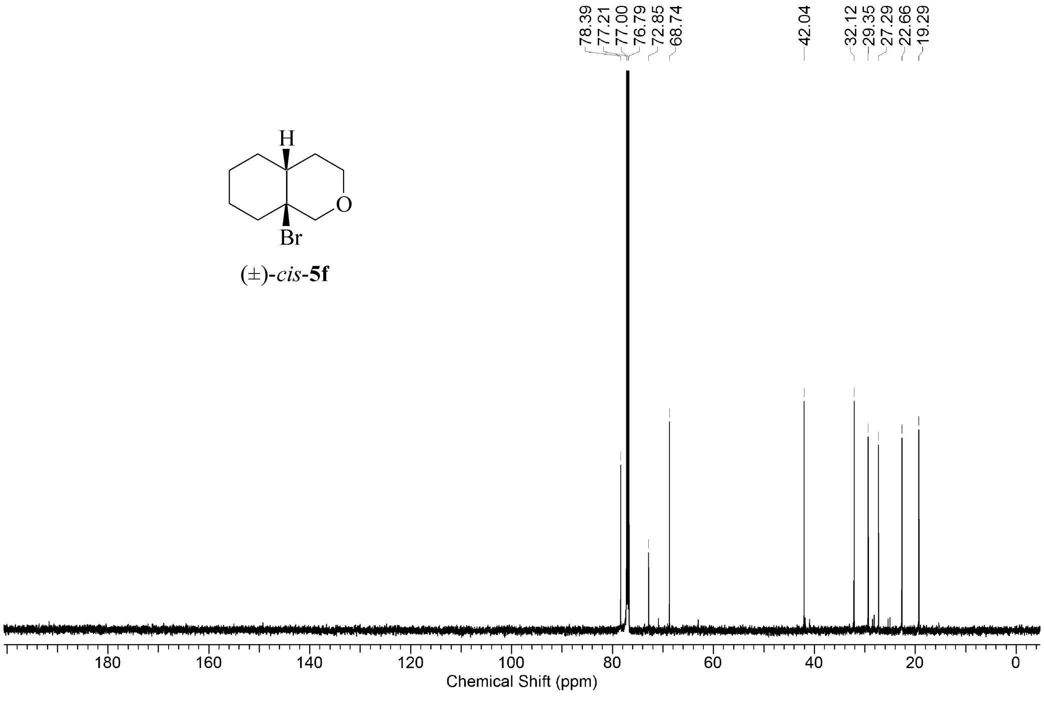


Figure S110. Carbon-13 NMR-spectrum of *cis*-(1-bromo)-3-oxabicyclo[4.4.0]decane *cis*-(**5f**) (150MHz, $CDCl_3$, 23 °C).

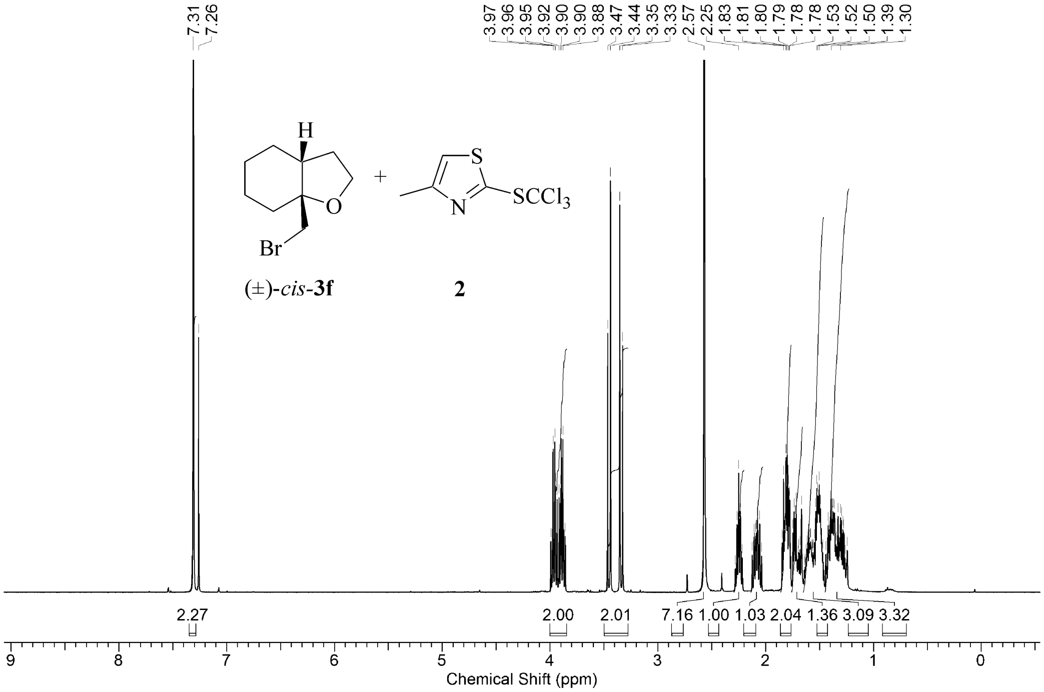


Figure S111. Proton-1 NMR-spectrum of *cis*-(1-bromomethyl)-9-oxabicyclo[4.3.0]nonane *cis*-(**3f**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (400MHz, $CDCl_3$, 23 °C).

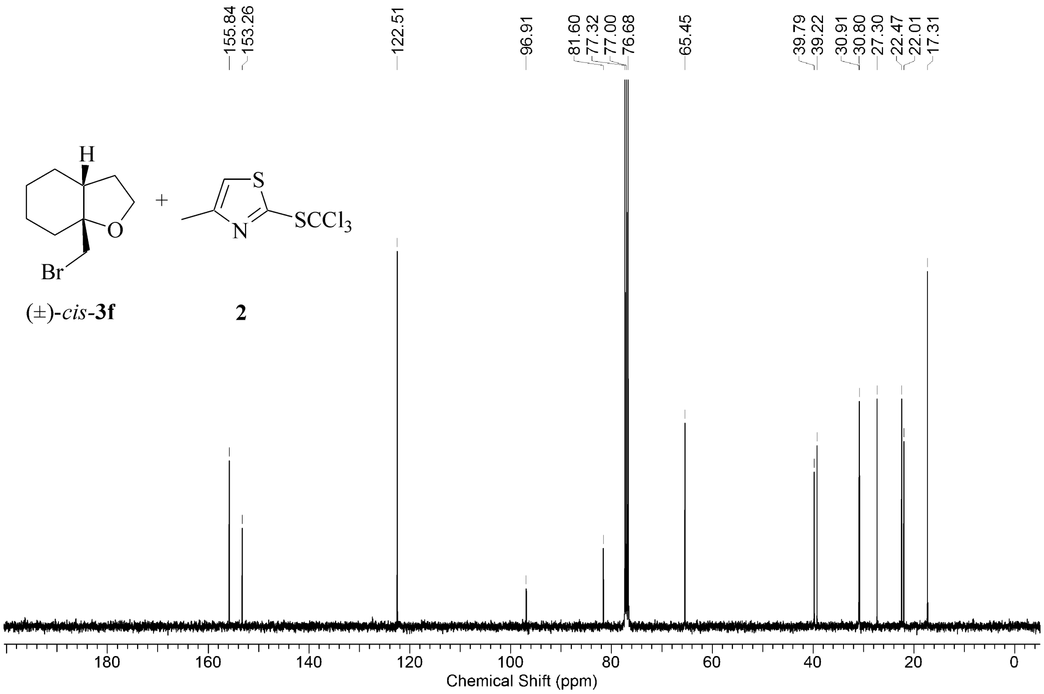


Figure S112. Carbon-13 NMR-spectrum of cis-(1-bromomethyl)-9-oxabicyclo[4.3.0]nonane *cis*-(**3f**) and 4-methyl-2-(trichloromethylsulfanyl)-thiazole (**2**) (100MHz, $CDCl_3$, 23 °C).

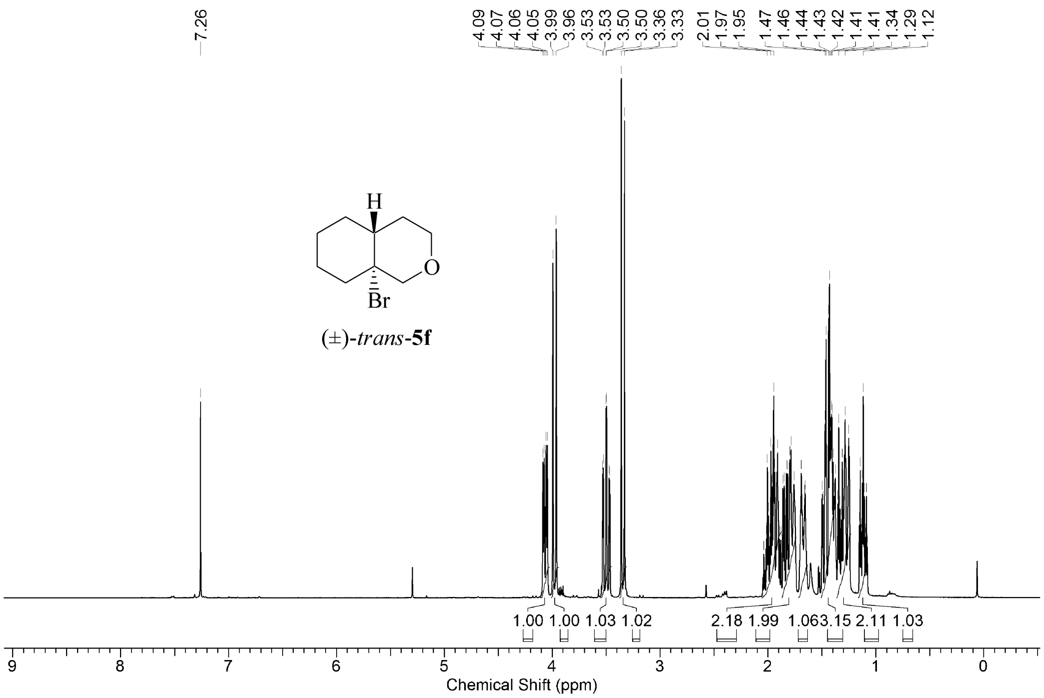


Figure S113. Proton-1 NMR-spectrum of *trans*-(1-bromo)-3-oxabicyclo[4.4.0]decane *trans*-(**5f**) (400MHz, $CDCl_3$, 23 °C).

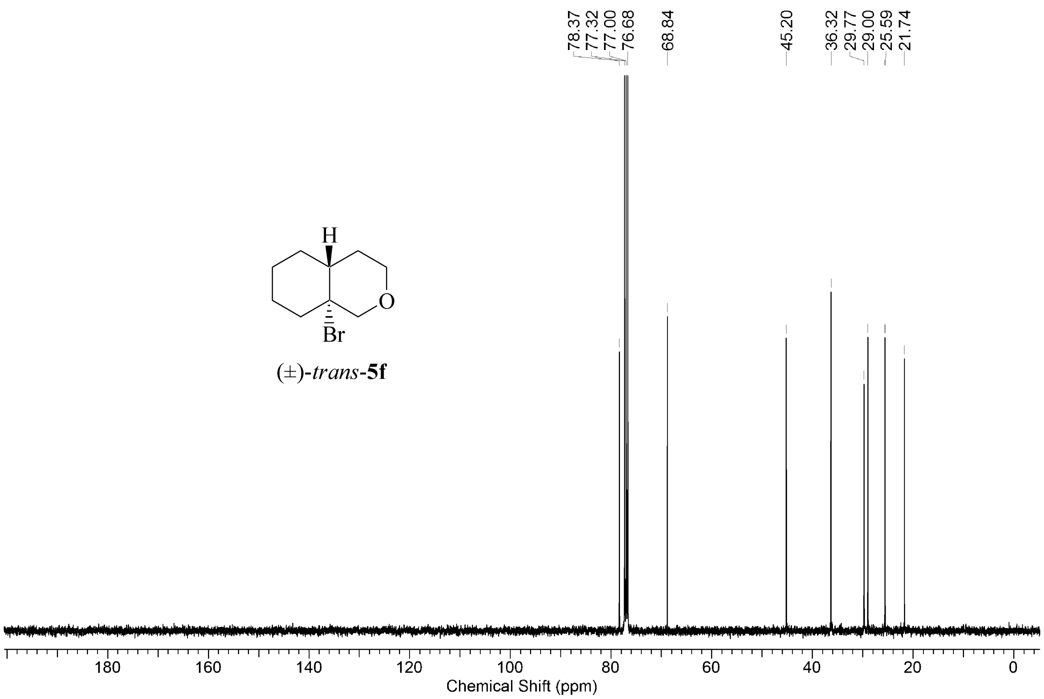


Figure S114. Carbon-13 NMR-spectrum of *trans*-(1-bromo)-3-oxabicyclo[4.4.0]decane *trans*-(**5f**) (100MHz, $CDCl_3$, 23 °C).

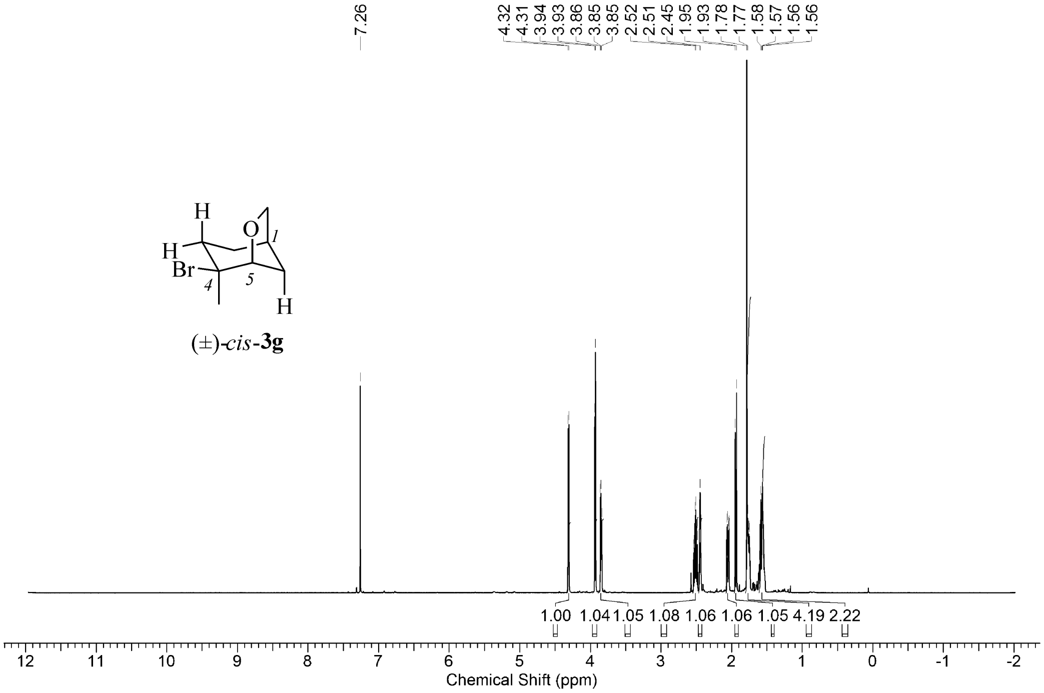


Figure S115. Proton-1 NMR-spectrum of, i.e *rel-(1R,4S,5R)*-**3g**, 4-bromo-4-methyl-6-oxa-bicyclo[3.2.1]octane *cis*-(**3g**) (400MHz, $CDCl_3$, 23 °C).

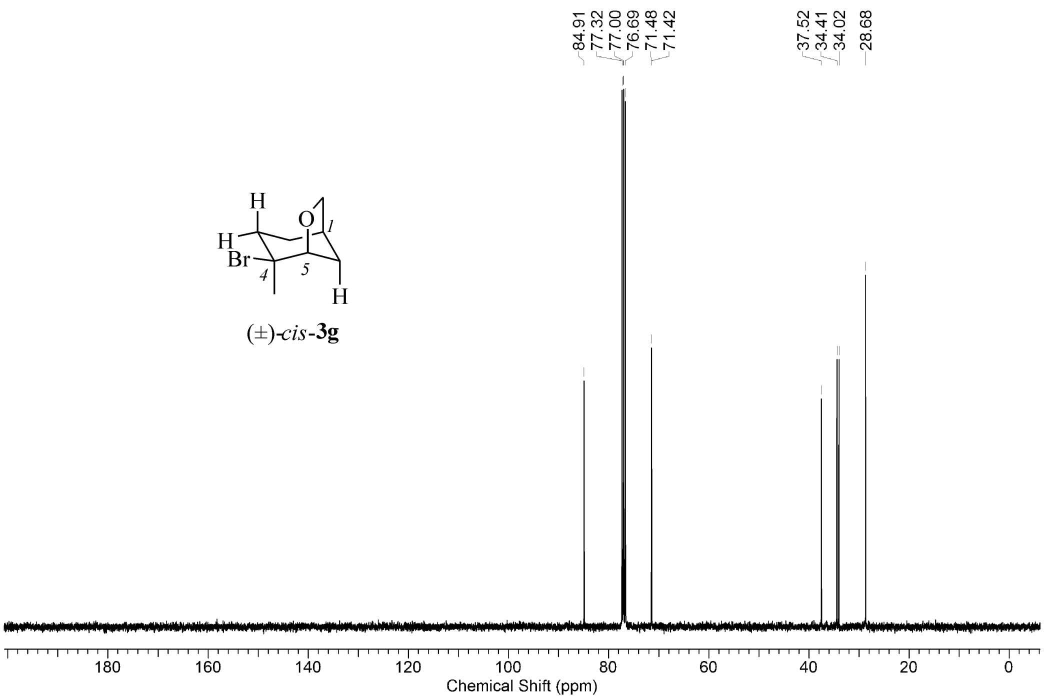


Figure S116. Carbon-13 NMR-spectrum of, i.e *rel-(1R,4S,5R)*-**3g**, 4-bromo-4-methyl-6-oxa-bicyclo[3.2.1]octane *cis*-(**3g**) (100MHz, $CDCl_3$, 23 °C).

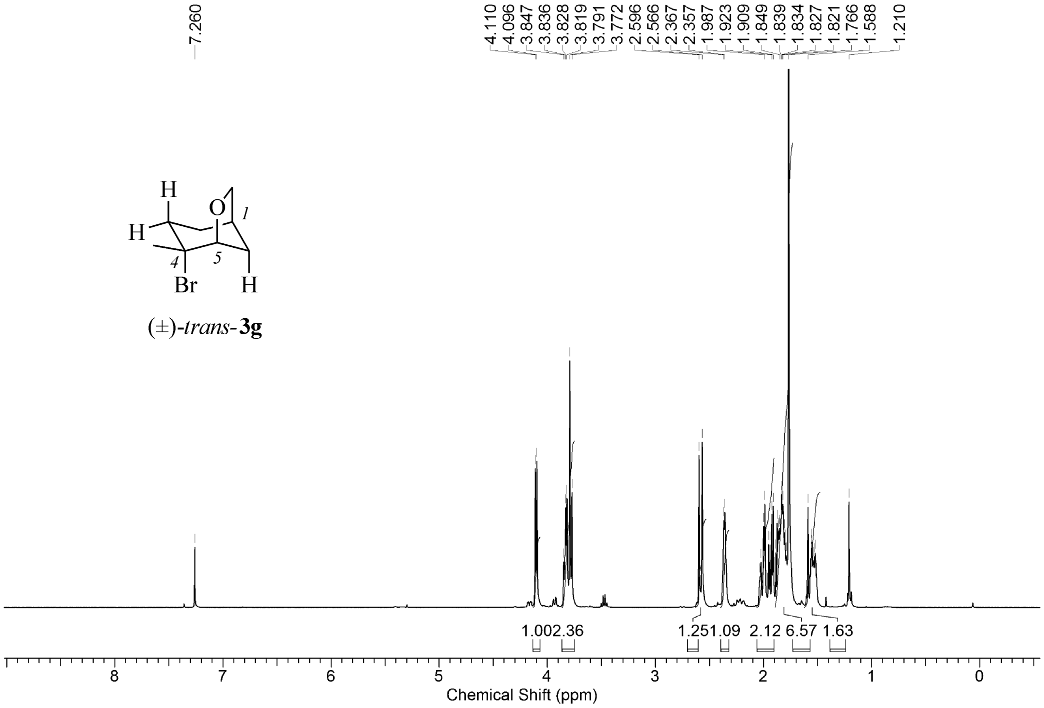


Figure S117. Proton-1 NMR-spectrum of, i.e. *rel-(1R,4R,5R)*-**3g**, 4-Bromo-4-methyl-6-oxa-bicyclo[3.2.1]octane *trans*-(**3g**) (400MHz, $CDCl_3$, 23 °C).

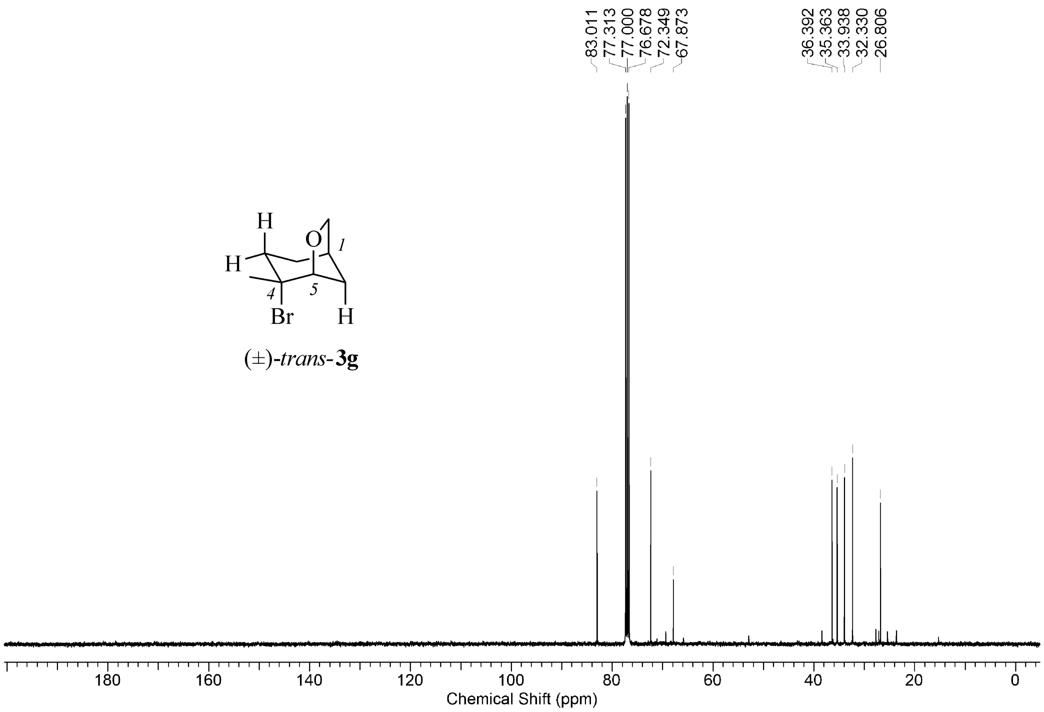


Figure S118. Carbon-13 NMR-spectrum of, i.e *rel-(1R,4R,5R)*-**3g**, 4-bromo-4-methyl-6-oxa-bicyclo[3.2.1]octane *trans*-(**3g**) (100MHz, $CDCl_3$, 23 °C).

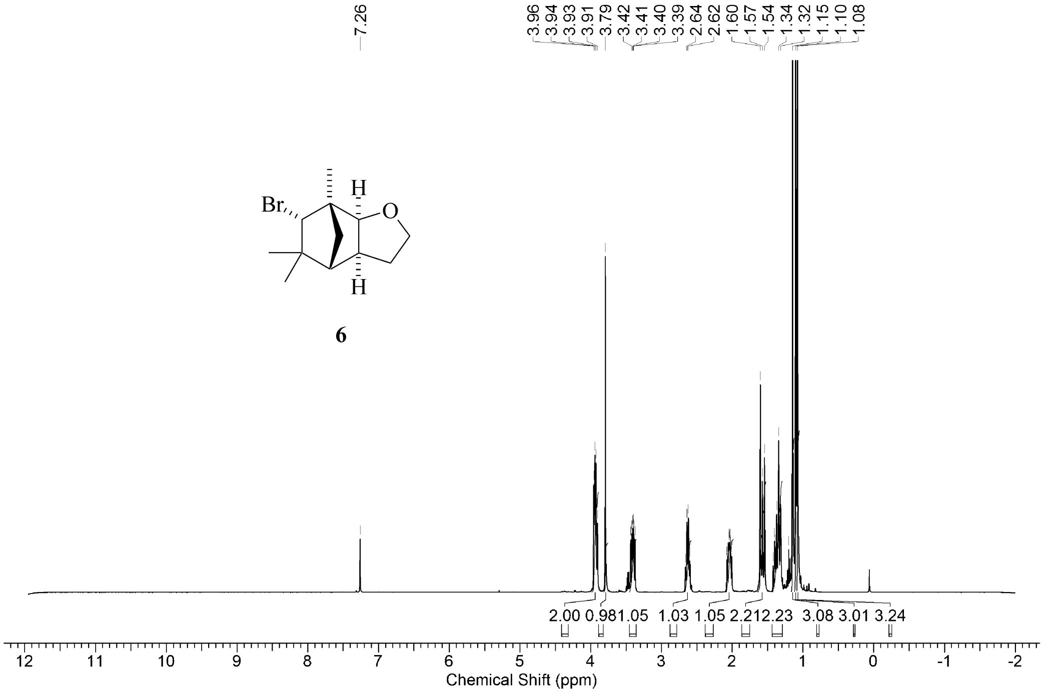


Figure S119. Proton-1 NMR-spectrum of i.e. *rel-(1R,2S,6S,7S,9S)*-9-bromo-1,8,8-trimethyl-3-oxatricyclo[5.2.1.0^{2,6}]-decane (**6**) (400MHz, $CDCl_3$, 23 °C).

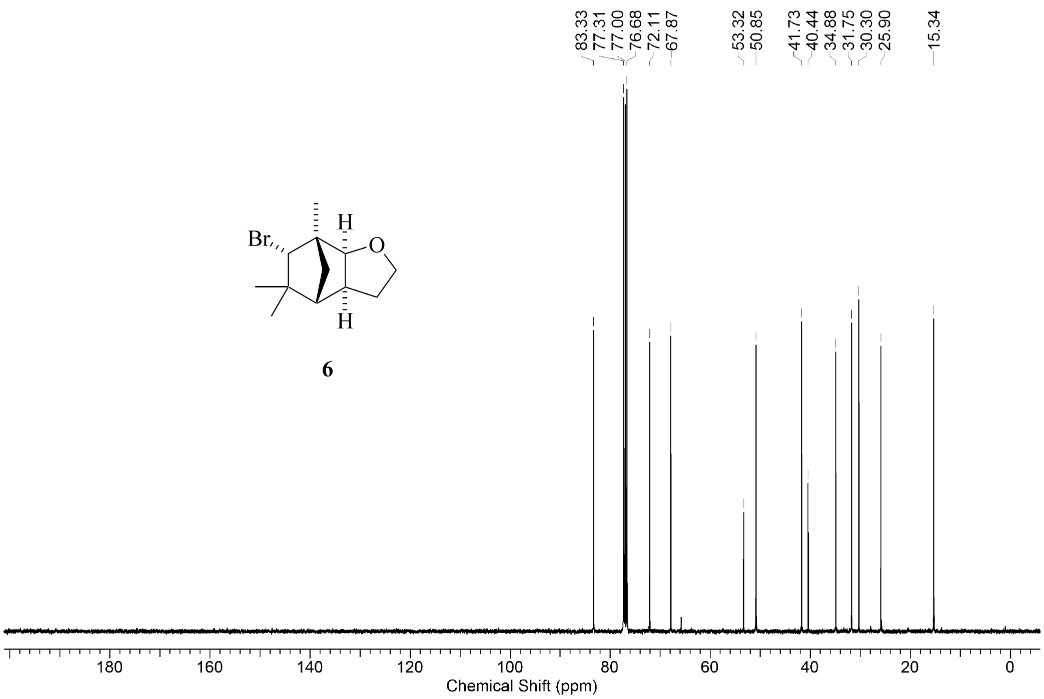


Figure S120. Proton-13 NMR-spectrum of i.e *rel-(1R,2S,6S,7S,9S)*-9-bromo-1,8,8-trimethyl-3-oxatricyclo[5.2.1.0^{2,6}]-decane (**6**) (100MHz, $CDCl_3$, 23 °C).

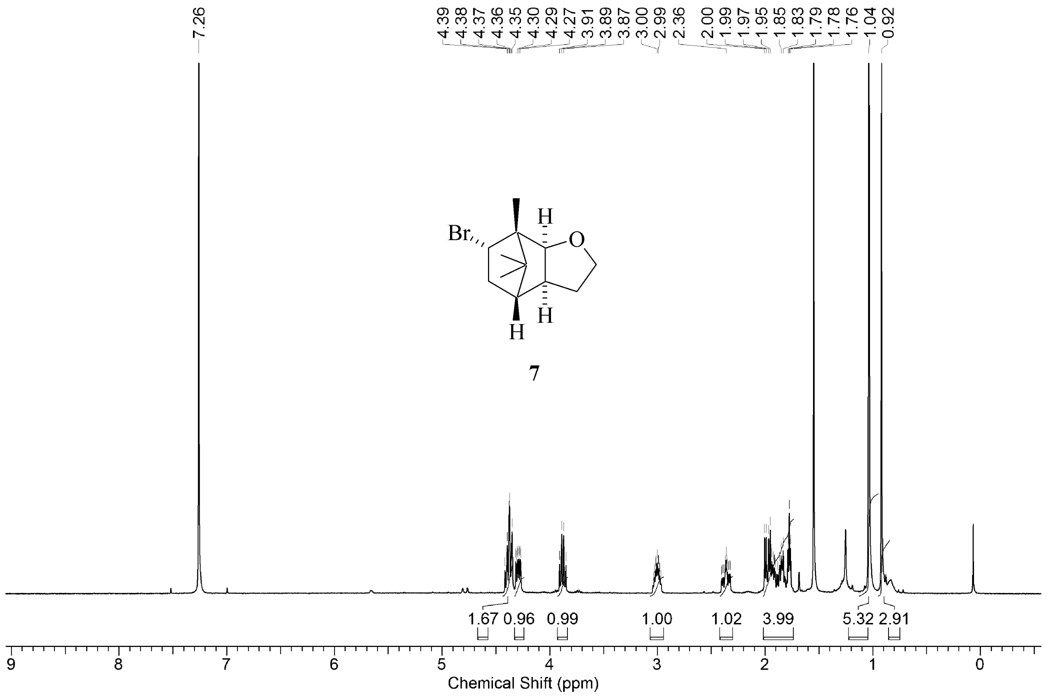


Figure S121. Proton-1 NMR-spectrum of i.e *rel-(1S,2S,6S,7S,9S)*-9-bromo-1,10,10-trimethyl-3-oxatricyclo[5.2.1.0^{2,6}]-decane (**7**) (400MHz, $CDCl_3$, 23 °C).

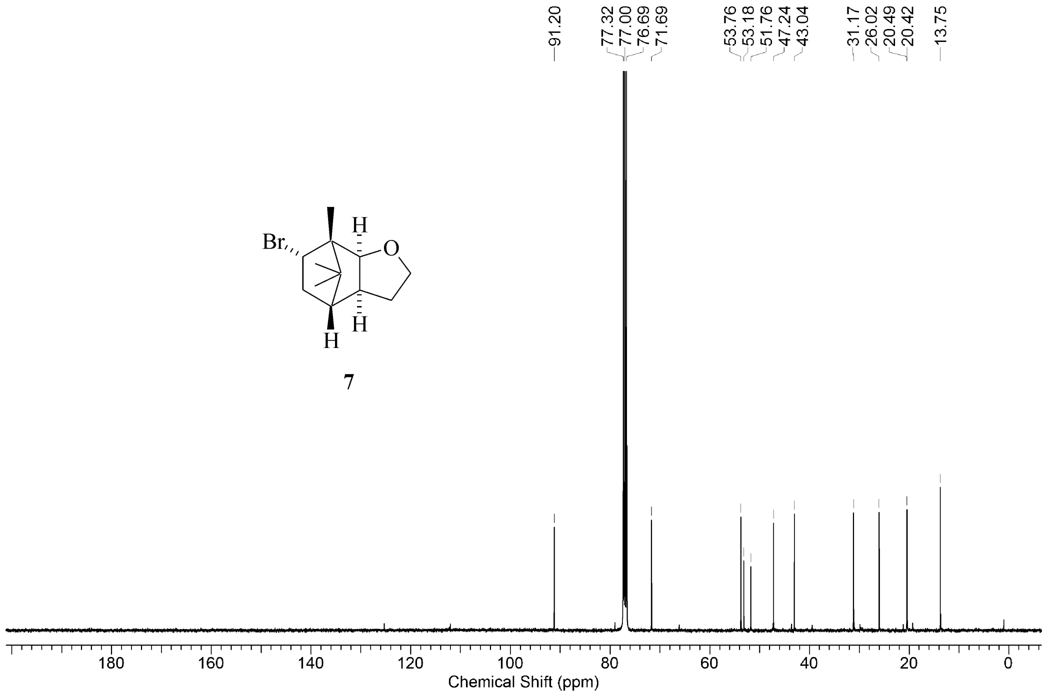


Figure S122. Carbon-13 NMR-spectrum of i.e *rel-(1S,2S,6S,7S,9S)*-9-bromo-1,10,10-trimethyl-3-oxatricyclo[5.2.1.0^{2,6}]-decane (**7**) (100MHz, $CDCl_3$, 23 °C).

8 Computational Chemistry

8.1 Computational Details

All calculations were carried out with Gaussian03[31], using the density functional/Hartree-Fock hybrid models B3LYP and BHandHLYP and split valance double-ζ basis set 6-31+G(d,p) and split valence triple-ζ basis set 6-311G(d,p). No symmetry or internal coordinate constraints were applied during energy function minimization. The ultrafine grid in combination with the tight option for energy function minimization was used. The absence of imaginary modes of vibration characterized computed structures as minima (for radicals **I, II,** and **VII** and for propene). Transition structures **TS-I** and **TS-VII** were located with the Berny algorithm. Hessian matrices of transition structures had exactly one negative stretching mode (Table 9 of the associated manuscript). Animations of eigenvector coordinates using Molden[32] were performed to verify that the imaginary mode correlates with the trajectory of C,O bond formation. Approximate Gibbs free energies ($G^{298.15}$) were obtained through thermochemical analysis for 298.15 K by unscaled frequency calculation from the thermal correction reported by Gaussian03. Likewise obtained Gibbs free energies take into account zero-point correction, thermal correction, and entropy. All transition structures were maxima on electronic potential energy hypersurface, which may not correspond to maxima on the free energy surface.

8.2 Ball-and-Stick Graphics from Modelled Structures

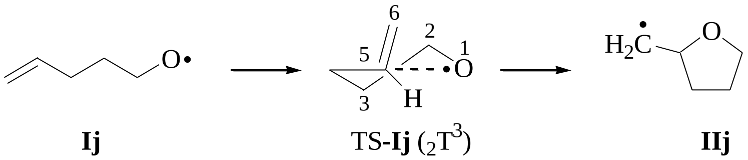
Graphics displaying computed equilibrium structures of oxygen radicals, addition products, and transition structures associated with oxygen radical additions were generated from B3LYP-calculated atomic coordinates. The results obtained from BHandHLYP-calculations provided almost identical conformations for the investigated structures. Oxygen is depicted in the ball-and-stick models in red, carbon in gray and hydrogen in white.

Table S1. Calculated zero point vibrational energy (ZPVE)-corrected electronic energies (*E*, 0 K) expectation values of spin the operator $\langle S^2 \rangle$ and free energies (*G*, 298.15K) for the 2-(cyclohexen-3-yl)-ethoxyl radical cyclization **Ii** → **Iii**.

method	**Ii**	parameter	**Ii**	TS-*cis*-**Ii**	TS-*trans*-**Ii**	*cis*-**IIi**	*trans*-**IIi**
B3LYP /6-31+G**	*pe*-**Ii**	*E* + ZPVE / a.u. [a]	–387.657312	–387.650940	–387.629477	–387.674108	–387.670439
		$\langle S^2 \rangle$	0.753802	0.778264	0.784693	0.753815	0.753984
		$G^{298.15}$ / a.u. [a]	–387.692413	–387.683999	–387.663009	–387.708058	–387.703786
BHandHLYP /6-31+G**	*pe*-**Ii**	*E* + ZPVE / a.u. [a]	–387.413367	–387.398398	–387.375607	–387.431051	–387.426977
		$\langle S^2 \rangle$	0.755213	0.826176	0.842594	0.755346	0.755562
		$G^{298.15}$ / a.u. [a]	–387.448360	–387.431259	–387.409043	–387.464567	–387.460005
BHandHLYP /6-311G**	*pe*-**Ii**	*E* + ZPVE / a.u. [a]	–387.481233	–387.465775	–387.442897	–387.498255	–387.494066
		$\langle S^2 \rangle$	0.754665	0.826681	0.842829	0.7554	0.755584
		$G^{298.15}$ / a.u. [a]	–387.516054	–387.498638	–387.476661	–387.531833	–387.527097
B3LYP /6-31+G**	*pa*-**Ii**	*E* + ZPVE / a.u. [a]	–387.655174	–387.648548	– [b]	-387.672979	– [b]
		$\langle S^2 \rangle$	0.753686	0.776177	– [b]	0.753956	– [b]
		$G^{298.15}$ / a.u. [a]	–387.690292	–387.681779	– [b]	–387.706516	– [b]
BHandHLYP /6-31+G**	*pa*-**Ii**	*E* + ZPVE / a.u. [a]	–387.410795	–387.395737	– [b]	–387.430001	– [b]
		$\langle S^2 \rangle$	0.755156	0.820896	– [b]	0.755609	– [b]
		$G^{298.15}$ / a.u. [a]	–387.445688	–387.428809	– [b]	–387.463260	– [b]
BHandHLYP /6-311G**	*pa*-**Ii**	*E* + ZPVE / a.u. [a]	–387.478854	–387.463263	– [b]	–387.497527	– [b]
		$\langle S^2 \rangle$	0.754575	0.821789	– [b]	0.755641	– [b]
		$G^{298.15}$ / a.u. [a]	–387.513728	–387.496441	– [b]	–387.530694	– [b]

[a] 1 a.u. = 1 Hartree = 2625.5 kJ mol^{-1}. [b] Identical with *trans*-**Ii** from *pe*-**Ii**.

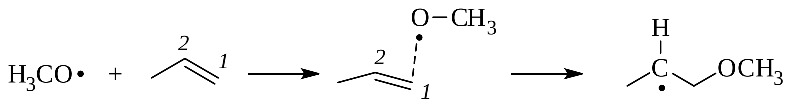
Table S2. Calculated zero point vibrational energy (ZPVE)-corrected electronic energies (*E*, 0 K) expectation values of spin the operator $\langle S^2 \rangle$ and free energies (*G*, 298.15K) for the 4-pentenoxyl radical 5-exo-cyclization.



method	parameter	**Ij**	TS-**Ij**	**IIj**
B3LYP/6-31+G**	E + ZPVE / a.u. [a]	–270.975247	–270.967723	–270.990673
	$\langle S^2 \rangle$	0.753684	0.778657	0.753834
	$G^{298.15}$ / a.u. [a]	–271.007703	–270.997697	–271.021685
BHandHLYP/6-31+G**	E + ZPVE / a.u. [a]	–270.804872	–270.789272	–270.821432
	$\langle S^2 \rangle$	0.755148	0.826588	0.755247
	$G^{298.15}$ / a.u. [a]	–270.837439	–270.819113	–270.852280
BHandHLYP/6-311G**	E + ZPVE / a.u. [a]	–270.853885	–270.838018	–270.869791
	$\langle S^2 \rangle$	0.754563	0.826641	0.755332
	$G^{298.15}$ / a.u. [a]	–270.886313	–270.867816	–270.900557

[a] 1 a.u. = 1 Hartree = 2625.5 kJ mol^{-1}

Table S3. Calculated zero point vibrational energy (ZPVE)-corrected electronic energies (*E*, 0 K) expectation values of spin the operator $\langle S^2 \rangle$ and free energies (*G*, 298.15K) for the methoxyl radical transition structure TS^1-**VII**, and addition product *iso*-**VIII**.

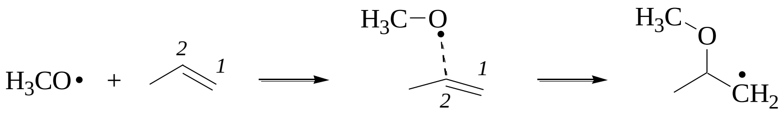


Ik *propene* TS^1-**VII** *iso*-**VIII**

method	parameter	**Ik**	*propene*	TS^1-**VII**	*iso*-**VIII**
B3LYP/6-31+G**	*E* + ZPVE / a.u. [a]	–115.026987	–117.843255	–232.863588	–232.892586
	$\langle S^2 \rangle$	0.753499	0	0.774311	0.753954
	$G_{298.15}$ / a.u. [a]	–115.049934	–117.868282	–232.895907	–232.924574
BHandHLYP/6-31+G**	*E* + ZPVE / a.u. [a]	–114.961999	-117.755443	–232.703774	–232.741734
	$\langle S^2 \rangle$	0.754977	0	0.821343	0.755624
	$G_{298.15}$ / a.u. [a]	–114.984919	–117.780411	–232.735641	–232.773478
BHandHLYP/6-311G**	*E* + ZPVE / a.u. [a]	–114.985163	–117.775341	–232.746863	–232.784295
	$\langle S^2 \rangle$	0.754332	0	0.822071	0.755667
	$G_{298.15}$ / a.u. [a]	–115.008074	–117.800297	–232.778726	–232.815991

[a] 1 a.u. = 1 Hartree = 2625.5 kJ mol^{-1} .

Table S4. Calculated zero point vibrational energy (ZPVE)-corrected electronic energies (E, 0 K) expectation values of spin the operator $\langle S^2 \rangle$ and free energies (G, 298.15K) for the methoxyl radical, transition structure TS^2-**VII**, and addition product **VIII**.



Ik *propene* TS^2-**VII** **VIII**

method	parameter	**Ik**	*propene*	TS^2-**VII**	**VIII**
B3LYP/6-31+G**	E + ZPVE / a.u. [a]	–115.026987	–117.843255	–232.862433	–232.890748
	$\langle S^2 \rangle$	0.753499	0	0.775952	0.753661
	$G_{298.15}$ / a.u. [a]	–115.049934	–117.868282	–232.893984	–232.921330
BHandHLYP/6-31+G**	E + ZPVE / a.u. [a]	–114.961999	–117.755443	–232.703249	–232.740760
	$\langle S^2 \rangle$	0.754977	0	0.823151	0.754984
	$G_{298.15}$ / a.u. [a]	–114.984919	–117.780411	–232.734388	–232.771144
BHandHLYP/6-311G**	E + ZPVE / a.u. [a]	–114.985163	–117.775341	–232.746689	–232.783726
	$\langle S^2 \rangle$	0.754332	0	0.823321	0.755082
	$G_{298.15}$ / a.u. [a]	–115.008074	–117.800297	–232.777810	–232.814067

[a] 1 a.u. = 1 Hartree = 2625.5 kJ mol^{-1} .

8.3 The 2-(Cyclohexen-3-yl)-ethane-1-oxyl Radical Cyclization

8.3.1 2-(Cyclohexen-3-yl)-ethane-1-oxyl radical *pe*-(Ij)

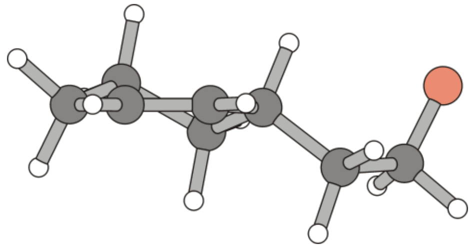


Figure S123. Ball-and-stick model showing the computed equilibrium structure of alkenoxyl radical *pe*-**Ij**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic            Coordinates (Angstroms)
Number     Number         Type           X           Y           Z
---------------------------------------------------------------------
   1          6             0         2.747885   -0.256934    0.110777
   2          6             0         2.158245    1.116702   -0.094916
   3          6             0         0.847895    1.341920   -0.261108
   4          6             0        -0.216312    0.266110   -0.224944
   5          6             0         0.352276   -1.045928    0.352082
   6          6             0         1.738080   -1.364248   -0.227487
   7          6             0        -1.462312    0.767702    0.538204
   8          6             0        -2.671934   -0.165532    0.431133
   9          8             0        -3.170931   -0.345463   -0.833906
  10          1             0         2.848808    1.958661   -0.114481
  11          1             0         0.502111    2.361250   -0.432759
  12          1             0        -0.545001    0.077763   -1.260665
  13          1             0         0.433228   -0.950178    1.445226
  14          1             0        -0.333917   -1.878119    0.156565
  15          1             0         2.095098   -2.331183    0.146004
  16          1             0         1.656729   -1.457776   -1.318844
  17          1             0         3.086542   -0.357198    1.153900
  18          1             0         3.652014   -0.365918   -0.502843
  19          1             0        -1.755754    1.748535    0.143257
  20          1             0        -1.213692    0.910216    1.599514
  21          1             0        -3.525360    0.242943    1.016325
  22          1             0        -2.496300   -1.154047    0.897615
---------------------------------------------------------------------
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\Thermal= 0.2016454\Dipole=-0.3969692,0.7057764,-0.2554294\PG=C01
[X(C8H13O1)]\ NImag=0\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
 Center     Atomic        Atomic           Coordinates (Angstroms)
 Number     Number         Type           X             Y             Z
---------------------------------------------------------------------
    1          6              0        2.143476    1.102893   -0.095854
    2          6              0        0.847299    1.332028   -0.272079
    3          6              0       -0.218311    0.268357   -0.235776
    4          6              0        0.336826   -1.032597    0.349112
    5          6              0        1.713739   -1.358290   -0.218583
    6          6              0        2.720331   -0.265067    0.124240
    7          1              0        2.833091    1.934535   -0.116146
    8          1              0        0.512043    2.344548   -0.451177
    9          6              0       -1.448257    0.779202    0.520443
   10          1              0       -0.538470    0.076372   -1.263027
   11          1              0        0.412499   -0.931932    1.433957
   12          1              0       -0.346300   -1.856771    0.154848
   13          1              0        2.060008   -2.319767    0.154797
   14          1              0        1.638479   -1.450085   -1.302127
   15          1              0        3.040880   -0.360712    1.164090
   16          1              0        3.622809   -0.381714   -0.474671
   17          6              0       -2.656727   -0.139458    0.445229
   18          8              0       -3.124165   -0.373058   -0.825310
   19          1              0       -1.737853    1.749982    0.119749
   20          1              0       -1.194690    0.937427    1.569682
   21          1              0       -3.490389    0.248235    1.040650
   22          1              0       -2.449038   -1.128063    0.871466
---------------------------------------------------------------------
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Thermal=0.20881\Dipole=0.0279442,0.6627,-0.4279888\PG=C01 [X(C8H13O1)]\
NImag=0\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
 Center     Atomic         Atomic           Coordinates (Angstroms)
 Number     Number          Type           X            Y            Z
---------------------------------------------------------------------
   1          6              0        2.137025     1.098996    -0.102435
   2          6              0        0.846774     1.329489    -0.278911
   3          6              0       -0.221831     0.271312    -0.232680
   4          6              0        0.328173    -1.028213     0.356730
   5          6              0        1.702615    -1.359917    -0.209775
   6          6              0        2.710486    -0.267589     0.126158
   7          1              0        2.829134     1.926689    -0.129476
   8          1              0        0.513530     2.340076    -0.464721
   9          6              0       -1.446977     0.788368     0.523570
  10          1              0       -0.548874     0.074869    -1.254914
  11          1              0        0.404406    -0.923316     1.439807
  12          1              0       -0.357294    -1.849256     0.165487
  13          1              0        2.046821    -2.319321     0.166613
  14          1              0        1.625793    -1.455160    -1.291537
  15          1              0        3.031352    -0.357306     1.165169
  16          1              0        3.611449    -0.389494    -0.471623
  17          6              0       -2.659522    -0.125092     0.440611
  18          8              0       -3.082536    -0.394752    -0.832755
  19          1              0       -1.729920     1.759907     0.122962
  20          1              0       -1.196096     0.945326     1.572204
  21          1              0       -3.498302     0.268576     1.021370
  22          1              0       -2.452164    -1.107699     0.881094
---------------------------------------------------------------------
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[X(C8H13O1)] \NImag=0\\@
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8.3.2 2-(Cyclohexen-3-yl)-ethoxyl radical – *pa*-(Ij)

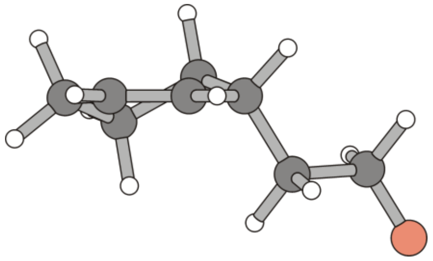

Figure S124. Ball-and-stick model showing the computed equilibrium structure of alkenoxyl radical *pa*-**Ij**

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic              Coordinates (Angstroms)
Number     Number         Type                         Y           Z
---------------------------------------------------------------------
   1          6             0        2.209017    1.057979   -0.221320
   2          6             0        0.993282    1.401643    0.224121
   3          6             0       -0.077326    0.414134    0.637752
   4          6             0        0.514396   -1.007497    0.780930
   5          6             0        1.480183   -1.350696   -0.363330
   6          6             0        2.662218   -0.370487   -0.394065
   7          1             0        2.921703    1.841233   -0.475500
   8          1             0        0.732635    2.456773    0.302115
   9          1             0       -0.442730    0.729903    1.628192
  10          6             0       -1.285725    0.488594   -0.327886
  11          1             0        1.057874   -1.068014    1.733261
  12          1             0       -0.286172   -1.755427    0.838140
  13          1             0        1.842089   -2.379964   -0.257734
  14          1             0        0.947893   -1.303179   -1.322261
  15          1             0        3.382736   -0.622032    0.400004
  16          1             0        3.216459   -0.471438   -1.336384
  17          6             0       -2.566470   -0.139092    0.242236
  18          8             0       -3.644606   -0.125809   -0.602018
  19          1             0       -2.833442    0.287135    1.228952
  20          1             0       -2.410230   -1.222461    0.445603
  21          1             0       -1.504498    1.539132   -0.556198
  22          1             0       -1.044921    0.007348   -1.282674
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```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic          Coordinates (Angstroms)
Number     Number         Type            X           Y           Z
---------------------------------------------------------------------
   1          6             0        2.188672    1.052738   -0.221943
   2          6             0        0.985808    1.392105    0.226870
   3          6             0       -0.076822    0.409242    0.640846
   4          6             0        0.515575   -1.000088    0.780260
   5          6             0        1.463743   -1.338438   -0.365629
   6          6             0        2.639000   -0.367510   -0.399552
   7          1             0        2.893626    1.830925   -0.476854
   8          1             0        0.728455    2.439111    0.307744
   9          1             0       -0.436297    0.721549    1.624827
  10          6             0       -1.276345    0.481292   -0.316218
  11          1             0        1.066611   -1.056005    1.718880
  12          1             0       -0.275749   -1.744209    0.846660
  13          1             0        1.822403   -2.360739   -0.267282
  14          1             0        0.928381   -1.286222   -1.312953
  15          1             0        3.356071   -0.618861    0.385261
  16          1             0        3.182603   -0.464332   -1.338410
  17          6             0       -2.538392   -0.159304    0.241931
  18          8             0       -3.616455   -0.106653   -0.605411
  19          1             0       -2.813761    0.264208    1.213716
  20          1             0       -2.396693   -1.232643    0.424087
  21          1             0       -1.499915    1.524684   -0.533295
  22          1             0       -1.031527    0.015533   -1.268494
---------------------------------------------------------------------
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```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic            Coordinates (Angstroms)
Number     Number         Type            X             Y            Z
---------------------------------------------------------------------
   1          6             0        2.184269     1.049823    -0.224674
   2          6             0        0.988594     1.390714     0.225808
   3          6             0       -0.075157     0.411643     0.641124
   4          6             0        0.514110    -0.996818     0.785496
   5          6             0        1.456952    -1.339595    -0.361807
   6          6             0        2.631324    -0.369904    -0.403442
   7          1             0        2.890517     1.824488    -0.481319
   8          1             0        0.733439     2.436807     0.308274
   9          1             0       -0.434758     0.726912     1.622484
  10          6             0       -1.272700     0.480159    -0.315496
  11          1             0        1.067792    -1.049107     1.721146
  12          1             0       -0.277139    -1.738387     0.857397
  13          1             0        1.814878    -2.360500    -0.262347
  14          1             0        0.918448    -1.289328    -1.305846
  15          1             0        3.352666    -0.620357     0.376020
  16          1             0        3.168642    -0.467887    -1.344319
  17          6             0       -2.537563    -0.152025     0.243426
  18          8             0       -3.605164    -0.112051    -0.610117
  19          1             0       -2.814976     0.283322     1.208578
  20          1             0       -2.393346    -1.221379     0.442312
  21          1             0       -1.493064     1.521211    -0.540798
  22          1             0       -1.030761     0.006635    -1.263256
---------------------------------------------------------------------
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Thermal= 0.2087976\Dipole=0.0100209,0.6723876,-0.5265333\PG=C01
[X(C8H13O1)]\\@
```

8.3.3 Transition structure TS^1-*cis*-**Ij** ($_3$T^4)

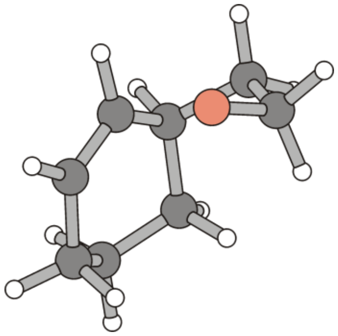

Figure S125. Ball-and-stick model of computed transition structure TS^1-*cis*-**Ij** showing $_3$T^4-conformation of the cyclohexyl-annulated tetrahydrofuran subunit.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic             Coordinates (Angstroms)
Number     Number           Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0        1.059457   -1.381949    0.389305
   2          6             0       -0.059410   -0.749735    0.888483
   3          6             0       -0.291296    0.738319    0.743204
   4          6             0        0.663015    1.390573   -0.280550
   5          6             0        2.088323    0.831154   -0.198852
   6          6             0        2.086312   -0.684995   -0.453386
   7          1             0        1.182989   -2.446122    0.576510
   8          1             0       -0.637017   -1.258428    1.653284
   9          6             0       -1.777159    0.933350    0.369608
  10          1             0       -0.119314    1.199112    1.728230
  11          1             0        0.281119    1.222211   -1.295445
  12          1             0        0.664701    2.476258   -0.125373
  13          1             0        2.737655    1.336144   -0.923335
  14          1             0        2.508977    1.028772    0.796627
  15          1             0        1.881251   -0.884945   -1.518422
  16          1             0        3.076324   -1.116719   -0.258527
  17          6             0       -2.076806   -0.059048   -0.768083
  18          8             0       -1.560449   -1.308446   -0.433927
  19          1             0       -3.169308   -0.168235   -0.885374
  20          1             0       -1.680654    0.315352   -1.729045
  21          1             0       -1.990598    1.970672    0.081246
  22          1             0       -2.407151    0.687475    1.232669
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NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic          Coordinates (Angstroms)
Number     Number         Type            X            Y            Z
---------------------------------------------------------------------
   1          6             0        1.052368   -1.372691    0.386576
   2          6             0       -0.071383   -0.751074    0.870171
   3          6             0       -0.296030    0.732552    0.737912
   4          6             0        0.651916    1.381342   -0.276625
   5          6             0        2.068434    0.830013   -0.187411
   6          6             0        2.071331   -0.672870   -0.452412
   7          1             0        1.179121   -2.427803    0.573049
   8          1             0       -0.635362   -1.254138    1.637237
   9          6             0       -1.768179    0.925181    0.362250
  10          1             0       -0.121161    1.184116    1.716603
  11          1             0        0.279252    1.211120   -1.285674
  12          1             0        0.649067    2.459016   -0.123614
  13          1             0        2.716714    1.338675   -0.897686
  14          1             0        2.476372    1.020375    0.805640
  15          1             0        1.866094   -0.863420   -1.509628
  16          1             0        3.055113   -1.097524   -0.259576
  17          6             0       -2.056111   -0.061673   -0.763949
  18          8             0       -1.526059   -1.297735   -0.425085
  19          1             0       -3.134428   -0.191553   -0.887879
  20          1             0       -1.657362    0.303340   -1.714431
  21          1             0       -1.981852    1.952589    0.071121
  22          1             0       -2.397176    0.682406    1.216447
---------------------------------------------------------------------
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(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic              Coordinates (Angstroms)
Number     Number           Type              X           Y           Z
---------------------------------------------------------------------
   1          6              0         1.041007   -1.371515    0.388588
   2          6              0        -0.079465   -0.748816    0.871069
   3          6              0        -0.298588    0.735712    0.739092
   4          6              0         0.656601    1.386226   -0.266311
   5          6              0         2.066894    0.821979   -0.184345
   6          6              0         2.053785   -0.677589   -0.459788
   7          1              0         1.168274   -2.424136    0.579936
   8          1              0        -0.634488   -1.243515    1.648026
   9          6              0        -1.765263    0.930479    0.347488
  10          1              0        -0.131885    1.183535    1.718911
  11          1              0         0.283349    1.231541   -1.276222
  12          1              0         0.663360    2.460590   -0.101186
  13          1              0         2.717618    1.329619   -0.890906
  14          1              0         2.477602    0.999650    0.808423
  15          1              0         1.831491   -0.858135   -1.514086
  16          1              0         3.035234   -1.111440   -0.284349
  17          6              0        -2.036074   -0.066733   -0.772014
  18          8              0        -1.516473   -1.296334   -0.410531
  19          1              0        -3.111828   -0.193862   -0.911067
  20          1              0        -1.623873    0.290299   -1.718917
  21          1              0        -1.973320    1.955176    0.048179
  22          1              0        -2.403130    0.692884    1.194831
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-387.6664803\S2=0.826681\S2-1=0.\
S2A=0.750703\RMSD=8.488e-09\RMSF=4.588e-07\ZeroPoint=0.2007052\Thermal=
0.2083489\Dipole=0.6728622,-0.5200177,0.0203533\PG=C01 [X(C8H13O1)]\\@
```

8.3.4 Transition structure TS^1-*trans*-**Ij** ($^3T_4$)

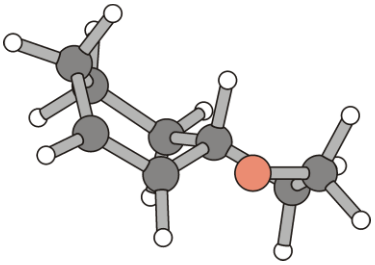

Figure S126. Ball-and-stick model of computed transition structure TS^1-*trans*-**Ij** showing, $^3T_4$-conformation of the cyclohexyl-annulated tetrahydrofuran subunit.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type              X           Y           Z
---------------------------------------------------------------------
   1          6              0        1.013337   -1.457806   -0.364381
   2          6              0       -0.119558   -0.706264   -0.612946
   3          6              0       -0.193967    0.620802    0.090699
   4          6              0        1.061699    1.442554   -0.253748
   5          6              0        2.342507    0.630237    0.126082
   6          6              0        2.053725   -0.854381    0.535083
   7          1              0        1.201871   -2.391558   -0.887435
   8          1              0       -0.640649   -0.843071   -1.555738
   9          6              0       -1.594327    1.170541   -0.146509
  10          1              0       -0.128325    0.407750    1.168353
  11          1              0        1.065487    1.681729   -1.324191
  12          1              0        1.042990    2.398002    0.283248
  13          1              0        3.035730    0.623238   -0.721639
  14          1              0        2.869497    1.118098    0.953560
  15          1              0        2.981787   -1.433332    0.514810
  16          1              0        1.700975   -0.873494    1.577746
  17          6              0       -2.518494    0.040960    0.390614
  18          8              0       -1.962530   -1.218120    0.103456
  19          1              0       -2.627323    0.171279    1.481637
  20          1              0       -3.516741    0.115703   -0.069139
  21          1              0       -1.784596    2.113087    0.378741
  22          1              0       -1.769992    1.337675   -1.216961
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-387.8231135\S2=0.784693\S2-1=0.\
S2A=0.750181\RMSD=2.449e-09\RMSF=8.718e-07\ZeroPoint=0.1936369\Thermal=
0.2017788\Dipole=0.8133663,0.8276342,-0.2953951\PG=C01 [X(C8H13O1)]\\@
```

(*ii*) BHandHLYP/6-31+G//BHandHLYP/6-31+G****

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type           X           Y           Z
---------------------------------------------------------------------
    1         6             0         0.997846   -1.445068   -0.373903
    2         6             0        -0.128073   -0.695291   -0.617705
    3         6             0        -0.193344    0.620949    0.091811
    4         6             0         1.052385    1.436003   -0.245984
    5         6             0         2.320507    0.622096    0.128087
    6         6             0         2.028307   -0.848940    0.532403
    7         1             0         1.188576   -2.366099   -0.900850
    8         1             0        -0.639006   -0.817511   -1.558426
    9         6             0        -1.585464    1.163525   -0.143442
   10         1             0        -0.130825    0.400846    1.159172
   11         1             0         1.057303    1.677731   -1.307422
   12         1             0         1.037913    2.382075    0.291114
   13         1             0         3.006718    0.613687   -0.714777
   14         1             0         2.847700    1.104426    0.947820
   15         1             0         2.948970   -1.424405    0.512496
   16         1             0         1.673957   -0.873574    1.564645
   17         6             0        -2.495893    0.036109    0.377054
   18         8             0        -1.915832   -1.213422    0.122557
   19         1             0        -2.629183    0.162482    1.454555
   20         1             0        -3.476935    0.078406   -0.098541
   21         1             0        -1.781139    2.093610    0.384763
   22         1             0        -1.755021    1.339401   -1.204925
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-387.576392\S2=0.842594\S2-1=0.\
S2A=0.750957\RMSD=8.244e-09\RMSF=5.707e-07\ZeroPoint=0.2007846\Thermal=
0.2087024\Dipole=0.7542893,0.7530258,-0.1558416\PG=C01 [X(C8H13O1)]\\@
```

(*iii*) **BHandHLYP/6-311G**//BHandHLYP/6-311G****

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type           X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.992232   -1.439601    0.382750
   2          6             0        0.133156   -0.692111    0.616163
   3          6             0        0.193570    0.622003   -0.096572
   4          6             0       -1.050559    1.436481    0.240158
   5          6             0       -2.317213    0.620743   -0.129498
   6          6             0       -2.022975   -0.850803   -0.525698
   7          1             0       -1.182212   -2.355623    0.915448
   8          1             0        0.643099   -0.805711    1.557107
   9          6             0        1.583746    1.164977    0.137992
  10          1             0        0.130808    0.395360   -1.160996
  11          1             0       -1.054390    1.680006    1.299746
  12          1             0       -1.038765    2.379917   -0.298467
  13          1             0       -3.002425    0.616121    0.712359
  14          1             0       -2.843772    1.098200   -0.950582
  15          1             0       -2.941620   -1.426659   -0.503476
  16          1             0       -1.668067   -0.880041   -1.556173
  17          6             0        2.498583    0.028257   -0.356369
  18          8             0        1.892408   -1.213476   -0.144499
  19          1             0        2.676152    0.164368   -1.425211
  20          1             0        3.459620    0.059502    0.157273
  21          1             0        1.781985    2.086170   -0.401470
  22          1             0        1.743867    1.356527    1.196866
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-387.6429368\S2=0.842829\S2-1=0.\
S2A=0.750915\RMSD=7.917e-09\RMSF=6.073e-07\ZeroPoint=0.2000403\Thermal=
0.2080349\Dipole=0.6627798,0.6975946,-0.1386777\PG=C01 [X(C8H13O1)]\\@
```

8.3.5 Transition structure TS^2-*cis*-**Ij** ($^2T_3$)

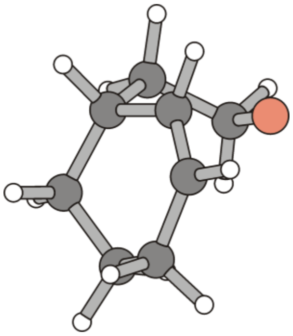

Figure S127 Ball-and-stick model showing the computed transition structure TS^2-*cis*-**Ij**, displaying $^2T_3$-conformation of the cyclohexyl-annulated tetrahydrofuran subunit.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic             Coordinates (Angstroms)
Number     Number           Type             X           Y           Z
---------------------------------------------------------------------
   1          6              0        1.154390   -1.286075   -0.537144
   2          6              0       -0.039284   -0.766116   -0.995052
   3          6              0       -0.377657    0.708702   -0.907531
   4          6              0        0.738650    1.530538   -0.212959
   5          6              0        1.487621    0.764664    0.888918
   6          6              0        2.106922   -0.527121    0.336765
   7          1              0        1.392603   -2.322233   -0.766946
   8          1              0       -0.608555   -1.351523   -1.709456
   9          1              0       -0.466686    1.080253   -1.938078
  10          6              0       -1.782589    0.830287   -0.265231
  11          1              0        1.470072    1.834601   -0.974247
  12          1              0        0.312690    2.457204    0.189957
  13          1              0        2.270028    1.401376    1.318029
  14          1              0        0.804477    0.512002    1.706231
  15          1              0        3.013460   -0.293239   -0.247234
  16          1              0        2.450106   -1.173017    1.156147
  17          6              0       -1.840490   -0.156499    0.908463
  18          8              0       -1.322340   -1.381605    0.492240
  19          1              0       -2.000346    1.862148    0.038299
  20          1              0       -2.535900    0.534848   -1.005442
  21          1              0       -2.890443   -0.328041    1.204415
  22          1              0       -1.318163    0.248178    1.793041
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-387.8427554\S2=0.776177\S2-1=0.\
S2A=0.750128\RMSD=2.966e-09\RMSF=7.733e-07\ZeroPoint=0.1942075\Thermal=
0.2021442\Dipole=0.7596247,0.6361151,-0.0474504\PG=C01 [X(C8H13O1)]\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic             Coordinates (Angstroms)
Number     Number           Type             X            Y            Z
---------------------------------------------------------------------
   1          6              0         1.150698   -1.277605   -0.529571
   2          6              0        -0.047632   -0.772680   -0.970574
   3          6              0        -0.383566    0.696970   -0.903310
   4          6              0         0.723623    1.518852   -0.219682
   5          6              0         1.470875    0.766365    0.877809
   6          6              0         2.099535   -0.509597    0.329920
   7          1              0         1.389852   -2.306249   -0.751322
   8          1              0        -0.606429   -1.357437   -1.681273
   9          1              0        -0.468918    1.054338   -1.929632
  10          6              0        -1.774477    0.818933   -0.263122
  11          1              0         1.449168    1.816242   -0.977078
  12          1              0         0.299702    2.440365    0.174762
  13          1              0         2.240651    1.406479    1.303625
  14          1              0         0.794625    0.509741    1.688446
  15          1              0         2.989983   -0.265919   -0.257147
  16          1              0         2.450048   -1.142946    1.144169
  17          6              0        -1.822436   -0.154413    0.904528
  18          8              0        -1.295841   -1.368069    0.488110
  19          1              0        -1.993777    1.842385    0.036369
  20          1              0        -2.524598    0.519878   -0.992838
  21          1              0        -2.856717   -0.340208    1.206490
  22          1              0        -1.296581    0.246927    1.774573
---------------------------------------------------------------------
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S2A=0.750663\RMSD=8.091e-09\RMSF=6.372e-07\ZeroPoint=0.2014988\Thermal=
0.2091774\Dipole=0.7493036,0.5447043,0.0068533\PG=C01 [X(C8H13O1)]\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        1.158882   -1.268696   -0.530906
   2          6           0       -0.046745   -0.779361   -0.961755
   3          6           0       -0.392359    0.688123   -0.905430
   4          6           0        0.703615    1.520862   -0.219302
   5          6           0        1.458019    0.774121    0.875738
   6          6           0        2.101319   -0.490652    0.323416
   7          1           0        1.408889   -2.293000   -0.753640
   8          1           0       -0.599642   -1.368556   -1.671320
   9          1           0       -0.474695    1.038067   -1.932769
  10          6           0       -1.784486    0.800738   -0.270764
  11          1           0        1.425500    1.827668   -0.974428
  12          1           0        0.269372    2.435212    0.176397
  13          1           0        2.217897    1.421156    1.305132
  14          1           0        0.784471    0.504103    1.682301
  15          1           0        2.984952   -0.234226   -0.266529
  16          1           0        2.463822   -1.119518    1.134136
  17          6           0       -1.812783   -0.161403    0.905379
  18          8           0       -1.263266   -1.364716    0.500740
  19          1           0       -2.018850    1.823127    0.015324
  20          1           0       -2.527607    0.480696   -0.996868
  21          1           0       -2.842745   -0.362713    1.208063
  22          1           0       -1.298005    0.263314    1.770027
---------------------------------------------------------------------
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S2A=0.75064\RMSD=4.929e-09\RMSF=7.479e-07\ZeroPoint=0.200816\Thermal=
0.2085137\Dipole=0.6657645,0.5032555,0.0077008\PG=C01 [X(C8H13O1)]\\@
```

8.3.6 *cis*-7-Oxabicyclo[4.3.0]bicyclonon-5-yl radical *cis*-IIj (axial)

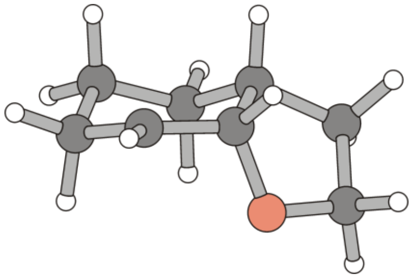

Figure S128. Ball-and-stick model showing the computed equilibrium structure of carbon radical *cis*-**IIj** (axial).

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic            Coordinates (Angstroms)
Number     Number         Type            X            Y            Z
---------------------------------------------------------------------
   1          6             0       -0.358950    0.739792    0.637461
   2          6             0        0.650278    1.392399   -0.324287
   3          6             0       -0.278320   -0.803388    0.586268
   4          6             0        2.077644    0.881200   -0.092319
   5          6             0        1.086661   -1.377979    0.421322
   6          6             0        2.154609   -0.640730   -0.320167
   7          1             0       -0.155714    1.089564    1.657328
   8          6             0       -1.830827    1.004879    0.234948
   9          1             0        0.354248    1.175368   -1.359832
  10          1             0        0.606739    2.482681   -0.206598
  11          1             0       -0.752054   -1.227448    1.488895
  12          8             0       -1.114900   -1.141548   -0.553124
  13          1             0        2.780669    1.394502   -0.759002
  14          1             0        2.388937    1.112120    0.936133
  15          1             0        1.232194   -2.426428    0.668457
  16          1             0        2.047225   -0.835360   -1.404168
  17          1             0        3.144185   -1.027442   -0.046376
  18          6             0       -2.276795   -0.312087   -0.457667
  19          1             0       -2.658525   -0.168003   -1.472294
  20          1             0       -3.051366   -0.823870    0.133739
  21          1             0       -1.908622    1.867994   -0.434411
  22          1             0       -2.454517    1.214197    1.109763
---------------------------------------------------------------------
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S2A=0.75001\RMSD=2.850e-09\RMSF=6.468e-07\ZeroPoint=0.195877\Thermal=
0.2040855\Dipole=-0.5584699,-0.2602332,0.0623216\PG=C01 [X(C8H13O1)]\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6            0       -0.379119    0.705385    0.689093
   2          6            0        0.561385    1.389266   -0.303079
   3          6            0       -0.259347   -0.819554    0.626743
   4          6            0        2.002642    0.924761   -0.132622
   5          6            0        1.121411   -1.340586    0.453521
   6          6            0        2.116643   -0.583861   -0.355478
   7          1            0       -0.157774    1.059141    1.694645
   8          6            0       -1.854479    0.895848    0.337294
   9          1            0        0.236059    1.172055   -1.321038
  10          1            0        0.490373    2.468526   -0.176096
  11          1            0       -0.707537   -1.258335    1.522046
  12          8            0       -1.065074   -1.179270   -0.502872
  13          1            0        2.654122    1.452929   -0.825930
  14          1            0        2.347278    1.169399    0.872818
  15          1            0        1.311622   -2.372313    0.703469
  16          1            0        1.951682   -0.792651   -1.419387
  17          1            0        3.124155   -0.930815   -0.134077
  18          6            0       -2.135524   -0.257902   -0.637141
  19          1            0       -2.162928    0.071569   -1.673122
  20          1            0       -3.078440   -0.755535   -0.416608
  21          1            0       -2.059077    1.868712   -0.101786
  22          1            0       -2.470608    0.801340    1.228047
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-387.634349\S2=0.755346\S2-1=0.\
S2A=0.75002\RMSD=3.020e-09\RMSF=8.680e-07\ZeroPoint=0.2032979\Thermal=
0.2112579\Dipole=-0.6223805,-0.2238857,0.0965257\PG=C01 [X(C8H13O1)]\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic          Coordinates (Angstroms)
Number     Number         Type           X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.383583    0.705319    0.692949
   2          6             0        0.553403    1.389715   -0.300645
   3          6             0       -0.258430   -0.818420    0.624622
   4          6             0        1.994760    0.926563   -0.138424
   5          6             0        1.125414   -1.331940    0.470320
   6          6             0        2.108879   -0.582067   -0.355714
   7          1             0       -0.165357    1.058891    1.697312
   8          6             0       -1.857362    0.889644    0.335445
   9          1             0        0.224276    1.172639   -1.315808
  10          1             0        0.482887    2.467561   -0.173742
  11          1             0       -0.720108   -1.261956    1.509298
  12          8             0       -1.037685   -1.166784   -0.522069
  13          1             0        2.640068    1.452308   -0.837076
  14          1             0        2.345748    1.174179    0.862652
  15          1             0        1.324598   -2.354867    0.741130
  16          1             0        1.927478   -0.796232   -1.414565
  17          1             0        3.118770   -0.925363   -0.147336
  18          6             0       -2.131435   -0.274427   -0.630106
  19          1             0       -2.194442    0.051542   -1.663820
  20          1             0       -3.057340   -0.790017   -0.383848
  21          1             0       -2.060092    1.857057   -0.112369
  22          1             0       -2.474880    0.802200    1.224036
---------------------------------------------------------------------
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S2A=0.75002\RMSD=5.613e-09\RMSF=9.426e-07\ ZeroPoint=0.2026525\Thermal=
0.2106306\Dipole=-0.5607397,-0.2060243,0.052826\PG=C01 [X(C8H13O1)]\\@
```

8.3.7 *trans*-7-Oxabicyclo[4.3.0]bicyclonon-5-yl radical *trans*-IIj

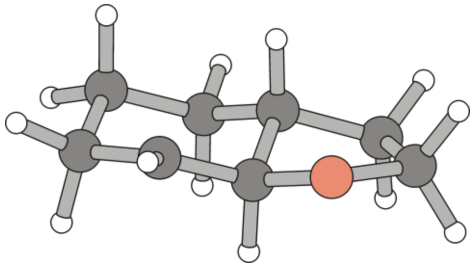

Figure S129. Ball-and-stick model showing the computed equilibrium structure of carbon radical *trans*-**IIj**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic             Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0        2.231815    0.680023   -0.256150
   2          6             0        0.976529    1.463162    0.190810
   3          6             0       -0.269104    0.719407   -0.288911
   4          6             0       -0.294324   -0.704969    0.288879
   5          6             0        0.894102   -1.483152   -0.131399
   6          6             0        2.205527   -0.814558    0.167848
   7          1             0        2.303823    0.732283   -1.350516
   8          1             0        3.136181    1.154704    0.142854
   9          1             0        0.956815    1.554067    1.286909
  10          1             0        1.011228    2.483457   -0.210859
  11          6             0       -1.683156    1.186852    0.077696
  12          1             0       -0.210499    0.612485   -1.381728
  13          1             0       -0.280142   -0.608213    1.400363
  14          8             0       -1.559263   -1.223635   -0.106828
  15          1             0        0.820209   -2.528130   -0.413682
  16          1             0        2.404276   -0.861944    1.255987
  17          1             0        3.032970   -1.350577   -0.309838
  18          6             0       -2.503498   -0.129925   -0.040953
  19          1             0       -2.065165    1.972435   -0.581278
  20          1             0       -1.707282    1.569832    1.105124
  21          1             0       -3.169897   -0.274899    0.818868
  22          1             0       -3.105756   -0.167461   -0.954490
---------------------------------------------------------------------
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0.2035768\Dipole=-0.7266069,-0.2555679,0.1878537\PG=C01 [X(C8H13O1)]\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic         Atomic              Coordinates (Angstroms)
Number     Number          Type              X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.887495   -1.475088   -0.135065
   2          6             0        0.294270   -0.698098    0.289060
   3          6             0        0.268309    0.712883   -0.282484
   4          6             0       -0.967993    1.452467    0.194049
   5          6             0       -2.212376    0.677140   -0.258908
   6          6             0       -2.192490   -0.805018    0.160566
   7          1             0       -0.818056   -2.528623   -0.347840
   8          1             0        0.274968   -0.608844    1.390536
   9          8             0        1.545557   -1.208400   -0.099985
  10          6             0        1.671863    1.174909    0.084239
  11          1             0        0.212360    0.609380   -1.367539
  12          1             0       -0.951953    1.536852    1.282318
  13          1             0       -0.999876    2.466645   -0.200286
  14          1             0       -3.111964    1.149510    0.130575
  15          1             0       -2.275784    0.731234   -1.345403
  16          1             0       -2.390160   -0.858201    1.239075
  17          1             0       -3.012995   -1.333553   -0.318447
  18          6             0        2.482137   -0.132243   -0.054787
  19          1             0        1.697275    1.539453    1.109648
  20          1             0        2.051679    1.963458   -0.558571
  21          1             0        3.163872   -0.279134    0.780642
  22          1             0        3.058829   -0.162695   -0.974841
---------------------------------------------------------------------
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0.2108076\.\Dipole=0.5778732,0.503979,0.2104386\PG=C01 [X(C8H13O1)]\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic             Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.884448   -1.472635   -0.135359
   2          6             0        0.295155   -0.697127    0.291601
   3          6             0        0.267600    0.712991   -0.279854
   4          6             0       -0.968022    1.451423    0.194902
   5          6             0       -2.210356    0.675834   -0.259423
   6          6             0       -2.189516   -0.805782    0.158190
   7          1             0       -0.811972   -2.524979   -0.344736
   8          1             0        0.272756   -0.606497    1.391911
   9          8             0        1.543321   -1.207060   -0.097649
  10          6             0        1.670398    1.174411    0.083797
  11          1             0        0.211790    0.605884   -1.363326
  12          1             0       -0.953310    1.534753    1.281907
  13          1             0       -1.000674    2.464416   -0.198283
  14          1             0       -3.109702    1.146474    0.128561
  15          1             0       -2.271921    0.730468   -1.344643
  16          1             0       -2.388393   -0.860651    1.235203
  17          1             0       -3.007932   -1.333645   -0.321929
  18          6             0        2.477953   -0.132792   -0.057981
  19          1             0        1.697243    1.537440    1.108164
  20          1             0        2.047891    1.961311   -0.559695
  21          1             0        3.165060   -0.275815    0.772422
  22          1             0        3.050005   -0.160619   -0.979601
---------------------------------------------------------------------
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0.2101704\\Dipole=0.521324,0.442767,0.189645\PG=C01 [X(C8H13O1)]\\@
```

8.3.8 *cis*-7-Oxabicyclo[4.3.0]bicyclonon-5-yl Radical *cis*-IIj (equatorial)

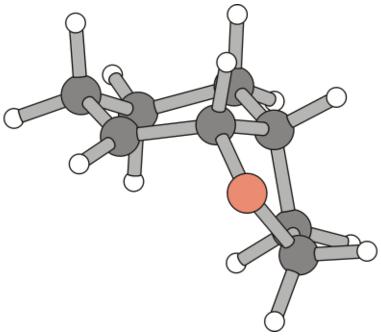

Figure S130. Equilibrium structure of carbon radical *cis*-**IIj** (equatorial).

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic         Atomic            Coordinates (Angstroms)
Number     Number          Type              X           Y           Z
---------------------------------------------------------------------
   1          6             0        2.303237   -0.129909   -0.448907
   2          8             0        1.764768    1.006439    0.253420
   3          6             0        0.414156    0.733942    0.674843
   4          6             0        0.261601   -0.805511    0.605461
   5          6             0        1.155800   -1.136488   -0.603969
   6          6             0       -1.197688   -1.290972    0.546778
   7          6             0       -2.056584   -0.543479   -0.483997
   8          6             0       -1.992433    0.982022   -0.255782
   9          6             0       -0.576787    1.459012   -0.181630
  10          1             0        0.340088    1.080723    1.721390
  11          1             0        0.734683   -1.230956    1.500486
  12          1             0       -1.214807   -2.370095    0.346839
  13          1             0       -1.648690   -1.158110    1.540642
  14          1             0       -1.712734   -0.769530   -1.500977
  15          1             0       -3.095347   -0.889719   -0.419567
  16          1             0       -2.538396    1.515317   -1.042348
  17          1             0       -2.526740    1.208663    0.687917
  18          1             0       -0.285745    2.428173   -0.577160
  19          1             0        1.505999   -2.173709   -0.598210
  20          1             0        2.711468    0.209605   -1.407315
  21          1             0        3.126510   -0.548293    0.146720
  22          1             0        0.617758   -0.965285   -1.542559
---------------------------------------------------------------------
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0.2038027\Dipole=0.7501928,0.0036996,-0.383314\PG=C01[X(C8H13O1)]\
NImag=0\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic            Coordinates (Angstroms)
Number     Number         Type            X            Y            Z
---------------------------------------------------------------------
   1          6             0        0.416935     0.724675     0.673612
   2          6             0        0.259251    -0.800766     0.601035
   3          6             0       -1.190906    -1.278374     0.546556
   4          6             0       -2.041322    -0.535336    -0.479187
   5          6             0       -1.974346     0.977934    -0.254580
   6          6             0       -0.561974     1.447244    -0.188718
   7          1             0        0.331047     1.072290     1.708324
   8          8             0        1.752394     0.983694     0.265827
   9          6             0        1.139832    -1.125988    -0.605413
  10          1             0        0.732341    -1.227331     1.485279
  11          1             0       -1.211928    -2.349586     0.350707
  12          1             0       -1.637436    -1.141127     1.532564
  13          1             0       -1.699907    -0.762925    -1.487659
  14          1             0       -3.072707    -0.877146    -0.415370
  15          1             0       -2.515597     1.506538    -1.035775
  16          1             0       -2.496259     1.209738     0.683481
  17          1             0       -0.276000     2.416600    -0.564267
  18          6             0        2.279554    -0.124147    -0.452961
  19          1             0        1.489022    -2.154764    -0.606310
  20          1             0        2.669604     0.225028    -1.405403
  21          1             0        3.105622    -0.545170     0.119217
  22          1             0        0.600900    -0.953137    -1.533465
---------------------------------------------------------------------
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0.2110232\Dipole=0.4324314,0.0510036,0.7106391\PG=C01 [X(C8H13O1)]\\@
```

(*iii*) BHandHLYP/6-311G//BHandHLYP/6-311G****

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        0.419322    0.721667    0.674249
   2          6           0        0.257576   -0.802284    0.598880
   3          6           0       -1.192364   -1.275824    0.547531
   4          6           0       -2.041401   -0.531511   -0.476745
   5          6           0       -1.968402    0.980904   -0.254702
   6          6           0       -0.555898    1.443777   -0.189826
   7          1           0        0.330282    1.067124    1.707868
   8          8           0        1.752597    0.980327    0.267866
   9          6           0        1.133486   -1.122568   -0.610685
  10          1           0        0.733347   -1.231509    1.478577
  11          1           0       -1.217648   -2.345719    0.353187
  12          1           0       -1.636155   -1.135967    1.532993
  13          1           0       -1.702794   -0.761201   -1.484220
  14          1           0       -3.072492   -0.869151   -0.411068
  15          1           0       -2.508033    1.509421   -1.035085
  16          1           0       -2.487695    1.216283    0.682598
  17          1           0       -0.265352    2.409573   -0.566242
  18          6           0        2.275421   -0.126539   -0.450121
  19          1           0        1.478389   -2.151086   -0.620313
  20          1           0        2.671329    0.219333   -1.399884
  21          1           0        3.095446   -0.556959    0.121869
  22          1           0        0.594149   -0.938495   -1.534703
---------------------------------------------------------------------
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S2A=0.750023\RMSD=7.457e-09\RMSF=6.944e-07\ZeroPoint=0.2025178\Thermal=
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```

8.4 The 4-Pentenoxyl Radical Cyclization

8.4.1 4-Pentenoxyl radical (Ij)

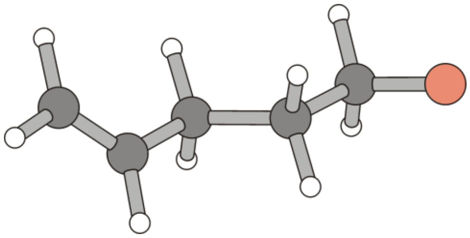

Figure S131. Equilibrium structure of alkenoxyl radical **Ij**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic             Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0        3.002765   -0.021861   -0.431860
   2          6             0        1.946396   -0.261177    0.350656
   3          6             0        0.650646    0.503218    0.319475
   4          6             0       -0.562098   -0.389227   -0.005333
   5          6             0       -1.880583    0.390047    0.004449
   6          8             0       -3.010696   -0.346030   -0.236400
   7          1             0        3.909612   -0.615313   -0.361311
   8          1             0        2.996920    0.778212   -1.169227
   9          1             0        1.999456   -1.076305    1.074278
  10          1             0        0.488779    0.975710    1.300830
  11          1             0        0.723455    1.318303   -0.412511
  12          1             0       -0.430866   -0.849474   -0.991813
  13          1             0       -0.635749   -1.209109    0.719775
  14          1             0       -2.050452    0.865517    0.996576
  15          1             0       -1.858344    1.254696   -0.689718
---------------------------------------------------------------------
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Thermal= 0.1342282\Dipole=-0.0665706,-0.6850188,-0.4549922\PG=C01
[X(C5H9O1)]\ NImag=0\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        2.978525   -0.036079   -0.429519
   2          6           0        1.931156   -0.252697    0.352672
   3          6           0        0.645193    0.511464    0.303372
   4          6           0       -0.559876   -0.381238    0.008758
   5          6           0       -1.864502    0.396005    0.008679
   6          8           0       -2.984578   -0.358243   -0.235357
   7          1           0        3.876649   -0.625907   -0.345847
   8          1           0        2.973148    0.740439   -1.179655
   9          1           0        1.982556   -1.044126    1.089690
  10          1           0        0.490317    1.008685    1.263482
  11          1           0        0.719039    1.297948   -0.446987
  12          1           0       -0.434660   -0.863905   -0.958391
  13          1           0       -0.627995   -1.175658    0.750462
  14          1           0       -2.033971    0.893662    0.972273
  15          1           0       -1.851434    1.210068   -0.725940
---------------------------------------------------------------------
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0.1389779\Dipole=-0.0479158,-0.648385,-0.4352557\PG=C01[X(C5H9O1)]\
NImag=0\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        2.968360   -0.042085   -0.433376
   2          6           0        1.931316   -0.247714    0.355690
   3          6           0        0.645861    0.514318    0.304608
   4          6           0       -0.558331   -0.378105    0.013745
   5          6           0       -1.863911    0.396104    0.000541
   6          8           0       -2.977226   -0.363102   -0.232034
   7          1           0        3.866277   -0.630099   -0.349975
   8          1           0        2.957459    0.724705   -1.191746
   9          1           0        1.986002   -1.029347    1.101069
  10          1           0        0.490806    1.014443    1.261834
  11          1           0        0.718502    1.297280   -0.447571
  12          1           0       -0.429117   -0.868436   -0.947696
  13          1           0       -0.631106   -1.165648    0.760468
  14          1           0       -2.034443    0.900825    0.959745
  15          1           0       -1.846342    1.205987   -0.737099
---------------------------------------------------------------------
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S2A=0.750016\RMSD=6.138e-09\RMSF=1.988e-07\ZeroPoint=0.1310322\Thermal=
0.1385375\Dipole=-0.0482987,-0.600967,-0.3910608\PG=C01 [X(C5H9O1)]\
NImag=0\\@
```

8.4.2 Transition structure TS-Ij

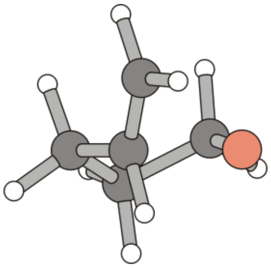

Figure S132. Ball-and-stick model of computed transition structure TS-**Ij**, showing $_2T^3$-conformation of the distorted tetrahydrofuran nucleus

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic             Coordinates (Angstroms)
Number     Number           Type               X            Y            Z
---------------------------------------------------------------------
   1          8              0        -0.218440   -1.341831   -0.316148
   2          6              0        -1.299215   -0.754709    0.343768
   3          6              0        -1.398322    0.710961   -0.089756
   4          6              0         0.025782    1.274149    0.084125
   5          6              0         1.027929    0.276129   -0.443264
   6          6              0         2.075669   -0.196800    0.313602
   7          1              0        -1.213795   -0.834621    1.442497
   8          1              0        -2.198724   -1.319062    0.043429
   9          1              0        -2.134109    1.278339    0.492803
  10          1              0        -1.692754    0.755213   -1.144904
  11          1              0         0.225307    1.466235    1.145447
  12          1              0         0.134371    2.228259   -0.446663
  13          1              0         1.081715    0.161974   -1.522137
  14          1              0         2.116102   -0.023639    1.385452
  15          1              0         2.838349   -0.836432   -0.117594
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S2A=0.750143\RMSD=6.659e-09\RMSF=8.393e-07\ZeroPoint=0.1286182\Thermal=
0.1345837\Dipole=0.6178429,-0.337967,0.4867433\PG=C01
[X(C5H9O1)\NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          8           0       -0.202708   -1.321345   -0.317738
   2          6           0       -1.280902   -0.754350    0.348631
   3          6           0       -1.396796    0.695908   -0.086321
   4          6           0        0.013331    1.263575    0.074590
   5          6           0        1.007429    0.260778   -0.440648
   6          6           0        2.064785   -0.177627    0.313792
   7          1           0       -1.173080   -0.827020    1.435209
   8          1           0       -2.163194   -1.332226    0.063123
   9          1           0       -2.128389    1.252671    0.495490
  10          1           0       -1.697429    0.732419   -1.131399
  11          1           0        0.214998    1.463794    1.125354
  12          1           0        0.121954    2.204553   -0.461560
  13          1           0        1.067249    0.145726   -1.510535
  14          1           0        2.108110    0.014325    1.373846
  15          1           0        2.824372   -0.813187   -0.107885
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-270.9226156\S2=0.826588\S2-1=0.\
S2A=0.750709\RMSD=3.664e-09\RMSF=4.925e-07\ZeroPoint=0.1333433\Thermal=
0.1391357\Dipole=0.5691574,-0.3174852,0.5117178\PG=C01[X(C5H9O1)]\
NImag=1\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          8           0       -0.190664   -1.312299   -0.325013
   2          6           0       -1.266752   -0.761342    0.350179
   3          6           0       -1.401377    0.687016   -0.081706
   4          6           0        0.005272    1.262952    0.070605
   5          6           0        1.001573    0.260628   -0.440750
   6          6           0        2.055296   -0.170013    0.318179
   7          1           0       -1.153658   -0.832639    1.435468
   8          1           0       -2.145081   -1.346035    0.070823
   9          1           0       -2.133466    1.237910    0.502389
  10          1           0       -1.705948    0.719385   -1.124421
  11          1           0        0.208969    1.469508    1.118288
  12          1           0        0.108657    2.199674   -0.470915
  13          1           0        1.071850    0.154182   -1.509346
  14          1           0        2.088544    0.019551    1.377633
  15          1           0        2.821379   -0.798584   -0.098847
----------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-270.9708623\S2=0.826641\S2-1=0.\
S2A=0.750674\RMSD=8.909e-09\RMSF=5.677e-07\ZeroPoint=0.1328445\Thermal=
0.1386177\Dipole=0.5187926,- 0.2920208,0.456006\PG=C01[X(C5H9O1)]\
NImag=1\\@
```

8.4.3 Tetrahydrofur-2-yl methyl radical IIj

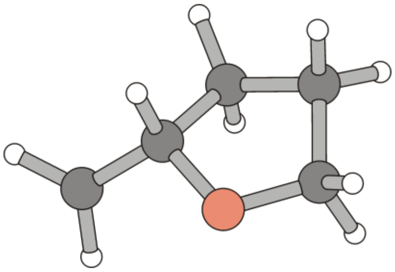

Figure S133. Ball-and-stick model for computed equilibrium structure of cyclized radical **IIj**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic             Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          8             0        0.052527   -1.145763   -0.109224
   2          6             0       -1.323108   -0.829684    0.166240
   3          6             0       -1.484039    0.678088   -0.079708
   4          6             0       -0.066021    1.199110    0.188922
   5          6             0        0.804905    0.053910   -0.387324
   6          6             0        2.171364   -0.063720    0.176831
   7          1             0       -1.538915   -1.093004    1.210712
   8          1             0       -1.962145   -1.440520   -0.481454
   9          1             0       -2.241880    1.130370    0.567237
  10          1             0       -1.769280    0.871677   -1.120226
  11          1             0        0.118440    1.297167    1.264968
  12          1             0        0.150445    2.160122   -0.286173
  13          1             0        0.869091    0.184109   -1.481832
  14          1             0        2.325218   -0.611143    1.100615
  15          1             0        3.010200    0.441104   -0.289822
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-271.1201629\S2=0.753834\S2-1=0.\
S2A=0.75001\RMSD=4.547e-09\RMSF=7.534e-07\ZeroPoint=0.1294895\Thermal=
0.1360879\Dipole=0.6334341,-0.0681858,0.5155249\PG=C01 [X(C5H9O1)]\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X            Y            Z
---------------------------------------------------------------------
   1          8            0        0.052199   -1.128943   -0.089913
   2          6            0       -1.313638   -0.826027    0.151690
   3          6            0       -1.472137    0.676163   -0.074941
   4          6            0       -0.062085    1.188057    0.192697
   5          6            0        0.791376    0.049041   -0.383533
   6          6            0        2.160680   -0.066891    0.162400
   7          1            0       -1.551553   -1.103001    1.177736
   8          1            0       -1.933801   -1.421275   -0.513854
   9          1            0       -2.223063    1.117753    0.573147
  10          1            0       -1.757363    0.880130   -1.104730
  11          1            0        0.121682    1.278502    1.261237
  12          1            0        0.154975    2.143727   -0.274076
  13          1            0        0.843701    0.173006   -1.470439
  14          1            0        2.333416   -0.662542    1.041971
  15          1            0        2.969236    0.503186   -0.261565
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-270.9557763\S2=0.755247\S2-1=0.\
S2A=0.750018\RMSD=5.353e-09\RMSF=2.900e-07\ZeroPoint=0.1343445\Thermal=
0.1407878\Dipole=0.6451734,-0.0555184,0.5012758\PG=C01[X(C5H9O1)]\
NImag=0\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X            Y            Z
---------------------------------------------------------------------
   1          8            0        0.051487   -1.128320   -0.118038
   2          6            0       -1.301808   -0.825179    0.170428
   3          6            0       -1.472004    0.669627   -0.076173
   4          6            0       -0.065801    1.189006    0.188069
   5          6            0        0.791325    0.052794   -0.388114
   6          6            0        2.151995   -0.066860    0.174530
   7          1            0       -1.505460   -1.078327    1.209299
   8          1            0       -1.945118   -1.433081   -0.458371
   9          1            0       -2.225553    1.115560    0.563244
  10          1            0       -1.752548    0.856770   -1.109087
  11          1            0        0.117018    1.280566    1.255392
  12          1            0        0.147268    2.143674   -0.278919
  13          1            0        0.856643    0.188992   -1.471421
  14          1            0        2.313681   -0.691304    1.034150
  15          1            0        2.959934    0.527386   -0.212421
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-271.0036263\S2=0.755332\S2-1=0.\
S2A=0.750018\RMSD=2.634e-09\RMSF=2.162e-07\ZeroPoint=0.1338352\Thermal=
0.1402611\Dipole=0.5829622,-0.0744891,0.4608763\PG=C01 [X(C5H9O1)]\
NImag=0\\@
```

8.5 Methoxyl Radical Addition to Propene

8.5.1 Methoxyl radical (Ik)

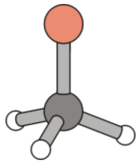

Figure S134. Ball-and-stick model of computed equilibrium structure of the methoxyl radical (**Im**).

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic              Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          8             0       -0.011028    0.793737    0.000000
   2          6             0       -0.011028   -0.577119    0.000000
   3          1             0        1.060625   -0.867662    0.000000
   4          1             0       -0.453118   -1.009759    0.911434
   5          1             0       -0.453118   -1.009759   -0.911434
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A'\HF=-115.0632975\S2=0.753499\S2-
1=0.\ S2A=0.750009\RMSD=0.000e+00\RMSF=5.714e-06\ZeroPoint=0.0363109\
Thermal= 0.0393505\Dipole=0.092549,0.,0.8822571\ PG=CS
[SG(C1H1O1),X(H2)]\NImag=0\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type              X           Y           Z
---------------------------------------------------------------------
   1          8             0       -0.008725    0.791541    0.000000
   2          6             0       -0.008725   -0.579110    0.000000
   3          1             0        1.048205   -0.870123    0.000000
   4          1             0       -0.463024   -0.993773    0.900153
   5          1             0       -0.463024   -0.993773   -0.900153
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A'\HF=-115.0001926\S2=0.754977\S2-
1=0.\ S2A=0.750019\RMSD=0.000e+00\RMSF=5.596e-06\ZeroPoint=0.0381938\
Thermal= 0.0411873\Dipole=0.0777085,0.,0.852451\ PG=CS
[SG(C1H1O1),X(H2)]\NImag=0\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic            Coordinates (Angstroms)
Number     Number         Type            X            Y            Z
---------------------------------------------------------------------
   1          8             0       -0.009067    0.789824    0.000000
   2          6             0       -0.009067   -0.576052    0.000000
   3          1             0        1.046992   -0.869045    0.000000
   4          1             0       -0.460025   -0.996617    0.898929
   5          1             0       -0.460025   -0.996617   -0.898929
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A'\HF=-115.0231817\S2=0.754332\S2-
1=0.\S2A =0.750014\RMSD=0.000e+00\RMSF=7.207e-06\ZeroPoint=0.038019\
Thermal= 0.0410064\Dipole=0.0716673,0.,0.7884664\ PG=CS
[SG(C1H1O1),X(H2)]\NImag=0\\@
```

8.5.2 Propene

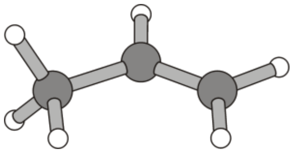

Figure S135. Ball-and-stick model showing the computed equilibrium of propene.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic             Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0       -1.285471    0.220790    0.000000
   2          6             0       -0.132616   -0.455269   -0.000001
   3          6             0        1.236630    0.163272    0.000000
   4          1             0       -2.244615   -0.288910    0.000004
   5          1             0       -1.308206    1.308661   -0.000001
   6          1             0       -0.164982   -1.545627    0.000001
   7          1             0        1.811424   -0.151766   -0.880247
   8          1             0        1.183715    1.256617   -0.000023
   9          1             0        1.811405   -0.151729    0.880274
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=1-A\HF=-117.9227982\RMSD=2.970e-09\RMSF=
1.478e-06\ZeroPoint=0.0795432\Thermal=0.0836416\Dipole=0.0634245,
0.0000044,0.1625806\PG=C01 [X(C3H6)]\NImag=0\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic             Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0       -1.275050    0.220283    0.000000
   2          6             0       -0.133510   -0.453067    0.000000
   3          6             0        1.228770    0.161772    0.000000
   4          1             0       -2.227580   -0.284092    0.000001
   5          1             0       -1.294308    1.299828   -0.000001
   6          1             0       -0.167753   -1.534660    0.000000
   7          1             0        1.797085   -0.150868   -0.874490
   8          1             0        1.174223    1.246710   -0.000013
   9          1             0        1.797074   -0.150846    0.874505
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=1-A\HF=-117.8377786\RMSD=8.955e-09\RMSF=
1.350e-06\ZeroPoint=0.0823352\Thermal=0.0863587\Dipole=0.0586603,
0.0000021,0.156776\PG=C01 [X(C3H6)]\NImag=0\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic           Coordinates (Angstroms)
Number     Number        Type           X            Y            Z
---------------------------------------------------------------------
   1          6             0       -1.270865     0.220030     0.000000
   2          6             0       -0.135388    -0.451678     0.000000
   3          6             0        1.226329     0.160971     0.000000
   4          1             0       -2.223283    -0.281976     0.000001
   5          1             0       -1.288706     1.298445    -0.000001
   6          1             0       -0.169537    -1.532055     0.000000
   7          1             0        1.793922    -0.152523    -0.873439
   8          1             0        1.173235     1.244677    -0.000012
   9          1             0        1.793912    -0.152505     0.873452
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=1-A\HF=-117.8573314\RMSD=2.797e-09\RMSF=
1.918e-06\ZeroPoint=0.0819904\Thermal=0.0860096\Dipole=0.0443792,
0.0000019,0.1390108\PG=C01 [X(C3H6)]\NImag=0\\@
```

8.5.3 Transition structure for methoxyl addition to the terminal carbon of propene

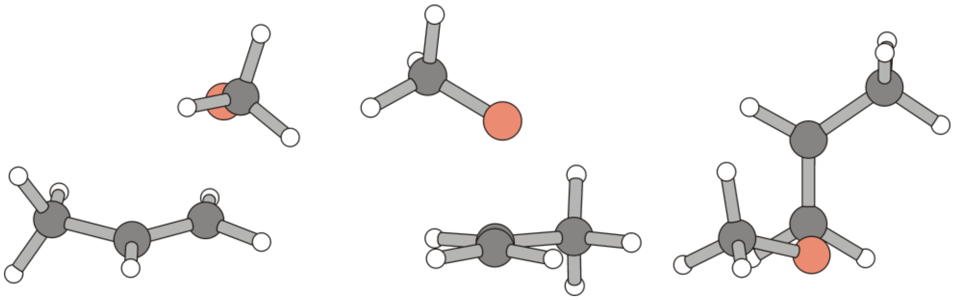

Figure S136. Ball-and-stick models showing different projections of computed transition structure TS^1-**VII** (left: side-on view; center: end-on view (center); right: top view.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic              Coordinates (Angstroms)
Number     Number           Type              X           Y           Z
---------------------------------------------------------------------
   1          6              0        0.316309    1.130301    0.022919
   2          6              0        1.131378    0.175308    0.561792
   3          6              0        2.128631   -0.623748   -0.214665
   4          8              0       -1.280498    0.023485   -0.715246
   5          6              0       -2.087098   -0.491704    0.298377
   6          1              0       -0.316406    1.742376    0.656781
   7          1              0        0.478857    1.490485   -0.986756
   8          1              0        1.005579   -0.086248    1.612374
   9          1              0        3.124514   -0.563914    0.244098
  10          1              0        1.852788   -1.686996   -0.225646
  11          1              0        2.200385   -0.282374   -1.251139
  12          1              0       -2.991923   -0.876333   -0.201905
  13          1              0       -1.630314   -1.335965    0.838245
  14          1              0       -2.414817    0.270148    1.025377
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-232.9827193\S2=0.774311\S2-1=0.\
S2A=0.750115\RMSD=4.084e-09\RMSF=1.701e-07\ZeroPoint=0.1191318\Thermal=
0.1265417\Dipole=-0.4009503,0.3081397,0.5377889\PG=C01 [X(C4H9O1)]\
NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6             0        0.274893    1.122975    0.084931
   2          6             0        1.093930    0.147113    0.569442
   3          6             0        2.074735   -0.608451   -0.257929
   4          8             0       -1.282751    0.142741   -0.695486
   5          6             0       -1.980704   -0.571630    0.267018
   6          1             0       -0.331257    1.706655    0.756639
   7          1             0        0.457626    1.552216   -0.884709
   8          1             0        0.971012   -0.171544    1.595241
   9          1             0        3.065313   -0.588385    0.194625
  10          1             0        1.787437   -1.656698   -0.340229
  11          1             0        2.144935   -0.200954   -1.261643
  12          1             0       -2.895357   -0.914057   -0.221360
  13          1             0       -1.443276   -1.451504    0.622386
  14          1             0       -2.271552    0.042305    1.122172
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-232.8273665\S2=0.821343\S2-1=0.\
S2A=0.750641\RMSD=8.780e-09\RMSF=4.567e-07\ZeroPoint=0.1235929\Thermal=
0.1307706\Dipole=-0.4122284,0.226645,0.5381189\PG=C01
[X(C4H9O1)]\NImag=1\\@
```

(*ii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6             0        0.265742    1.121707    0.064261
   2          6             0        1.088274    0.164506    0.571075
   3          6             0        2.058335   -0.613462   -0.245122
   4          8             0       -1.254006    0.111231   -0.700976
   5          6             0       -1.974250   -0.554528    0.274897
   6          1             0       -0.338803    1.720035    0.722616
   7          1             0        0.454835    1.535229   -0.909374
   8          1             0        0.968091   -0.131382    1.602464
   9          1             0        3.050890   -0.594975    0.200651
  10          1             0        1.760651   -1.659142   -0.306999
  11          1             0        2.125959   -0.225824   -1.255502
  12          1             0       -2.877430   -0.918914   -0.217430
  13          1             0       -1.453120   -1.419381    0.686054
  14          1             0       -2.287624    0.095168    1.094657
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-232.8698526\S2=0.822071\S2-1=0.\
S2A=0.750607\RMSD=8.678e-09\RMSF=2.587e-07\ZeroPoint=0.1229893\Thermal=
0.1301643\Dipole=-0.3853017,0.2110959,0.4576732\PG=C01[X(C4H9O1)]
\NImag=1\\@
```

8.5.4 Transition structure for methoxyl addition to the inner carbon of propene

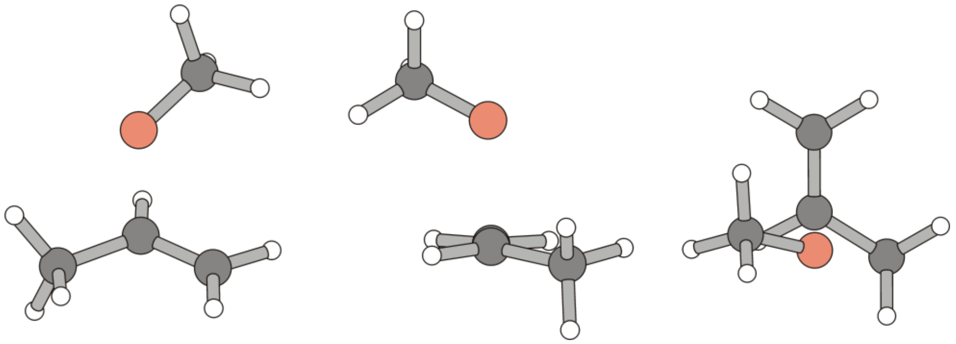

Figure S137. Ball-and-stick models showing different projections of computed transition structure TS^2-**VII** (left: side-on view; center: end-on view (center); right: top view.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic            Coordinates (Angstroms)
Number     Number         Type            X           Y           Z
---------------------------------------------------------------------
   1          6             0        2.097983   -0.076794    0.098252
   2          8             0        0.900994   -0.634797   -0.352539
   3          6             0       -0.802703    0.215154    0.436027
   4          6             0       -0.705437    1.444261   -0.162410
   5          6             0       -1.743882   -0.856040   -0.032811
   6          1             0        2.122808    0.074250    1.190544
   7          1             0        2.357878    0.866531   -0.405212
   8          1             0        2.886180   -0.807395   -0.148716
   9          1             0       -0.114690    2.243185    0.274420
  10          1             0       -1.147380    1.627186   -1.137832
  11          1             0       -0.424115    0.106823    1.450471
  12          1             0       -2.003185   -0.722332   -1.086916
  13          1             0       -1.292000   -1.843203    0.092665
  14          1             0       -2.669214   -0.826154    0.556542
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-232.9815166\S2=0.775952\S2-1=0.\
S2A=0.750124\RMSD=6.870e-09\RMSF=2.181e-07\ZeroPoint=0.1190836\Thermal=
0.1263569\Dipole=0.5128292,-0.0592211,-0.2007177\PG=C01 [X(C4H9O1)]
\NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic          Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6            0        2.055773   -0.071552    0.061157
   2          8            0        0.862390   -0.692415   -0.278150
   3          6            0       -0.770947    0.216838    0.429501
   4          6            0       -0.650864    1.443917   -0.158469
   5          6            0       -1.734477   -0.819567   -0.051067
   6          1            0        2.115081    0.175905    1.123369
   7          1            0        2.255994    0.822201   -0.529323
   8          1            0        2.842141   -0.798163   -0.153076
   9          1            0       -0.061725    2.226492    0.289592
  10          1            0       -1.067257    1.632890   -1.134857
  11          1            0       -0.432985    0.110770    1.449395
  12          1            0       -1.939379   -0.699048   -1.110343
  13          1            0       -1.333556   -1.813961    0.111661
  14          1            0       -2.674347   -0.735589    0.492056
---------------------------------------------------------------------
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S2A=0.750651\RMSD=7.433e-09\RMSF=2.658e-07\ZeroPoint=0.1234463\Thermal=
0.1304837\Dipole=0.4593215,0.0043118,-0.2735085\PG=C01[X(C4H9O1)]\
NImag=1\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic          Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6            0        2.046021   -0.074618    0.069507
   2          8            0        0.854424   -0.674234   -0.298562
   3          6            0       -0.758496    0.214630    0.427061
   4          6            0       -0.660215    1.441454   -0.158357
   5          6            0       -1.719663   -0.827457   -0.042618
   6          1            0        2.101662    0.142687    1.138139
   7          1            0        2.264420    0.833343   -0.491389
   8          1            0        2.829355   -0.799715   -0.157227
   9          1            0       -0.077855    2.229959    0.284975
  10          1            0       -1.087561    1.625504   -1.129452
  11          1            0       -0.415753    0.113813    1.444546
  12          1            0       -1.918155   -0.720750   -1.103328
  13          1            0       -1.316054   -1.816699    0.134380
  14          1            0       -2.661330   -0.738324    0.494295
---------------------------------------------------------------------
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S2A=0.750616\RMSD=5.379e-09\RMSF=2.567e-07\ZeroPoint=0.122879\Thermal=
0.1298972\Dipole=0.0166082,0.3860869,0.3017036\Polar=65.3333003,10.4831
885,50.7814032,12.8518568,0.7358499,60.3796669\PG=C01 [X(C4H9O1)]
\NImag=1\\@
```

8.5.5 1-Methoxprop-2-yl radical *iso*-(VIII)

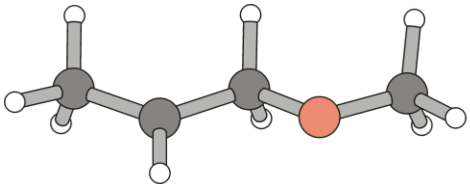

Figure S138. Ball-and-stick models showing computed equilibrium structure of carbon radical *iso*-**VIII**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic             Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0        2.398331   -0.185298   -0.003971
   2          8             0        1.170099    0.513232   -0.069710
   3          6             0        0.040462   -0.336825    0.056502
   4          6             0       -1.206907    0.471671    0.015015
   5          6             0       -2.542907   -0.188782   -0.038361
   6          1             0        3.194974    0.554823   -0.106478
   7          1             0        2.514721   -0.707985    0.958606
   8          1             0        2.487346   -0.923085   -0.816865
   9          1             0        0.038741   -1.095663   -0.750946
  10          1             0        0.113692   -0.908494    1.008165
  11          1             0       -1.119743    1.531554    0.235286
  12          1             0       -3.331779    0.522124   -0.302674
  13          1             0       -2.564094   -1.006304   -0.772512
  14          1             0       -2.828525   -0.637433    0.929991
---------------------------------------------------------------------
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S2A=0.750011\RMSD=6.031e-09\RMSF=1.492e-07\ZeroPoint=0.1209638\Thermal=
0.1284394\Dipole=0.5185199,0.0604196,-0.2626168\PG=C01[X(C4H9O1)]\
NImag=0\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6            0        2.378423   -0.182097    0.000409
   2          8            0        1.161879    0.504734   -0.051788
   3          6            0        0.043170   -0.334716    0.037830
   4          6            0       -1.197143    0.473861   -0.005410
   5          6            0       -2.525954   -0.189500   -0.023337
   6          1            0        3.170451    0.553941   -0.073926
   7          1            0        2.488092   -0.728332    0.939910
   8          1            0        2.472766   -0.889426   -0.826424
   9          1            0        0.051254   -1.066865   -0.780684
  10          1            0        0.095282   -0.920469    0.969595
  11          1            0       -1.107841    1.527324    0.202226
  12          1            0       -3.314573    0.507687   -0.290378
  13          1            0       -2.553005   -1.014731   -0.735228
  14          1            0       -2.788429   -0.612280    0.952263
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-232.8672925\S2=0.755624\S2-1=0.\
S2A=0.750023\RMSD=2.485e-09\RMSF=1.626e-07\ZeroPoint=0.1255586\Thermal=
0.1329041\Dipole=0.5187985,0.0504959,-
0.2788378\PG=C01[X(C4H9O1)]\NImag=0\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6            0        2.373235   -0.180650    0.002185
   2          8            0        1.159560    0.504751   -0.057538
   3          6            0        0.045321   -0.335320    0.038657
   4          6            0       -1.194145    0.471393   -0.007543
   5          6            0       -2.523181   -0.187804   -0.024110
   6          1            0        3.166372    0.552122   -0.076382
   7          1            0        2.483659   -0.720170    0.944886
   8          1            0        2.471617   -0.895235   -0.817194
   9          1            0        0.050597   -1.073877   -0.773145
  10          1            0        0.096371   -0.915287    0.973689
  11          1            0       -1.103514    1.517943    0.225704
  12          1            0       -3.303666    0.498615   -0.335527
  13          1            0       -2.538567   -1.041470   -0.699612
  14          1            0       -2.806727   -0.566369    0.962750
---------------------------------------------------------------------
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S2A=0.750023\RMSD=4.869e-09\RMSF=4.236e-07\ZeroPoint=0.1250554\Thermal=
0.1323703\Dipole=0.4609028,0.047443,-0.2628264\PG=C01[X
(C4H9O1)]\NImag=0\\@
```

8.5.6 The 2-Methoxprop-1-yl radical (VIII)

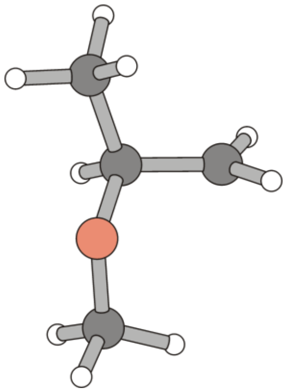

Figure S139. Ball-and-stick models showing computed equilibrium structure of carbon radical **VIII**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic         Atomic              Coordinates (Angstroms)
Number     Number          Type              X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.588502    1.477054   -0.110997
   2          6             0       -0.437818    0.051278    0.314670
   3          6             0       -1.673492   -0.794321   -0.029833
   4          8             0        0.670388   -0.587305   -0.329518
   5          6             0        1.938925   -0.111571    0.090994
   6          1             0       -0.402172    1.748249   -1.146192
   7          1             0       -1.033427    2.214627    0.549447
   8          1             0       -0.283322    0.012127    1.407917
   9          1             0       -1.521603   -1.826296    0.302623
  10          1             0       -2.564752   -0.390203    0.459611
  11          1             0       -1.838119   -0.795607   -1.111591
  12          1             0        2.076909    0.953565   -0.141252
  13          1             0        2.079831   -0.256809    1.173532
  14          1             0        2.688874   -0.695851   -0.446966
---------------------------------------------------------------------
Version=AM64L-G03RevE.01\State=2-A\HF=-233.0118568\S2=0.753661\S2-1=0.\
S2A=0.750008\RMSD=4.273e-09\RMSF=5.654e-07\ZeroPoint=0.1211087\Thermal=
0.128218\Dipole=-0.0156316,0.3308128,0.3590719\PG=C01[X(C4H9O1)]\
NImag=0\\@
```

(ii) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -0.585808    1.467636   -0.104568
   2          6           0       -0.430636    0.044896    0.311448
   3          6           0       -1.656868   -0.791589   -0.033267
   4          8           0        0.665950   -0.573105   -0.327815
   5          6           0        1.920855   -0.111333    0.091301
   6          1           0       -0.360155    1.749880   -1.120081
   7          1           0       -1.092341    2.175229    0.530148
   8          1           0       -0.277326    0.002994    1.395512
   9          1           0       -1.507953   -1.817089    0.292921
  10          1           0       -2.542127   -0.391417    0.452663
  11          1           0       -1.818647   -0.789716   -1.107280
  12          1           0        2.057868    0.947829   -0.126387
  13          1           0        2.060137   -0.267652    1.163169
  14          1           0        2.667689   -0.682878   -0.447627
---------------------------------------------------------------------
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1=0.\ S2A=0.750016\RMSD=5.787e-09\RMSF=8.737e-08\ZeroPoint=0.1255823\
Thermal= 0.132513\Dipole=-0.1952881,-0.4069541,-0.225176\PG=C01
[X(C4H9O1)] \NImag=0\\@
```

(ii) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -0.590567    1.466672   -0.103174
   2          6           0       -0.428183    0.045627    0.310696
   3          6           0       -1.650259   -0.795962   -0.031477
   4          8           0        0.665001   -0.566255   -0.334013
   5          6           0        1.916406   -0.111130    0.094302
   6          1           0       -0.351886    1.749053   -1.114202
   7          1           0       -1.116215    2.167042    0.521710
   8          1           0       -0.273065    0.003868    1.393536
   9          1           0       -1.493559   -1.818807    0.295224
  10          1           0       -2.538448   -0.401926    0.451452
  11          1           0       -1.807757   -0.796662   -1.104921
  12          1           0        2.053182    0.951834   -0.100833
  13          1           0        2.057707   -0.287474    1.162173
  14          1           0        2.665655   -0.668128   -0.454116
---------------------------------------------------------------------
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S2A=0.750016\RMSD =1.461e-09\RMSF=7.103e-08\ZeroPoint=0.1250384\
Thermal= 0.1319545\Dipole=-0.1968934,-0.3672109,-0.2047589\PG=C01
[X(C4H9O1)]\ NImag=0\\@
```

8.6 Transition structure models for 2-allylcyclohexyl-1-oxyl radical cyclizations

8.6.1 2,4-Cis-cyclization of the *cis*-2-(propen-3-yl)-cyclohexyl-1-oxyl radical *cis*-Ic– favored conformer of transition structure *TS*^{1}-*cis*-Ic

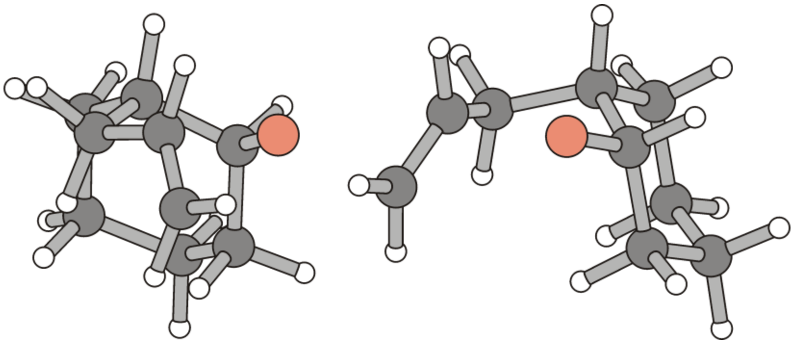

Figure S140. Projections of the ball-and-stick model for computed transition structure TS^1-*cis*-**Ic**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic         Atomic             Coordinates (Angstroms)
Number     Number          Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.152681    0.855917   -0.716508
   2          6             0       -1.588435    1.312485   -0.395685
   3          6             0       -2.254587    0.491401    0.722134
   4          6             0       -2.174757   -1.015597    0.431410
   5          6             0       -0.717547   -1.466123    0.240561
   6          6             0       -0.016814   -0.677503   -0.880928
   7          8             0        1.335368   -0.985644   -1.029507
   8          6             0        0.907085    1.250061    0.338490
   9          6             0        2.191283    0.507672    0.072012
  10          6             0        2.833373   -0.239530    1.033785
  11          1             0       -1.591479    2.380869   -0.141900
  12          1             0       -2.193735    1.214350   -1.307714
  13          1             0       -3.299893    0.804889    0.832785
  14          1             0       -1.768761    0.699249    1.685629
  15          1             0       -2.751467   -1.239407   -0.478570
  16          1             0       -2.644141   -1.585998    1.242101
  17          1             0       -0.658990   -2.535332    0.007035
  18          1             0       -0.160043   -1.323413    1.175608
  19          1             0       -0.486720   -0.956687   -1.844858
  20          1             0        0.155999    1.306019   -1.669182
  21          1             0        1.087278    2.331963    0.291459
  22          1             0        0.555903    1.026975    1.351859
  23          1             0        2.760985    0.817409   -0.799230
  24          1             0        3.803853   -0.686126    0.845070
  25          1             0        2.346753   -0.482306    1.974333
---------------------------------------------------------------------
 Zero-point correction=                      0.222220 (Hartree/Particle)
```

```
 Thermal correction to Energy=              0.231299
 Thermal correction to Enthalpy=            0.232244
 Thermal correction to Gibbs Free Energy=   0.187914
 Sum of electronic and zero-point Energies=          -426.939071
 Sum of electronic and thermal Energies=             -426.929991
 Sum of electronic and thermal Enthalpies=           -426.929047
 Sum of electronic and thermal Free Energies=        -426.973376

Version=AM64L-G03RevE.01\State=2-A\HF=-427.1612907\S2=0.778927\S2-1=0.\
S2A=0.750149\RMSD=3.650e-09\RMSF=7.905e-07\Dipole=-0.137655,0.5613339,
0.6226988\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type           X            Y            Z
---------------------------------------------------------------------
   1          6             0       -0.158957    0.859034   -0.707305
   2          6             0       -1.587306    1.297945   -0.382552
   3          6             0       -2.236148    0.468841    0.724678
   4          6             0       -2.142917   -1.024276    0.423063
   5          6             0       -0.691569   -1.453166    0.225974
   6          6             0       -0.016670   -0.656278   -0.887260
   7          8             0        1.333381   -0.946677   -1.033782
   8          6             0        0.888373    1.240000    0.345333
   9          6             0        2.161648    0.494101    0.071337
  10          6             0        2.803833   -0.243517    1.032443
  11          1             0       -1.597754    2.356008   -0.122567
  12          1             0       -2.190942    1.200841   -1.285686
  13          1             0       -3.276206    0.768316    0.840419
  14          1             0       -1.751949    0.672364    1.680205
  15          1             0       -2.715336   -1.244787   -0.480235
  16          1             0       -2.599317   -1.601763    1.224657
  17          1             0       -0.622125   -2.512386   -0.011270
  18          1             0       -0.136446   -1.308726    1.152234
  19          1             0       -0.476790   -0.936801   -1.842628
  20          1             0        0.144457    1.319500   -1.647073
  21          1             0        1.074017    2.312749    0.313783
  22          1             0        0.538646    1.006903    1.347895
  23          1             0        2.734780    0.816934   -0.782184
  24          1             0        3.767578   -0.684834    0.844502
  25          1             0        2.318615   -0.487014    1.963935
---------------------------------------------------------------------

Zero-point correction=                     0.230391 (Hartree/Particle)
Thermal correction to Energy=              0.239135
Thermal correction to Enthalpy=            0.240079
Thermal correction to Gibbs Free Energy=   0.196369
Sum of electronic and zero-point Energies=          -426.660375
Sum of electronic and thermal Energies=             -426.651630
Sum of electronic and thermal Enthalpies=           -426.650686
Sum of electronic and thermal Free Energies=        -426.694397

Version=AM64L-G03RevE.01\State=2-A\HF=-426.8907654\S2=0.827049\S2-1=0.\
S2A=0.750736\RMSD=1.004e-09\RMSF=3.563e-07\ Dipole=-0.1224624,
0.5154782,0.6274927\PG=C0 1 [X(C9H15O1)]\NImag=1\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type             X           Y           Z
---------------------------------------------------------------------
   1          6             0        -0.161510    0.864551   -0.703166
   2          6             0        -1.589369    1.297132   -0.374888
   3          6             0        -2.234130    0.459018    0.726440
   4          6             0        -2.136286   -1.030719    0.415247
   5          6             0        -0.684602   -1.452655    0.216908
   6          6             0        -0.011146   -0.648020   -0.890450
   7          8             0         1.336895   -0.930297   -1.034634
   8          6             0         0.886091    1.240080    0.349639
   9          6             0         2.155543    0.489400    0.073303
  10          6             0         2.790414   -0.251624    1.032812
  11          1             0        -1.603503    2.351969   -0.108263
  12          1             0        -2.192615    1.203928   -1.277082
  13          1             0        -3.273630    0.753927    0.844943
  14          1             0        -1.750478    0.657520    1.681782
  15          1             0        -2.705800   -1.246283   -0.489483
  16          1             0        -2.591941   -1.613949    1.211040
  17          1             0        -0.609671   -2.508756   -0.025844
  18          1             0        -0.131455   -1.310885    1.143203
  19          1             0        -0.468170   -0.925427   -1.846755
  20          1             0         0.140289    1.329321   -1.639561
  21          1             0         1.076716    2.310509    0.320240
  22          1             0         0.536507    1.006145    1.350514
  23          1             0         2.735195    0.822071   -0.770038
  24          1             0         3.753930   -0.691778    0.848653
  25          1             0         2.299442   -0.498921    1.958654
---------------------------------------------------------------------

Zero-point correction=                     0.229641 (Hartree/Particle)
Thermal correction to Energy=              0.238379
Thermal correction to Enthalpy=            0.239323
Thermal correction to Gibbs Free Energy=   0.195648
Sum of electronic and zero-point Energies=           -426.734639
Sum of electronic and thermal Energies=              -426.725901
Sum of electronic and thermal Enthalpies=            -426.724957
Sum of electronic and thermal Free Energies=         -426.768631

Version=AM64L-G03RevE.01\State=2-A \HF=-426.9642794\S2=0.826958\S2-
1=0.\ S2A=0.750702\RMSD=4.351e-09\RMSF=2.866e-07\Dipole=-0.1243078,
0.4861921, 0.5485657\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

8.6.2 2,4-Cis-cyclization of the *cis*-2-(propen-3-yl)-cyclohexyl-1-oxyl radical *cis*-Ic – disfavored conformer of transition structure *TS*^{1}-*cis*-Ic

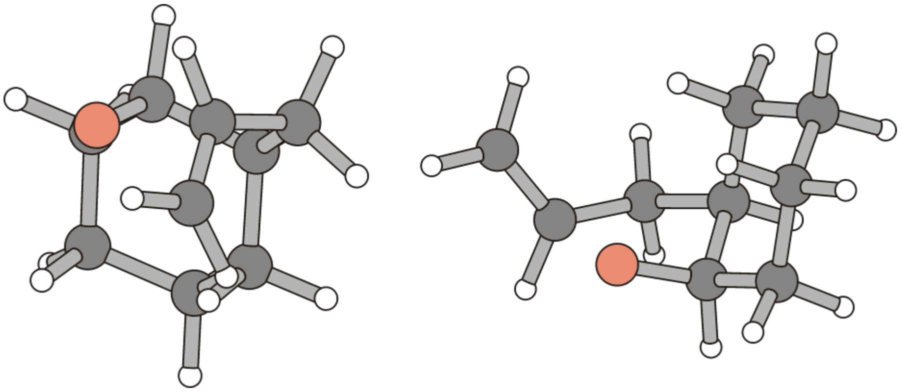

Figure S141. Projections of the ball-and-stick model for computed transition structure TS^1-*cis*-**Ic**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic              Coordinates (Angstroms)
Number     Number           Type              X           Y           Z
---------------------------------------------------------------------
   1          6              0       -2.046643    1.184906   -0.327709
   2          6              0       -2.283368   -0.273147   -0.747359
   3          6              0       -1.712915   -1.246677    0.290844
   4          6              0       -0.224975   -0.980989    0.621945
   5          6              0        0.047994    0.505673    0.955760
   6          6              0       -0.551640    1.451674   -0.098665
   7          8              0        0.566770   -1.330381   -0.472855
   8          6              0        1.591252    0.616896    1.051610
   9          6              0        2.251327   -0.263390    0.007633
  10          6              0        2.665339    0.210287   -1.217290
  11          1              0       -3.355859   -0.463524   -0.878522
  12          1              0       -1.804950   -0.455667   -1.717119
  13          1              0       -1.815630   -2.284175   -0.045419
  14          1              0       -2.273571   -1.159063    1.233031
  15          1              0        0.044536   -1.587883    1.508851
  16          1              0       -0.401861    0.740666    1.931171
  17          1              0       -0.019753    1.320765   -1.048825
  18          1              0       -0.390517    2.490707    0.218039
  19          1              0       -2.436698    1.870603   -1.089877
  20          1              0       -2.604537    1.395338    0.597352
  21          1              0        1.902641    1.660436    0.922569
  22          1              0        1.921036    0.302450    2.047829
  23          1              0        2.682195   -1.197670    0.354372
  24          1              0        3.190765   -0.432032   -1.916451
  25          1              0        2.409820    1.210702   -1.554773
---------------------------------------------------------------------
```

```
Zero-point correction=                           0.222239 Hartree/Particle)
Thermal correction to Energy=                    0.231425
Thermal correction to Enthalpy=                  0.232370
Thermal correction to Gibbs Free Energy=         0.187773
Sum of electronic and zero-point Energies=           -426.935676
Sum of electronic and thermal Energies=              -426.926490
Sum of electronic and thermal Enthalpies=            -426.925545
Sum of electronic and thermal Free Energies=         -426.970142

Version=AM64L-G03RevE.01\State=2-A\HF=-427.1579149\S2=0.783393\S2-1=0.\
S2A=0.750174\RMSD=9.577e-09\RMSF=3622e-07\Dipole=0.2271718,0.083556,-
0.6967465\ PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic          Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6            0       -2.039282    1.158194   -0.348558
   2          6            0       -2.259198   -0.299096   -0.740395
   3          6            0       -1.687892   -1.240534    0.312647
   4          6            0       -0.220484   -0.949676    0.638503
   5          6            0        0.041868    0.526794    0.945343
   6          6            0       -0.557854    1.440542   -0.122708
   7          8            0        0.563063   -1.300327   -0.456441
   8          6            0        1.571749    0.647320    1.027813
   9          6            0        2.218623   -0.270710    0.017669
  10          6            0        2.663106    0.168290   -1.202997
  11          1            0       -3.320911   -0.500489   -0.872212
  12          1            0       -1.777097   -0.492996   -1.696653
  13          1            0       -1.778155   -2.277225   -0.002766
  14          1            0       -2.252353   -1.141519    1.241305
  15          1            0        0.064351   -1.544585    1.514948
  16          1            0       -0.404376    0.778409    1.908585
  17          1            0       -0.025073    1.294423   -1.060718
  18          1            0       -0.407307    2.479078    0.170704
  19          1            0       -2.431153    1.820726   -1.118205
  20          1            0       -2.596950    1.377558    0.564503
  21          1            0        1.881360    1.676184    0.856529
  22          1            0        1.909695    0.373321    2.024341
  23          1            0        2.637536   -1.189128    0.394351
  24          1            0        3.190132   -0.492001   -1.870543
  25          1            0        2.421986    1.154112   -1.566543
---------------------------------------------------------------------

Zero-point correction=                           0.230385 Hartree/Particle)
Thermal correction to Energy=                    0.239244
Thermal correction to Enthalpy=                  0.240189
Thermal correction to Gibbs Free Energy=         0.196165
Sum of electronic and zero-point Energies=           -426.657211
Sum of electronic and thermal Energies=              -426.648351
Sum of electronic and thermal Enthalpies=            -426.647407
Sum of electronic and thermal Free Energies=         -426.691431

Version=AM64L-G03RevE.01\State=2-A\HF=-426.8875955\S2=0.837039\S2-1=0.\
S2A=0.750851\RMSD=2.340e-09\RMSF=7.723e-08\ Dipole=0.2566768,0.1
```

```
270104,-0.636262\ PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic          Atomic              Coordinates (Angstroms)
Number     Number           Type              X           Y           Z
---------------------------------------------------------------------
   1          6              0       -2.025971    1.162331   -0.345471
   2          6              0       -2.246112   -0.291362   -0.745992
   3          6              0       -1.688134   -1.237340    0.308171
   4          6              0       -0.222046   -0.952131    0.637143
   5          6              0        0.044988    0.519627    0.957138
   6          6              0       -0.546887    1.440787   -0.107446
   7          8              0        0.554644   -1.289130   -0.462566
   8          6              0        1.574492    0.626376    1.036160
   9          6              0        2.204342   -0.279309    0.004676
  10          6              0        2.639209    0.180110   -1.209072
  11          1              0       -3.305112   -0.488694   -0.892493
  12          1              0       -1.751273   -0.483191   -1.694455
  13          1              0       -1.778296   -2.271127   -0.011936
  14          1              0       -2.257600   -1.139906    1.232363
  15          1              0        0.062909   -1.555381    1.506429
  16          1              0       -0.398450    0.768160    1.920572
  17          1              0       -0.009939    1.298772   -1.041796
  18          1              0       -0.396832    2.476199    0.191902
  19          1              0       -2.409817    1.828554   -1.113906
  20          1              0       -2.589857    1.378040    0.563048
  21          1              0        1.893739    1.653557    0.883319
  22          1              0        1.912722    0.329299    2.024369
  23          1              0        2.630903   -1.198968    0.364825
  24          1              0        3.160004   -0.468006   -1.891180
  25          1              0        2.396462    1.171192   -1.552380
---------------------------------------------------------------------

Zero-point correction=                           0.229626 Hartree/Particle)
Thermal correction to Energy=                    0.238470
Thermal correction to Enthalpy=                  0.239414
Thermal correction to Gibbs Free Energy=         0.195476
Sum of electronic and zero-point Energies=              -426.731832
Sum of electronic and thermal Energies=                 -426.722988
Sum of electronic and thermal Enthalpies=               -426.722044
Sum of electronic and thermal Free Energies=            -426.765981

Version=AM64L-G03RevE.01\State=2-A\HF=-426.9614577\S2=0.837013\S2-1=0.\
S2A=0.750816\RMSD=3.002e-09\RMSF=1.890e-07\ Dipole=0.2596675,0.0672917,
-0.5929465\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

8.6.3 2,4-Trans-cyclization of the *cis*-2-(propen-3-yl)-cyclohexyl-1-oxyl radical *cis*-Ic – favored conformer of transition structure *TS^2*-*cis*-Ic

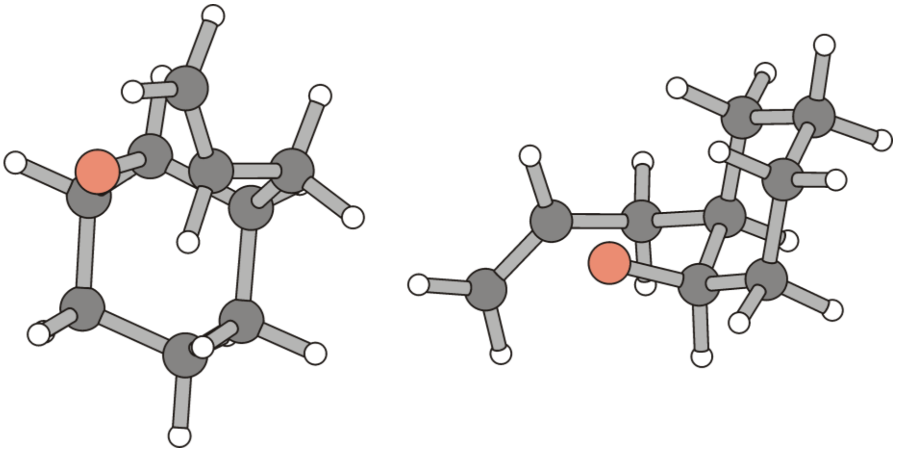

Figure S142. Projections of the ball-and-stick model for computed transition structure of TS^2-*cis*-**Ic**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -2.340459    0.863904   -0.318391
   2          6           0       -2.344848   -0.659723   -0.510351
   3          6           0       -1.486153   -1.354278    0.554071
   4          6           0       -0.047767   -0.785489    0.643937
   5          6           0       -0.018969    0.756756    0.732773
   6          6           0       -0.906893    1.414595   -0.339413
   7          8           0        0.657474   -1.168164   -0.500942
   8          6           0        1.475025    1.118915    0.574153
   9          6           0        2.099240    0.292563   -0.526021
  10          6           0        3.209084   -0.493536   -0.324268
  11          1           0       -3.370134   -1.047236   -0.462311
  12          1           0       -1.957984   -0.903217   -1.507389
  13          1           0       -1.425036   -2.432223    0.370363
  14          1           0       -1.944270   -1.221706    1.544801
  15          1           0        0.420420   -1.208518    1.552061
  16          1           0       -0.373565    1.076100    1.723853
  17          1           0       -0.475948    1.235569   -1.332652
  18          1           0       -0.911132    2.501839   -0.187017
  19          1           0       -2.940132    1.349126   -1.098198
  20          1           0       -2.815976    1.113000    0.642373
  21          1           0        1.588828    2.187412    0.347812
  22          1           0        2.006374    0.927932    1.514137
  23          1           0        1.838621    0.550549   -1.547952
  24          1           0        3.695250   -1.004282   -1.148738
  25          1           0        3.575328   -0.701275    0.677453
---------------------------------------------------------------------
```

```
Zero-point correction=                          0.222461 (Hartree/Particle)
Thermal correction to Energy=                   0.231577
Thermal correction to Enthalpy=                 0.232521
Thermal correction to Gibbs Free Energy=        0.188147
Sum of electronic and zero-point Energies=           -426.939500
Sum of electronic and thermal Energies=              -426.930385
Sum of electronic and thermal Enthalpies=            -426.929440
Sum of electronic and thermal Free Energies=         -426.973815


Version=AM64L-G03RevE.01\State=2-A\HF=-427.1619615\S2=0.77813\S2-1=0.\
S2A=0.75014\RMSD=3.597e-09\RMSF=5.468e-07\Dipole=0.2770511,0.1469996,
-0.6333259\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic          Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6             0       -2.325483    0.845823   -0.316652
   2          6             0       -2.316711   -0.667520   -0.504806
   3          6             0       -1.461448   -1.345882    0.558762
   4          6             0       -0.045209   -0.768451    0.644984
   5          6             0       -0.020791    0.759406    0.728571
   6          6             0       -0.906159    1.403221   -0.339000
   7          8             0        0.651963   -1.139501   -0.502145
   8          6             0        1.458868    1.119031    0.560039
   9          6             0        2.068449    0.273562   -0.525401
  10          6             0        3.183148   -0.493644   -0.314657
  11          1             0       -3.330921   -1.060730   -0.461478
  12          1             0       -1.925165   -0.907296   -1.491789
  13          1             0       -1.393375   -2.416155    0.380308
  14          1             0       -1.923386   -1.215047    1.538508
  15          1             0        0.438030   -1.184355    1.535403
  16          1             0       -0.371677    1.079317    1.711108
  17          1             0       -0.476209    1.225331   -1.323746
  18          1             0       -0.917815    2.482467   -0.190585
  19          1             0       -2.924314    1.320575   -1.091765
  20          1             0       -2.799031    1.090654    0.636511
  21          1             0        1.575966    2.174843    0.318346
  22          1             0        1.992030    0.940393    1.491697
  23          1             0        1.819177    0.526433   -1.542434
  24          1             0        3.664428   -1.012036   -1.126194
  25          1             0        3.548575   -0.681660    0.682223
---------------------------------------------------------------------

Zero-point correction=                          0.230582 (Hartree/Particle)
Thermal correction to Energy=                   0.239372
Thermal correction to Enthalpy=                 0.240316
Thermal correction to Gibbs Free Energy=        0.196530
Sum of electronic and zero-point Energies=           -426.661020
Sum of electronic and thermal Energies=              -426.652230
Sum of electronic and thermal Enthalpies=            -426.651286
Sum of electronic and thermal Free Energies=         -426.695072

Version=AM64L-G03RevE.01\State=2-A\HF=-426.8916022\S2=0.825906\S2-1=0.\
```

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S2A=0.750706\RMSD=2.398e-09\RMSF=6.920e-07\ Dipole=0.2868565,0.1732445,
-0.6016817\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(iii) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type           X            Y            Z
---------------------------------------------------------------------
   1          6             0       -2.320750     0.838495   -0.320322
   2          6             0       -2.304577    -0.674158   -0.504201
   3          6             0       -1.453505    -1.344449    0.566021
   4          6             0       -0.040832    -0.761990    0.647523
   5          6             0       -0.020009     0.764923    0.732268
   6          6             0       -0.905333     1.402729   -0.337459
   7          8             0        0.644376    -1.124511   -0.505384
   8          6             0        1.458183     1.122022    0.555690
   9          6             0        2.059040     0.268105   -0.527803
  10          6             0        3.166049    -0.503993   -0.313467
  11          1             0       -3.316017    -1.071157   -0.469190
  12          1             0       -1.902295    -0.914631   -1.485092
  13          1             0       -1.379204    -2.413384    0.390764
  14          1             0       -1.918610    -1.212144    1.542572
  15          1             0        0.448951    -1.177776    1.532745
  16          1             0       -0.367954     1.087416    1.713143
  17          1             0       -0.471710     1.225389   -1.319037
  18          1             0       -0.923179     2.480761   -0.191497
  19          1             0       -2.917108     1.307670   -1.098676
  20          1             0       -2.799868     1.083165    0.628572
  21          1             0        1.576509     2.174557    0.307129
  22          1             0        1.994445     0.947273    1.484554
  23          1             0        1.819855     0.527932   -1.543818
  24          1             0        3.647024    -1.023953   -1.122434
  25          1             0        3.524553    -0.695131    0.683846
---------------------------------------------------------------------

Zero-point correction=                           0.229847 (Hartree/Particle)
Thermal correction to Energy=                    0.238622
Thermal correction to Enthalpy=                  0.239566
Thermal correction to Gibbs Free Energy=         0.195836
Sum of electronic and zero-point Energies=           -426.735746
Sum of electronic and thermal Energies=              -426.726971
Sum of electronic and thermal Enthalpies=            -426.726027
Sum of electronic and thermal Free Energies=         -426.769757

Version=AM64L-G03RevE.01\State=2-A\HF=-426.9655932\S2=0.825796\S2-1=0.\
S2A=0.750672\RMSD=9.647e-09\RMSF=2.600e-07\ Dipole=0.289737,0.1225767,-
0.5574019\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

8.6.4 2,4-Trans-cyclization of the *cis*-2-(propen-3-yl)-cyclohexyl-1-oxyl radical *cis*-Ic–disfavored conformer of transition structure TS^2-*cis*-Ic

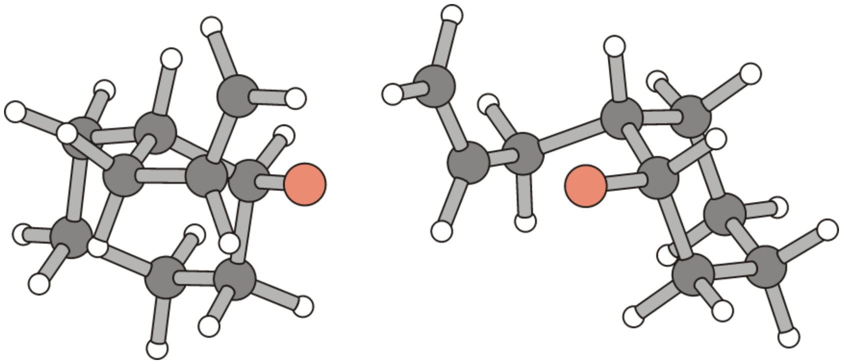

Figure S143. Projections of the ball-and-stick model for computed transition structure of TS^2-*cis*-**Ic**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic         Atomic              Coordinates (Angstroms)
Number     Number          Type              X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.080694   -0.688968   -0.549603
   2          6             0        1.281062   -1.404981   -0.601757
   3          6             0        2.322540   -0.820227    0.367024
   4          6             0        2.465835    0.696411    0.172446
   5          6             0        1.113062    1.403655    0.345828
   6          6             0        0.043968    0.860041   -0.624932
   7          8             0       -1.209798    1.416959   -0.372150
   8          6             0       -0.939900   -0.994974    0.697431
   9          6             0       -2.150899   -0.091197    0.692258
  10          6             0       -3.217110   -0.299271   -0.149539
  11          1             0        1.138218   -2.477067   -0.412040
  12          1             0        1.673647   -1.325833   -1.625030
  13          1             0        3.286521   -1.320366    0.213208
  14          1             0        2.031118   -1.026442    1.406261
  15          1             0        2.862032    0.897176   -0.834046
  16          1             0        3.197317    1.106023    0.879630
  17          1             0        1.210622    2.483435    0.185365
  18          1             0        0.753786    1.275315    1.375305
  19          1             0        0.340400    1.109213   -1.660951
  20          1             0       -0.667064   -0.995535   -1.425263
  21          1             0       -1.247855   -2.047791    0.677143
  22          1             0       -0.364791   -0.845988    1.615914
  23          1             0       -2.287264    0.579431    1.534192
  24          1             0       -4.095539    0.335727   -0.109118
  25          1             0       -3.179948   -1.045893   -0.938315
---------------------------------------------------------------------
```

```
Zero-point correction=                           0.222155 (Hartree/Particle)
Thermal correction to Energy=                    0.231375
Thermal correction to Enthalpy=                  0.232319
Thermal correction to Gibbs Free Energy=         0.187557
Sum of electronic and zero-point Energies=           -426.936270
Sum of electronic and thermal Energies=              -426.927050
Sum of electronic and thermal Enthalpies=            -426.926105
Sum of electronic and thermal Free Energies=         -426.970867

Version=AM64L-G03RevE.01\State=2-A\HF=-427.1584244\S2=0.778523\S2-1=0.\
S2A=0.750143\RMSD=3.844e-09\RMSF=1.157e-06\ Dipole=-0.285087,0.5675337,
0.6335652\\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -0.067174   -0.690357   -0.561013
   2          6           0        1.291641   -1.390129   -0.599293
   3          6           0        2.306269   -0.799870    0.377787
   4          6           0        2.434088    0.708480    0.189453
   5          6           0        1.079942    1.393555    0.346369
   6          6           0        0.045286    0.839954   -0.632643
   7          8           0       -1.215235    1.381004   -0.406643
   8          6           0       -0.921173   -0.995161    0.674864
   9          6           0       -2.107950   -0.069296    0.679072
  10          6           0       -3.208051   -0.302670   -0.102561
  11          1           0        1.158085   -2.455407   -0.413790
  12          1           0        1.693963   -1.305092   -1.609329
  13          1           0        3.270754   -1.284201    0.236593
  14          1           0        2.005972   -1.009773    1.404745
  15          1           0        2.835974    0.914262   -0.804590
  16          1           0        3.146900    1.121119    0.900761
  17          1           0        1.165294    2.467001    0.192511
  18          1           0        0.712296    1.257273    1.363140
  19          1           0        0.343342    1.105692   -1.652839
  20          1           0       -0.642704   -1.003619   -1.431076
  21          1           0       -1.248339   -2.032729    0.649757
  22          1           0       -0.345970   -0.864309    1.586405
  23          1           0       -2.214715    0.607212    1.509763
  24          1           0       -4.073764    0.334642   -0.047796
  25          1           0       -3.202481   -1.067153   -0.863325
---------------------------------------------------------------------

Zero-point correction=                           0.230229 (Hartree/Particle)
Thermal correction to Energy=                    0.239133
Thermal correction to Enthalpy=                  0.240077
Thermal correction to Gibbs Free Energy=         0.195773
Sum of electronic and zero-point Energies=           -426.657300
Sum of electronic and thermal Energies=              -426.648396
Sum of electronic and thermal Enthalpies=            -426.647452
Sum of electronic and thermal Free Energies=         -426.691756

Version=AM64L-G03RevE.01\State=2-A \HF=-426.8875294\S2=0.831067\S2-
1=0.\ S2A=0.750779\RMSD=1.057e-09\RMSF=6.016e-07\ Dipole=-
```

```
0.2447059,0.5226366, 0.6258052\ PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(*iii*) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X           Y           Z
---------------------------------------------------------------------
   1          6            0       -0.072995   -0.691850   -0.548277
   2          6            0        1.282852   -1.393849   -0.591531
   3          6            0        2.305213   -0.799464    0.372881
   4          6            0        2.435651    0.705568    0.170442
   5          6            0        1.085900    1.393737    0.334989
   6          6            0        0.037811    0.837680   -0.627541
   7          8            0       -1.213219    1.381447   -0.376521
   8          6            0       -0.921218   -0.984752    0.692152
   9          6            0       -2.113542   -0.067504    0.675616
  10          6            0       -3.188505   -0.305311   -0.133198
  11          1            0        1.149098   -2.456274   -0.398656
  12          1            0        1.677382   -1.315995   -1.603797
  13          1            0        3.265891   -1.287370    0.229451
  14          1            0        2.011489   -0.999291    1.402348
  15          1            0        2.827102    0.901114   -0.828366
  16          1            0        3.156065    1.121733    0.869646
  17          1            0        1.170689    2.464684    0.173599
  18          1            0        0.727543    1.264898    1.354538
  19          1            0        0.321071    1.098918   -1.651606
  20          1            0       -0.653214   -1.008237   -1.412165
  21          1            0       -1.240962   -2.023439    0.686004
  22          1            0       -0.348272   -0.832093    1.599996
  23          1            0       -2.248657    0.594730    1.511471
  24          1            0       -4.062686    0.319040   -0.092159
  25          1            0       -3.153782   -1.059536   -0.901332
---------------------------------------------------------------------

Zero-point correction=                       0.229526 (Hartree/Particle)
Thermal correction to Energy=                0.238410
Thermal correction to Enthalpy=              0.239354
Thermal correction to Gibbs Free Energy=     0.195181
Sum of electronic and zero-point Energies=           -426.731636
Sum of electronic and thermal Energies=              -426.722752
Sum of electronic and thermal Enthalpies=            -426.721808
Sum of electronic and thermal Free Energies=         -426.765981

Version=AM64L-G03RevE.01\State=2-A\HF=-426.9611614\S2=0.830117\S2-1=0.\
S2A=0.750727\RMSD=2.042e-09\RMSF=5.079e-07\ Dipole=-0.2518872,
0.4899384, 0.5523471\ PG=C01 [X(C9H15O1)]\NImag=1\\@
```

8.6.5 2,4-Cis-cyclization of the *trans*-2-(propen-3-yl)-cyclohexyl-1-oxyl radical *trans*-Ic – transition structure TS^1-*trans*-Ic

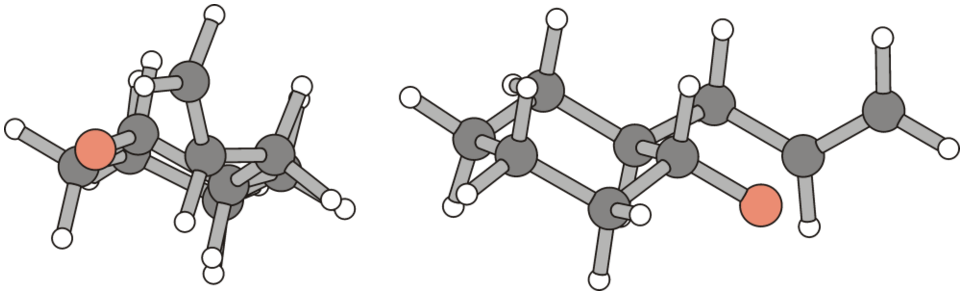

Figure S144. Projections of the ball-and-stick model for computed transition structure TS^1-*trans*-**Ic**.

(*i*) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -1.269145    1.487036    0.191899
   2          6           0       -0.066135    0.707719   -0.345332
   3          6           0       -0.017982   -0.722780    0.211324
   4          6           0       -1.298352   -1.492988   -0.166465
   5          6           0       -2.532278   -0.729697    0.354086
   6          6           0       -2.572456    0.730549   -0.132374
   7          1           0       -1.300613    2.498149   -0.234002
   8          1           0       -1.172356    1.607490    1.281142
   9          1           0       -0.166065    0.615574   -1.437641
  10          6           0        1.329759    1.280757   -0.043101
  11          8           0        1.113224   -1.354020   -0.303831
  12          1           0        0.024979   -0.673029    1.318137
  13          1           0       -1.259981   -2.504525    0.251664
  14          1           0       -1.338705   -1.592597   -1.258768
  15          1           0       -2.526488   -0.743939    1.453181
  16          1           0       -3.444647   -1.252881    0.042670
  17          1           0       -3.430181    1.249246    0.312879
  18          1           0       -2.730332    0.743507   -1.220271
  19          6           0        2.367299    0.236186   -0.385517
  20          6           0        3.325808   -0.183773    0.513203
  21          1           0        1.513288    2.194384   -0.623147
  22          1           0        1.405447    1.545838    1.019472
  23          1           0        2.547147    0.059920   -1.442106
  24          1           0        4.124277   -0.853530    0.212033
  25          1           0        3.249340    0.060495    1.569065
---------------------------------------------------------------------
```

```
Zero-point correction=                           0.222307 (Hartree/Particle)
Thermal correction to Energy=                    0.231434
Thermal correction to Enthalpy=                  0.232378
Thermal correction to Gibbs Free Energy=         0.187942
Sum of electronic and zero-point Energies=            -426.941556
Sum of electronic and thermal Energies=               -426.932430
Sum of electronic and thermal Enthalpies=             -426.931485
Sum of electronic and thermal Free Energies=          -426.975921

Version=AM64L-G03RevE.01\State=2-A\HF=-427.163863 8\S2=0.779033\S2-
1=0.\ S2A=0.750145\RMSD=3.631e-09\RMSF=6.053e-07\ Dipole=-0.4920779,-
0.2430848,-0.6047289\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(*ii*) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic           Coordinates (Angstroms)
Number     Number        Type            X            Y           Z
---------------------------------------------------------------------
   1          6            0       -1.262342    1.475193    0.189203
   2          6            0       -0.067331    0.705187   -0.349589
   3          6            0       -0.017679   -0.711211    0.203832
   4          6            0       -1.281367   -1.482448   -0.162170
   5          6            0       -2.507316   -0.729377    0.360264
   6          6            0       -2.554291    0.719074   -0.128116
   7          1            0       -1.297811    2.478341   -0.233470
   8          1            0       -1.162215    1.594206    1.269887
   9          1            0       -0.169533    0.613649   -1.433327
  10          6            0        1.316529    1.273966   -0.049912
  11          8            0        1.108010   -1.333382   -0.316657
  12          1            0        0.041179   -0.660461    1.299402
  13          1            0       -1.238758   -2.485952    0.253773
  14          1            0       -1.328475   -1.582872   -1.245941
  15          1            0       -2.493790   -0.738867    1.451070
  16          1            0       -3.413455   -1.251766    0.059624
  17          1            0       -3.406766    1.231409    0.313998
  18          1            0       -2.712855    0.727280   -1.207484
  19          6            0        2.342311    0.222706   -0.378296
  20          6            0        3.295727   -0.180819    0.523586
  21          1            0        1.508520    2.176048   -0.628981
  22          1            0        1.389348    1.541319    1.003711
  23          1            0        2.533174    0.048224   -1.424505
  24          1            0        4.086004   -0.852318    0.234845
  25          1            0        3.215914    0.075195    1.567833
 --------------------------------------------------------------------


Zero-point correction=                          0.230395 (Hartree/Particle)
Thermal correction to Energy=                   0.239204
Thermal correction to Enthalpy=                 0.240148
Thermal correction to Gibbs Free Energy=        0.196275
Sum of electronic and zero-point Energies=            -426.662633
Sum of electronic and thermal Energies=               -426.653825
Sum of electronic and thermal Enthalpies=             -426.652880
Sum of electronic and thermal Free Energies=          -426.696754

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S2A=0.750716\RMSD=1.834e-09\RMSF=4.142e-07\Dipole=-0.4556083,
-0.2385617, -0.6033449\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(iii) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type            X           Y            Z
---------------------------------------------------------------------
   1          6             0       -1.264157    1.473962    0.191220
   2          6             0       -0.069204    0.708078   -0.348916
   3          6             0       -0.012951   -0.707690    0.202645
   4          6             0       -1.273044   -1.482038   -0.162735
   5          6             0       -2.500655   -0.734505    0.359555
   6          6             0       -2.552499    0.713674   -0.126178
   7          1             0       -1.304250    2.476100   -0.229589
   8          1             0       -1.163657    1.591771    1.270643
   9          1             0       -0.173324    0.614040   -1.430850
  10          6             0        1.314793    1.275546   -0.053913
  11          8             0        1.109663   -1.323005   -0.322037
  12          1             0        0.045548   -0.657109    1.297250
  13          1             0       -1.225354   -2.484582    0.251237
  14          1             0       -1.317339   -1.581086   -1.245458
  15          1             0       -2.485971   -0.745064    1.448969
  16          1             0       -3.404515   -1.258160    0.059706
  17          1             0       -3.405851    1.221309    0.315997
  18          1             0       -2.710715    0.722755   -1.204216
  19          6             0        2.336818    0.219269   -0.376922
  20          6             0        3.281797   -0.183662    0.529553
  21          1             0        1.509221    2.172237   -0.637777
  22          1             0        1.389112    1.547850    0.996868
  23          1             0        2.538039    0.051585   -1.420704
  24          1             0        4.073742   -0.853345    0.246180
  25          1             0        3.192625    0.069947    1.572197
---------------------------------------------------------------------

Zero-point correction=                      0.229616 (Hartree/Particle)
Thermal correction to Energy=               0.238423
Thermal correction to Enthalpy=             0.239367
Thermal correction to Gibbs Free Energy=    0.195515
Sum of electronic and zero-point Energies=           -426.736508
Sum of electronic and thermal Energies=              -426.727701
Sum of electronic and thermal Enthalpies=            -426.726757
Sum of electronic and thermal Free Energies=         -426.770609
```

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S2A=0.75068\RMSD=4.126e-09\RMSF=2.859e-07\ Dipole=-0.4301163,
-0.2379023,-0.5309277\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

8.6.6 2,4-Trans-cyclization of the *trans*-2-(propen-3-yl)-cyclohexyl-1-oxyl radical *trans*-Ic – transition structure TS^{2}-*trans*-Ic

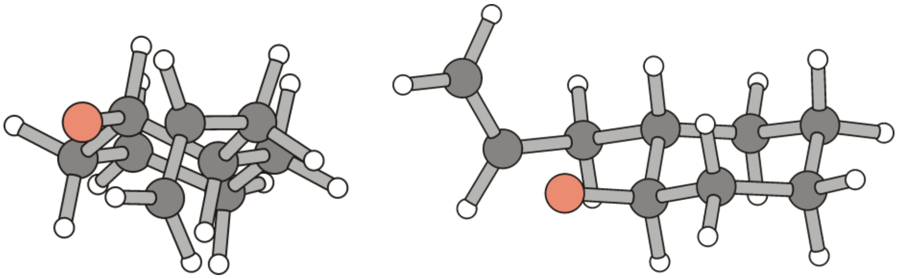

Figure S145. Projections of the ball-and-stick model for computed transition structure TS^{2}-*trans*-**Ic**.

(i) B3LYP/6-31+G**//B3LYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic        Atomic           Coordinates (Angstroms)
Number     Number         Type           X           Y           Z
---------------------------------------------------------------------
   1          6             0        1.215797    1.501487   -0.128538
   2          6             0       -0.046238    0.670926    0.116799
   3          6             0        0.092562   -0.751700   -0.463683
   4          6             0        1.287423   -1.472635    0.184374
   5          6             0        2.576392   -0.659417   -0.039600
   6          6             0        2.447691    0.789408    0.464002
   7          1             0        1.107902    2.501398    0.311393
   8          1             0        1.355404    1.646505   -1.209799
   9          1             0       -0.183616    0.552596    1.201933
  10          6             0       -1.361282    1.213424   -0.470822
  11          8             0       -1.109155   -1.426734   -0.267398
  12          1             0        0.298614   -0.643904   -1.549473
  13          1             0        1.385307   -2.478393   -0.238993
  14          1             0        1.084634   -1.591222    1.256786
  15          1             0        2.814512   -0.648620   -1.112850
  16          1             0        3.418628   -1.155520    0.457855
  17          1             0        3.357876    1.353000    0.225602
  18          1             0        2.362204    0.783529    1.560055
  19          6             0       -2.422500    0.141233   -0.325700
  20          6             0       -3.079884   -0.074217    0.866698
  21          1             0       -1.667299    2.130457    0.047315
  22          1             0       -1.220049    1.465992   -1.528137
  23          1             0       -2.867135   -0.255699   -1.232381
  24          1             0       -3.872608   -0.810493    0.944637
  25          1             0       -2.760900    0.413191    1.784067
---------------------------------------------------------------------
```

```
Zero-point correction=                     0.222034 (Hartree/Particle)
Thermal correction to Energy=              0.231254
Thermal correction to Enthalpy=            0.232199
Thermal correction to Gibbs Free Energy=   0.187429
Sum of electronic and zero-point Energies=          -426.938864
Sum of electronic and thermal Energies=             -426.929644
Sum of electronic and thermal Enthalpies=           -426.928699
Sum of electronic and thermal Free Energies=        -426.973469

Version=AM64L-G03RevE.01\State=2-A\HF=-427.1608981\S2=0.780578\S2-
1=0.\ S2A=0.750155\RMSD=2.934e-09\RMSF=6.527e-07\Dipole=-0.621196,
-0.1364414,-0.5910704\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(ii) BHandHLYP/6-31+G**//BHandHLYP/6-31+G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic            Coordinates (Angstroms)
Number     Number        Type            X            Y            Z
---------------------------------------------------------------------
   1          6            0        1.215713     1.490569    -0.123185
   2          6            0       -0.038993     0.669253     0.128272
   3          6            0        0.092405    -0.735954    -0.448360
   4          6            0        1.276049    -1.463973     0.177940
   5          6            0        2.557309    -0.660407    -0.052488
   6          6            0        2.438184     0.776250     0.456725
   7          1            0        1.115720     2.483173     0.313935
   8          1            0        1.348040     1.633205    -1.197319
   9          1            0       -0.171566     0.553711     1.205923
  10          6            0       -1.343838     1.209878    -0.451594
  11          8            0       -1.100347    -1.408625    -0.228930
  12          1            0        0.277588    -0.639348    -1.528034
  13          1            0        1.365922    -2.460597    -0.247564
  14          1            0        1.085186    -1.584823     1.243770
  15          1            0        2.782921    -0.644328    -1.119817
  16          1            0        3.396011    -1.157688     0.430826
  17          1            0        3.343457     1.331734     0.218952
  18          1            0        2.357906     0.764342     1.544698
  19          6            0       -2.387891     0.125546    -0.337316
  20          6            0       -3.097891    -0.069437     0.821072
  21          1            0       -1.664487     2.106306     0.075110
  22          1            0       -1.199065     1.480350    -1.495604
  23          1            0       -2.796776    -0.272724    -1.250310
  24          1            0       -3.883907    -0.802979     0.873791
  25          1            0       -2.820453     0.428313     1.736696
---------------------------------------------------------------------

Zero-point correction=                     0.230126 (Hartree/Particle)
Thermal correction to Energy=              0.239044
Thermal correction to Enthalpy=            0.239988
Thermal correction to Gibbs Free Energy=   0.195687
Sum of electronic and zero-point Energies=          -426.659649
Sum of electronic and thermal Energies=             -426.650731
Sum of electronic and thermal Enthalpies=           -426.649787
Sum of electronic and thermal Free Energies=        -426.694088
```

```
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S2A=0.750804\RMSD=1.350e-09\RMSF=5.612e-07\Dipole=-0.5568576,
-0.1484082,-0.589441\PG=C01 [X(C9H15O1)]\NImag=1\\@
```

(iii) BHandHLYP/6-311G**//BHandHLYP/6-311G**

```
Standard orientation:
---------------------------------------------------------------------
Center     Atomic       Atomic              Coordinates (Angstroms)
Number     Number        Type              X           Y           Z
---------------------------------------------------------------------
   1          6            0        1.215024    1.489608   -0.126243
   2          6            0       -0.041572    0.672312    0.118676
   3          6            0        0.088826   -0.731586   -0.459365
   4          6            0        1.262312   -1.463609    0.177185
   5          6            0        2.547807   -0.666130   -0.041387
   6          6            0        2.429827    0.771484    0.462767
   7          1            0        1.116745    2.481602    0.308971
   8          1            0        1.354568    1.630375   -1.198285
   9          1            0       -0.177014    0.554638    1.194335
  10          6            0       -1.344879    1.208583   -0.463400
  11          8            0       -1.106034   -1.398181   -0.257969
  12          1            0        0.288374   -0.629469   -1.535204
  13          1            0        1.350710   -2.459549   -0.246681
  14          1            0        1.058788   -1.583080    1.239511
  15          1            0        2.782195   -0.652979   -1.105475
  16          1            0        3.379949   -1.163892    0.449310
  17          1            0        3.337951    1.321906    0.230987
  18          1            0        2.341354    0.762381    1.548782
  19          6            0       -2.386027    0.125233   -0.325103
  20          6            0       -3.055325   -0.073138    0.852973
  21          1            0       -1.663320    2.111890    0.049771
  22          1            0       -1.203853    1.460713   -1.511010
  23          1            0       -2.828604   -0.259772   -1.226053
  24          1            0       -3.843955   -0.799949    0.927366
  25          1            0       -2.741573    0.414089    1.760807
---------------------------------------------------------------------

Zero-point correction=                         0.229373 (Hartree/Particle)
Thermal correction to Energy=                  0.238275
Thermal correction to Enthalpy=                0.239219
Thermal correction to Gibbs Free Energy=       0.195020
Sum of electronic and zero-point Energies=          -426.733601
Sum of electronic and thermal Energies=             -426.724700
Sum of electronic and thermal Enthalpies=           -426.723755
Sum of electronic and thermal Free Energies=        -426.767955

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S2A=0.750755\RMSD=3.158e-09\RMSF=6.183e-07\ Dipole=-0.5402038,
-0.1407461,-0.5158939\PG=C01 [X(C9H15O1)]\NImag=1\\@


TWO ROADS DIVERGED IN A WOOD, AND I--
I TOOK THE ONE LESS TRAVELED BY,
AND THAT HAS MADE ALL THE DIFFERENCE.
       -- ROBERT FROST
```

9 Crystallography

The applied model for solving the crystal structure uses restraints for fixing carbons 2 and 4, nitrogen N3/N3a, and oxygen 1/1a in a plane. Treating residual electron density as systematic disordering leads to a 78/22-ratio of diastereomers of 3-[(1-methylcyclohex-1-en-4-yl)-methyloxy]-4-methylthiazole-2(3*H*)-thione (**1g**) at crystallographic independent positions. The diastereomers differ in configuration at C8 and C8a with respect to configuration at the stereogenic N,O-bond. The minor diastereomer (population of 22%) is depicted in Figure S146 and the major (population of 78%) in Figure 2 of the associated article.

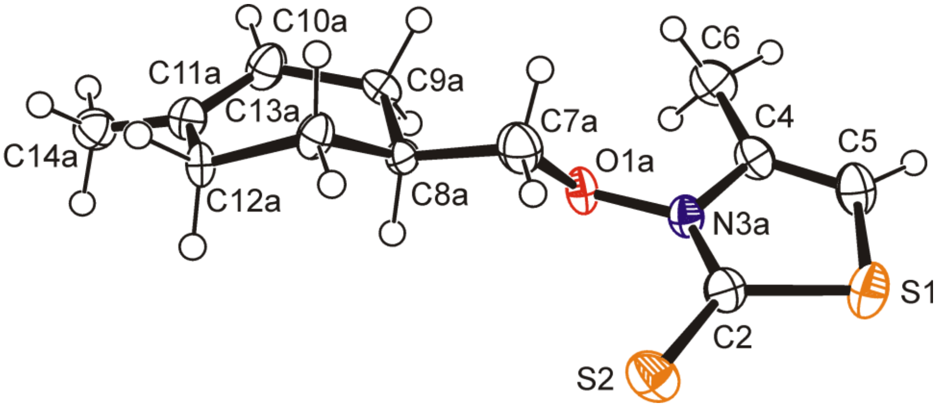

Figure S146. Ellipsoid graphic of (*S*,*P*)/(*R*,*M*)-3-[(1-methylcyclohex-1-en-4-yl)-methyloxy]-4-methylthiazole-2(3*H*)-thione (*S*,*P*)/(*R*,*M*)-(**1g**) in the solid state [minor diastereomer at 150 K; the (*S*,*P*)-isomer was arbitrarily chosen from the racemate for presentation (50% probability level); hydrogen atoms are drawn as circles of an arbitrary radius; oxygen is depicted in red, nitrogen in blue, and sulfur in orange; for depiction of the minor diastereomer see the ESI].

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