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Supporting Information

Brønsted Acid Catalysis in Visible-Light-Induced [2+2] Photocycloaddition Reactions of Enone Dithianes

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1. General Information

All reactions sensitive to air and moisture were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk techniques.

Commercially available chemicals were used without further purification, if not further mentioned. Diisopropylamine (*Merck*, technical grade, 99%) for lithium diisopropylamine (LDA) preparation was refluxed over CaH_2 and distilled.

For moisture sensitive reactions tetrahydrofuran (THF), diethyl ether (Et_2O), pentane (P) and dichloromethane (CH_2Cl_2) were purified using a MBSPS 800 *MBraun* solvent purification system. The following columns were used:

THF: 2 × MB-KOL-M type 2 (3 Å molecular sieve)
Et_2O: 1 × MB-KOL-A type 2 (aluminium oxide), 1 × MB-KOL-M type 2 (3 Å molecular sieve)
CH_2Cl_2: 2 × MB-KOL-A type 2 (aluminium oxide)

Dichloromethane for photochemical reactions was additionally dried over activated molecular sieve (4 Å).

For fluorescence experiments *Merck* dichloromethane for spectroscopy Uvasol® was used. For moisture sensitive experiments it was dried by passing through a pad of activated basic aluminium oxide under argon atmosphere.

The following dry solvents are commercially available and were used without further purification:

Methanol: *Acros Organics*, 99.8%, extra dry, over molecular sieve.
Pyridine: *Acros Organics*, 99.5% extra dry, over molecular sieve.

Technical solvents for column chromatography (pentane, dichloromethane, diethyl ether) were used after simple distillation.

Flash column chromatography was performed on silica 60 (*Merck*, 230-400 mesh) with the indicated eluent mixture.

Photochemical experiments using a LED were carried out in a Schlenk tube (diameter = 1 cm) with a polished quartz rod as an optical fibre, which was roughened by sandblasting at one end. The roughed end has to be completely submerged in the solvent during the reaction, in order to guarantee optimal and reproducible irradiation conditions.[1] Photochemical experiments at λ = 366 nm were performed in Duran tubes (Æ = 1.0 cm) in an RPR-100 photochemical reactor (Southern New England Ultra Violet Company, Branford, CT, USA) equipped with 16 fluorescence lamps (Philips Lighting, Black Light Blue, 8 W, λ = 366 nm). For low temperature irradiation the reaction vessel was placed in the photoreactor for 20 minutes prior to irradiation to assure proper cooling of the solution.

2. Analytical Methods

Thin layer chromatography (TLC) was performed on silica coated glass plates (*Merck*, silica 60 F254) with detection by UV-light (λ = 254 nm) and/or by staining with a potassium permanganate solution [$KMnO_4$] followed by heat treatment.

> $KMnO_4$-staining solution: 3.00 g potassium permanganate, 20.0 g potassium carbonate and 5.00 mL 5% sodium hydroxide solution in 300 mL water.

Infrared spectra (IR) were recorded on a *JASCO* IR-4100 spectrometer or a *Perkin Elmer* Frontier IR-FTR spectrometer by ATR technique. The signal intensity is assigned using the following abbreviations: s (strong), m (medium), w (weak), br (broad).

Nuclear magnetic resonance-spectra were recorded at room temperature either on a *Bruker* AVHD-300, AVHD-400, AVHD-500 or an AV-500 cryo. ^{1}H-NMR spectra were calibrated to the residual solvent signal of chloroform-d_1 ($CHCl_3$ δ = 7.26 ppm) or benzene-d_6 (C_6HD_5 δ = 7.16 ppm). ^{13}C-NMR spectra were calibrated to the ^{13}C-D triplet of $CDCl_3$ (δ = 77.16 ppm) or C_6D_6 (δ = 128.1 ppm). Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). Following abbreviations for single multiplicities were used: *br*-broad, s-singlet, d-doublet, t-triplet, q-quartet, quin.-quintet. Assignment and multiplicity of the ^{13}C-NMR signals were determined by two dimensional NMR experiments (COSY, HSQC, HMBC) or DEPT experiments (DEPT-90 and DEPT-135).

Mass spectroscopy (MS) was performed on a *Agilent* MS5977A MSD spectrometer coupled to a *Agilent* 7890 B gas chromatograph using a HP-5MS UI column (30 m, 0.25 mm, 0.25 µm, 5% diphenyl- 95% dimethylpolysiloxane).

High resolution mass spectroscopy (HR-MS) was performed on a *Thermo Scientific* DFS-HRMS spectrometer.

UV/Vis Spectroscopy was performed on a *Perkin Elmer* Lambda 35 UV/Vis spektometer. If not further mentioned, spectra were recorded using a *Hellma* precision cell made of quartz SUPRASIL® with a pathway of 1 mm. Solvents and concentrations are given for each spectrum.

Gas chromatography (GC) was performed on an *Agilent* 7890 B gas chromatograph using a HP-5 column (30 m, 0.32 mm, 0.25 µm, 5% diphenyl- 95% dimethylpolysiloxane) with a flame ionisation detector.

X-ray crystallography was performed on a *Bruker* D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource (λ = 0.71073 Å). The data was analyzed using a *Bruker* SAINT software package using a narrow-frame algorithm.

Fluoreszence spectroscopy was carried at on a *Horiba Scientific* Fluoromax-4 Spectrofuorometer. Spectra were recorded using a *Hellma* precisions cell made of quartz SUPRASIL® (exc.: 4 mm/emi.: 10 mm or exc.: 2 mm/emi.: 10 mm).

3. General Procedures

General Procedure 1: Gringardaddition to 3-ethoxycycloalkenones

A solution of alkylbromide (1.35 eq.) in dry THF [0.96 M] was added dropwise to a suspension of magnesium (1.30 eq.) and catalytic amounts of iodine in THF (1 mL). After full conversion of the magnesium the corresponding 3-ethoxycycloalkenone (1.00 eq.) in THF [0.89 M] was added and the reaction was stirred at room temperature for the time given below. After full conversion the reaction was quenched with saturated aqueous ammonium chloride solution and extracted three times with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was evaporated in vacuo. The crude material was purified by column chromatography.

Lower equivalents of alkyl bromides and magnesium were used, if the bromide was not commercially available. Equivalents are given in the respective procedures below.

General Procedure 2: Synthesis of dithiols and dithianes

Reactions were carried out in flame dried flask under argon atmosphere. To a stirred solution of the corresponding cycloalkenone (1.00 eq.) in dry methanol [0.18 M] was added 1,3-propanedithiol (1.50 eq.) and boron trifluoride diethyl etherate (1.20 eq.) at room temperature. After the time indicated in the individual procedures, the reaction was quenched with saturated aqueous sodium bicarbonate solution. After extraction with Et_2O (three times), the combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified using column chromatography.

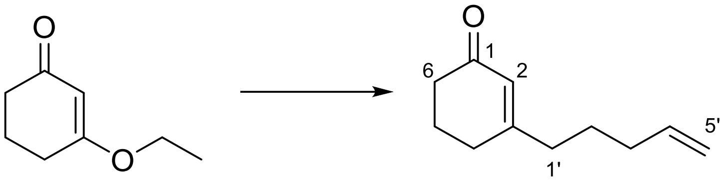
General Procedure 3: Brønsted acid catalysed photocycloadditions using LED-setup

Catalysts were stored in a glove box. For irradiations using 398 or 405 nm LEDs a polished quartz rod was used as an optical fibre, which was roughened by sandblasting at one end. The roughed end has to be completely submerged in the solvent during the reaction, in order to guarantee optimal and reproducible irritation conditions.[1]

A solution of the respective 1,3-dithiane (1.00 eq) in dry CH_2Cl_2 [10 mM] was precooled to −78 °C before addition of catalyst and irradiation was started under continuous stirring. After the time given below, the reaction was stopped by addition of triethylamine (1.00 eq.). The mixture was allowed to warm to room temperature and the solvent was removed in vacuo. The crude product was purified by column chromatography as given below.

4. Synthesis of Irradiation Precursors

3-(Pent-4-en-1-yl)cyclohex-2-en-1-one (9a)



$C_{11}H_{16}O$
MW = 164.12 g/mol

Following *GP1* 3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**9a**) was synthesized using 564 mg magnesium (23.3 mmol, 1.30 eq.), 2.97 mL 5-bromopent-1-ene (3.61 g, 24.2 mmol, 1.35 eq.) in 25 mL THF and 2.60 mL 3-ethoxycyclohex-2-en-1-one (2.50 g, 17.9 mmol, 1.00 eq.) in 20 mL THF. The reaction was quenched after three hours. After column chromatography (SiO_2, P/Et_2O = 4/1) the title compound **9a** was obtained as a colorless oil in 74% yield (2.20 g, 13.2 mmol).

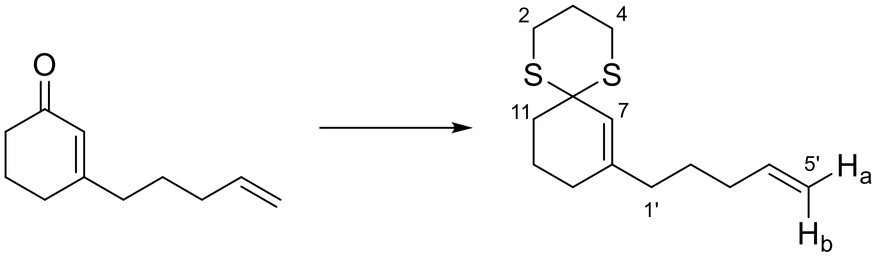
TLC: R_f = 0.29 (P/Et_2O = 4/1) [UV/$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.61 (*virt.* quin, $^{3}J \approx 7.5$ Hz, 2H, H-2’), 1.99 (*virt.* quin., $^{3}J \approx 6.2$ Hz, 2H, H-5), 2.08 (*virt.* qt, $^{3}J \approx 7.1$ Hz, $^{4}J \approx 1.3$ Hz, 2H, H-3’), 2.22 (t, $^{3}J = 7.7$ Hz, 2H, H-1’), 2.28 (t, $^{3}J = 6.0$ Hz, 2H, H-4), 2.36 (t, $^{3}J = 6.7$ Hz, 2H, H-6), 4.97 – 5.05 (m, 2H, H-5’), 5.78 (ddt, $^{3}J = 16.9$ Hz, $^{3}J = 10.2$ Hz, $^{3}J = 6.7$ Hz, 2H, H-4’), 5.88 (s, 1H, H-2).

^{13}C NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 22.9 (t, C-5), 26.2 (t, C-2’), 29.8 (t, C-4), 33.1 (t, C-3’), 37.5 (t, C-6), 37.5 (t, C-1’), 115.4 (t, C-5’), 125.9 (d, C-2), 138.0 (d, C-4’), 166.3 (s, C-3), 200.0 (s, C-1).

The obtained data match with those reported in the literature.[2]

8-(Pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1a)



$C_{14}H_{22}S_2$
MW = 254.45 g/mol

A solution of 300 mg 3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**9a**) (1.83 mmol, 1.00 eq.), 274 µL 1,3-propandithiol (296 mg, 2.74 mmol, 1.50 eq.) and 277µL boron trifluoride diethyl etherate (311 µg, 219 µmol, 1.20 eq.) was stirred in dry methanol (4.6 mL) for three hours according to *GP2*. Column chromatography (SiO_2, P/Et_2O = 100/0 → 99.5/0.5) afforded the title compound **1a** as a colorless oil in 79% yield (367 mg, 1.45 mmol).

TLC: R_f = 0.21 (P/Et_2O = 99.5/0.5) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2972 (s, sp^3-CH), 1635 (w, C=C), 1424 (m, sp^3-CH), 908 (s, sp^2-CH), 886 (s, sp^2-CH), 801 (m, C-S).

MS (EI, 70 eV): *m/z* (%) = 254 (61) $[M]^+$, 213 (19) $[M\text{-}C_3H_5]^+$, 200 (7) $[M\text{-}C_2H_4\text{-}C_3H_5]^+$, 179 (68), 52 (100), 137 (26), 91 (34) $[C_7H_7]^+$, 55 (5) $[C_4H_3]^+$.

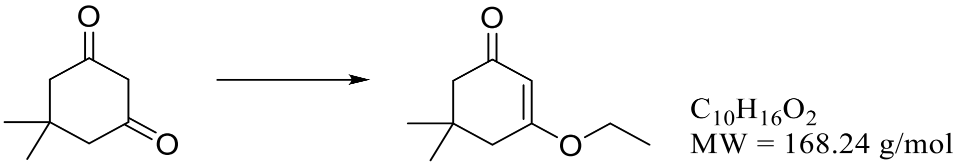
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.53 (*virt.* quin., $^3J \approx 7.5$ Hz, 2H, H-2’), 1.75-1.82 (m, 2H, H-10), 1.89 (dtt, $^2J = 14.0$ Hz, $^3J = 10.8$ Hz, $^3J = 3.2$ Hz, 1H, H-3), 1.96-2.09 (m, 7H, H-3, H-9, H-1’, H-3’), 2.19-2.2 (m, 2H, H-11), 2.75 (ddd, $^2J = 14.2$ Hz, $^3J = 6.0$ Hz, $^3J = 3.2$ Hz, 2H, H-2, H-4), 2.98 (ddd, $^2J = 14.2$ Hz, $^3J = 10.8$ Hz, $^3J = 2.9$ Hz, 2H, H-2, H-4), 4.95 (ddt, $^2J = 2.2$ Hz, $^3J = 10.2$ Hz, $^4J = 1.2$ Hz, 1H, H-5’a), 5.01 (*virt.* dq, $^3J = 17.0$ Hz, $^2J \approx {}^4J \approx 1.6$ Hz, 1H, H-5’b), 5.80 (ddt, $^3J = 17.0$ Hz, $^3J = 10.2$ Hz, $^3J = 6.7$ Hz, 1H, H-4’).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.9 (t, C-10), 25.1 (t, C-3), 26.6 (t-C-2’), 26.9 (t, C-2, C-4), 28.8 (t,C-9), 33.4 (t, C-3’), 36.0 (t, C-11), 37.1 (t, C-1’), 49.0 (s, C-6), 114.9 (d, C-5’), 123.4 (d, C-7), 138.8 (d, C-4’), 142.4 (s,C-8).

HRMS (EI, 70 eV): calculated: ($C_{14}H_{22}{}^{32}S_2$): 254.1157; found: 254.1154

calculated: ($C_{13}{}^{13}CH_{22}{}^{32}S_2$): 255.1191; found: 255.1191.

3-Ethoxy-5,5-dimethylcyclohex-2-en-1-one (10)



In 25 mL dry toluene 2.00 g 5,5-dimethyl-cyclohexan-1,3-dione (14.3 mmol, 1.00 eq.), 16.0 mL ethanol (12.6 g, 27.4 mmol, 1.92 eq.) und 54.3 mg *para*-toluenesulfonic acid monohydrat (28.6 µmol, 0.02 eq.) were refluxed for 6.5 hours and the solvent was evaporated in vacuo. After column chromatography (SiO_2, P/Et_2O = 2/1) the title compound was obtained as a colorless solid in 85% yield (2.04 g, 12.1 mmol).

TLC: R_f = 0.28 (P/Et_2O = 2/1) [UV].

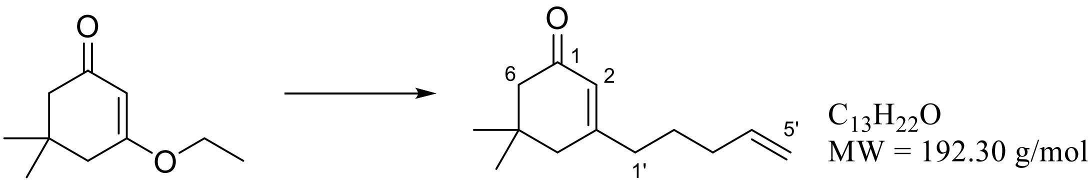
M.P.: 59 – 61 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.06 [s, 6H, $(CH_3)_2$], 1.36 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 2.20 (s, 2H, H_6), 2.26 (s, 2H, H-4), 3.89 (q, ^3J = 7.0 Hz, 2H, CH_2CH_3), 5.33 (s, 1H, H-2).

^{13}C NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 12.3 (q, CH_2CH_3), 28.4 [q, $(CH_3)_2$], 32.6 (s, C-5), 43.1 (t, C-4), 50.9 (t, C-6), 64.4 (t, CH_2CH_3), 101.7 (d, C-2), 176.3 (s, C-3), 199.2 (s, C-1).

The obtained data match with those reported in the literature.[3]

5,5-Dimethyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (9b)



Following *GP1* 5,5-dimethyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**9b**) was prepared using 187 mg magnesium (7.73 mmol, 1.30 eq.), 950 µL 5-bromopent-1-ene (1.95 g, 8.02 mmol, 1.35 eq.) in 8.3 mL THF and 1.00 g 3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (5.94 mmol, 1.00 eq.) in 6.6 mL THF. The reaction was quenched after four hours. After column chromatography (SiO_2, P/Et_2O = 10/1 → 4/1) the title compound was obtained as a yellowish oil in 51% yield (580 mg, 3.02 mmol).

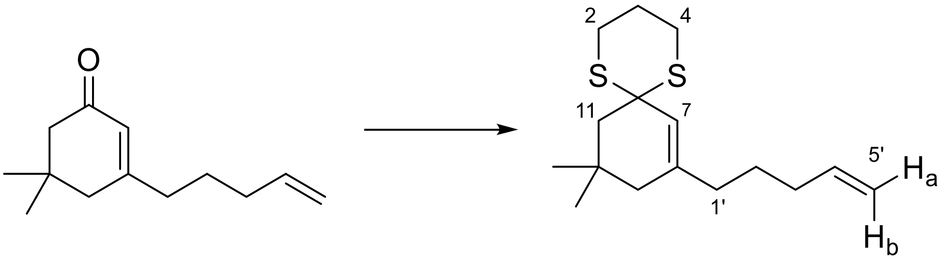
TLC: R_f = 0.31 (P/Et_2O = 10/1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.03 (s, 6H, C*H*$_3$), 1.60 (*virt.* quin., $^3J \approx 7.4$ Hz, 2H, H-2’), 2.07 (*virt.* qt, $^3J \approx 7.3$ Hz, $^4J \approx 1.2$ Hz, 2H, H-3’), 2.17 (s, 2H, H-4), 2.19 (*t*, $^3J = 8.0$ Hz, 2H, H-1’), 2.21 (s, 2H, H-6), 4.97 – 5.05 (m, 2H, H-5’), 5.79 (ddt, $^3J = 16.9$ Hz, $^3J = 10.2$ Hz, $^3J = 6.7$ Hz, 1H, H-4’), 5.88 (*virt.* quin., $^4J \approx 1.4$ Hz, 1H, H-2).

^{13}C NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 26.2 (t, C-2’), 28.4 (q, *C*H$_3$), 33.3 (t, C-3’), 33.8 (t, C-5), 37.5 (t, C-1’), 44.1 (t, C-4), 51.2 (t, C-6), 115.4 (t, C-5’), 125.0 (d, C-2), 138.0 (d, C-4’), 163.8 (s, C-3), 200.1 (s, C-1).

The obtained data match with those reported in the literature.[4]

10,10-Dimethyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1b)



$C_{16}H_{26}S_2$
MW = 282.50 g/mol

According to *GP2* a solution of 448 mg 5,5-dimethyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**10**) (2.33 mmol, 1.0 eq.), 350 µL 1,2-propanedithiol (378 µg, 3.49 mmol, 1.50 eq.) and 396 µL $BF_3 \cdot Et_2O$ (353 µg, 2.79 mmol, 1.2 eq.) was stirred in dry methanol (8 mL) for five hours. After column chromatography (SiO_2, P/Et_2O = 100/0 → 99.5/0.5) **1b** was obtained in 81% yield (360 mg, 1.89 mmol).

TLC: R_f = 0.21 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3074 (w, sp^2-CH), 2928 (s, sp^3-CH), 1654 (w, C=C), 1436 (m, sp^3-CH), 906 (s, sp^2-CH).

MS (EI, 70 eV): *m/z* (%) = 282 (65) $[M]^+$, 241 (100) $[M-C_3H_5]^+$, 207 (29), 152 (93), 107 (54) 91 (32) $[C_7H_7]^+$, 51 (10) $[C_4H_3]^+$.

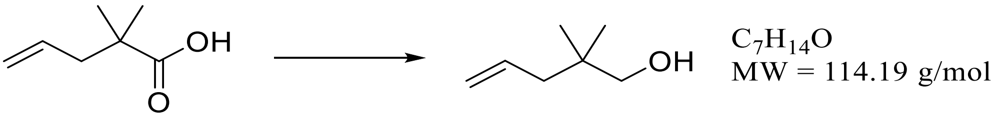
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.02 (s, 6H, C*H*$_3$), 1.50-1.56 (m, 2H, H-2’), 1.81 (s, 2H, H-9), 1.97-2.09 (m, 6H, H-3, H-1’, H-4’), 2.05 (s, 2H, H-11), 2.85-2.91 (m, 2H, H-2, H-4), 2.97-3.03 (m, 2H, H-2, H-4), 4.96 (ddt, $^2J = 2.2$ Hz, $^3J = 10.2$ Hz, $^4J = 1.1$ Hz, 1H, H-5’a), 5.02 (*virt.* dq, $^3J = 17.1$ Hz, $^2J \approx {}^4J \approx 1.6$ Hz, 1H, H-5’b), 5.76-5.86 (m, 2H, H-7, H-4’).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 25.1 (t, C-3), 26.6 (t, C-2’), 27.3 (t, C-2, C-4), 30.0 (q, CH_3), 31.2 (s, C-10), 33.4 (t, C-3’), 37.5 (t, C-1’), 42.4 (t, C-9), 47.5 (s, C-6), 49.4 (t, C-11), 114.8 (t, C-5’), 121.6 (d, C-7), 137.6 (s, C-8), 138.8 (d, C-4’).

HRMS (EI, 70 eV): calculated: ($C_{16}H_{26}{}^{32}S_2$): 282.1470; found: 282.1468,

calculated: ($C_{15}{}^{13}CH_{26}{}^{32}S_2$): 283.1504; found: 283.1504.

2,2-Dimethylpent-4-en-1-ol (11)



To a suspension of 638 mg lithium aluminium hydride (15.9 mmol, 1.02 eq.) in 40 mL of dry THF were added 2.00 g 2,2-dimethylpent-4-enoic acid (15.6 mmol 1.00 eq.) in 10 mL THF dropwise at 0 °C. The mixture was warmed to room temperature and stirred for 23 hours. After addition of 1 mL water, 2 mL NaOH (10 wt-% aqueous solution) and 1 mL water the precipitate was filtered of and washed with ethyl acetate. The filtrate was dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The title compound **11** was obtained as a colorless liquid in 79% yield (1.40 g, 12.3 mmol) and was used without further purification.[5]

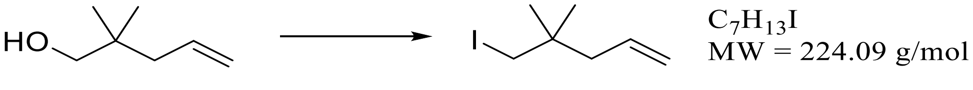
TLC: R_f = 0.15 (P/Et_2O = 10/1) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.89 (s, 6H, CH_3), 2.02 (*virt*. dt, ^3J = 7.5 Hz, $^4J \approx$ 1.1 Hz, 2H, H-3), 3.33 (s, 2H, H-1), 5.02-5.09 (m, 2H, H-5), 5.80-5.90 (m, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.0 (q, CH_3), 36.7 (s, C-2), 43.5 (t, C-3), 71.9 (t, C-1), 117.3 (t, C-5), 135.5 (s, C-4).

The obtained data match with those reported in the literature.[6]

5-Iodo-4,4-dimethylpent-1-ene (12)



To a solution of 1.66 g 2,2-Dimethylpent-4-en-1-ol (**11**) (14.5 mmol, 1.00 eq.) in 7.7 mL dry pyridine were added 4.19 g triphenylphosphine (15.9 mmol, 1.10 eq.) and 3.69 g iodine (15.5 mmol, 1.00 eq.). The mixture was stirred under reflux for 14 hours. The crude product was purified by column chromatography (SiO_2, P) without any further work up. The product **12** was obtained in 63% yield (2.05 g, 9.15 mmol) as a colorless oil.

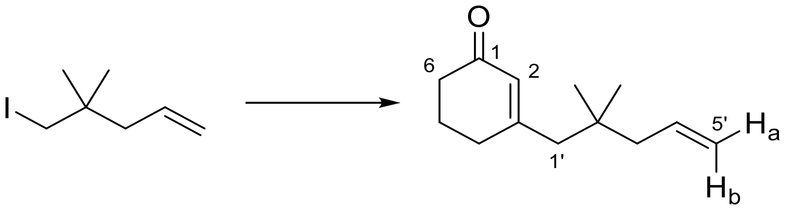
TLC: R_f = 0.85 (P) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.06 (s, 6H, C*H*$_3$), 2.10 (virt. dt, ^3J = 7.5 Hz, $^4J \approx$ 1.0 Hz, 2H, H-3), 3.14 (s, 2H, H-5), 5.06-5.14 (m, 2H, H-5), 5.75 (ddt, ^3J = 16.7 Hz, ^3J = 14.4 Hz, ^3J = 7.5 Hz, 1H, H-2).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.0 (t, C-5), 26.9 (q, *C*H$_3$), 33.8 (s, C-4), 45.3 (t, C-3), 118.3 (t, C-1), 134.4 (d, C-2).

The obtained data match with those reported in the literature.[7]

3-(2,2-Dimethylpent-4-en-1-yl)cyclohex-2-en-1-one (9c)



$C_{13}H_{20}O$
MW = 192.30 g/mol

To a solution of 700 mg 5-iodo-4,4-dimethylpent-1-ene (**12**) (3.12 mmol, 1.00 eq.) in 12 mL dry pentane and 8 mL dry Et_2O were added 3.37 mL *t*-BuLi (2.5 M in heptane, 410 mg, 6.40 mmol, 2.05 eq.) dropwise at −78°C. The mixture was stirred at −78°C for one hour, 477 µL 3-ethoxycyclohex-2-en-1-one (460 mg, 3.28 mmol, 1.05 eq.) were added and the solution was stirred for three hours at room temperature before 12 mL saturated aqueous ammonium chloride solution were added. The aqueous phase was extracted with Et_2O (3 × 20 mL). Combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified using column chromatography (SiO_2, P/Et_2O = 4/1). Remaining 3-(*tert*-butyl)cyclohex-2-en-1-one was removed by distillation (4 mbar, 100°C). Pure ketone **9c** was obtained as a colorless oil in 50% yield (222 mg, 1.60 mmol).

TLC: R_f = 0.33 (P/Et_2O = 4/1) [UV/$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077 (w, sp^2-CH), 2957 (s, sp^3-CH), 1671 (s, C=O), 1618 (m, C=C), 1468 (m, sp^3-CH), 1324 (m, sp^2-CH).

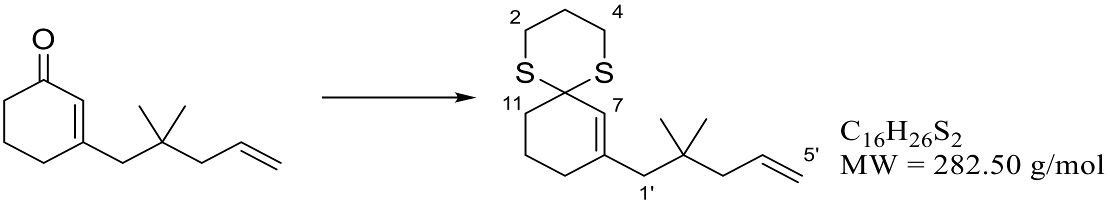
MS (EI, 70 eV): *m/z* (%) = 192 (17) [M]$^+$, 164 (14) [M-C_2H_4]$^+$, 151 (18) [M-C_3H_5]$^+$, 110 (100), 55 (52).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.93 (s, 6H, CH_3), 1.94-2.00 (m, 2H, H-5), 2.01 (d, ^3J = 7.3 Hz, 2H, H-3’), 2.13 (s, 2H, H-1’), 2.32-2.38 (m, 4H, H-4, H-6), 5.01-5.08 (m, 1H, H-5’b), 5.08 (ddt, ^2J = 0.8 Hz, ^3J = 10.2 Hz, ^4J = 1.9 Hz, 1H, H-5’a), 5.82 (ddt, ^3J = 17.5 Hz, ^3J = 10.2 Hz, ^3J = 7.3 Hz, 1H, H-4’), 5.85 (s, 1H, H-2).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 23.2 (t, C-5), 27.4 (q, CH_3), 32.7 (t, C-4), 35.2 (s, C-2’), 37.4 (t, C-6), 47.6 (t, C-3’), 50.2 (t, C-1’), 117.9 (t, C-5’), 129.3 (d, C-2), 134.9 (d, C-4’), 164.8 (s, C-3), 199.9 (s, C-1).

HRMS (EI, 70 eV): calculated: ($C_{13}H_{20}O$): 192.1509; found: 192.1504.

8-(2,2-Dimethylpent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1c)



A solution of 2.15 mg 3-(2,2-dimethylpent-4-en-1-yl)cyclohex-2-en-1-one (**9c**) (1.12 mmol, 1.00 eq.), 170 µL 1,3-propandithiol (181 mg, 1.68 mmol, 1.50 eq.) and 170 µL boron trifluoride diethyl etherate (190 µg, 1.34 mmol, 1.30 eq.) was stirred in dry methanol (6.2 mL) for four hours according to *GP2*. Column chromatography (SiO_2, P/Et_2O = 99/1) afforded the title **1c** compound as a colorless oil in 95% yield (300 mg, 1.06 mmol).

TLC: R_f = 0.26 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3073 (s, sp^2-CH), 2931 (s, sp^3-CH), 1638 (m, C=C), 1423 (m, sp^3-CH), 911 (m, sp^2-CH).

MS (EI, 70 eV): *m/z* (%) = 282 (69) $[M]^+$, 241 (13) $[M\text{-}C_3H_5]^+$, 208 (36) $[C_{13}H_{20}S]^+$, 207 (100), 180 (72), 167 (13) $[C_{10}H_{15}S]^+$, 126 (62) $[C_7H_{10}S]^+$.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.88 (s, 6H, CH_3), 1.73-1.86 (m, 2H, H-10), 1.85-1.94 (m, 1H, H-3), 1.90 (s, 2H, H-1’), 1.97 (d, ^3J = 7.4 Hz, 2H, H-3’), 2.02-2.09 (m, 3H, H-3, H-9, H-9), 2.21-2.23 (m, 2H, H-11), 2.75 (ddd, ^2J = 14.3 Hz, ^3J = 6.0 Hz, ^3J = 3.2 Hz, 2H, H-2, H-4), 2.98 (ddd, ^2J = 14.3 Hz, ^3J = 10.8 Hz, ^3J = 2.8 Hz, 2H, H-2, H-4), 4.98-5.06 (m, 2H, H-5’), 5.50 (s, 1H, H-7), 5.82 (ddt, ^3J = 17.6 Hz, ^3J = 10.2 Hz, ^3J = 7.4 Hz, 1H, H-4’).

^{13}C NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.2 (t, C-10), 25.1 (t, C-3), 26.9 (t, C-2, C-4), 27.5 (q, CH_3), 31.9 (t, C-9), 34.6 (s, C-2’), 35.9 (t, C-11), 47.5 (t, C-3’), 49.2 (s, C-6), 49.5 (t, C-1’), 117.2 (t, C-5’), 127.2 (d, C-7), 135.7 (d, C-4’), 140.0 (s, C-8).

HRMS (EI, 70 eV): calculated: ($C_{16}H_{26}{}^{32}S_2$): 282.1470; found: 282.1471,

calculated: ($C_{15}{}^{13}CH_{26}{}^{32}S_2$): 283.1504; found: 283.1500.

(5-Bromopent-1-yn-1-yl)trimethylsilane (13)

$C_8H_{15}BrSi$
MW = 219.20 g/mol

To 66 mL of dry THF were added 5.18 g 5-(trimethylsilyl)pent-4-yn-1-ol (33.1 mmol, 1.00 eq.) and 5.97 mL NEt_3 (4.36 g, 43.1 mmol, 1.30 eq.). At 0 °C were 3.33 mL methanesulfonyl chloride (4.93 g, 43.1 mmol, 1.03 eq.) added dropwise. After stirring for three hours at room temperature 50 mL water were added. The aqueous phase was extracted using CH_2Cl_2 (4×40 mL), combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude mesylate was dissolved in 35 mL acetone, 8.64 g LiBr (99.5 mmol, 3.00 eq.) were added and the heterogeneous mixture was stirred for 15 hours at 60 °C. After cooling the reaction mixture to room temperature about 50% of acetone were removed in vacuo and 40 mL water were added. The aqueous phase was extracted using Et_2O (3×20 mL), combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (SiO_2, P/Et_2O = 100/0 → 99/1) bromide **13** was obtained as a colorless oil in 76% yield (5.50 g, 25. mmol).

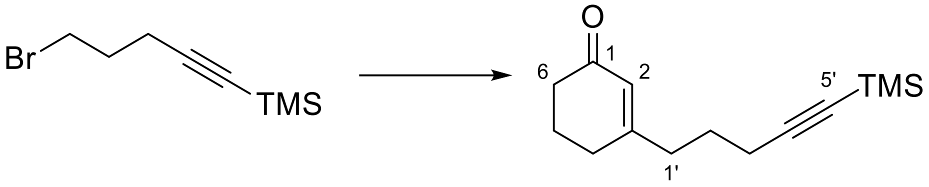
TLC: R_f = 0.47 (P) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.15 [s, 9H, Si(CH_3)$_3$], 2.05 (*virt.* p, $^3J \approx 6.7$ Hz, 2H, H-4), 2.41 (t, $^3J = 6.8$ Hz, 2H, H-3), 3.51 (t, $^3J = 6.5$ Hz, 2H, H-5).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.2 [q, Si(CH_3)$_3$], 18.8 (t, C-3), 31.6 (t, C-4), 32.5 (t, C-5), 85.9 (s, C-1), 105.2 (s,C-2).

The obtained data match with those reported in the literature.[8]

3-(5-(Trimethylsilyl)pent-4-yn-1-yl)cyclohex-2-en-1-one (14)



$C_{14}H_{22}OSi$
MW = 234.41 g/mol

Following *GP2* the title compound was prepared using 225 mg magnesium (9.27 mmol, 1.30 eq.), 2.11 g (5-bromopent-1-yn-1-yl)trimethylsilane (**13**) (9.60 mmol, 1.35 eq.) in 12 mL dry THF and 961 µL 3-ethoxycyclohex-2-en-1-on (1.00 g, 7.13 mmol, 1.00 eq.) in 12.8 mL THF. After stirring for 3.5 hours stirring at room temperature, the reaction was quenched using saturated aqueous NH_4Cl solution. Purification by column chromatography (SiO_2, P/Et_2O = 5/1) yielded in 98% of cyclohexenone **14** (1.64 g, 6.82 mmol) as a colorless oil.

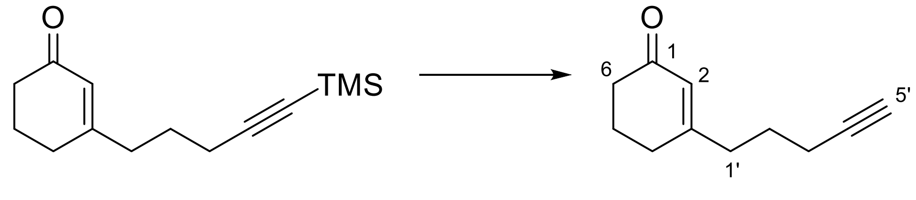
TLC: R_f = 0.33 (P/Et_2O = 3/1) [UV/$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.15 [s, 9H, Si(C*H*$_3$)$_3$], 1.72 (*virt.* p, $^3J \approx 7.3$ Hz, 2H, H-2’), 2.00 (*virt.* p, $^3J \approx 6.3$ Hz, 2H, H-5), 2.26 (t, $^3J = 7.0$ Hz, 2H, H-3’), 2.28-2.35 (m, 4H, H-4, H-1’), 2.37 (t, $^3J = 6.6$ Hz, 2H, H-6), 5.89 (s, 1H, H-2).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.3 [q, Si(*C*H$_3$)$_3$], 19.6 (t, C-3’), 22.8 (t, C-5), 26.0 (t, C-2’), 29.8 (t, C-4), 37.0 (t, C-1’), 37.5 (t,C-6), 85.7 (s, C-5’), 106.3 (s, C-4’), 126.2 (d, C-2), 165.6 (s, C-3), 200.0 (s, C-1).

The obtained data match with those reported in the literature.[9]

3-(Pent-4-yn-1-yl)cyclohex-2-en-1-one (15)



$C_{11}H_{14}O$
MW = 162.23 g/mol

A solution of 1.20 g 3-(5-(trimethylsilyl)pent-4-yn-1-yl)cyclohex-2-en-1-one (**14**) (5.12 mmol, 1.00 eq.) in 5.0 mL dry THF was cooled to 0 °C and 10.2 mL tetrabutylammonium fluoride (1.0 M in THF, 2.68 g, 10.2 mmol, 2.00 eq.) were slowly added. After stirring for five hours 20 mL water were added. The aqueous phase was extracted using Et_2O (4×20 mL), combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After purification by column chromatography (SiO_2, P/Et_2O = 3/1 → 2/1) the deprotected alkyne **15** was obtained as a colorless oil in 89% yield (742 mg, 4.57 mmol).

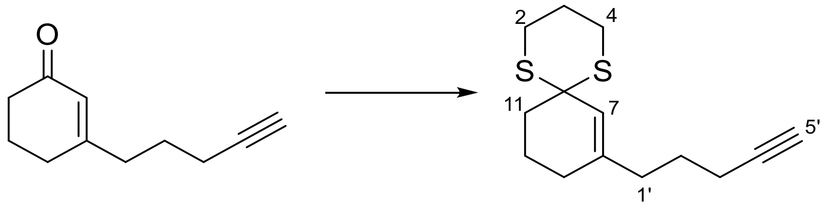
TLC: R_f = 0.17 (P/Et_2O = 3/1) [UV/$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.74 (*virt.* p, $^3J \approx 7.0$ Hz, 2H, H-2’), 1.96-.2.04 (m, 3H, H-5, H-5’), 2.23 (td, $^3J = 6.9$ Hz, $^4J = 2.6$ Hz, 2H, H-3’), 2.26-2.41 (m, 6H, H-4, H-6, H.1’), 5.89 (s, 1H, H-2).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.2 (t, C-3’), 22.9 (t, C-5), 25.8 (t, C-2’), 29.9 (t, C-4), 36.9 (t, C-1’), 37.5 (t,C-6), 69.3 (d, C-5’), 83.5 (s, C-4’), 126.2 (d, C-2), 165.3 (s, C-3), 199.8 (s, C-1).

The obtained data match with those reported in the literature.[10]

8-(Pent-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (16)



$C_{14}H_{20}S_2$
MW = 252.43 g/mol

According to *GP1* 730 µg ketone **15** (4.50 mmol. 1.00 eq.), 676 µL propane dithiol (730 mg, 6.75 mmol, 1.50 eq.) and 684 µL $BF_3{\cdot}OEt_2$ (766 mg, 5.40 mmol, 1.20 eq.) in 12 mL dry methanol were stirred for four hours at room temperature. After aqueous work up and column chromatography (SiO_2, P/Et_2O = 98/2) the title compound **16** was obtained as a yellowish oil in 92% yield (1.05 g, 4.14 mmol).

TLC: R_f = 0.21 (P/Et_2O = 98/2) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3290 (m, sp-CH), 3292 (s, sp^3-CH), 1653 (m, C=C), 1424 (m, sp^3-CH), 1274 (m, sp^2-CH), 886 (m), 652 (m, C-S).

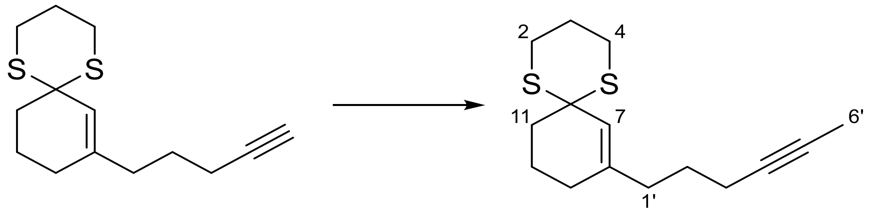
MS (EI, 70 eV): *m/z* (%) = 252 (7) $[M]^+$, 177 (24), 150 (100) $[C_9H_{10}S]^+$, 149 (36), 135 (36).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.66 (*virt.* p, $^3J \approx 7.2$ Hz, 2H, H-2’), 1.77-1.82 (m, 2H, H-10), 1.89 (dtt, $^2J = 14.6$ Hz, $^3J = 6.1$ Hz, $^3J = 3.0$ Hz, 1H, H-3), 1.95 (t, $^4J = 2.7$ Hz, 1H, H-5’), 1.99 (t, $^3J = 5.7$ Hz, 2H, H-9), 2.05 (dtt, $^2J = 14.6$ Hz, $^3J = 6.1$ Hz, $^3J = 3.0$ Hz, 1H, H-3), 2.10 (t, $^3J = 7.6$ Hz, 2H, H-1), 2.18 (td, $^3J = 7.1$ Hz, $^4J = 2.7$ Hz, 2H, H-3’), 2.20-2.22 (m, 2H, H-11), 2.76 (ddt, ^2J = 14.2 Hz, ^3J = 6.1 Hz, ^3J = 3.2 Hz, 2H, H-2, H-4), 2.97 (ddt, ^2J = 14.2 Hz, ^3J = 10.7 Hz, ^3J = 3.0 Hz, 2H, H-2 H-4), 5.55 (s, 1H, H-7).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.11 (t, C-3'), 19.9 (t, C-10), 25.1 (t, C-3), 26.3 (t, C-2'), 26.9 (t, C-2, C-4), 28.7 (t, C-9), 35.9 (t, C-11), 36.6 (t, C-1'), 48.9 (s, C-6), 68.7 d, C-5'), 84.4 (s, C-4'), 124.0 (d, C-7), 141.4 (s, C-8).

HRMS (EI, 70 eV): calculated: ($C_{14}H_{20}S_2$): 252.1001; found: 252.0995.

8-(Hex-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1d)



$C_{15}H_{22}S_2$
MW = 266.46 g/mol

A solution of 300 mg 8-(pent-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**16**) (1.19 mmol, 1.00 eq.) in 12 mL dry THF was cooled to −78 °C. After dropwise addition of 713 µL *n*-BuLi (2.5 M in hexane, 114 mg, 1.78 mmol, 1.50 eq.) the reaction mixture was stirred for 1.5 hours and 295 µL methyl iodine (674 mg, 4.75 mmol, 4.00 eq.) were added. After stirring for 1.5 hours at −78 °C and additional 1.5 hours at room temperature 15 mL water were added. Aqueous phase was extracted using Et_2O (3×20 mL), combined organic layers were dried over Na_2SO_4, filtered and solvent was removed in vacuo. Purification by column chromatography (SiO_2, P/Et_2O = 98/2) yielded in 97% of product **1d** (308 mg, 1.16 mmol) as a colorless oil.

TLC: R_f = 0.31 (P/Et_2O = 98/2) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2933 (s, sp^3-CH), 2190 (w, C≡C), 1653 (w, C=C), 1423 (m, sp^3-CH), 1273 (m), 885 (m).

MS (EI, 70 eV): *m/z* (%) = 266 (8), $[M]^+$, 238 (15) $[M-C_2H_4]^+$, 207 (27), 191 (31), 164 (100), $[C_{10}H_{12}S]^+$, 149 (35) $[C_9H_9S]^+$.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.60 (*virt*. q, $^3J \approx$ 7.4 Hz, 2H, H-2'), 1.76-1.81 (m, 2H, H-10), 1.78 (t, ^5J = 2.5 Hz, 3H, H-6'), 1.89 (dtt, ^2J = 13.9 Hz, ^3J = 10.8 Hz, ^3J = 3.2 Hz, 1H, H-3), 1.99 (td, ^3J = 6.3 Hz, ^4J = 1.5 Hz, 2H, H-9), 2.01-2.05 (m, 1H, H-3), 2.05-2.10 (m, 2H, H-1'), 2.09-2.13 (m, 2H, H-3), 2.20 (tq, ^3J = 6.1 Hz, ^4J = 2.5 Hz, 2H, H-11), 2.75 (ddd,

^2J = 14.2 Hz, ^3J = 6.1 Hz, ^3J = 3.2 Hz, 2H, H-2, H-4), 2.97 (ddd, ^2J = 14.2 Hz, ^3J = 10.8 Hz, ^3J = 2.8 Hz, 2H, H-2, H-4), 5.51-5.53 (m, 1H, H-7).

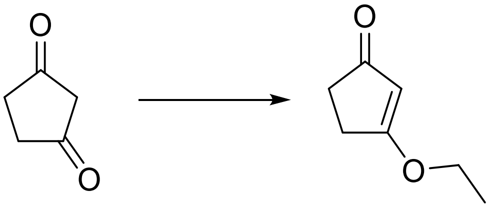
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 3.5 (q, C-6’), 18.5 (t, C-3’), 19.9 (t, C-10), 25.1 (t, C-3), 26.9 (t, C-2’), 26.9 (t, C-2, C-4), 28.8 (t, C-9), 36.0 (t, C-11), 36.8 (t, C-1’), 49.0 (s, C-6), 76.0 (s, C-5’*), 79.0 (s, C-4’*), 123.6 (d, C-7), 141.9 (s, C-8).

* assignment is interconvertible

HRMS (EI, 70 eV): calculated: ($C_{15}H_{22}{}^{32}S_2$): 266.1157; found: 266.1155,

calculated: ($C_{14}{}^{13}CH_{22}{}^{32}S_2$): 267.1191; found: 267.1192.

3-Ethoxycyclopent-2-en-1-one (17)



$C_7H_{10}O_2$
MW = 126.07 g/mol

In dry toluene (28 mL) 2.00 g cyclopentane-1,3-dione (20.4 mmol, 1.00 eq.), 9.15 mL ethanol (154 mmol, 7.6 eq.) and 71.0 mg *para*-toluenesulfonic acid monohydrat (407 µmol, 2.0 mol-%) were stirred at 90 °C for 10 hours. After removal of volatile compounds in vacuo the crude product was subjected to column chromatography (SiO_2, CH_2Cl_2/EtOAc = 3/1). The title compound **17** was obtained in 99% yield (2.54 g, 20.1 mmol) as a colorless oil.

TLC: R_f = 0.27 (CH_2Cl_2/EtOAc = 3/1) [UV/$KMnO_4$].

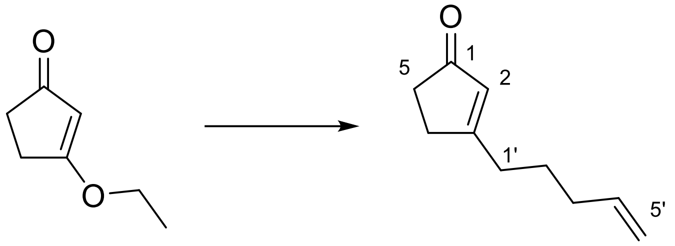
^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ (ppm) = 1.31 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 2.27-2.31 (m, 2H, H-4*), 2.53-2.58 (m, 2H, H-5*), 4.07 (q, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.36 (s, 1H, H-2).

^{13}C NMR (126 MHz, DMSO-d_6, 300 K): δ (ppm) = 14.1 (q, OCH_2CH_3), 27.9 (t, C-4*), 33.8 (t, C-5*), 67.5 (t, OCH_2CH_3), 104.4 (d, C-2), 189.9 (s, C-3), 204.6 (s, C-1).

* assignment is interconvertible

The obtained data match with those reported in the literature.[11]

3-(Pent-4-en-1-yl)cyclopent-2-en-1-one (9e)



$C_{10}H_{14}O$
MW = 150.22 g/mol

The synthesis was carried out according to *GP1* using 250 mg magnesium (10.3 mmol, 1.30 eq.), 1.27 mL 5-bromopentene (1.59 g, 10.7 mmol, 1.35 eq.) in dry THF (11 mL) and 1.00 g vinylogous ester **17** (7.93 mmol, 1.00 eq.) in dry THF (9 mL). The reaction mixture was stirred for 20 hours. After column chromatography (SiO_2, P/Et_2O = 3/1) the enone **9e** was obtained as a yellowish oil in 70% yield (755 mg, 7.0 mmol).

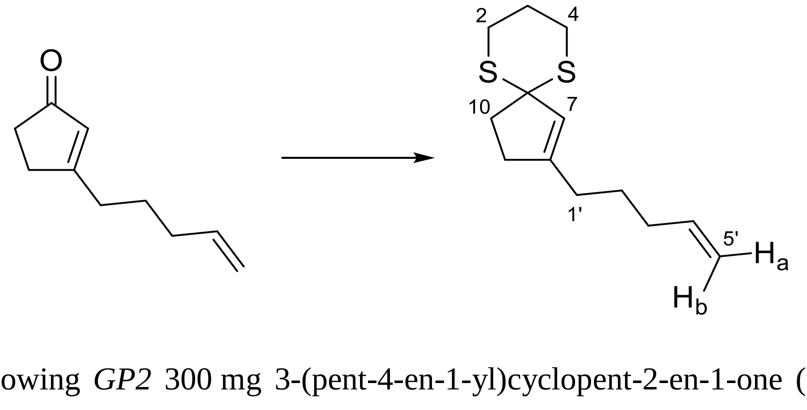
TLC: R_f = 0.26 (P/Et_2O = 2/1) [UV/$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.69 (*virt*. p, $^3J \approx$ 7.5 Hz, 2H, H-2'), 2.12 (*virt*. q, $^3J \approx$ 7.1 Hz, 2H, H-3'), 2.38-2.45 (m, 4H, H-5, H-1'), 2.55-2.60 (m, 2H, H-4), 4.98-5.06 (m, 2H, H-5'), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, H-4'), 5.95 (s, 1H, H-2).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 26.3 (t, C-2'), 31.7 (t, C-4), 32.9 (t, C-1'), 33.4 (t, C-3'), 35.4 (t, C-5), 115.6 (t, C-5'), 129.7 (d, C-4'), 182.9 (s, C-3), 210.3 (s, C-5).

The obtained data match with those reported in the literature.[12]

2-(Pent-4-en-1-yl)-6,10-dithiaspiro[4.5]dec-1-ene (1e)



$C_{13}H_{20}S_2$
MW = 240.42 g/mol

Following *GP2* 300 mg 3-(pent-4-en-1-yl)cyclopent-2-en-1-one (**9e**) (2.00 mmol, 1.00 eq.), 300 µL 1,3-propandithiol (324 mg, 3.00 mmol, 1.5 eq.) and 304 µL boron trifluoride diethyl etherate (340 mg, 2.40 mmol, 1.2 eq.) were stirred in dry methanol (10 mL) for three hours.

After column chromatography (SiO_2, P/Et_2O = 99.5/0.5 → 99/1) the irradiation precursor **1e** was obtained as a colorless oil in 56% yield (256 mg, 1.12 mmol).

TLC: R_f = 0.28 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3074 (w, sp^2-CH), 2940 (s, sp^3-CH), 1640 (m, C=C), 1422 (m, sp^3-CH), 1272 (m), 907 (m, sp^2-CH).

MS (EI, 70 eV): *m/z* (%) = 240 (100) $[M]^+$, 199 (22) $[M-C_3H_5]^+$, 186 (58), 166 (49) $[C_{10}H_{14}S]^+$, 124 (74), 91 (68).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.57 (*virt.* p, ^3J = 7.7 Hz, 2H, H-2'), 1.99-2.17 (m, 6H, H-3, H-1', H-3'), 2.43-2.54 (m, 4H, H-9, H-10), 2.88-2.98 (m, 4H, H-2, H-4), 4.96 (ddt, ^2J = 2.2 Hz, ^3J = 10.2 Hz, ^4J = 1.2 Hz, 1H, H-5'a), 5.01 (*virt.* dq, ^3J = 17.0 Hz, $^2J \approx {}^4J \approx$ 1.6 Hz, 1H, H-5'b), 5.63 (s, 1H, H-7), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, H-4').

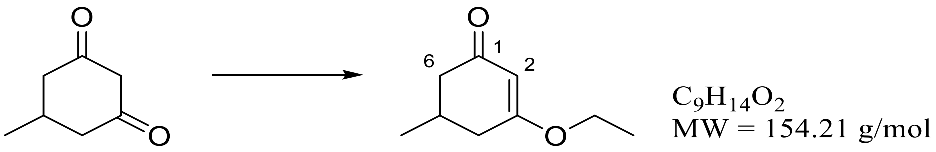
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 25.2 (t, C-3), 26.6 (t, C-2'), 28.8 (t, C-2, C-4), 30.5 (t, C-1'), 33.5 (t, C-3'), 34.3 (t, C-9*), 41.4 (t, C-10*), 59.8 (s, C-6), 115.0 (t, C-5'), 126.8 (d, C-7), 138.6 (d, C-4'), 147.4 (s, C-8).

* assignment is interconvertible

HRMS (EI, 70 eV): calculated: ($C_{13}H_{20}{}^{32}S_2$): 240.1001; found: 240.1003,

calculated: ($C_{12}{}^{13}CH_{20}{}^{32}S_2$): 241.1035; found: 241.1032.

3-Ethoxy-5-methylcyclohex-2-en-1-one (18)



A solution of 2.50 g 5-methylcyclohexane-1,3-dione (19.8 mmol, 1.00 eq.), 11.6 mL ethanol (198 mmol, 10.0 eq.) and 75.4 mg *p*TsOH·H_2O (396 µmol, 2.0 mol%) in 25 mL toluene was stirred at 85°C for six hours. All volatile compounds were removed in vacuo and the product purified using column chromatography (SiO_2, P/Et_2O = 1/2). Vinylogous ester **18** was obtained as a yellowish oil in 82% yield (2.51 g, 16.3 mmol).

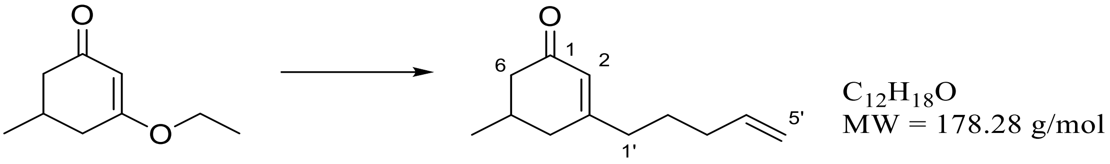
TLC: R_f = 0.51 (P/Et_2O = 1/2) [UV/$KMnO_4$].

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.07 (d, ^3J = 6.3 Hz, 3H, CHCH_3), 1.36 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 2.03 (dd, ^2J =16.3 Hz, ^3J =11.4 Hz, 1H, H-6), 2.10-2.18 (m, 1H, H-4), 2.18-2.29 (m, 1H, H-5), 2.36-2.41 (m, 2H, H-4, H-6), 3.83-3.95 (m, 2H, OCH_2CH_3), 5.33 (s, 1H, H-2).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 14.3 (q, OCH_2CH_3), 21.1 (q, CHCH_3), 29.0 (d, C-5), 37.4 (t, C-4), 45.3 (t, C-6), 64.4 (t, OCH_2CH_3), 102.5 (d, C-2), 177.4 (s, C-3), 199.9 (s, C-1).

The obtained data match with those reported in the literature.[13]

5-Methyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (9f)



According to *GP1* this *Grignard*-reaction was carried out using 143 mg magnesium (5.45 mmol, 1.30 eq.), 725 µL 5-bromopent-1-en (913 mg, 6.13 mmol, 1.35 eq.) in 9.2 mL dry THF and 700 mg vinylogous ester **18** (6.13 mmol, 1.00 eq.). The reaction was quenched after 21 hours by addition of 20 mL saturated aqueous ammonium chloride solution. Usual work up and column chromatography (SiO_2, P/Et_2O = 5/1) yielded in 47% of the title compound **9f** (380 mg, 2.13 mmol) as a colorless oil.

TLC: R_f = 0.27 (P/Et_2O = 5/1) [UV/$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077 (w, sp^2-CH), 2654 (m, sp^3-CH), 1666 (s, C=O), 1626 (m, C=C), 911 (m), 799 (m).

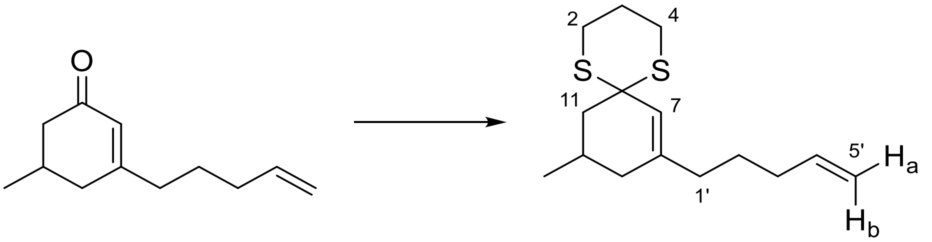
MS (EI, 70 eV): *m/z* (%) = 178 (21) $[M]^+$, 163 (9) $[M-CH_3]^+$, 136 (50) $[C_9H_{12}O]^+$, 108 (61) $[C_7H_8O]^+$, 82 (100) $[C_7H_8O-C_2H_4]^+$, 93 (32).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.06 (d, ^3J = 6.6 Hz, 3H, CH_3), 1.57-1.65 (m, 2H, H-2’), 1.97-2.06 (m, 2H, H-4, H-6), 2.07-2.11 (m, 2H, C-3’), 2.12-2.9 (m, 1H, H-5), 2.21 (t, ^3J = 8.0 Hz, 2H, H-1’), 2.30 (dd, ^2J = 17.6 Hz, ^3J = 4.1 Hz, 1H, H-4), 2.43 (dd, ^2J = 16.2 Hz, ^3J = 3.7 Hz, 1H, H-6), 4.96-5.06 (m, 2H, H-5’), 5.79 (ddt, ^3J = 16.9 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, H-4’), 5.87 (*br* s, 1H, H-2).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 21.3 (q, CH_3), 26.2 (t, C-2’), 30.4 (d, C-5), 33.3 (t, C-3’), 37.4 (t, C-1’), 38.3 (t, C-4), 45.7 (t, C-6), 115.4 (t, C-5’), 125.6 (d, C-2), 138.0 (d, C-4’), 165.6 (s, C-3), 200.4 (s, C-1).

HRMS (EI, 70 eV): calculated: ($C_{12}H_{18}O$): 178.1352; found: 178.1347.

10-Methyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1f)



$C_{15}H_{24}S_2$
MW = 268.48 g/mol

Following *GP3* the title compound was prepared using 240 mg 5-methyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**9f**) (1.1 mmol, 1.0 eq.), 0.21 mL 1,3-propanedithiol (0.22 g, 1.7 mmol, 1.5 eq.) and 0.21 mL $BF_3{\cdot}OEt_2$ (1.4 mmol, 1.2 eq.) in 7.7 mL dry methanol in 2.5 hours. After work up and column chromatography product **1f** was obtained as a colorless oil in 66% yield (342 mg, 0.73 mmol).

TLC: R_f = 0.32 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3074 (w, sp^2-CH), 2904 (s, sp^3-CH), 1654 (m, C=C), 1422 (s, sp^3-CH), 902 (s), 888 (s, CSC).

MS (EI, 70 eV): *m/z* (%) = 268 (53) $[M]^+$, 227 (10) $[M\text{-}C_3H_5]^+$, 193 (45) $[C_{12}H_{17}S]^+$, 152 (100) $[C_{12}H_{17}S\text{-}C_3H_5]^+$, 137 (28) $[C_{12}H_{17}S\text{-}C_3H_5\text{-}CH_3]$, 105 (31).

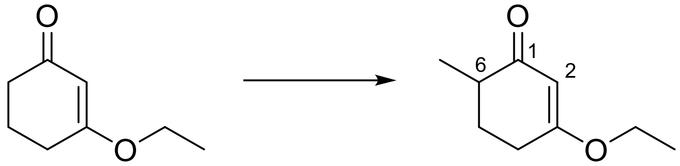
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.00 (d, ^3J = 6.4 Hz, 3H, CH_3), 1.47-1.59 (m, 3H, H-9, H-2’,H-2’), 1.62-1.72 (m, 1H, H-11), 1.90 (*virt.* dtt, ^2J = 13.8 Hz, $^3J \approx$ 10.5 Hz, $^3J \approx$ 3.2 Hz, 1H, H-3), 1.96-2.09 (m, 7H, H-3, H-10, H-11, H-1’, H-1’, H-3’, H-3’), 2.51 (ddt, ^2J = 13.3 Hz, ^3J = 2.7 Hz, ^4J = 1.6 Hz, 1H, H-9), 2.71 (ddd, ^2J = 14.3 Hz, ^3J = 6.0 Hz, ^3J = 3.1 Hz, 1H, H-2), 2.83 (ddd, ^2J = 14.7 Hz, ^3J = 6.3 Hz, ^3J = 3.3 Hz, 1H, H-4), 2.92-3.03 (m, 2H, H-2, H-4), 4.95 (ddt, ^2J = 2.1 Hz, ^3J = 10.2 Hz, ^4J = 1.2 Hz, 1H, H-5’a), 5.01 (*virt.* qd, $^2J \approx {}^4J \approx$ 1.6 Hz, ^3J = 17.0 Hz, 1H, H-5’b), 5.52 (s, 1H, H-7), 5.79 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, H-4’).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 21.6 (q, *C*H_3), 25.1 (t, C-3), 26.3 (t, C-4*), 26.5 (t, C-2'*), 26.6 (d, C-10), 27.4 (t, C-2), 33.4 (t, C-3'), 36.9 (t, C-1'), 37.7 (t, C-11), 44.5 (t, C-9), 49.6 (s, C-6), 114.9 (t, C-5'), 123.1 (d, C-7), 138.8 (d, C-4'), 141.8 (s, C-8).

* assignment is interconvertible

HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}S_2$): 268.1314; found: 268.1307.

3-Ethoxy-6-methylcyclohex-2-en-1-one (19)



$C_9H_{14}O_2$
MW = 154.21 g/mol

This compound was synthesized following literate procedure.[13] To a solution of 2.43 mL diisopropylamine (1.73 g, 17.1 mmol, 1.20 eq.) in 8.6 ml dry THF were added 6.85 mL *n*-BuLi (2.5 M in hexane, 1.10 g, 17.1 mmol, 1.20 eq.) at –78 °C. After complete addition the mixture was allowed to warm to 0 °C. Freshly prepared LDA was added dropwise to a solution of 2.08 mL 3-ethoxycyclohexenone (2.00 g, 14.0 mmol, 1.00 eq.) in 14 mL dry THF at –78 °C. After stirring for two hours 1.06 mL MeI (2.43 g, 17.1 mmol, 1.20 eq.) were added. The reaction mixture was allowed to warm to room temperature and was stirred for an additional hour, before 10 mL of saturated aqueous ammonium chloride solution were added. The aqueous phase was extracted four times with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (SiO_2, P/Et_2O = 10/1→5/1→4/1→3/1→2/1) the title compound **19** was obtained as a colorless oil in 96% yield (2.12 g, 13.7 mmol).[14]

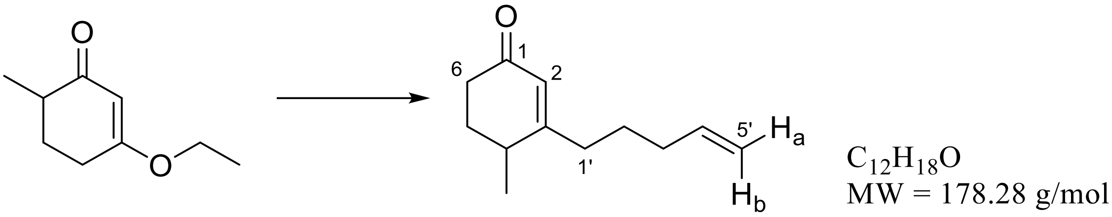
TLC: R_f = 0.22 (P/Et_2O = 3/1) [UV].

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.14 (d, ^3J = 6.9 Hz, 3H, C*H*$_3$), 1.35 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.69 (*virt.* dtd, ^2J = 13.3 Hz, ^3J ≈ 10.6 Hz, ^3J = 5.3 Hz, 1H, H-5), 2.04 (*virt.* dq, ^2J = 13.3 Hz, ^3J ≈ 4.9 Hz, 1H, H-5), 2.28 (dqd, ^3J = 11.5 Hz, ^3J = 6.9 Hz, ^3J = 4.8 Hz, 1H, H-6), 2.38 (*virt.* dt, ^2J = 17.0 Hz, ^3J ≈ 5.0 Hz, 1H, H-4), 2.47 (dddd, ^2J = 17.0 Hz, ^3J = 10.5 Hz, ^3J = 5.1 Hz, ^4J = 1.0 Hz, 1H, H-4), 3.81-3.94 (m, 2H, OC*H*$_2$CH$_3$), 5.31 (s, 1H, H-2).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 14.3 (q, OCH_2CH_3), 15.5 (q, CH_3), 28.6 (t, C-4), 29.4 (t, C-5), 40.3 (d, C-6), 64.3 (t, OCH_2CH_3), 102.2 (d, C-2), 177.0 (s, C-3), 202.2 (s, C-1).

The obtained data match with those reported in the literature.[14]

4-Methyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (9g)



Following *GP1* 4-methyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**9g**) was synthesized using 113 mg magnesium (4.65 mmol, 1.30 eq.), 639 mL 5-bromopent-1-ene (719 mg, 4.83 mmol, 1.35 eq.) dissolved in 6.4 mL THF and 600 mg vinylogous ester **19** (3.90 mmol, 1.00 eq.) in 6.0 mL THF. The reaction was quenched after 21 hours. After column chromatography (SiO_2, P/Et_2O = 2/1→4/1) the title compound **9g** was obtained as a colorless oil in 85% yield (539 mg, 3.02 mmol).

TLC: R_f = 0.30 (P/Et_2O = 5/1) [UV/$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3078 (w, sp^2-CH), 2933 (m, sp^3-CH), 1670 (s, C=O), 1623 (m, O=C-C=C), 1457 (m, sp^3-CH), 1417 (m, sp^2-CH), 880 (m, C=C).

MS (EI, 70 eV): *m/z* (%) = 178 (9) $[M]^+$, 163 (23) $[M-CH_3]^+$, 150 (7) $[M-C_2H_7]^+$, 136 (100) $[M-C_3H_5]^+$, 96 (82) $[M-C_2H_4-C_4H_7]^+$.

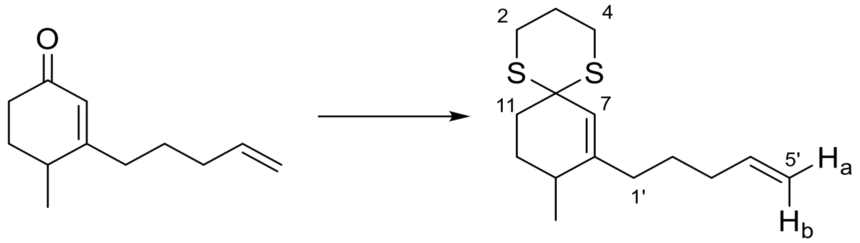
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.19 (d, ^3J = 7.1 Hz, 3H, CH_3), 1.54-1.60 (m, 1H, H-2'), 1.60-1.68 (m, 1H, H-2'), 1.78 (*virt.* ddt, ^2J = 13.3 Hz, ^3J = 6.7 Hz, $^3J \approx$ 3.2 Hz, 1H, H-5), 2.05-2.15 (m, 3H, H-5, H-3', H-3'), 2.20-2.26 (m, 2H, H-1'), 2.32 (ddd, ^2J = 17.1 Hz, ^3J = 6.7 Hz, ^3J = 4.9 Hz, 1H, H-6), 2.40-2.46 (m, 1H, H-4), 2.49 (ddd, ^2J = 17.1 Hz, ^3J = 10.6 Hz, ^3J = 4.9 Hz, 1H, H-6), 4.97-5.00 (m, 1H, H-5'a), 5.04 (*virt.* qd, $^2J \approx {}^3J \approx$ 1.6 Hz, ^3J = 17.4 Hz, 1H, H-5'b), 5.74-5.84 (m, 1H, H-4'), 5.82 (s, 1H, H-2).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.0 (q, CH_3), 26.4 (t, C-2'), 30.4 (t, C-5), 33.2 (t, C-4), 33.4 (t, C-3') 34.4 (t, C-6), 35.0 (t, C-1'), 115.4 (t, C-5'), 25.2 (d, C-2), 138.0 (d, C-4'), 170.4 (s, C-3), 199.9 (s, C-1).

HRMS (EI, 70 eV): calculated: ($C_{12}H_{18}O$): 178.1352; found: 178.1357,

calculated: ($C_{11}{}^{13}CH_{18}O$): 179.1386; found: 179.1396.

9-Methyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1g)



$C_{15}H_{24}S_2$
MW = 268.48 g/mol

Following *GP2* 200 mg 4-methyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (1.12 mmol, 1.00 eq.) were dissolved in 3.0 mL MeOH and 168 µL 1,3-propanedithiol (182 mg, 1.68 mmol, 1.50 eq.) and 171 µL boron trifluoride diethyl etherate (191 mg, 1.35 mmol, 1.30 eq.) were added. The reaction was quenched after three hours. After column chromatography (SiO_2, P/Et_2O = 99/1) dithiane **1g** was obtained as a colorless oil in 90% yield (0.27g, 1.0 mmol).

TLC: R_f = 0.27 (P/Et_2O = 98/2) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3074 (w, sp^2-CH), 2932 (s, sp^2-CH), 1640 (m, C=C), 1441 (m, sp^3-CH), 909 (m, sp^3-CH).

MS (EI, 70 eV): *m/z* (%) = 268 (24) $[M]^+$, 193 (28), 179 (5) $[C_{11}H_{15}S]^+$, 152 (100), 137 (15), 91 (19).

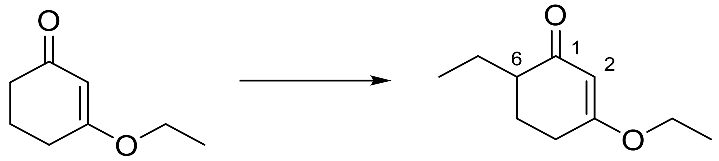
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.03 (d, ^3J = 7.1 Hz, 3H, CH_3), 1.44-1.66 (m, 3H, H-10, H-2’, H-2’), 1.85-1.94 (m, 2H, H-3, H-10), 1.95-2.01 (m, 1H, H-1’), 2.01-2.12 (m, 4H, H-3, H-11, H-1’, H-3’), 2.14-2.21 (m, 2H, H-9, H-3’), 2.28 (ddd, ^2J = 12.6 Hz, ^3J = 9.3 Hz, ^3J = 3.0 Hz, 1H, H-11), 2.71-2.78 (m, 2H, H-2, H-4), 2.94-3.02 (m, 2H, H-2, H-4), 4.95 (*virt.* ddt, ^2J = 2.2 Hz, ^3J = 10.2 Hz, $^4J \approx$ 1.2 Hz, 1H, H-5’a), 5.01 (*virt.* dq, $^2J \approx {}^3J \approx$ 1.6 Hz, ^3J = 17.0 Hz, 1H, H-5’b), 5.47 (s, 1H, H-7), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, H-4’).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.3 (q, CH_3), 25.1 (C-3), 26.9 (t, C-2, C-4), 27.0 (t, C-2’), 28.3 (t, C-10), 32.1 (d, C-9), 33.5 (t, C-3’), 33.5 (t, C-11), 34.4 (t, C-1’), 49.2 (s, C-6), 114.9 (t, C-5’), 123.4 (d, C-7), 138.8 (d, C-4’), 146.4 (s, C-8).

HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}{}^{32}S_2$): 268.1314; found: 268.1309,

calculated: ($C_{14}{}^{13}CH_{24}{}^{32}S_2$): 269.1348; found: 269.1343.

3-Ethoxy-6-ethylcyclohex-2-en-1-one (20)



$C_{10}H_{16}O_2$
MW = 168.24 g/mol

To a solution of 2.42 mL diisopropylamine (1.73 g, 17.1 mmol, 1.20 eq.) in 8.6 ml dry THF were added 6.85 mL *n*-BuLi (2.5 M in hexane, 1.10 g, 17.1 mmol, 1.20 eq.) at 0 °C. After stirring for 30 minutes, LDA was added dropwise to a solution of 2.08 mL 3-Ethoxycyclohexenone (2.00 g, 14.3 mmol, 1.00 eq.) in 13 mL dry THF at –78°C. After stirring for two hours 1.37 mL ethyl iodine (2.67 g, 17.1 mmol, 1.20 eq.) were added. The reaction mixture was allowed to warm to room temperature. After stirring for 14 hours 10 mL of saturated aqueous ammonium chloride solution were added, the aqueous phase was extracted four times with $Et_2O$and the combined organic layers were dried over $NaSO_4$, filtered and the solvent was removed in vacuo. After column chromatography (SiO_2, P/Et_2O = 6/1→5/1→4/1→3/1→2/1) the title compound **20** was obtained as a colorless oil in 61% yield (1.47 g, 8.74 mmol).

TLC: R_f = 0.19 (P/Et_2O = 3/1) [UV/$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2937 (w, sp_3-CH), 1651 (s, O=C-C=C), 1604 (s, C=C), 1377 (m, sp^3-CH), 1184 (s, C-O), 814 (m).

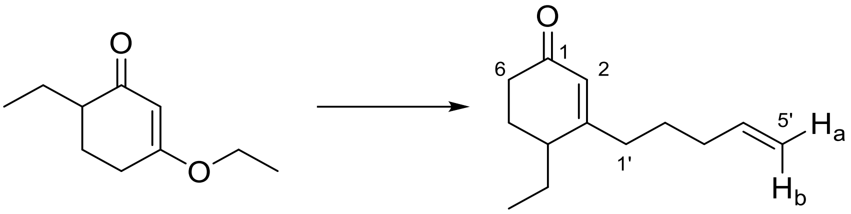
MS (EI, 70 eV): *m/z* (%) = 168 (39) $[M]^+$, 140 (100) $[M-C_2H_4]^+$, 112 (53) $[M-C_4H_8]^+$, 84 (64), 69 (48).

^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.94 (t, ^3J = 7.5 Hz, 3H, $CHCH_2CH_3$), 1.35 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.45 (*virt*. dq, ^2J = 14.5 Hz, $^3J \approx$ 7.5 Hz, 1H, $CHCH_2CH_3$), 1.68-1.79 (m, 1H, H-5), 1.81-1.96 (m, 1H, $CHCH_2CH_3$), 2.00-2.18 (m, 2H, H-5, H-6), 2.39-2.44 (m, 2H, H-4), 3.88 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 5.30 (s, 1H, H-2).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 11.7 (q, $CHCH_2CH_3$), 14.3 (q, OCH_2CH_3), 22.6 (t, $CHCH_2CH_3$), 25.8 (t, C-5), 28.1 (t, C-4), 46.7 (d, C-6), 64.3 (t, OCH_2CH_3), 102.4 (d, C-2), 176.9 (s, C-3), 201.9 (s, C-1).

HRMS (EI, 70 eV): calculated: ($C_{10}H_{16}O_2$): 168.1145; found: 168.1146.

4-Ethyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (9h)



$C_{13}H_{20}O$
MW = 192.30 g/mol

According to *GP1* 4-ethyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**9g**) was prepared using 116 mg magnesium (4.79 mmol, 1.30 eq.), 658 µL 5-bromopent-1-ene (741 mg, 4.98 mmol, 1.35 eq.) in 6.4 mL THF and 620 mg vinylogous ester **20** (3.69 mmol, 1.00 eq.) in 6 mL THF. The reaction was quenched after 20 hours. After column chromatography (SiO_2, P/Et_2O = 4/1) the title compound **9h** was obtained as a colorless oil in 80% yield (570 mg, 2.96 mmol).

TLC: R_f = 0.25 (P/Et_2O = 4/1) [UV/ $KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3074 (w, sp^2-CH), 2931 (m, sp^3-CH), 1670 (s, C=O), 1460 (m, sp^3-CH), 1247 (m), 912 (m,sp^2-CH), 882 (m, C=C).

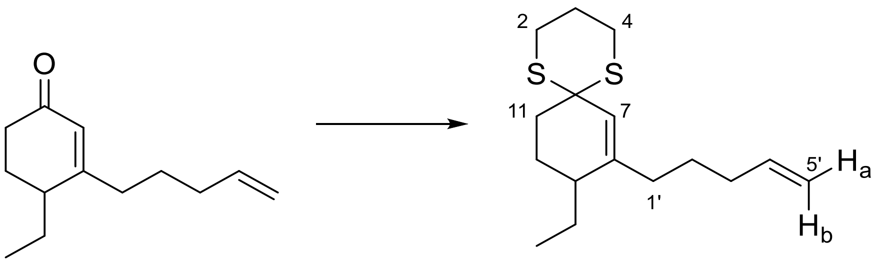
MS (EI, 70 eV): *m/z* (%) = 192 (11) $[M]^+$, 177 (4) $[M-CH_3]^+$, 163 (35) $[M-C_2H_5]^+$, 136 (100) $[M-C_4H_8]^+$, 121 (40), 82 (71).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.00 (t, ^3J = 7.3 Hz, 3H, CH_2CH_3), 1.42-1.49 (m, 1H, CH_2CH_3), 1.51-1.59 (m, 1H, H-2'), 1.61-1.70 (m, 2H, H-2', CH_2CH_3), 1.92-1.98 (m, 1H, H-5), 1.99-2.04 (m, 1H, H-5), 2.05-2.13 (m, 2H , H-3'), 2.17 (*virt.* dq, ^3J = 8.7 Hz, $^3J \approx$ 4.3 Hz, 1H, H-4), 2.21-2.26 (m, 2H, H-1'), 2.29 (*virt.* dt, ^2J = 17.2 Hz, $^3J \approx$ 5.1 Hz, 1H, H-6), 2.44 (ddd, ^2J = 17.2 Hz, ^3J = 11.5 Hz, ^3J = 5.3 Hz, 1H, H-6), 4.99 (ddt, ^2J = 2.0 Hz, ^3J = 10.2 Hz, ^4J = 1.2 Hz, 1H, H-5'a), 5.02 (*virt.* dq, ^3J = 17.0 Hz, $^3J \approx$ 1.6 Hz, 1H, H-5'b), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.2 Hz, 1H, H-4'), 5.82 (s, 1H, H-2).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.7 (q, CH_2CH_3), 24.0 (t, CH_2CH_3), 25.6 (t, C-5), 26.6 (t, C-2'), 33.4 (t, C-3'), 33.7 (t, C-6), 35.3 (t, C-1'), 39.9 (d, C-4), 115.4 (t, C-5'), 125.4 (d, C-2), 138.0 (d, C-4'), 170.1 (s, C-3), 199.9 (s, C-1).

HRMS (EI, 70 eV): calculated: ($C_{13}H_{20}O$): 192.1509; found: 192.1495.

9-Ethyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1h)



$C_{16}H_{26}S_2$
MW = 282.50 g/mol

According to *GP2* dithiane formation was carried out using 214 mg 4-ethyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (**9h**) (1.11 mmol, 1.00 eq.), 167 µL propanedithiol (180 mg, 1.67 mmol, 1.50 eq.) and 190 µL $BF_3 \cdot OEt_2$ (169 mg, 1.34 mmol, 1.20 eq.) in 6.2 mL methanol. The reaction mixture was stirred for 2.5 hours before quenching. After purification using column chromatography (SiO_2, P/CH_2Cl_2 = 4/1) the irradiation precursor **1h** was obtained as a colorless oil in 42% yield (132 mg, 46.7 mmol).

TLC: R_f = 0.29 (P/CH_2Cl_2 = 4/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3074 (w, sp^2-CH), 2931 (s, sp^3-CH), 1640 (m, C=C), 1441 (m, sp^3-CH), 1273 (m), 907 (s, sp^2-CH), 872 (s).

MS (EI, 70 eV): *m/z* (%) = 282 (30) $[M]^+$, 241 (8) $[M\text{-}C_3H_5]^+$, 207 (38) $[C_{13}H_{19}S]^+$, 152 (100) $[C_{13}H_{19}S\text{-}C_4H_7]^+$, 119 (15), 91 (20).

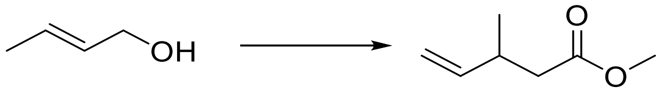
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.90 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3), 1.26 (ddq, ^2J = 14.4 Hz, ^3J = 9.5 Hz, ^3J = 7.3 Hz, 1H, CH_2CH_3), 1.42-1.51 (m, 1H, H-2’), 1.51-1.56 (m, 1H, H-2’), 1.57-1.61 (m, 1H, CH_2CH_3), 1.68 (dddd, ^2J = 14.4 Hz, ^3J = 8.3 Hz, ^3J = 5.7 Hz, ^3J = 3.1 Hz, 1H, H-10), 1.82 (*virt.* ddt, ^2J = 14.4 Hz, ^3J = 9.3 Hz, $^3J \approx$ 3.1 Hz, 1H, H-10), 1.86-1.93 (m, 1H, H-3), 1.95-2.01 (m, 2H, H-9, H-1’), 2.01-2.12 (m, 4H, H-3, H-1’, H-3’, H-3’), 2.16 (ddd, ^2J = 13.3 Hz, ^3J = 8.3 Hz, ^3J = 3.1 Hz, 1H, H-11), 2.26 (ddd, ^2J = 13.3 Hz, ^3J = 9.3 Hz, ^3J = 3.1 Hz, 1H, H-11), 2.74 (ddd, ^2J = 14.2 Hz, ^3J = 5.9 Hz, ^3J = 3.1 Hz, 2H, H-2, H-4), 2.98 (ddd, ^2J = 14.2 Hz, ^3J = 10.9 Hz, ^3J = 2.8 Hz, 2H, H-2, H-4), 4.95 (ddt, ^2J = 2.1 Hz, ^3J = 10.2 Hz, ^4J = 1.1 Hz, 1H, H-5’a), 5.01 (*virt.* dq, ^3J = 17.0 Hz, , $^2J \approx {}^4J \approx$ 1.6 Hz, 1H, H-5’b), 5.49 (s, 1H, H-7), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, H-4’).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 11.9 (q, CH_2CH_3), 23.6 (t, C-10), 24.9 (t, CH_2CH_3), 25.1 (t, C-3), 26.9 (t, C-2’), 27.1 (t, C-2), 27.1 (t, C-4), 33.3 (t, C-3’*), 33.5 (t, C-11*), 34.5 (t, C-1’), 38.5 (d, C-9), 49.1 (s, C-6), 114.8 (t, C-5’), 124.1 (d, C-7), 138.8 (d, C-4’), 145.7 (s, C-8).

* assignment is interconvertible

HRMS (EI, 70 eV): calculated: ($C_{12}H_{26}{}^{32}S_2$): 282.1470; found: 282.1476.

Methyl 3-methylpent-4-enoate (21)



$C_7H_{12}O_2$
MW = 128.17 g/mol

This compound was prepared following literature procedure.[15] A solution of 8.28 mL but-2-en-1-ol (7.00 g, 97.1 mmol, 1.00 eq.), 12.4 mL trimethyl orthoacetate (11.7 g, 97.1 mmol, 1.00 eq.) and 436 µL propionic acid (431 mg, 5.82 mmol, 6.0 mol-%) was stirred at 135 °C until distillation of methanol was complete. After stirring for five hours at 145 °C the mixture was cooled to room temperature, the organic layer was washed with saturated aqueous $NaHCO_3$ solution (3×40 mL), dried over Na_2SO_4 and filtered. Volatile compounds were removed in vacuo. The title compound **21** was obtained by distillation (115°C, 400 mbar) as a colorless oil in 50% yield (6.16 g, 48.1 mmol).

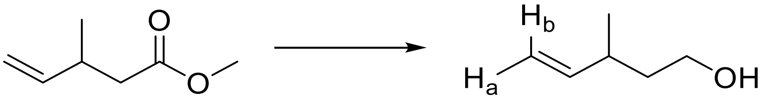
B.P.: 115°C (400 mbar).

^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.05 (d, ^3J = 6.8 Hz, 3H, CHC*H*$_3$), 2.21-2.41 (m, 2H, H-2), 2.60-2.76 (m, 1H, H-3), 3.66 (s, 3H, COOC*H*$_3$), 4.91-5.12 (m, 2H, H-5), 5.77 (ddd, ^3J = 17.3 Hz, ^3J = 10.4 Hz, ^3J = 6.9 Hz, 1H, H-4).

^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.9 (q, CH*C*H$_3$), 34.5 (d, C-3), 41.5 (t, C-2), 51.6 (q, COO*C*H$_3$), 112.5 (t, C-5), 142.6 (d, C-4), 173.1 (s, C-1).

The obtained data match with those reported in the literature.[16]

3-Methylpent-4-en-1-ol (22)



$C_6H_{12}O$
MW = 100.16 g/mol

To a suspension of 1.82 g $LiAlH_4$ (48.6 mmol, 1.00 eq.) in 120 mL dry THF at 0 °C was a solution of 6.16 g ester **21** (48.6 mmol, 1.00 eq.) in 20 mL THF added dropwise. The mixture was allowed to warm to room temperature and was stirred for 19 hours before 2 mL ethyl acetate, 2.4 mL water, 1.5 mL NaOH (2 M in water) and 2.4 mL water were added carefully at 0 °C. The precipitate was removed by filtration over a short pad of celite and washed with diethyl ether. The filtrate was diluted with 20 mL water and was extracted using diethyl ether (5×30 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After purification by column chromatography (SiO_2, P/Et_2O = 2/1) alcohol **22** was obtained as a colorless oil in 75% yield (3.56 g, 35.5 mmol).

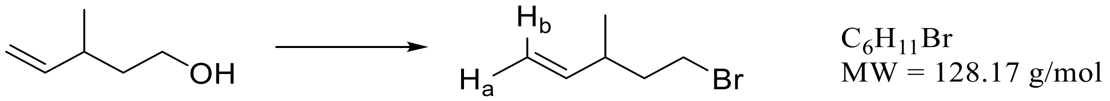
TLC: R_f = 0.21 (P/Et_2O = 4/1) [$KMnO_4$].

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.20 (d, ^3J = 6.8 Hz, 3H, C*H*$_3$), 1.38 (*br*. s, 1H, O*H*), 1.52-1.62 (m, 2H, H-2), 2.30 (*virt*. hept, ^3J ≈ 7.2 Hz, 2H, H-3), 3.66 (td, ^3J = 6.6 Hz, ^4J = 1.6 Hz, 2H, H-1), 4.94 (ddd, ^2J = 1.7 Hz, ^3J = 10.3Hz, ^4J = 0.7 Hz, 1H, H-5a), 5.04 (*virt*. dt, ^3J = 17.4 Hz, ^2J ≈ ^4J ≈ 1.4 Hz, 1H, H-5b), 5.72 (ddd, ^3J = 17.4 Hz, ^3J = 10.3 Hz, ^3J = 7.9 Hz, 1H, H-4).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.6 (q, *C*H$_3$), 35.1 (d, C-3), 39.4 (t, C-2), 61.4 (t, C-1), 113.3 (t, C-5), 144.4 (s, C-4).

The obtained data match with those reported in the literature.[17]

5-Bromo-3-methylpent-1-ene (23)



To a solution of 2.00 g alcohol (**22**) (20.0 mmol, 1.00 eq.), 3.60 mL triethyl amine (2.63 g, 26.0 mmol, 1.30 eq.) and 40 mL dry THF at 0 °C were added 2.01 mL methanesulfonyl chloride (2.97 g, 26.0 mmol, 1.30 eq.) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for four hours, before 50 mL water were added. The aqueous layer was extracted using CH_2Cl_2 (4×30 mL), combined organic layers were dried over Na_2SO_4, filtrated and solvent was removed in vacuo. The crude mesylate was used without any further purification and was dissolved in 30 mL acetone. To this solution 5.20 g LiBr (59.9 mmol, 3.00 eq.) were added and the suspension was stirred at 60 °C for 19 hours. After cooling to room temperature about 50% acetone were removed in vacuo. To the remaining suspension were added 40 mL water and the aqueous layer was extracted using pentane (3×30 mL). Combined organic layers were dried over Na_2SO_4, filtered and solvent was removed in vacuo. Column chromatography (SiO_2, P) yielded in 42% bromide **23** (1.37 g, 10.7 mmol) as a colorless oil.

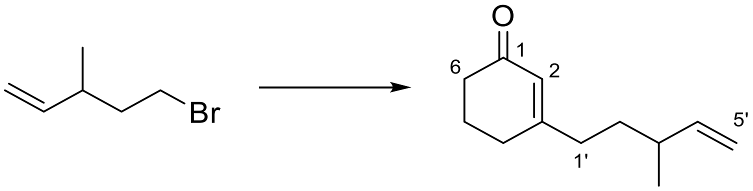
TLC: R_f = 0.80 (P) [$KMnO_4$].

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.03 (d, ^3J = 6.8 Hz, 3H, C*H*$_3$), 1.79-1.90 (m, 2H, H-4), 2.37 (*virt*. hept., $^3J \approx$ 7.6 Hz, 1H, H-3), 3.33-3.45 (m, 2H, H-5), 4.99 (ddd, ^2J = 1.7 Hz, ^3J = 10.3 Hz, ^4J = 0.7 Hz) 1H, H-1a), 5.05 (ddd, ^2J = 1.7 Hz, ^3J = 17.3 Hz, ^4J = 0.7 Hz, 1H, H-1b), 5.63 (ddd, ^3J = 17.3 Hz, ^3J = 10.3 Hz, ^3J = 7.9 Hz, 1H, H-2).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.1 (q, *C*H$_3$), 32.0 (t, C-5), 36.7 (d, C-3), 39.4 (t, C-4), 114.3 (t, C-1), 142.8 (d, C-2).

The obtained data match with those reported in the literature.[18]

3-(3-Methylpent-4-en-1-yl)cyclohex-2-en-1-one (9i)



$C_{12}H_{18}O$
MW = 178.28 g/mol

Compound (**9i**) was prepared following *GP1* using 76.3 mg magnesium (3.14 mmol, 1.10 eq.), 558 mg bromide (**23**) (3.42 mmol, 1.20 eq.) in 5.8 mL THF and 415 µL 3-ethoxy-cyclohex-2-en-1-one (400 mg, 2.85 mmol, 1.00 eq.) in 4.5 mL THF. The reaction was quenched after four hours. After column chromatography (SiO_2, P/Et_2O = 4/1 → 3/1) the enone **9i** was obtained as a yellowish oil in 80% yield (406 mg, 2.28 mmol).

TLC: R_f = 0.23 (P/Et_2O = 4/1) [UV/ $KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3074 (w, sp^2-CH), 2928 (s, sp^3-CH), 1653 (w, C=O), 1639 (w, O=C-C=C), 1451 (m, sp^3-CH), 1421 (m, sp^2-CH), 995 (m), 907 (s, C=C), 884 (s, C=C).

MS (EI, 70 eV): *m/z* (%) = 178 (28) $[M]^+$, 163 (9) $[M-CH_3]^+$, 150 (29) $[M-C_2H_4]^+$, 123 (32) $[M-C_4H_7]^+$, 107 (55), 82 (100) $[M-C_2H_4-C_5H_8]^+$.

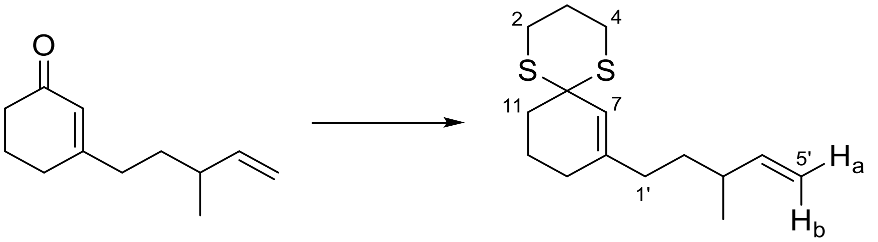
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.02 (d, ^3J = 6.7 Hz, 3H, C*H*$_3$), 1.43-1.55 (m, 2H, H-2’), 1.95-2.01 (m, 2H, H-5), 2.09-2.15 (m, 1H, H-3’), 2.16-2.25 (m, 2H, H-1’), 2.27 (t, ^3J = 5.9 Hz, 2H, H-4), 2.33-2.37 (m, 2H, H-6), 4.92-5.01 (m, 2H, H-5’), 5.65 (ddd, ^3J = 17.3 Hz, ^3J = 10.3 Hz, ^3J = 7.8 Hz, 1H, H-4’), 5.87 (*virt.* , $^3J \approx$ 1.4 Hz, 1H, H-2).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.4 (q, *C*H$_3$), 22.9 (t, C-5), 29.9 (t, C-4), 33.8 (t, C-2’), 35.9 (t, C-1’), 37.5 (t, C-6), 37.7 (d, C-3’), 113.7 (t, C-5’), 125.8 (d, C-2), 143.8 (d, C-4’), 166.8 (s, C-3), 200.1 (s, C-1).

HRMS (EI, 70 eV): calculated: ($C_{12}H_{18}O$): 178.1352; found: 178.1351,

calculated: ($C_{11}{}^{13}CH_{18}O$): 179.1391; found: 179.1386.

8-(3-Methylpent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1i)



$C_{15}H_{24}S_2$
MW = 268.48 g/mol

Following *GP2* 200 mg ketone **9i** (1.12 mmol, 1.00 eq.) dissolved in 6.3 mL dry methanol, 168 µL propanedithiol (182 mg, 1.68 mmol, 1.50 eq.) and 171 µL $BF_3{\cdot}OEt_2$ (191 mg, 1.35 mmol, 1.20 eq.) were stirred for four hours. The title compound **1i** was obtained as a colorless oil in 56% yield (170 mg, 63.3 µmol) after purification by column chromatography (SiO_2, P/Et_2O = 99/1).

TLC: R_f = 0.20 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2926 (s, sp^3-CH), 1444 (m), 1421 (m, sp^3-CH), 1274 (m), 906 (m, sp^2-CH), 809 (m, C-S).

MS (EI, 70 eV): *m/z* (%) = 268 (71) $[M]^+$, 253 (4) $[M-CH_3]^+$, 213 (8) $[M-C_4H_7]^+$, 193 (86), 166 (100) $[C_{10}H_{14}S]^+$, 151 (25), 139 (57) $[C_8H_{11}S]^+$, 91 (47).

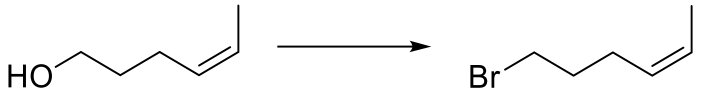
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.99 (d, ^3J = 6.7 Hz, 3H, CH_3), 1.38-1.44 (m, 2H, H-2’), 1.76-1.82 (m, 2H, H-10), 1.90 (dtt, ^2J = 14.0 Hz, ^3J = 10.8 Hz, ^3J = 3.2 Hz, 1H, H-3), 1.94-2.00 (m, 4H, H-9, H-1’), 2.00-2.06 (m, 1H, H-3), 2.07-2.14 (m, 1H, H-3’), 2.19-2.23 (m, 2H, H-11), 2.75 (ddd, ^2J = 14.4 Hz, ^3J = 6.0 Hz, ^3J = 3.2 Hz, 2H, H-2, H-4), 2.94-3.01 (m, 2H, H-2, H-4), 4.92 (ddd, ^2J = 1.9 Hz, ^3J = 10.3 Hz, ^4J = 0.7 Hz, 1H, H-5’a), 4.96 (ddd, ^2J = 1.9 Hz, ^3J = 17.6 Hz, ^3J = 1.2 Hz, 1H, H-5’b), 5.50 (*br.* s, 1H, H-7), 5.66 (ddd, ^3J = 17.6 Hz, ^3J = 10.3 Hz, ^3J = 7.7 Hz, 1H, H-4’).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.0 (t, C-10), 20.4 (q, CH_3), 25.1 (t, C-3), 27.0 (t, C-2, C-4), 28.9 (t, C-9), 34.3 (t, C-2’), 35.4 (t, C-1’), 36.0 (t, C-11), 37.6 (d, C-3’), 49.0 (s, C-6), 113.1 (t, C-5’), 123.1 (d, C-7), 142.8 (s, C-8), 144.5 (d, C4’).

HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}{}^{32}S_2$): 268.1312; found: 268.1312,

calculated: ($C_{14}{}^{13}CH_{24}{}^{32}S_2$): 269.1348; found: 269.1348.

(*Z*)-6-Bromohex-2-ene (24)



$C_6H_{11}Br$
MW = 163.06 g/mol

To a mixture of 2.33 mL (Z)-hex-4-en-1-ol (2.00 g, 20.0 mmol, 1.00 eq.), 3.60 mL triethylamine (2.63 g, 26.0 mmol, 1.30 eq.) and dry THF (40 mL) were added 2.01 mL methanesulfonyl chloride (2.97 g,26.0 mmol, 1.30 eq.) dropwise at 0 °C. The mixture was stirred for 40 minutes at 0 °C and additional 45 minutes at room temperature. The reaction was quenched with water (60 mL) and the aqueous layer was extracted with CH_2Cl_2 (4×50 mL). Combined organic layer were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude mesylate was dissolved in freshly distilled acetone (40 mL) and 5.2 g LiBr (59.9 mmol, 3.00 eq.) were added. After stirring the mixture under reflux for 23 hours, acetone was removed in vacuo up to 50%. The precipitate was dissolved in water and the aqueous layer was extracted with Et_2O (4×20 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The product **24** was obtained as a colorless oil in 70% overall yield (2.30 g, 14.0 mmol) and was used without further purification.

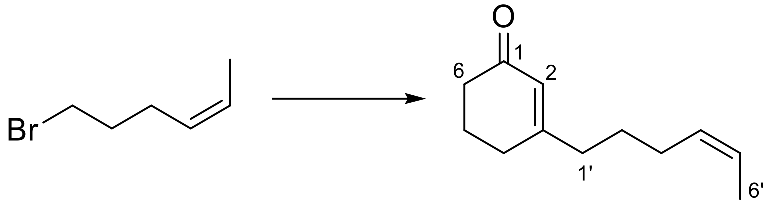
TLC: R_f = 0.34 (P) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.64 (ddt, ^3J = 6.8 Hz, ^4J = 1.9 Hz, ^5J = 1.0 Hz, 3H, H-1), 1.93 (*virt*. quin., $^3J \approx$ 7.0 Hz, 2H, H-5), 2.21 (*virt*. quin., $^3J \approx$ 7.4 Hz, 2H, H-4), 3.42 (t, ^3J = 6.7 Hz, 2H, H-6) 5.34 (dtq, ^3J = 11.6 Hz, ^3J = 7.3 Hz, ^4J = 1.9 Hz, 1H, H-3), 5.52 (dqt, ^3J = 11.6 Hz, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 1H, H-2).

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.0 (q, C-1), 25.5 (t, C-4), 32.7 (t, C-5), 33.6 (t, C-6), 125.7 (d, C-2), 128.5 (d, C-3).

The obtained data match with those reported in the literature.[19]

(*Z*)-3-(Hex-4-en-1-yl)cyclohex-2-en-1-one (9j)



$C_{12}H_{18}O$
MW = 178.28 g/mol

Following *GP1* 230 mg magnesium (9.90 mmol, 1.30 eq.), 1.60 g 5-bromopent-1-ene (9.60 mmol, 1.35 eq.) in 10 mL THF and 0.96 mL 3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (1.00 g, 7.10 mmol, 1.00 eq.) in 9 mL THF were used. The reaction was quenched after 5 hours. After column chromatography (SiO_2, P/Et_2O = 3/1) the title compound **9j** was obtained as a colorless oil in 65% yield (820 mg, 4.61 mmol).

TLC: R_f = 0.25 (P/Et_2O = 4/1) [UV/ $KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3013 (w, sp^2-CH), 2933 (m, sp^3-CH), 2864 (m, sp^3-CH), 1669 (s, C=O), 1623 (m, C=CCO), 1456 (w, sp^3-CH), 1252 (m), 1191 (m), 885 (m, sp^2-CH).

MS (EI, 70 eV): *m/z* (%) = 178 (16) $[M]^+$, 150 (34) $[M-C_2H_4]^+$, 123 (93) $[M-C_4H_7]^+$, 110 (77), 93 (23) $[C_9H_{10}O]^+$, 82 (100) $[C_6H_{10}]^+$, 68 (61) $[C_5H_8]^+$, 55 (29) $[C_4H_7]^+$.

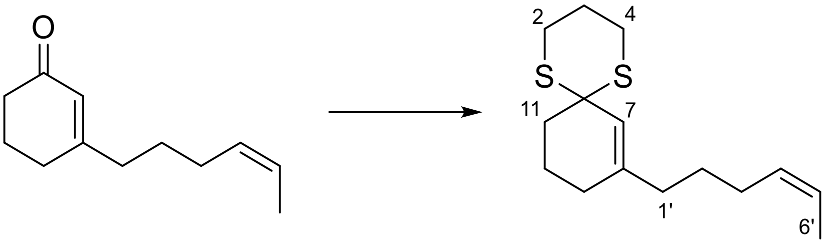
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.57 (*virt.* quin., $^3J \approx 7.5$ Hz, 2H, H-2’), 1.59 (*virt.* dq, $^3J = 7.2$ Hz, $^4J \approx {}^5J \approx 1.3$ Hz, 3H, H-6’), 1.98 (*virt.* quin., $^3J \approx 6.2$ Hz, 2H, H-5), 2.07 (*virt.* q, $^3J \approx 7.4$ Hz, 2H, H-3’), 2.22 (t, $^3J = 7.7$ Hz, 2H, H-1’), 2.28 (t, $^3J = 5.9$ Hz, 2H, H-4), 2.36 (t, $^3J = 6.2$ Hz, 2H, H-6), 5.36 (dtq, $^3J = 10.2$ Hz, $^3J = 7.1$ Hz, $^4J = 1.6$ Hz, 1H, H-4’), 5.49 (dqt, $^3J = 10.2$ Hz, $^3J = 7.2$ Hz, $^4J = 1.4$ Hz, 1H, H-5’), 5.91 (s, 1H, H-2).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.2 (q, C-6’), 23.1 (t, C-5), 26.7 (t, C-3’), 27.1 (t, C-2’), 30.1 (t, C-4), 37.8 (t, C-6), 37.9 (t, C-1’), 125.2 (d, C-5’), 126.1 (d, C-2), 129.9 (d, C-4’), 166.9 (s, C-3), 200.4 (s, C-1).

HRMS (EI, 70 eV): calculated: ($C_{12}H_{18}O$): 178.1352; found: 178.1349,

calculated: ($C_{11}{}^{13}CH_{18}O$): 179.1386; found: 179.1393.

(*Z*)-8-(Hex-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1j)



$C_{15}H_{24}S_2$
MW = 268.48 g/mol

Dithiane **1j** was prepared using 200 mg enone **9j** (1.12 mmol, 1.00 eq.), 169 µL propanedithiol (186 mg, 1.50 eq.) and 171 µL $BF_3{\cdot}OEt_2$ (191 mg, 1.35 mmol, 1.20 eq.) in 2.5 hours. After aqueous work up and column chromatography the title compound **1j** was obtained in 83% yield (254 mg, 946 µmol) as a colorless oil. Ration of *Z*/*E*-isomers was determined as 92/8 by GC.

TLC: R_f = 0.25 (P/CH_2Cl_2 = 3/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 301 (w, sp^2-CH), 2929 (s, sp^3-CH), 1654 (w, C=C), 1423 (m, sp^3-CH), 1273 (m), 865 (m, sp^2-CH).

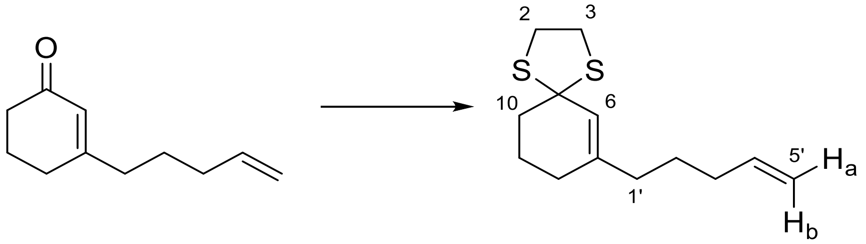
MS (EI, 70 eV): *m/z* (%) = 268 (59) $[M]^+$, 213 (10) $[M-C_4H_7]^+$, 193 (32), 166 (25), 139 (87) $[C_8H_{11}S]^+$, 126 (100) $[C_7H_{10}S]^+$, 91 (42).

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ (ppm) = 1.35 (*virt.* quin., $^3J \approx 7.5$ Hz, 2H, H-2’), 1.45-1.53 (m, 1H, H-3), 1.55 (ddt, $^3J = 7.0$ Hz, $^4J = 1.8$ Hz, $^5J = 0.9$ Hz, 3H, H-6’), 1.54-1.64 (m, 1H, H-3), 1.75-1.79 (m, 4H, H-9, H-10), 1.82 (*br.* t, $^3J = 7.6$ Hz, 2H, H-1’), 1.94 (*virt.* q, $^3J \approx 7.3$ Hz, 2H, H-3’), 2.19-2.24 (m, 2H, H-11), 2.31 (ddd, $^2J = 14.3$ Hz, $^3J = 5.6$ Hz, $^3J = 3.2$ Hz, 2H, H-2, H-4), 2.60 (ddd, $^2J = 14.3$ Hz, $^3J = 5.7$ Hz, $^3J = 2.7$ Hz, 2H, H-2, H-4), 5.37 (dtq, $^3J = 10.7$ Hz, $^3J = 7.0$ Hz, $^4J = 1.7$ Hz, 1H, H-4’), 5.43-5.52 (m, 1H, H-5’), 5.78 (*br.* s, 1H, H-7).

^{13}C NMR (126 MHz, C_6D_6, 300 K): δ (ppm) = 13.2 (q, C-6’), 20.3 (t, C-10), 25.2 (t, C-3), 26.7 (t, C-3’), 26.9 (t, C-2, C-4), 27.5 (t, C-2’), 28.9 (t, C-9), 36.4 (t, C-11), 37.3 (t, C-1’), 49.5 (s, C-6), 124.3 (d, C-5’), 124.5 (d, C-7), 130.6 (d, C-4’), 142.3 (s, C-8).

HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}{}^{32}S_2$): 268.1314; found: 268.1314,
calculated: ($C_{14}{}^{13}CH_{24}{}^{32}S_2$): 269.1348; found: 269.1346.

7-(Pent-4-en-1-yl)-1,4-dithiaspiro[4.5]dec-6-ene (25)



$C_{13}H_{20}S_2$
MW = 240.43 g/mol

Following *GP2* 500 mg enone **9a** (3.04 mmol, 1.00 eq.), 380 µL 1,2-ethandithiol (430 mg, 4.56 mmol, 1.50 eq.) and 458 µL boron trifluoride diethyl etherate (523 mg, 3.68 mmol, 1.20 eq.) were stirred in dry methanol (8.0 mL) for three hours. After column chromatography (SiO_2, P/Et_2O = 100/0 → 99.5/0.5 → 99/1) the title compound **25** was obtained as a colourless oil in 56% yield (413 mg, 1.70 mmol).

TLC: R_f = 0.21 (P/ Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2924 (s, sp^3-CH), 1638 (w, C=C), 1455 (w, sp^3-CH), 911 (m, sp^2-CH), 886 (m, sp^2-CH).

MS (EI, 70 eV): *m/z* (%) = 240 (19) $[M]^+$, 212 (72) $[M\text{-}C_2H_4]^+$, 179 (100), 152 (45), 123 (16) $[C_9H_{15}]^+$, 91 (34) $[C_7H_7]^+$, 55 (5) $[C_4H_3]^+$.

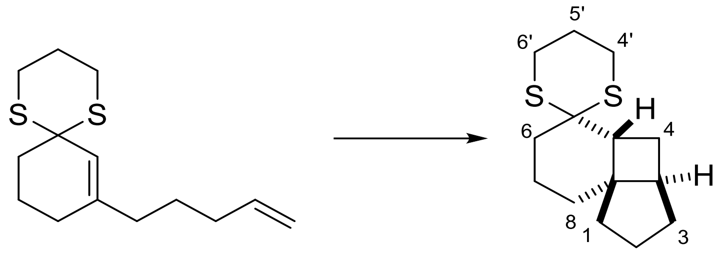
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.50 (*virt.* quin., ^3J = 7.6 Hz, 2H, H-2‘), 1.83-1.76 (m, 2H, H-9), 1.92 (t, ^3J = 6.2 Hz, 2H, H-8), 1.96 (t, ^3J = 7.6 Hz, 2H, H-1‘), 1.99-2.06 (m, 2H, H-4‘), 2.13-2.17 (m, 2H, H-10), 3.27-3.40 (m, 4H, H-2, H-3), 4.95 (ddt, ^3J = 10.2 Hz, ^3J = 2.1 Hz, ^4J = 1.1 Hz, 1H, H-5’a), 5.01 (*virt.* dq, ^3J = 17.0 Hz, $^2J \approx {}^4J \approx$ 1.6 Hz, 1H, H-5’b), 5.58 (s, 1H, H-6), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, H-4‘).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 23.0 (t, C-9), 26.8 (t, C-2‘), 27.7 (t, C-3‘), 37.0 (t, C-1‘), 40.0 (t, C-2, C-3), 41.7 (t, C-10), 66.0 (s, C-5), 114.8 (t, C-5‘), 126.3 (d,C-6), 138.8 (d, C-4‘), 139.9 (s,C-7).

HRMS (EI, 70 eV): calculated: ($C_{13}H_{20}{}^{32}S_2$): 240.1001; found: 240.0994.

5. Photoreactions of Dithianes

Octahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2a)



$C_{14}H_{22}S_2$
MW = 254.45 g/mol

Small Scale:

According to *GP3* 27.3 mg 8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**1a)** (107 µmol, 1.00 eq.) were dissolved in 10.7 mL CH_2Cl_2 and irradiated at 405 nm at −78 °C with 236 µg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (8.05 µmol, 7.5 mol-%) for 3.5 hours. After addition of 14.9 µL NEt_3 (10.9 mg, 107 µmol, 1.00 eq.) and column chromatography (SiO_2, P/Et_2O = 99.25/0.75) the title compound **2a** was obtained as a colorless oil in 85% yield (23.2 mg, 91.0 µmol).

Large Scale:

A large scale reaction was carried out following *GP3*, but and power of the LED was increased to 10 W and concentration of dithiane was increased to 20 mM. Therefore 407 mg 8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene **1a** (1.60 mmol, 1.00 eq.) were dissolved in 80 mL CH_2Cl_2 and precooled to −78 °C. After irradiation at 405 nm in presence of 35.2 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (120 µmol, 7.5 mol-%) for 16 hours, 223 µL NEt_3 (162 mg, 1.60 mmol, 1.00 eq.) were added. Purification by column chromatography (SiO_2, P/Et_2O = 99/1) yielded in 93% (379 mg, 14.9 µmol) of the title compound **2a** as a colorless oil.

TLC: R_f = 0.15 (P/Et_2O = 99.5/0.5) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2926 (s, sp^3-CH), 1444 (m, sp^3-CH), 1421 (m , sp^3-CH), 906 (w, C-S).

MS (EI, 70 eV): *m/z* (%) = 254 (100) $[M]^+$, 179 (87) $[C_{11}H_{15}S]^+$, 152 (46), 145 (21), 106 (41), 91 (28), 79 (23).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.17-1.26 (m, 1H, H-6*), 1.35-1.43 (m, 1H, H-8*), 1.48-1.58 (m, 2H, H-3*, H-4), 1.62-1.71 (m, 2H, H-3*, H-6*), 1.71-1.84 (m, 3H, H-2*, H-2*, H-7*), 1.86-2.01 (m, 5H, H-1*, H-1* , H-7 , H-5’, H-5’), 2.02-2.09 (m, 1H, H-4), 2.09-

2.16 (m, 2H, H-3a, H-8*), 2.57-2.62 (m, 1H, H-4a), 2.66-2.77 (m, 2H, H-4’, H-6’), 2.78-2.89 (m, 2H, H-4’, H-6’).

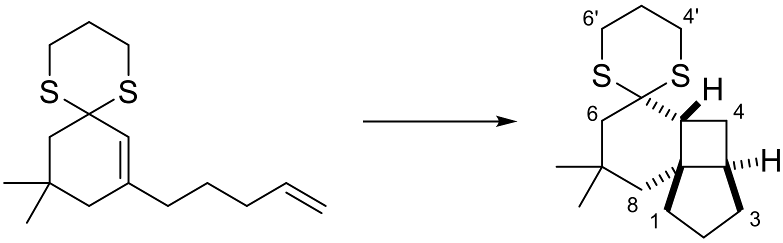
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.0 (t, C-2*), 25.6 (t, C-1*), 26.1 (t, C-7*), 26.2 (t, C-4’*), 26.6 (t, C-4), 26.7 (t, C-6’*), 30.0 (t, C-8*), 32.2 (t, C-5’*), 32.3 (t, C-3*), 39.0 (d, C-3a), 40.8 (t, C-6*), 41.2 (d, C-4a), 49.3 (s, C-8a), 51.8 (s, C-5).

*assignment is interconvertible

The relative configuration was confirmed upon deprotection by comparison with literature known NMR spectra.[20]

HRMS (EI, 70 eV): calculated: ($C_{14}H_{22}S_2$):254.1157; found: 254.1164.

7,7-Dimethyloctahydro-6H-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2b)



$C_{16}H_{26}S_2$
MW = 282.50 g/mol

26.2 mg 10,10-dimethyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**1b**) (92.7 µmol, 1.00 eq.) were dissolved in 9.3 mL CH_2Cl_2 and was cooled to −78 °C. After addition of 2.04 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (6.96 µmol, 7.5 mol-%) the solution was irradiated at λ = 405 nm for 4.5 h according to *GP3*. After column chromatography (SiO_2, P/Et_2O = 99/1) the title compound was obtained as a colorless oil in 80% yield (21.0 mg, 74.3 µmol).

TLC: R_f = 0.19 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2926 (s, sp^3-CH), 1456 (m, sp^3-CH), 1157 (m), 802 (m).

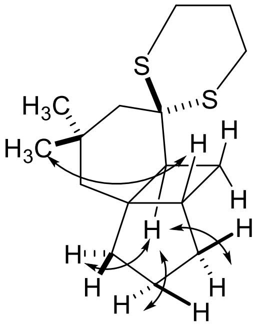
MS (EI, 70 eV): *m/z* (%) = 282 (42) $[M]^+$, 267 (13) $[M-CH_3]^+$, 207 (100) $[C_{13}H_7S]^+$, 152 (66) $[C_{13}H_7S-C_4H_8]^+$, 106 (31).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.12 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.16-1.24 (m, 2H, H-1, H-8), 1.42 (ddd, ^2J = 13.5 Hz, ^3J = 9.6 Hz, ^3J = 4.2 Hz 1H, H-4), 1.51-1.63 (m, 3H, H-1, H-3, H-3), 1.71-1.77 (m, 1H, H-2), 1.79-1.89 (m, 1H, H-2), 1.89-1.98 (m, 4H, H-6, H-8, H-5', H-5'), 2.03 (dd, ^2J = 14.9 Hz, ^4J = 1.7 Hz, 1H, H-6), 2.06-2.11 (m, 1H, H-4), 2.33-2.39 (m, 1H, H-3a), 2.44 (*virt.* t, $^3J \approx$ 8.0 Hz, 1H, H-4a), 2.74-2.85 (m, 4H, H-4', H-6').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.0 (t, C-2), 24.9 (t, C-4), 25.6 (t, C-5'), 26.1 (t, C-4'*), 26.2 (t, C-6'*), 30.5 (s, C-7), 33.3 (t, C-3), 34.7 (q, *C*H_3), 35.0 (q, *C*H_3), 37.6 (d, C-3a), 42.1 (d, C-4a), 42.4 (t, C-8), 42.6 (t, C-1), 43.7 (t, C-6), 48.7 (s, C-8a), 53.1 (s, C-5).

* assignment is interconvertible

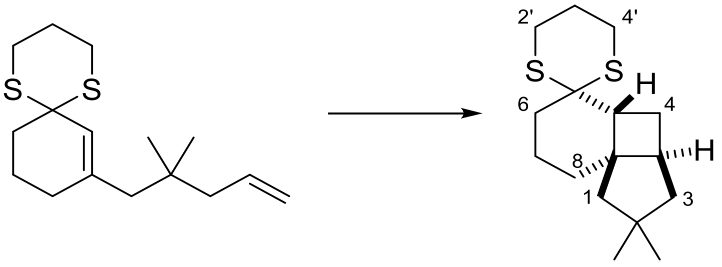
Important NOE contacts



HRMS (EI, 70 eV): calculated: ($C_{16}H_{26}{}^{32}S_2$): 282.1470; found: 282.1472,

calculated: ($C_{15}{}^{13}CH_{26}{}^{32}S_2$): 283.1506; found: 283.1504.

2,2-Dimethyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2c)



$C_{16}H_{26}S_2$
MW = 282.50 g/mol

According to *GP3* 23.0 mg 8-(2,2-dimethylpent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**1c**) (81.4 µmol, 1.00 eq.) were irradiated with a 405 nm LED at −78 °C in 8.1 mL CH_2Cl_2 in presence of 2.39 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (8.14 µmol, 10 mol-%) for 22 hours. After work up column chromatography (SiO_2, P/Et_2O = 99/1) yielded in an inseparable mixture of product and starting material (23.0 mg, 94/6). This mixture was dissolved in 0.3 mL 1,4-dioxane and 16.0 mg 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine (81.4 µmol, 1.00 eq.). After stirring for two hours at room temperature solvent was removed in vacuo and the crude product was submitted to column chromatography (SiO_2, P/Et_2O = 99/1) without any further work up. Cyclobutane **2c** was obtained as a colorless oil in 78% yield (18.0 mg, 63.7 µmol) over two steps.

TLC: R_f = 0.43 (P/Et_2O = 98/2) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2928 (s, sp^3-CH), 2857 (m, sp^3-CH), 1456 (w, sp^3-CH), 1275 (w).

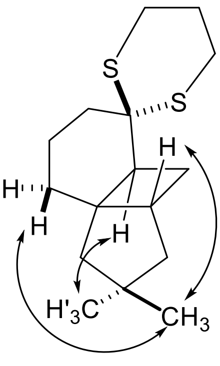
MS (EI, 70 eV): *m/z* (%) = 282 (100) $[M]^+$, 267 (4) $[M-CH_3]^+$, 225 (30), 207 (89) $[C_{13}H_{20}S]^+$, 180 (29) $[C_{13}H_{20}S-C_2H_4]^+$, 145 (31), 106 (91).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.87 (s, 3H, C*H*$_3$), 1.10 (s, 3H, C*H*'$_3$), 1.37 (dd, ^2J = 13.1 Hz, ^4J = 1.7 Hz, 1H, H-1), 1.47-1.53 (m, 1H, H-7), 1.55-1.59 (m, 1H, H-3), 1.60-1.66 (m, 3H, H-4*, H-7. H-8), 1.66-1.74 (m, 3H, H-1, H-3, H-6), 1.81-1.85 (m, 1H, H-8), 1.90-2.02 (m, 3H, H-4, H-3', H-3'*), 2.10-2.16 (m, 1H, H-3a), 2.17-2.22 (m, 1H, H-6), 2.72-2.84 (m, 5H, H-4a, H-2', H-2', H-4', H-4').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.4 (t, C-7), 24.9 (t, C-4*), 25.8 (t, C-3'*), 25.9 (t, C-2'), 26.8 (t, C-4'), 29.0 (q, *C*H$_3$), 29.7 (q, *C*H$_3$), 34.0 (t, C-6), 35.7 (t, C-8), 43.0 (d, C-3a), 45.1 (s, C-2), 47.3 (t, C-3), 47.3 (d, C-4a), 50.3 (s, C-8a), 51.2 (s, C-5), 57.1 (t, C-1).

* assignment is interconvertible

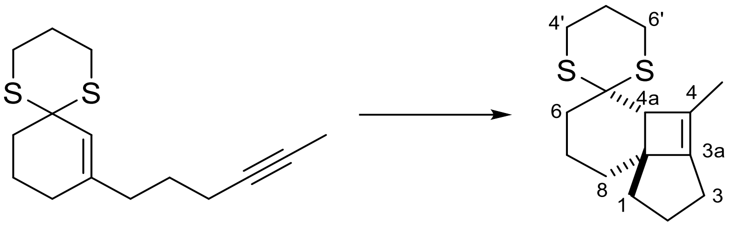
Important NOE contacts



HRMS (EI, 70 eV): calculated: ($C_{16}H_{26}{}^{32}S_2$): 282.1470; found: 282.1473,

calculated: ($C_{15}{}^{13}CH_{26}{}^{32}S_2$): 283.1504; found: 283.1504.

8-(Hex-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (2d)



$C_{15}H_{22}S_2$
MW = 266.46 g/mol

Following *GP3* a, precooled to −78 °C, solution of 28.3 mg 8-(hex-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**2d**) (106 µmol, 1.00 eq.) in 10.5 mL dry CH_2Cl_2 was irradiated at 405 nm, after addition of 3.11 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (10.6 µmol, 10 mol-%). Irradiation was stopped after 24 hours and quenched by addition of NEt_3. After column chromatography cyclobutene **2d** was obtained as a colorless oil in 86% yield (24.2 mg, 91.2 µmol).

TLC: R_f = 0.38 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2920 (s, sp^3-CH), 1436 (m, sp^3-CH), 1271 (w), 1032 (w), 951 (w).

MS (EI, 70 eV): *m/z* (%) = 266 (100) $[M]^+$, 251 (5) $[M-CH_3]^+$, 233 (22) $[C_{12}H_{16}S]^+$, 177 (9) $[C_{11}H_{13}S]^+$, 164 (49), 131 (24), 117 (22), 91 (20).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.99-1.06 (m, 1H, H-8), 1.18 (*virt.* td, $^2J \approx {}^3J \approx$ 12.2 Hz, ^3J = 5.5 Hz, 1H, H-8), 1.31-1.42 (m, 2H, H-6, H-7), 1.41-1.48 (m, 2H, H-1), 1.51-1.58 (m, 1H, H-7), 1.67 (t, ^3J = 1.7 Hz, 3H, CH_3), 1.89-1.99 (m, 2H, H-2), 1.99-2.07 (m, 1H, H-5’), 2.07-2.16 (m, 1H, H-3), 2.18-2.28 (m, 2H, H-3, H-5’), 2.34 (*virt.* td, $^2J \approx {}^3J \approx$ 12.7 Hz, ^3J = 5.9 Hz, 1H, H-6), 2.64 (*virt.* dt, ^2J = 15.6 Hz, $^3J \approx$ 4.7 Hz, 1H, H-4’), 2.75 (ddd, ^2J = 14.7 Hz, ^3J = 11.5 Hz, ^3J = 5.2 Hz, 1H, H-6’), 2.86 (ddd, ^2J = 14.7 Hz, ^3J = 6.1 Hz, ^3J = 2.7 Hz, 1H, H-6’), 2.97-3.03 (m, 1H, H-4’), 3.01 (s, 1H, H-4a).

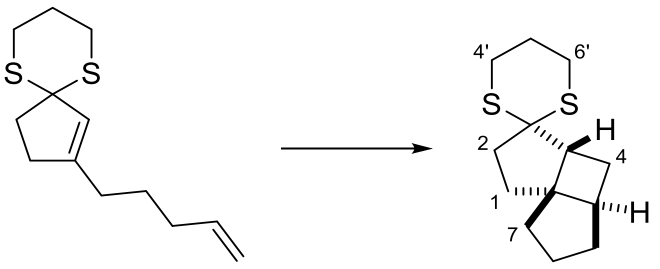
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.1 (q, CH_3), 20.9 (t, C-7), 23.2 (t, C-3), 24.1 (t, C-8), 25.6 (t, C-6), 25.6 (t, C-4), 27.0 (t, C-2), 33.9 (t, C-6*), 34.4 (t, C-1), 34.8 (t, C-5*), 57.4 (s, C-9), 65.4 (s, C-5), 75.5 (d, C-4a), 128.6 (s, C-4), 148.0 (s, C-3a).

* assignment is interconvertible

HRMS (EI, 70 eV): calculated: ($C_{15}H_{22}{}^{32}S_2$): 266.1157; found: 266.1156,

calculated: ($C_{14}{}^{13}CH_{22}{}^{32}S_2$): 267.1191; found: 267.1190.

Octahydrospiro{cyclobuta[1,2:1,4]di[5]annulene-3,2'-[1,3]dithiane} (2e)



$C_{13}H_{20}S_2$
MW = 240.42 g/mol

A solution of 24.3 mg 2-(pent-4-en-1-yl)-6,10-dithiaspiro[4.5]dec-1-ene (**1e**) (101 µmol, 1.00 eq) in 10 mL dry CH_2Cl_2 were cooled down to −78 °C in a duran tube. After addition of 2.22 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (7.58 µmol, 7.5 mol-%) the reaction mixture was irradiated at 366 nm at −78 °C for 21 hours and 14.0 µL NEt_3 (10.2 mg, 101 µmol, 1.00 eq.) were added. After warming to room temperature the solvent was removed in vacuo. Purification by column chromatography yielded in 78% of the title compound (19.0 mg, 79.0 µmol) as a colorless oil.

TLC: R_f = 0.27 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2927 (s, sp^3-CH), 1444 (m, sp3-CH), 907 (w, C-S).

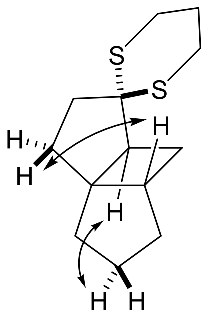
MS (EI, 70 eV): *m/z* (%) = 240 (100) [M]$^+$, 165 (36), 133 (27), 91 (33).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.35-1.41 (m, 1H, H-7), 1.44 (*virt.* dt, ^2J = 12.9 Hz, $^3J \approx$ 3.7 Hz, 1H, H-4), 1.47-1.52 (m, 1H, H-5), 1.52-1.61 (m, 2H, H-2, H-5), 1.61-1.66 (m, 1H, H-7), 1.79-1.86 (m, 2H, H-6), 1.90-2.04 (m, 3H, H-2, H-5', H-5'), 2.04-2.11 (m, 1H, H-4a), 2.11-2.21 (m, 2H, H-1, H-4), 2.25-2.32 (m, 1H, H-1), 2.47 (dd, ^3J = 9.3 Hz, ^3J = 5.3 Hz, 1H, H-3a), 2.66-2.74 (m, 2H, H-4'), 2.76-2.84 (m, 2H, H-6').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 25.8 (t, C-4), 26.1 (t, C-5'), 26.3 (t, C-6), 27.3 (t, C-6'), 28.1 (t, C-4'), 33.2 (t, C-5), 33.6 (t, C-2), 37.4 (t, C-7), 39.1 (d, C-4a), 39.5 (t, C-1), 49.3 (d, C-3a), 56.6 (s, C-7a), 59.5 (s, C-3).

* assignment is interconvertible

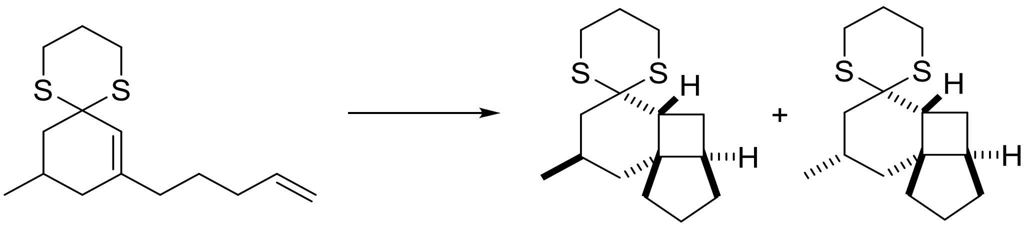
Important NOE contacts



HRMS (EI, 70 eV): calculated: ($C_{13}H_{20}{}^{32}S_2$): 240.1001; found: 240.0997,

calculated: ($C_{12}{}^{13}CH_{20}{}^{32}S_2$): 241.1035; found: 241.1030.

7-Methyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2f)



$C_{15}H_{24}S_2$
MW = 268.13 g/mol

Following *GP3* 30.0 mg 10-methyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene **(1f)** (112 µmol, 1.00 eq.) were converted into its corresponding cyclobutane by irradiation at 405 nm in presence of 3.28 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (11.2 µmol, 10 mol-%) in 11 mL dry CH_2Cl_2 at −78 °C. The reaction was finished after 24 hours. After column chromatography (SiO_2, P/Et_2O =99/1) the product **2f** was obtained in 90% yield (27.4 mg, 102 µmol) as a colorless oil in a diastereomeric ratio of 60/40 (determined by NMR).

TLC: R_f = 0.22 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2925 (s, sp^3-CH), 1454 (m, sp^3-CH), 905 (m), 790 (w, CSC).

MS (EI, 70 eV): *m/z* (%) = 268 (98) $[M]^+$, 253 (2) $[M\text{-}CH_3]^+$, 193 (100) $[C_{12}H_{17}S]^+$, 179 (9) $[C_{11}H_{15}S]^+$, 152 (69) $[C_6H_{12}S]^+$, 106 (63).

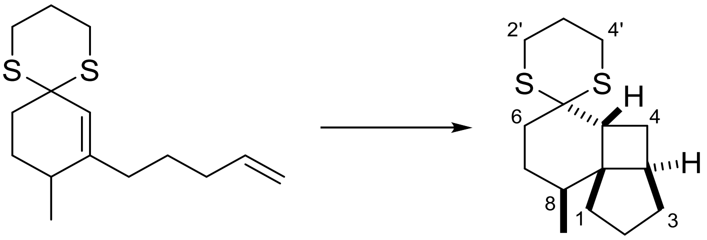
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.92 (d, ^3J = 6.6 Hz, 2H, CH_3-minor), 1.00 (d, ^3J = 6.2 Hz, 3H, CH_3-major), 1.15-1.28 (m, 2.7H, 2×H-major, 1×H-minor), 1.33-1.69 (m, 8.8H, 6×H-major, 4×H-minor), 1.71-1.89 (m, 6.2H, 2×H-major, 6×H-minor), 1.89-2.03 (m, 5.8H, 3×H-major, 4×H-minor), 2.04-2.24 (m, 4.4H, 3×H-major, 2×H-minor), 2.58-2.73 (m, 3.4H, 2×H-major, 2×H-minor), 2.73-2.82 (m, 2.4H, 1×H-major, 2×H-minor), 2.83-2.96 (m, 2H, 2×H-major).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 22.8 (q, CH_3-minor), 24.1 (q, CH_3-major), 25.2 (t, CH_2-major), 25.4 (t, CH_2-minor), 25.4 (d, CH-minor), 25.9 (t, CH_2-minor), 26.0 (t, CH_2-minor), 26.4 (d, CH-major), 26.5 (t, CH_2-minor), 26.6 (t, CH_2-major), 26.9 (t, CH_2-major), 27.0 (t, CH_2-major), 27.5 (t, CH_2-major), 28.1 (t, CH_2-minor), 31.7 (t, CH_2-minor), 32.7 (t, CH_2-major), 36.9 (d, CH-major), 37.2 (t, CH_2-major), 39.4 (d, CH-major), 40.2 (t, CH_2-major), 41.0 (t, CH_2-minor), 41.7 (d, CH-minor), 42.0 (t, CH_2-major), 42.4 (t, CH_2-minor), 42.5 (d, CH_2-minor), 42.9 (t, CH_2-minor), 49.8 (s, $C_{quar.}$-major), 51.1 (s, $C_{quar.}$-minor), 51.7 (s, $C_{quar.}$-major), 52.3 (s, $C_{quar.}$-minor).

HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}{}^{32}S_2$): 268.1314; found: 268.1308,

calculated: ($C_{14}{}^{13}CH_{24}{}^{32}S_2$): 269.1348; found: 269.1342.

8-Methyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2g)



$C_{15}H_{24}S_2$
MW = 268.48 g/mol

Following *GP3* 27.0 mg 9-ethyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**1g**) (100 µmol, 1.00 eq.) were dissolved in 10 mL CH_2Cl_2 and precooled to −78 °C. After addition of 2.95 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (10.1 µmol, 10 mol-%) irradiation at 405 nm was started and stopped after 21 hours followed by addition of 14 µL NEt_3 (10 mg, 100 µmol, 1.00 eq.). Column chromatography (SiO_2, P/Et_2O = 99/1) yielded in 89% of the compound **2g** (24.3 mg, 90.5 µmol) as a white solid.

TLC: R_f = 0.49 (P/Et_2O = 98/2) [$KMnO_4$].

M.P.: 59°C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2929 (s, sp^3-CH), 1444 (m, sp^3-CH).

MS (EI, 70 eV): *m/z* (%) = 268 (80) [M]$^+$, 163 (96), 152 (100) [$C_9H_{12}S$]$^+$, 145 (30), 106 (55).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.87 (d, ^3J = 7.0 Hz, 3H, C*H*$_3$), 1.34-1.40 (m, 1H, H-7), 1.44-1.47 (m, 1H, H-1), 1.49-1.54 (m, 1H, H-7), 1.55-1.58 (m, 1H, H-1), 1.58-1.61 (m, 1H, H-3), 1.61-1.64 (m, 1H, H-4), 1.72-1.78 (m, 1H, H-2), 1.78-1.83 (m, 1H, H-3), 1.83-1.87 (m, 1H, H-6), 1.88-2.06 (m, 5H, H-2, H-3a, H-8, H-3', H-3'), 2.16 (*virt.* td, $^2J \approx {}^3J \approx$ 11.3 Hz, ^3J = 8.3 Hz, 1H, H-4), 2.21-2.26 (m, 1H, H-6), 2.72-2.83 (m, 5H, H-4a, H-2', H-2', H-4', H-4').

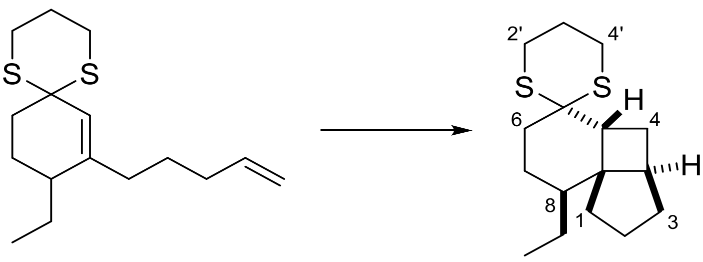
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 16.7 (q, *C*H$_3$), 26.0 (t, C-3'), 26.0 (t, C-2'), 26.9 (t, C-4'), 27.1 (t, C-4), 28.0 (t, C-7), 29.0 (t, C-2), 31.3 (t, C-3), 31.8 (t, C-1), 35.7 (t, C-6), 36.0 (d, C-8), 42.0 (d, C-3a), 43.6 (d, C-4a), 51.6 (s, C-5), 54.8 (s, C-9).

Relative configuration was determined by x-ray crystallography (chapter 7).

HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}{}^{32}S_2$): 268.1314; found: 268.1308,

calculated: ($C_{14}{}^{13}CH_{24}{}^{32}S_2$): 269.1348; found:269.1341.

8-Ethyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2h)



$C_{16}H_{26}S_2$
MW = 282.50 g/mol

Cyclobutane **2h** was prepared following *GP3* using 29.1 mg dithiane **1h** (103 µmol, 1.00 eq.) dissolved in 10.3 mL CH_2Cl_2. After irradiation at λ = 405 nm for 24 hours at −78°C in presence of 3.02 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (10.3 µmol, 10 mol-%), followed by column chromatography, 22.8 mg (80.7 µmol, 79%) of the title compound **2h** were obtained as a colorless oil.

TLC: R_f = 0.23 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2930 (s, sp^3-CH), 1422 (s, sp^3-CH).

MS (EI, 70 eV): *m/z* (%) = 282 (83) [M]$^+$, 253 (8) [M-C_2H_5]$^+$, 207 8100) [$C_{13}H_{19}S$]$^+$, 152 (85) [$C_9H_{12}S$]$^+$, 145 (40), 106 (61).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.84 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3), 1.07-1.17 (m, 1H, CH_2CH_3), 1.23-1.34 (m, 2H, H-2, CH_2CH_3), 1.37-1.61 (m, 6H, H-2, H-3, H-4, H-6*, H-6*, H-8), 1.69-1.81 (m, 3H, H-1, H-3, H-3’), 1.85-2.00 (m, 4H, H-3a, H-7*, H-7*, H-3’), 2.11 (*virt.* td, $^2J \approx {}^3J \approx$ 11.3 Hz, ^3J = 8.4 Hz, 1H, H-4), 2.16-2.21 (m, 1H, H-1), 2.64-2.79 (m, 5H, H-4a, H-2’, H-2’, H-4’, H-4’).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.1 (q, CH_2CH_3), 24.5 (t, CH_2CH_3), 24.8 (t, C-2), 26.0 (t, C-7*), 26.1 (t, C-4’), 27.0 (t, C-2’), 27.2 (t, C-4), 28.8 (t, C-3’), 31.2 (t, C-3), 32.0 (t, C-6*), 35.8 (t, C-1), 42.3 (d, C-3a), 43.1 (d, C-8), 43.8 (d, C-4a), 51.6 (s, C-8a**), 54.9 (s, C-5**).

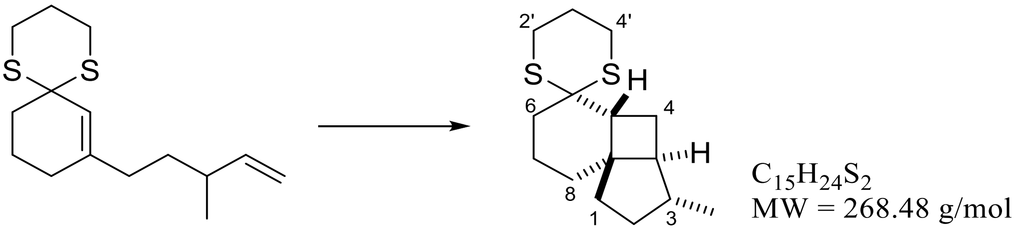
*/** assignment is interconvertible

Relative configuration was assumed to be the same as for compound **2g**.

HRMS (EI, 70 eV): calculated: ($C_{16}H_{26}{}^{32}S_2$): 282.1470; found: 282.1465.

calculated: ($C_{15}{}^{13}CH_{26}{}^{32}S_2$): 283.1504; found: 283.1498.

3-Methyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2i)



According to *GP*3 27.3 mg 8-(3-methylpent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (**1i**) (101 µmol, 1.00 eq.) in 10 mL CH_2Cl_2 were irradiated at −78 °C and λ = 405 nm in presence of 2.24 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (7.63 µmol, 7.5 mol-%) for 5.5 hours. After quenching and column chromatography (SiO_2, P/Et_2O = 99/1) the cyclobutane **2i** was obtained as a colorless oil in 85% yield (22.8 mg, 84.9 µmol) in a mixture of diastereoisomers of 90/10 (determined by GC).

TLC: R_f = 0.24 (P/Et_2O = 99/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2930 (s, sp^3-CH), 1455 (m, sp^3-CH), 1274 (w), 808 (w, C-S).

MS (EI, 70 eV): *m/z* (%) = 268 (100) $[M]^+$, 239 (13) $[M-C_2H_5]^+$, 193 (99) $[M-C_3H_7S]^+$, 166 (37), 106 (70).

HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}{}^{32}S_2$): 268.1314; found: 268.1312,

calculated: ($C_{14}{}^{13}CH_{24}{}^{32}S_2$): 269.1348; found: 269.1348.

Major Diastereoisomer

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.88 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.37-1.45 (m, 3H, H-2, H-7, H-8), 1.53-1.64 (m, 2H, H-4, H-7), 1.67-1.73 (m, 1H, H-3a), 1.73-1.82 (m, 2H, H-1), 1.84-2.07 (m, 6H, H-3, H-4, H-6, H-8, H-3', H-3'), 2.07-2.17 (m, 2H, H-2, H-6), 2.63 (*virt*. t, ^3J ≈ 9.0 Hz, 1H, H-4a), 2.67-2.77 (m, 2H, H-2', H-4'), 2.78-2.88 (m, 2H, H-2', H-4').

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.9 (t, C-1), 21.2 (q, CH_3), 25.6 (t, C-2'), 25.8 (t, C-4'), 26.1 (t, C-4), 26.7 (t, C-3'), 31.2 (t, C-8), 32.2 (t, C-6), 34.0 (t, C-2), 38.9 (t, C-7), 40.2 (d, C-3), 41.9 (d, C-4a), 47.5 (d, C-3a), 49.6 (s, C-8a), 51.8 (s, C-5).

Minor Diastereoisomer

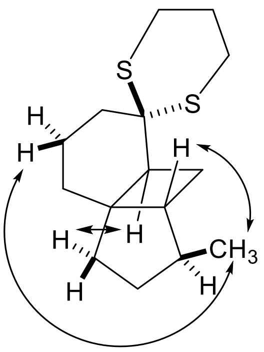
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.95 (d, ^3J = 6.7 Hz, 3H, CH_3), 1.2-1.4 (m, 4H), 2.47 (t, ^3J = 8.8 Hz, 1H, H-4a).

Remaining ^{1}H signals could not be identified due to their low signal intensity and overlap with the ^{1}H NMR signals of the major diastereoisomer.

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 14.8 (q, CH_3), 16.7, 19.7, 25.6, 26.2 26.6, 29.1, 31.3, 33.7, 36.3, 40.5, 41.3 (d, C-4a), 42.6, 49.2, 52.2.

Signals could not be assigned due to low signal intensities in 2D spectra. In addition most cross peaks overlap with the signals of the major diastereoisomer.

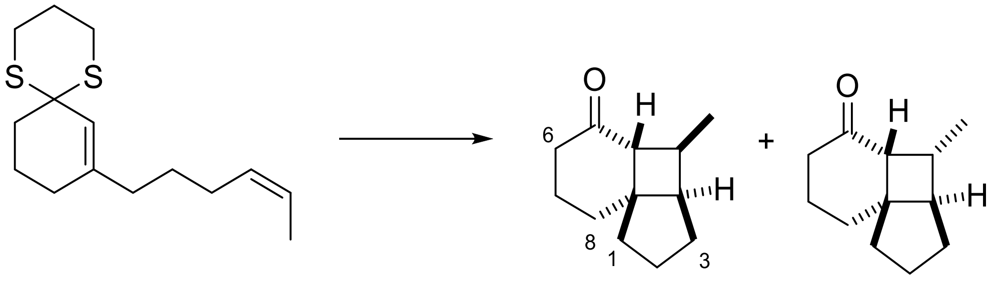
Important NOE contacts of the major diastereoisomer



HRMS (EI, 70 eV): calculated: ($C_{15}H_{24}{}^{32}S_2$): 268.1314; found: 268.1309,

calculated: ($C_{14}{}^{13}CH_{24}{}^{32}S_2$): 269.1348; found: 269.1341.

4-Methyloctahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (6)



cis-**6** *trans*-**6**

$C_{12}H_{18}O$
MW = 164.12 g/mol

This photochemical reaction was carried out following *GP3* by cooling a solution of 22.8 mg dithiane **1j** (84.9 µmol, 1.00 eq.) in 8.6 mL dry CH_2Cl_2 to −78 °C. After addition of 1.87 mg 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (**3**) (6.37 µmol, 7.5 mol-%) the solution was irradiated at $\lambda = 405$ nm for 15 hours. After addition of 11.8 µL NEt_3 (8.59 mg, 84.9 µmol, 1.00 eq.) The reaction solution was allowed to warm to room temperature and polar impurities were removed by column chromatography (SiO_2, P/Et_2O = 99/1). Small amounts of unpolar impurities were not separable and the dithiane was removed in order to isolate pure cyclobutane **6**. For the deprotection reaction the crude product was dissolved in 0.3 mL methanol, 0.3 mL THF and 40 µL water and cooled to −78 °C. After addition of 35.2 mg [bis(trifluoroacetoxy)-iodo]benzene (81.9 µmol, 1.10 eq.) the reaction solution was allowed to warm slowly to room temperature. After stirring at room temperature for two hours 10 mL saturated aqueous sodium bicarbonate solution were added and organic compounds were extracted by Et_2O (3×15 mL). The combined organic layers were dried over Na_2SO_4, filtered and solvent was removed in vacuo. The title compounds *cis*-**6** and *trans*-**6** were obtained as a colorless oil in 53% (7.1 mg, 39 µmol) over both steps after column chromatography (SiO_2, P/Et_2O = 10/1). The diastereomeric ratio (d.r.) was determined as 67/33 by GC.

TLC: R_f = 0.20 (P/Et_2O = 10/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2926 (s, sp^3-CH), 1694 (s, C=O), 1443 (m, sp^3-CH), 1315 (m, sp^3-CH), 1163 (m).

MS (EI, 70 eV): *m/z* (%) = 178 (31) $[M]^+$, 163 (9) $[M-CH_3]^+$, 150 (28) $[M-C_2H_4]^+$, 123 (100) $[M-C_4H_7]^+$, 110 (91), 79 (43).

HRMS (EI, 70 eV): calculated: ($C_{12}H_{18}O$): 178.1354; found: 178.1354.

*major Diastereoisomer cis-***6**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.98 (d, ^3J = 6.8 Hz, 3H, C*H*$_3$), 1.24-1.38 (m, 1H), 1.47-1.63 (m, 3H), 1.56-1.75 (m, 1H), 1.68-1.74 (m, 1H), 1.75-1.86 (m, 2H), 1.89-1.98 (m, 1H), 2.03-2.21 (m, 3H, H-4a), 2.33-2.46 (m, 2H, H-3a, H-4), 2.57 (*virt.* dt, ^2J = 17.8 Hz, ^3J ≈ 3.9 Hz, 1H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 14.7 (q, *C*H$_3$), 20.9 (t), 26.7 (t), 26.9 (t), 31.3 (d, C-4), 32.5 (t), 39.0 (t), 39.6 (t), 43.3 (d, C-3a), 47.4 (s, C-8a), 56.0 (d, C-4a), 214 (s, C-6).

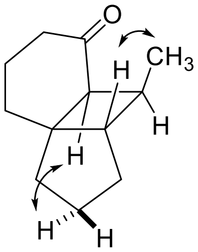
*minor Diastereoisomer trans-***6**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.94 (d, ^3J = 7.5 Hz, 3H, C*H*$_3$), 1.29-1.39 (m, 1H, H-3), 1.49-1.63(m, 5H, H-1, H-1, H-3, H-8, H-8), 1.75-1.84 (m, 2H, H-2), 1.89-1.98 (m, 2H, H-7), 1.98-2.04 (m, 1H, H-3a), 2.04-2.14 (m, 2H, H-4, H-6), 2.40 (virt. dt, ^2J = 18.4 Hz, ^3J ≈ 3.6 Hz, 1H, H-6). 2.52 (d, ^3J = 11.2 Hz, 1H, H-4a).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 17.3 (q, *C*H$_3$), 21.3 (t, C-7), 25.2 (t, C-2), 32.5 (t, C-8*), 33.0 (t, C-1*), 33.3 (d, C-4), 40.6 (t, C-3), 41.1 (t, C-6), 45.8 (s, C-8a), 47.9 (d, C-3a), 51.3 (d, C-4a), 214.9 (q, C-5).

* assignment is interconvertible

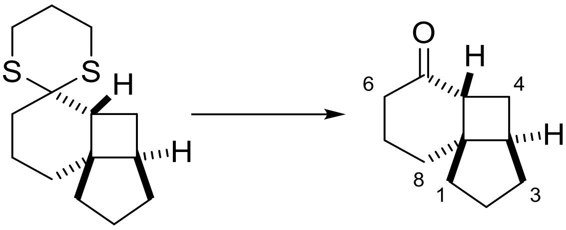
Important NOE contacts



Minor diastereoisomer *trans*-**6** was isolated in a different reaction in pure form. Therefore complete assignment was possible for this isomer. The major diastereoisomer *cis*-**6** was not isolated as a single product and an assignment of all NMR signals was not possible.

6. Deprotection of 1,3-Dithianes

Octahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (5)



$C_{11}H_{16}O$
MW = 164.25 g/mol

For oxidative deprotection 30.0 mg dithiane (2a) (11.8 µmol, 1.00 eq.) were dissolved in 0.45 mL MeOH and 0.05 mL water. To this solution 76.0 mg [bis(trifluoroacetoxy)iodo]benzene (17.7 µmol, 1.50 eq.) were added and the mixture was stirred for one hour at room temperature before 4.0 mL sat. $NaHCO_3$ solution were added. The aqueous phase was extracted with Et_2O (3×15 mL), combined organic layers were dried over Na_2SO_4, filtrated and the solvent was removed in vacuo. The corresponding ketone **5** was obtained as a colorless oil in 84% yield (16.0 mg, 99.0 µmol), after column chromatography (SiO_2, P/Et_2O = 10:1).

TLC: R_f = 0.26 (P/Et_2O = 10/1, [$KMnO_4$]).

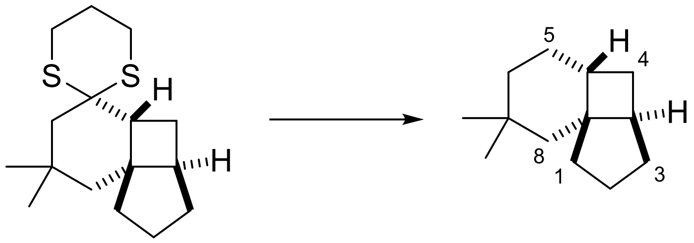
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.34 (*virt.* td, $^2J \approx {}^3J \approx$ 12.6 Hz, ^3J = 6.8 Hz, 1H, H-1), 1.50 – 1.58 (m, 2H, H-8), 1.58 – 1.65 (m, 3H, H-1, H-3), 1.77 – 1.85 (m, 2H, H-2, H-4), 1.85 – 1.93 (m, 1H, H-2), 1.94 – 2.05 (m, 2H, H-7), 2.05 – 2.11 (m, 1H, H-4), 2.17 (dddd, ^2J = 18.0 Hz, ^3J = 11.5 Hz, ^3J = 6.9 Hz, ^4J = 0.9 Hz, 1H, H-6), 2.36 – 2.43 (m, 1H, H-3a), 2.48 (dd, ^3J = 11.4 Hz, ^3J = 6.9 Hz, H-4a), 2.56 (dt, ^2J = 18.0 Hz, ^3J = 4.2 Hz, 1H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 21.3 (t, C-7), 25.1 (t, C-2), 27.0 (t, C-4), 33.0 (t, C-8*), 33.2 (t, C-3*), 39.6 (d, C-3a), 39.7 (t, C-6), 40.5 (t, C-1), 47.4 (d, C-4a), 50.1 (s, C-8a), 215.5 (s, C-5).

* assignment is interconvertible

The obtained data match with those reported in the literature.[20]

7,7-Dimethyldecahydrocyclopenta[1,4]cyclobuta[1,2]benzene (4)



$C_{13}H_{22}$
MW = 178.32 g/mol

Raney®-Ni (440 mg) was washed with dry methanol (3×1 mL) before use.

Dithiane **2b** (18.0 mg, 63.7 µmol) was dissolved in dry methanol (2.5 mL), *Raney*®-Ni was added and the mixture was stirred at 63°C for four hours in a closed flask. After cooling to room temperature, Ni was filtered off and washed with MeOH, water and pentane. Layers were separated and the organic layer was washed with water (3×5 mL), dried over Na_2SO_4 and filtered. Pentane was carefully removed in vacuo (20°C, 700 mbar). The product was obtained as a colorless oil in 75% yield (8.5 mg, 63 µmol).

TLC: R_f = 1.0 (P) [$KMnO_4$].

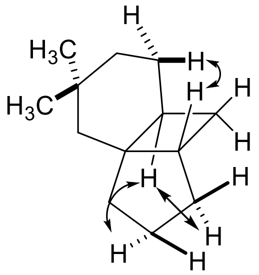
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2925 (s, sp^3-CH), 2854 (m, sp^3-CH), 1463 (w, sp^3-CH).

MS (EI, 70 eV): *m/z* (%) = 178 (19) $[M]^+$, 163 (100) $[M-CH_3]^+$, 136 (31) $[M-CH_3-C_2H_4]^+$, 122 (45), 93 (44), 81 (73).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ (ppm) = 0.85 (s, 3H, C*H*$_3$), 0.95 (s, 3H, C*H*$_3$), 1.07-1.14 (m, 1H, H-1), 1.14-1.20 (m, 1H, H-6), 1.22-1.27 (m, 2H, H-2, H-8), 1.39-1.46 (m, 2H, H-1, H-3), 1.51 (ddd, ^3J = 12.5 Hz, ^3J = 9.0 Hz, ^3J = 3.8 Hz, 1H, H-4), 1.55-1.60 (m, 2H, H-6, H-8), 1.60-1.62 (m, 1H, H-3), 1.62-1.67 (m, 1H, H-2), 1.74 (*virt.* dtd, ^2J = 8.6 Hz, $^3J \approx$ 6.9 Hz, ^3J = 5.2 Hz, 1H, H-5), 1.79-1.85 (m, 1H, H-4), 1.86-1.96 (m, 2H, H-4a, H-5), 2.12-2.18 (m, 1H, H-3a).

^{13}C NMR (126 MHz, CD_2Cl_2, 300 K): δ (ppm) = 25.9 (t, C-2), 26.9 (t, C-5), 28.8 (t, C-4), 29.6 (s, C-8a), 29.7 (q, *C*H$_3$), 32.5 (q, *C*H$_3$), 32.9 (t, C-3), 35.4 (d, C-4a), 35.5 (t, C-1), 43.1 (t, C-6), 44.0 (d, C-3a), 47.3 (t, C-8), 47.6 (s, C-7).

Important NOE contacts



HRMS (EI, 70 eV): calculated: ($C_{13}H_{22}$): 178.1716; found: 178.1708.

7. SC- XRD Determination of Compound 2g (CCDC 1528600)

A clear colorless plate-like specimen of $C_{15}H_{24}S_2$, approximate dimensions 0.019 mm x 0.124 mm x 0.181 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource (λ = 0.71073 Å).

A total of 2564 frames were collected. The total exposure time was 20.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 36482 reflections to a maximum θ angle of 25.08° (0.84 Å resolution), of which 2439 were independent (average redundancy 14.958, completeness = 99.8%, R_{int} = 8.47%, R_{sig} = 3.40%) and 2041 (83.68%) were greater than $2\sigma(F^2)$. The final cell constants of a = 34.16(2) Å, b = 6.682(4) Å, c = 12.551(9) Å, β = 105.66(4)°, volume = 2759.(3) Å^3, are based upon the refinement of the XYZ-centroids of 9938 reflections above 20 σ(I) with 4.945° < 2θ < 51.23°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.940. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9370 and 0.9930.

The final anisotropic full-matrix least-squares refinement on F^2 with 227 variables converged at R1 = 3.10%, for the observed data and wR2 = 6.84% for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was 0.284 $e^-/Å^3$ and the largest hole was -0.227 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.293 g/cm^3 and F(000), 1168 e^-.

Figure 1. Ortep drawing with 50% ellipsoids for BreCh2 AP8183-100.

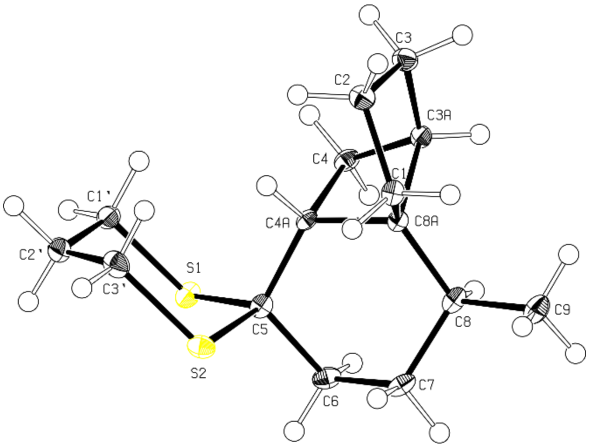


Table 2. Sample and crystal data for BreCh2 AP8183-100.

Identification code	BreCh2 AP8183-100	
Chemical formula	$C_{15}H_{24}S_2$	
Formula weight	268.46	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.019 x 0.124 x 0.181 mm	
Crystal habit	clear colorless plate	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 34.16(2) Å	α = 90°
	b = 6.682(4) Å	β = 105.66(4)°
	c = 12.551(9) Å	γ = 90°
Volume	2759.(3) Å^3	
Z	8	

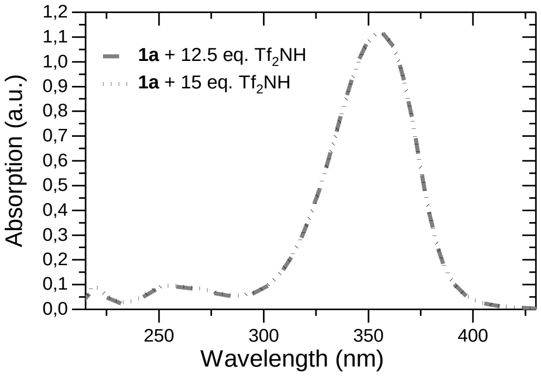
Density (calculated)	1.293 g/cm^3
Absorption coefficient	0.363 mm^{-1}
F(000)	1168

Table 1. Data collection and structure refinement for BreCh2 AP8183-100.

Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	2.48 to 25.08°	
Index ranges	-40<=h<=40, -7<=k<=7, -15<=l<=15	
Reflections collected	36482	
Independent reflections	2439 [R(int) = 0.0847]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9930 and 0.9370	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	Σ w(F$_o^2$ - F$_c^2$)^2	
Data / restraints / parameters	2439 / 0 / 227	
Goodness-of-fit on F^2	1.032	
Δ/σ_{max}	0.002	
Final R indices	2041 data; I>2σ(I)	R1 = 0.0310, wR2 = 0.0654
	all data	R1 = 0.0442, wR2 = 0.0684
Weighting scheme	w=1/[σ^2(F$_o^2$)+(0.0278P)^2+3.8302P] where P=(F$_o^2$+2F$_c^2$)/3	
Extinction coefficient	0.0007(1)	
Largest diff. peak and hole	0.284 and -0.227 eÅ^{-3}	
R.M.S. deviation from mean	0.048 eÅ^{-3}	

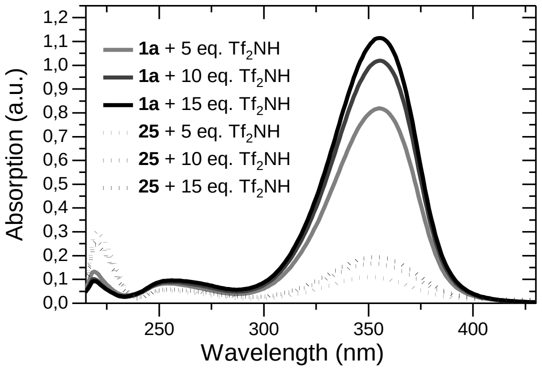
8. Additional UV/Vis Spectra

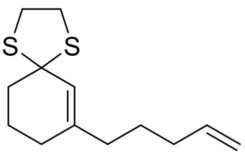
*a) Dithiane **1a** in the presence of more equivalents of Tf_2NH*



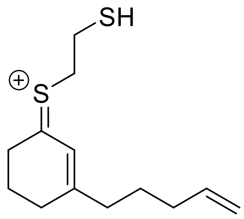
UV/Vis spectra were measured in CH_2Cl_2 [0.5 mM]

*b) Comparison of Dithiane **1a** and Dithiolane **25***





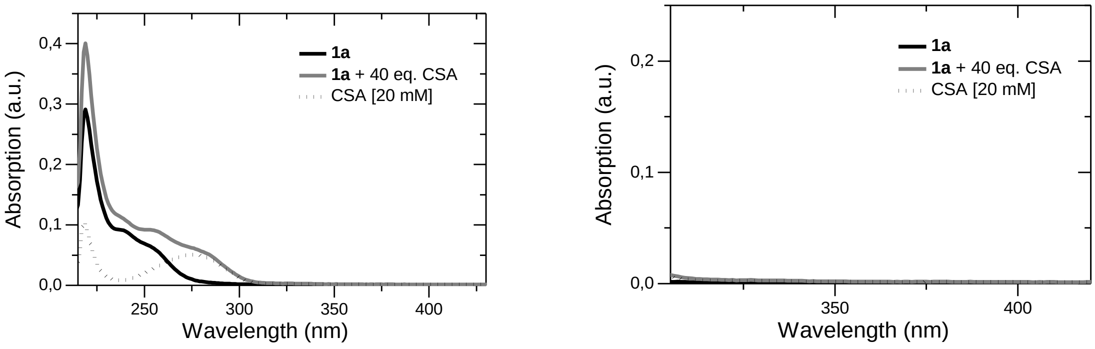
25

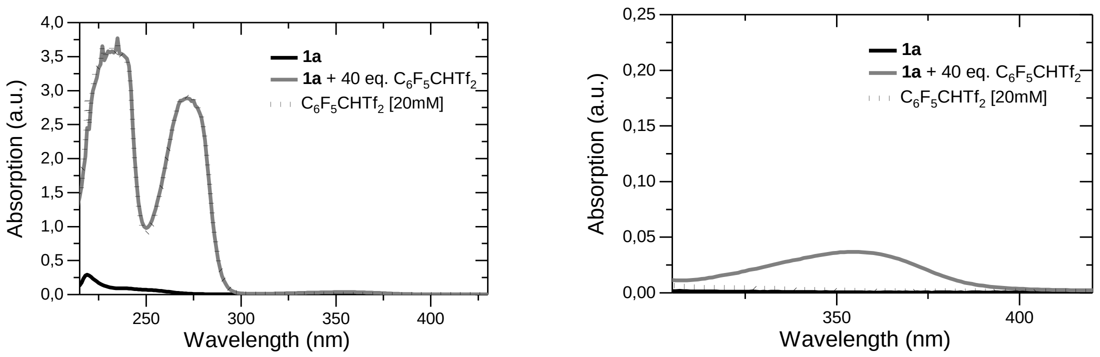


λ_{max} = 353 nm

UV/Vis spectra were measured in CH_2Cl_2 [0.5 mM]

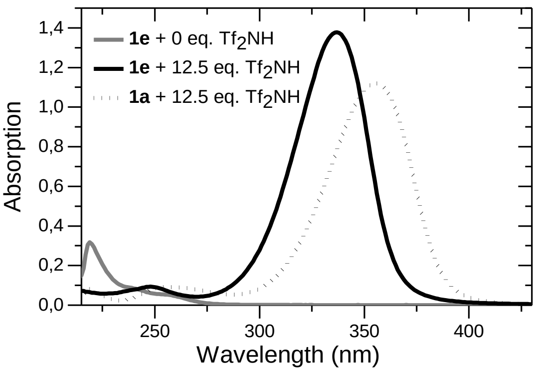
*c) Spectra of Dithiane **1a** in the presence of CSA and $C_6F_5CHTf_2$*

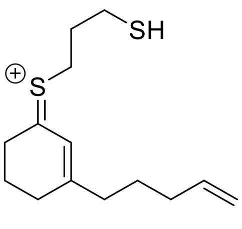




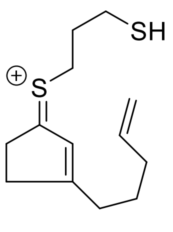
UV/Vis spectra were measured in CH_2Cl_2 [0.5 mM]

*d) Dithiane **1e** under acidic conditions*





λ_{max} = 356 nm



λ_{max} = 337 nm

UV/Vis spectra were measured in CH_2Cl_2 [0.5 mM]

9. Data Sheets and Emission Spectra of Light Sources

LED 398 nm

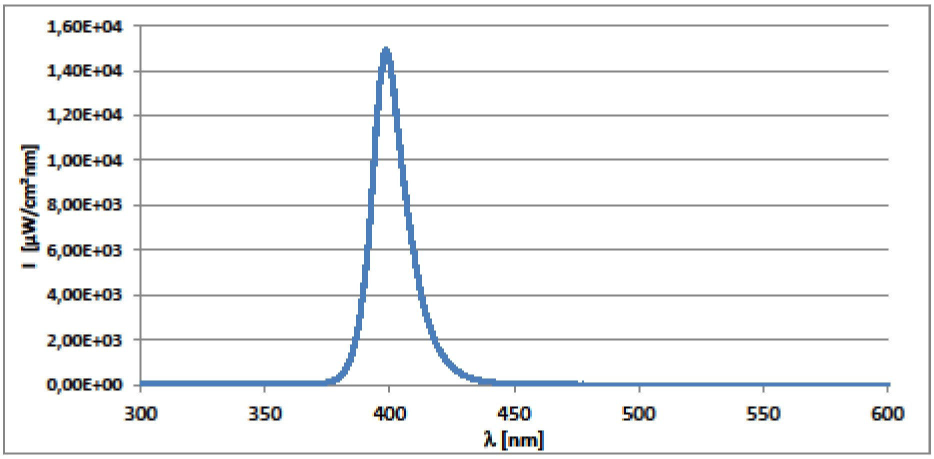
Lehrstuhl OC 1 - TUM

200 nm | 250 nm | 300 nm | 350 nm | 400 nm | 450 nm | 500 nm | 550 nm | 600 nm | 650 nm

Datasheet 400 / 10 W

Basic Information	Ultra-High-Power Violet (400)
Type	High-Power-LED
Description	
Manufacturer / Supplier	LED-Engine Mouser
Order number / Date of purch.	LZ4-40UA00-00U6 / 01/2016
Internal lot / serial number	2016-01 / LED026
Specification Manufacturer	
Type / size	quattro emitter / not spec.
Mechanical specification	
Electrical specification	700 mA @15 V
Wavelength (range, typ.)	
Spectral width (FWHM)	
Datasheet	LZ4-00UA-series.pdf
Characterization	
Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 500 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	398 nm
Measured spectral width	15 nm
Integral Reference intensity	272000 µW/cm² (360-480 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum



LED 405 nm

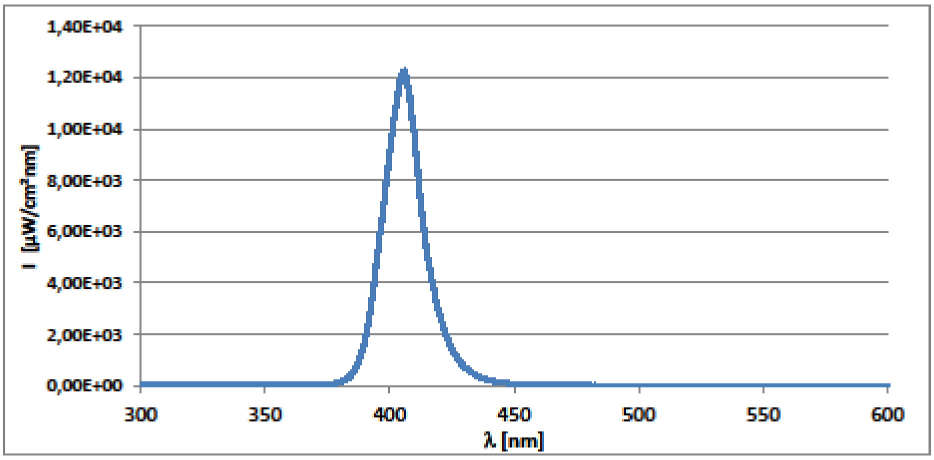
Lehrstuhl OC 1 - TUM

200 nm | 250 nm | 300 nm | 350 nm | 400 nm | 450 nm | 500 nm | 550 nm | 600 nm | 650 nm

Datasheet 405 / 10 W

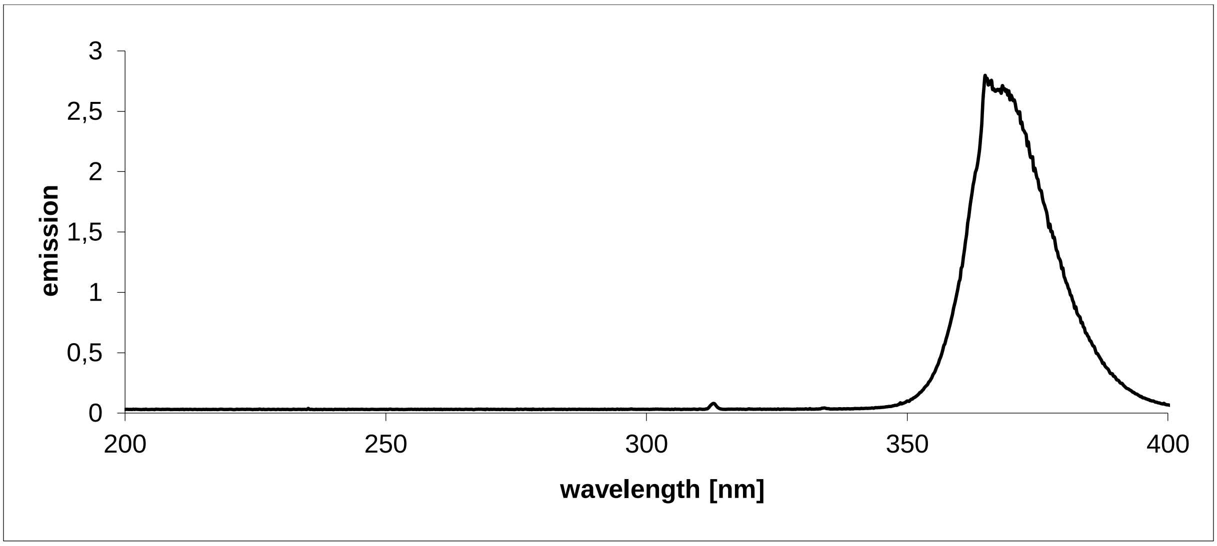
Basic Information	**Ultra-High-Power Violet (405)**
Type	**High-Power-LED**
Description	
Manufacturer / Supplier	**LED-Engine Mouser**
Order number / Date of purch.	**LZ4-40UA00-00U7 / 03/2016**
Internal lot / serial number	**2016-03 / LED037**
Specification Manufacturer	
Type / size	**quattro emitter / not spec.**
Mechanical specification	
Electrical specification	**700 mA @15 V**
Wavelength (range, typ.)	
Spectral width (FWHM)	
Datasheet	**LZ4-00UA-series.pdf**
Characterization	
Description of measurement	**Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 500 mA on a passive heat-sink at approx. 20 °C**
Measured wavelength	**405 nm**
Measured spectral width	**18 nm**
Integral Reference intensity	**247500 µW/cm² (360-480 nm @ 20 mm distance, 4 mmcosine corr.)**

Spectrum



Philips Lighting 366 nm fluorescence lamp

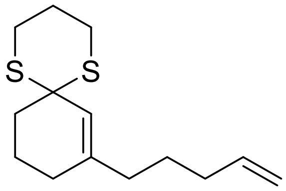
Black Light Blue, 8 W, λ = 366 nm



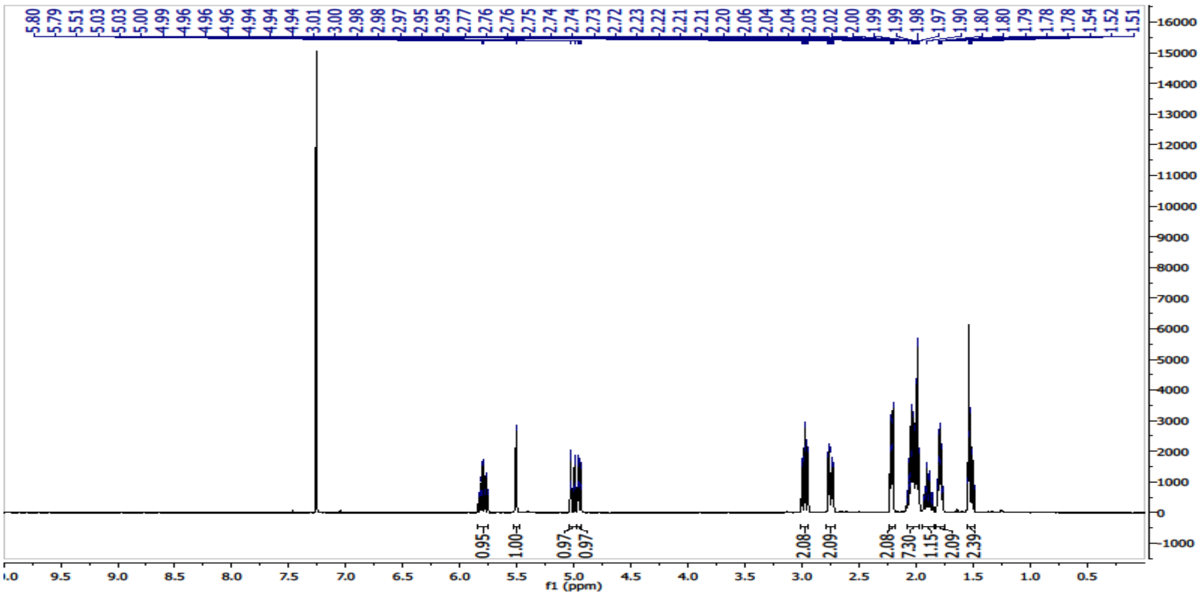
10. NMR Spectra of new Compounds

10.1. Substrates and Intermediate Compounds

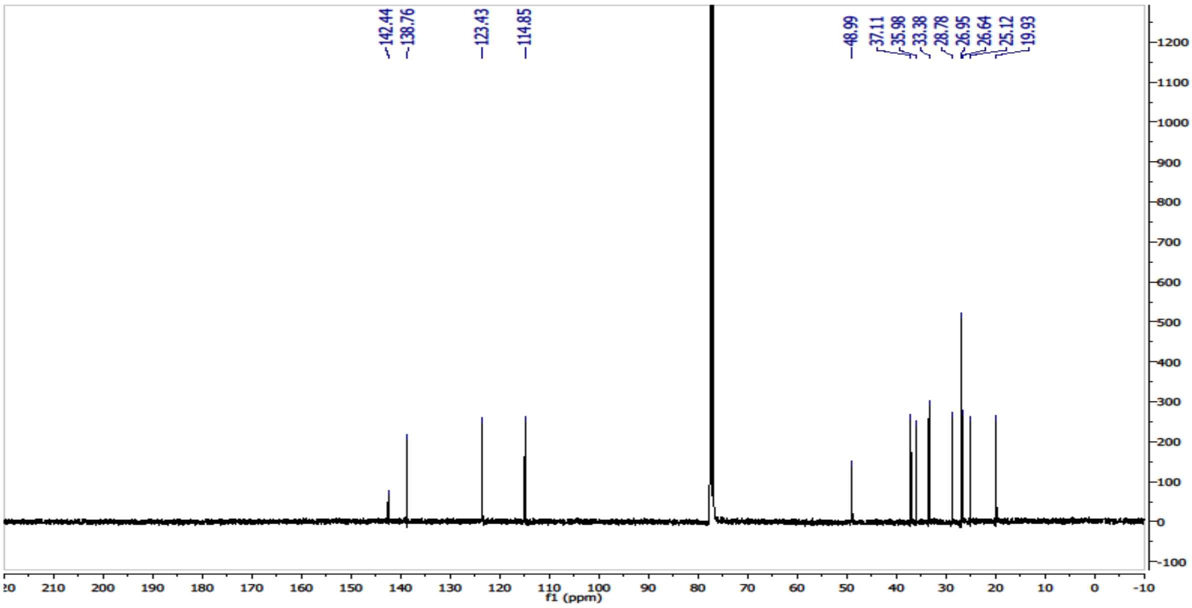
8-(Pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1a)



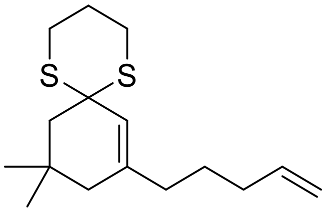
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



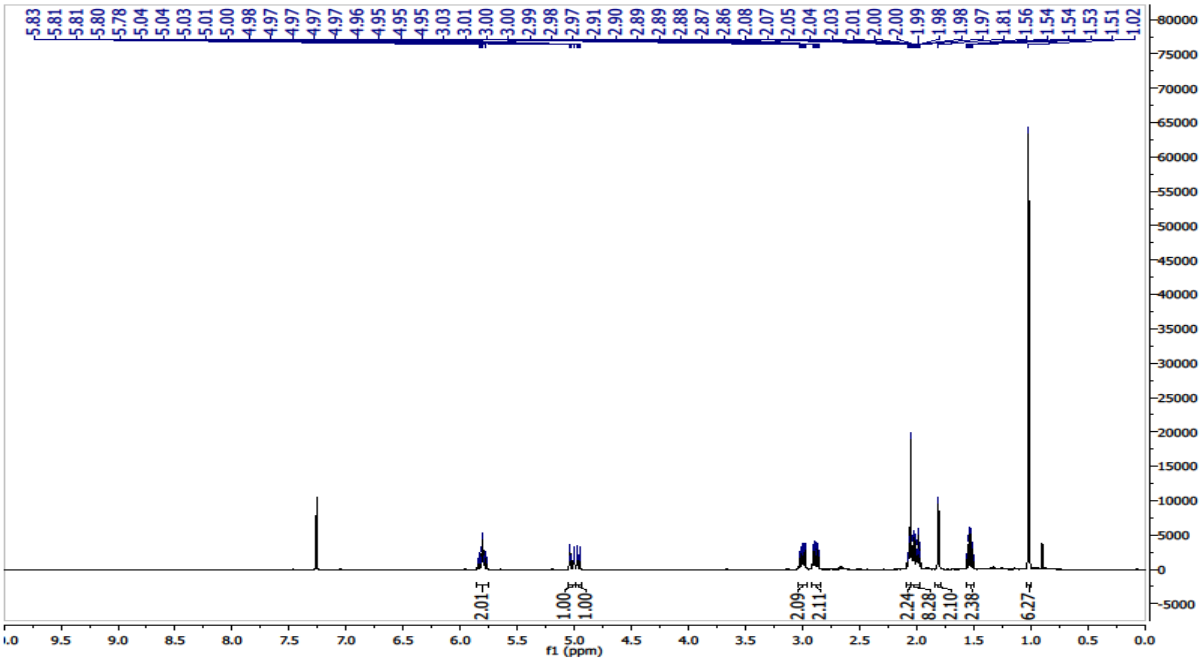
^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



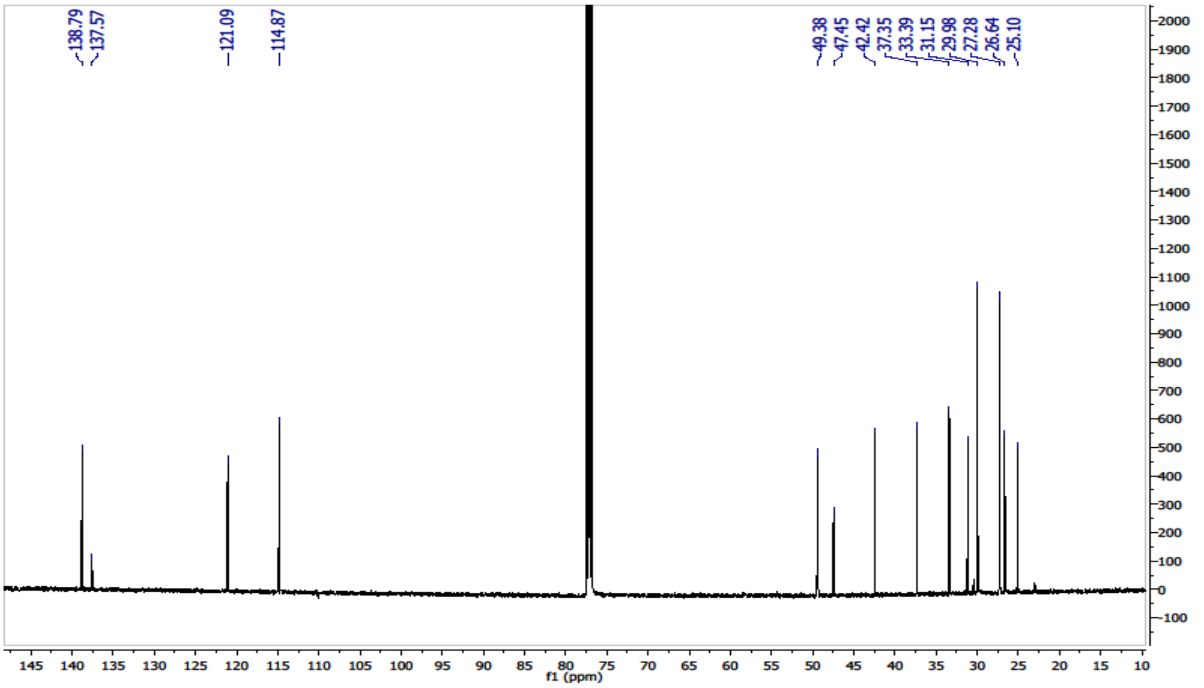
10,10-Dimethyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1b)



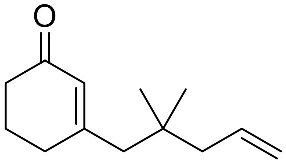
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



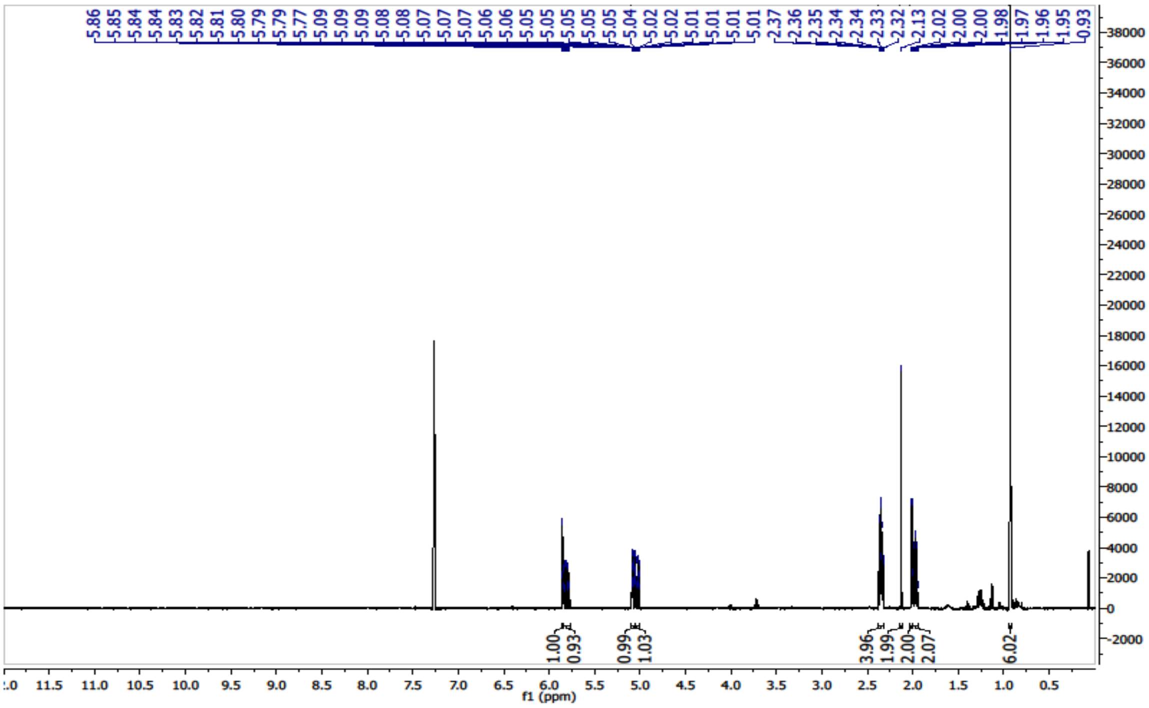
^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



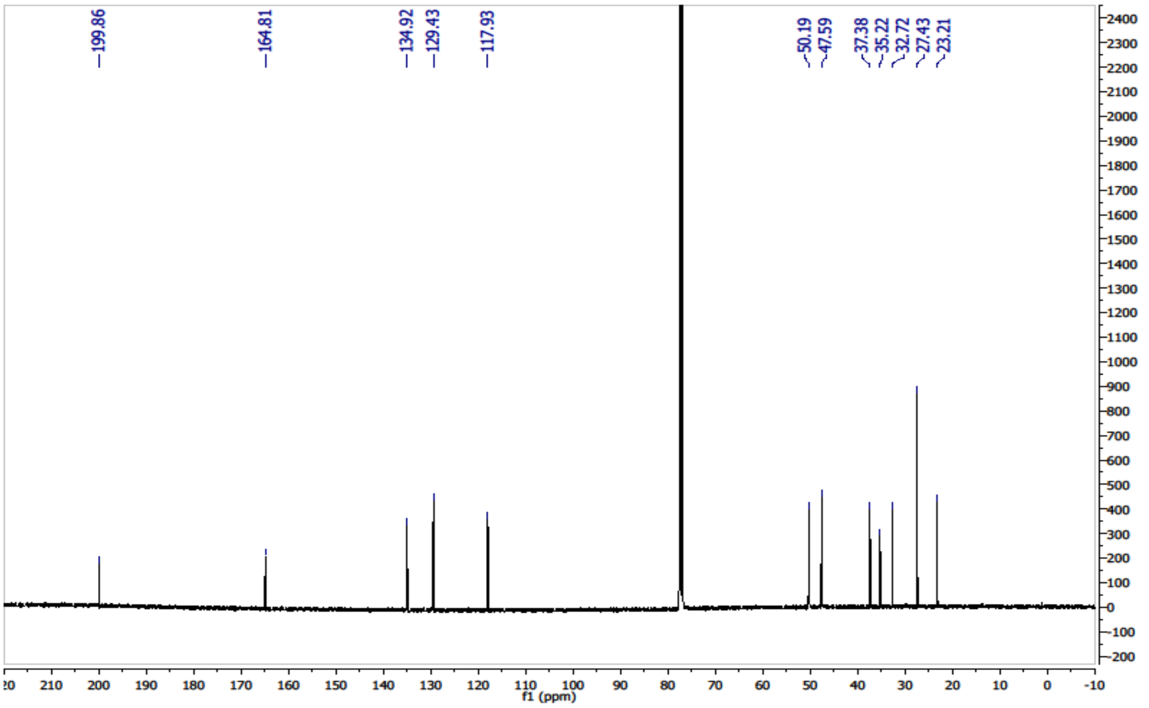
3-(2,2-Dimethylpent-4-en-1-yl)cyclohex-2-en-1-one (9c)



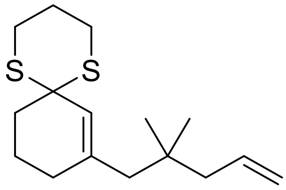
^{1}H NMR (500 MHz, CDCl$_3$, 298 K)



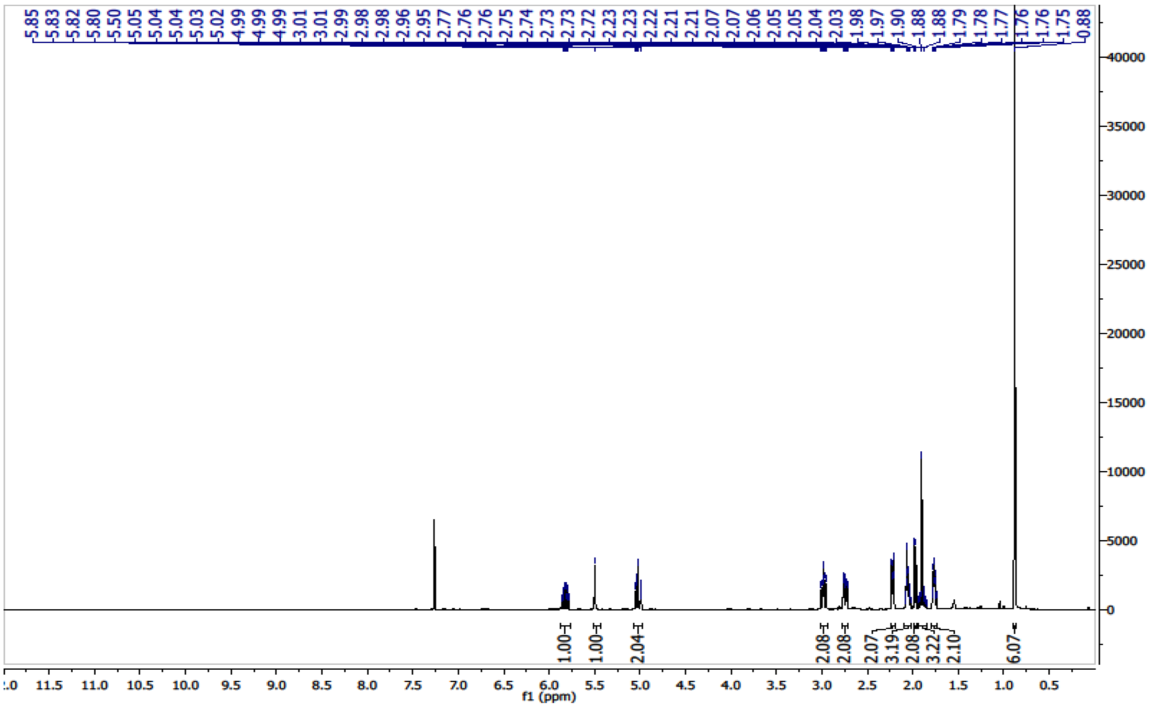
^{13}C NMR (126 MHz, CDCl$_3$, 300 K)



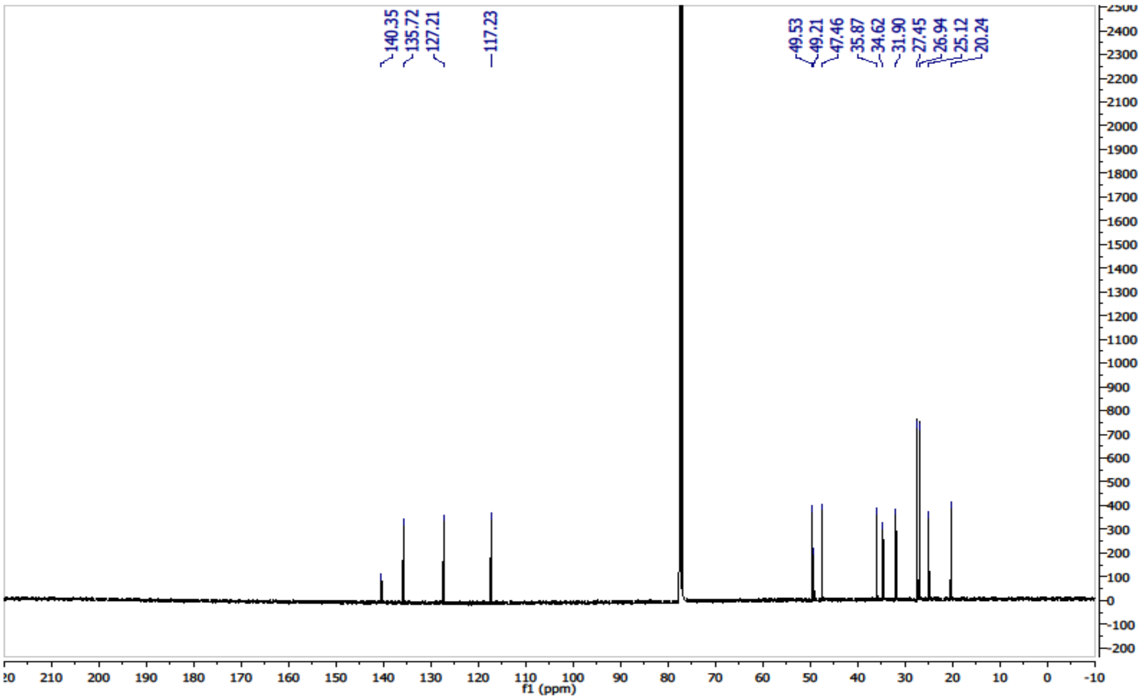
8-(2,2-Dimethylpent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1c)



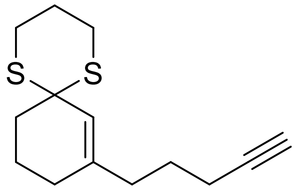
^{1}H NMR (500 MHz, CDCl$_3$, 298 K)



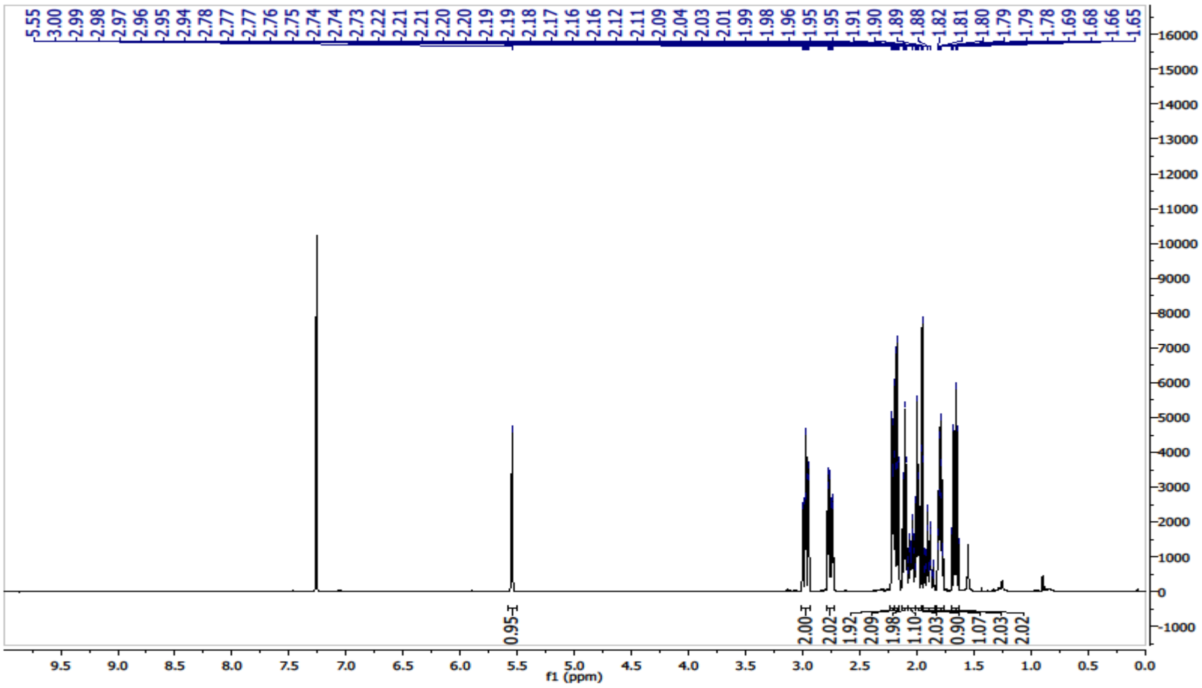
^{13}C NMR (126 MHz, CDCl$_3$, 300 K)



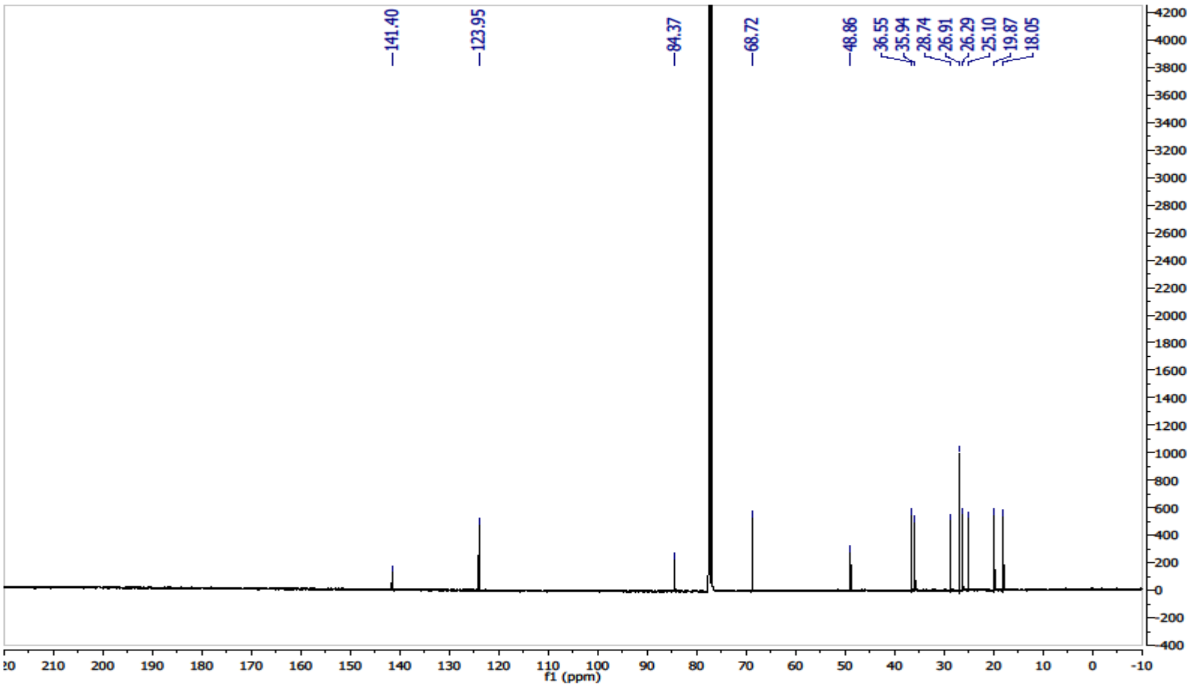
8-(Pent-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (16)



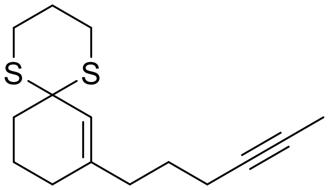
^{1}H NMR (500 MHz, CDCl$_3$, 298 K)



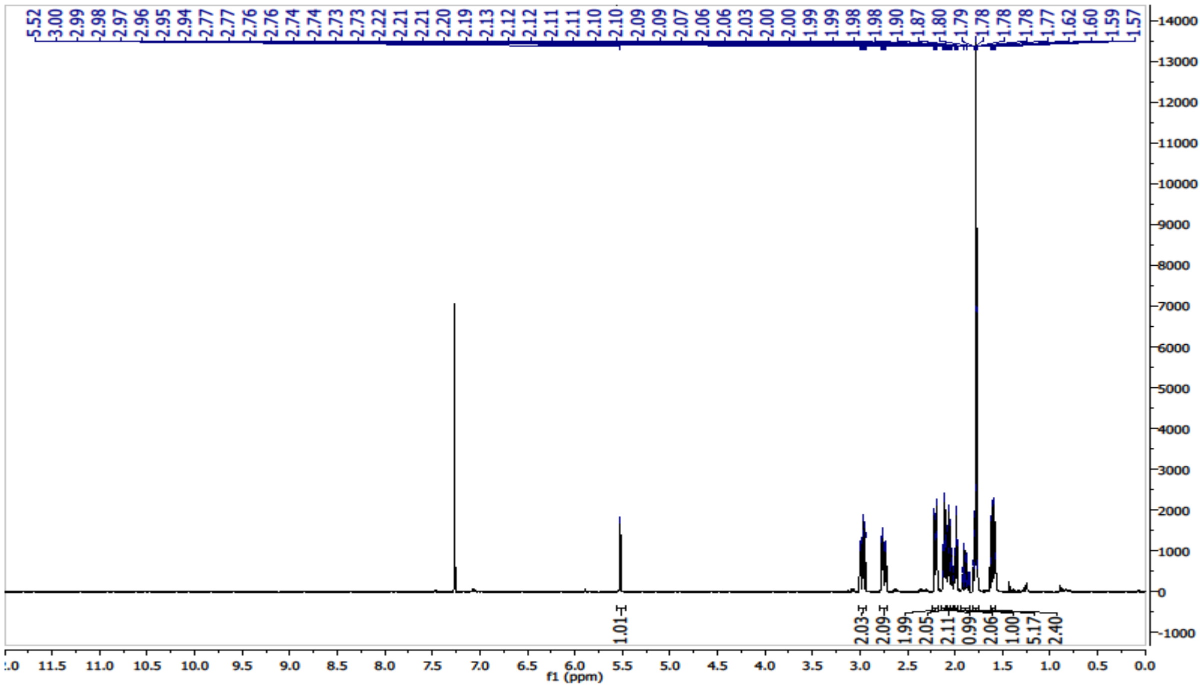
^{13}C NMR (126 MHz, CDCl$_3$, 300 K)



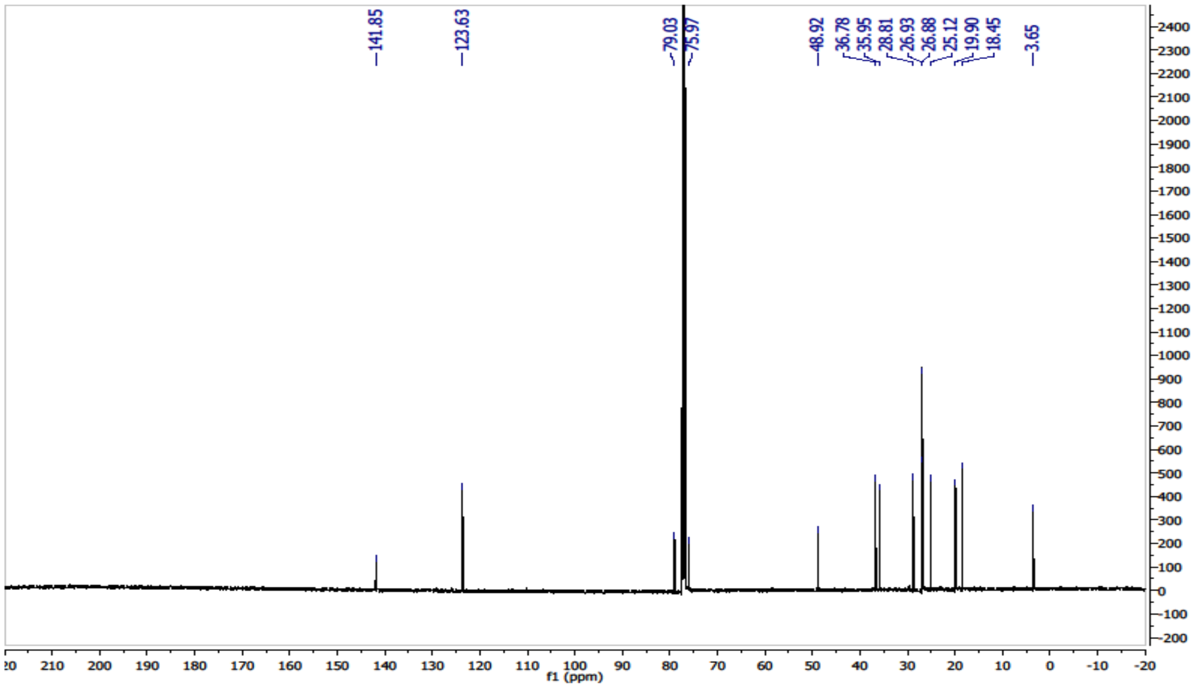
8-(hex-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1d)



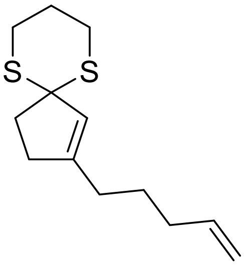
^{1}H NMR (500 MHz, CDCl$_3$, 298 K)



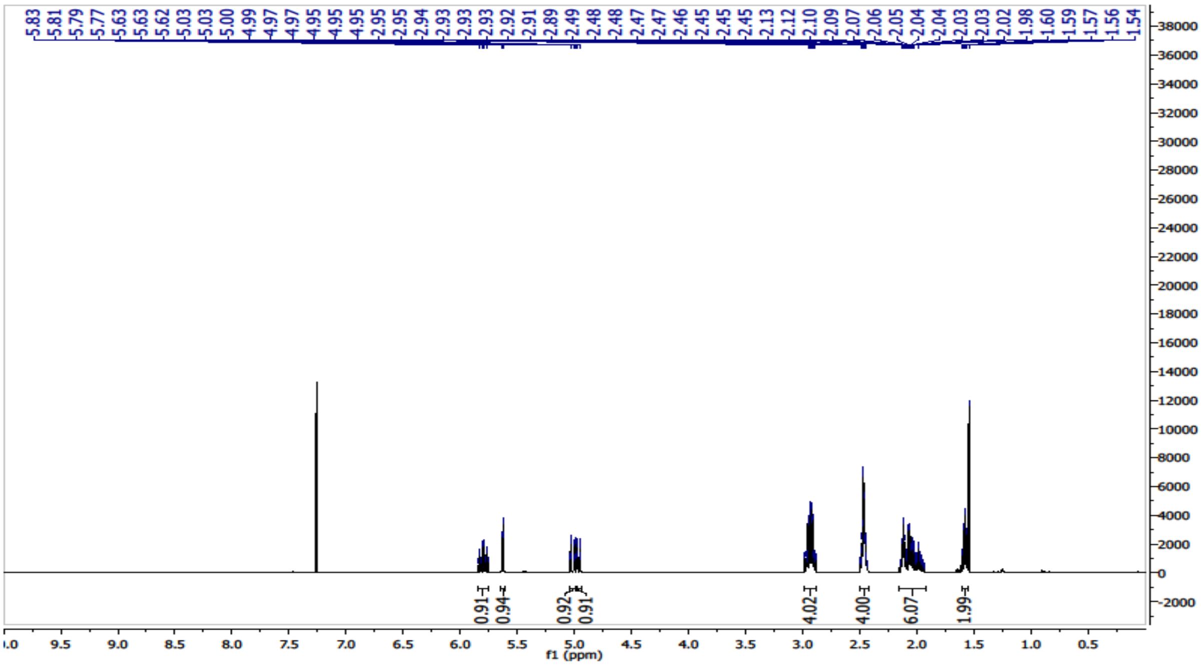
^{13}C NMR (126 MHz, CDCl$_3$, 300 K)



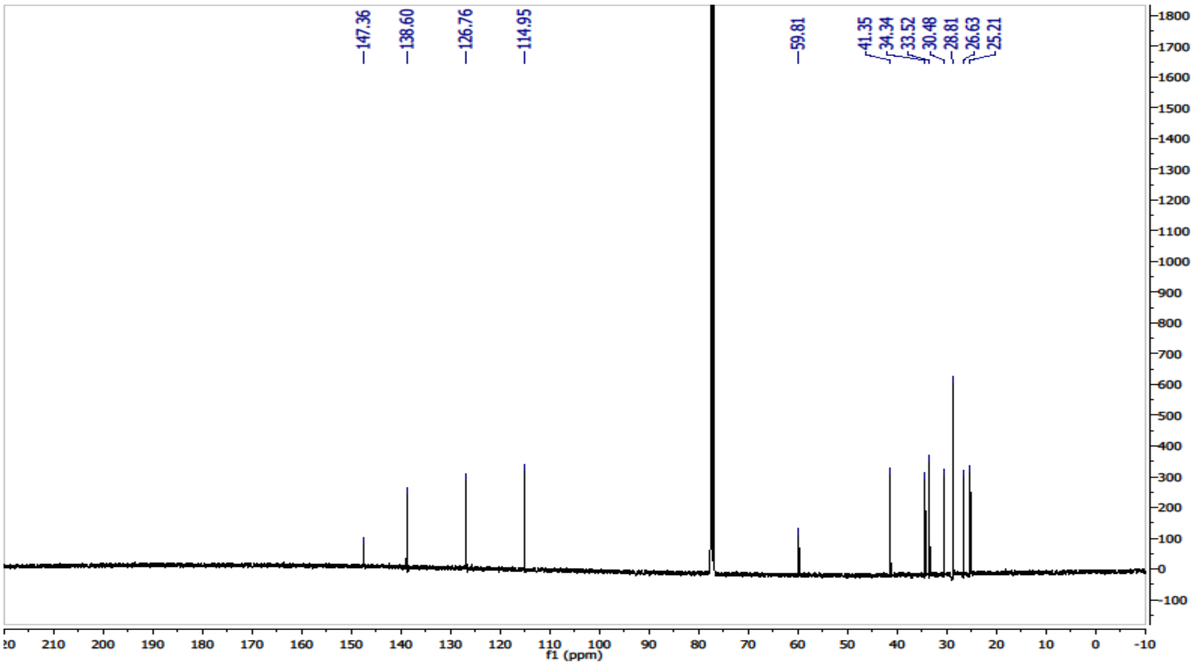
2-(Pent-4-en-1-yl)-6,10-dithiaspiro[4.5]dec-1-ene (1e)



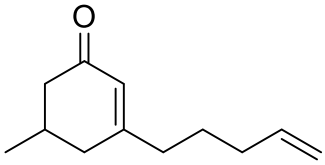
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



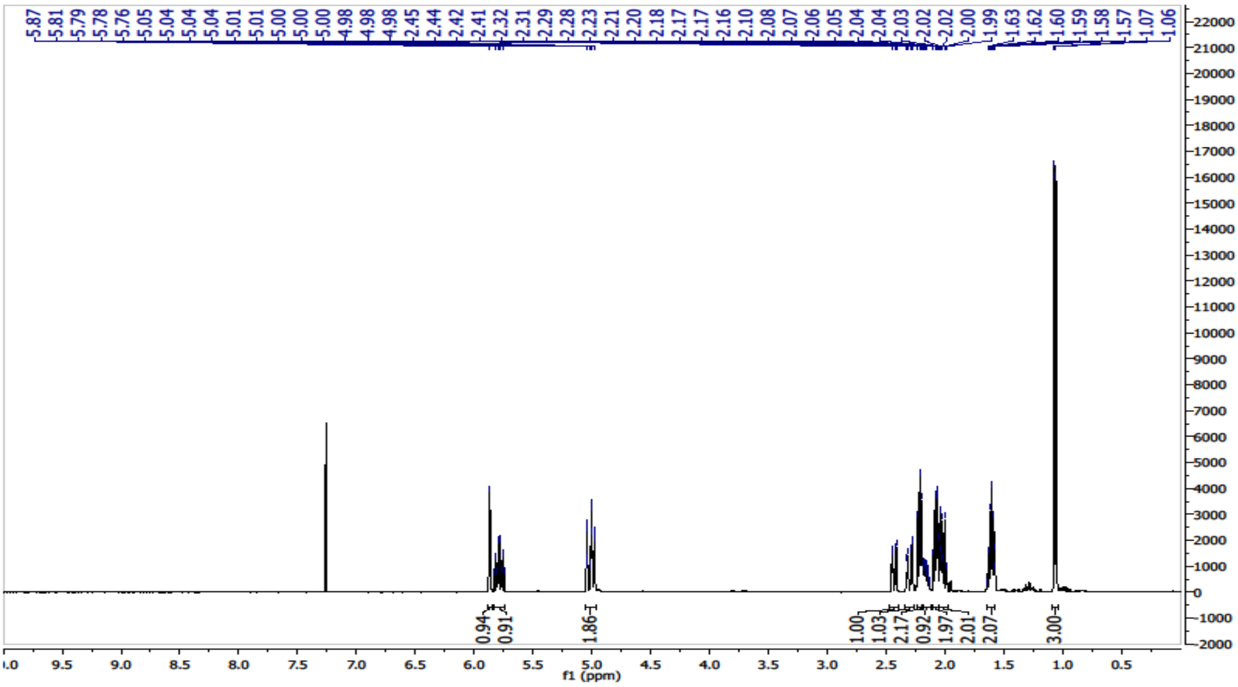
^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



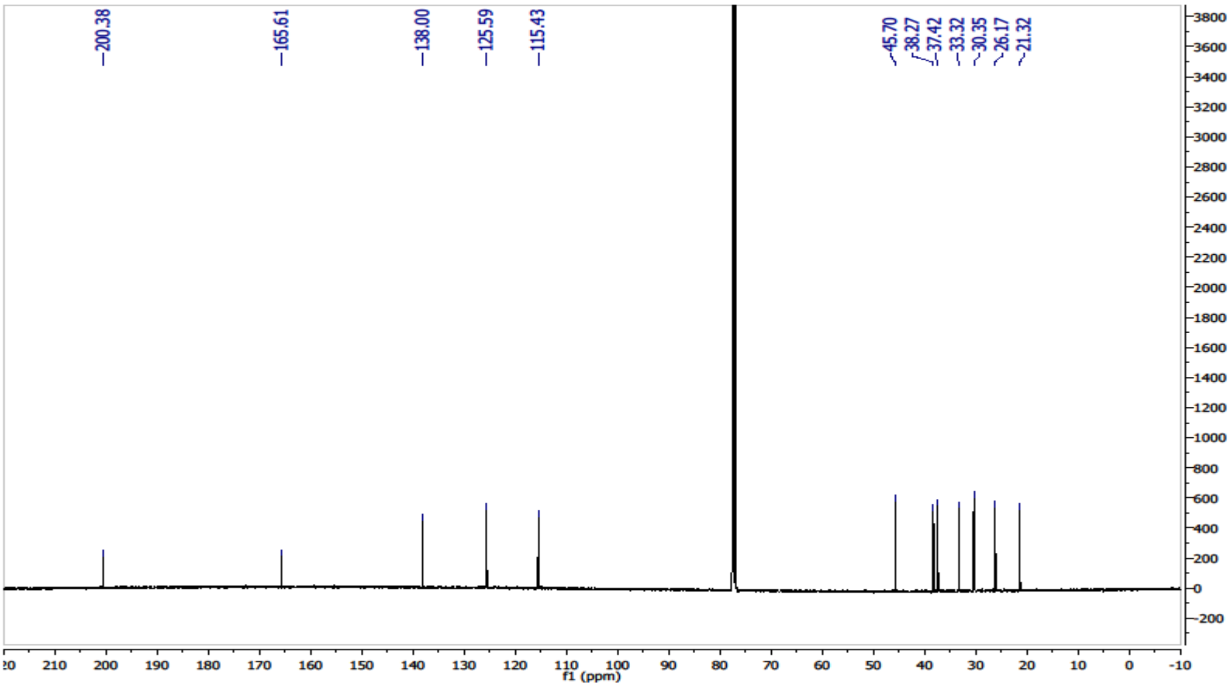
5-Methyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (9f)



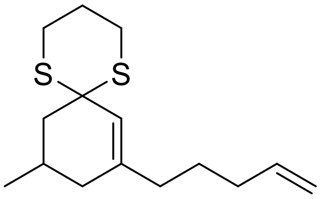
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



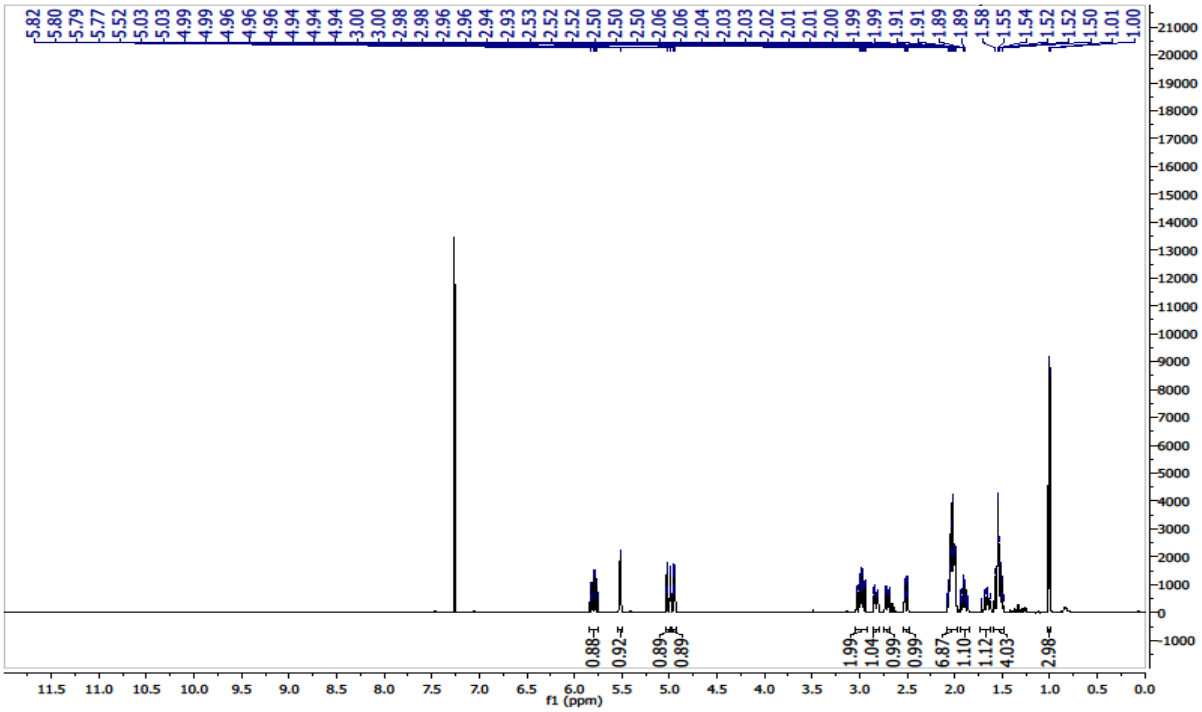
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



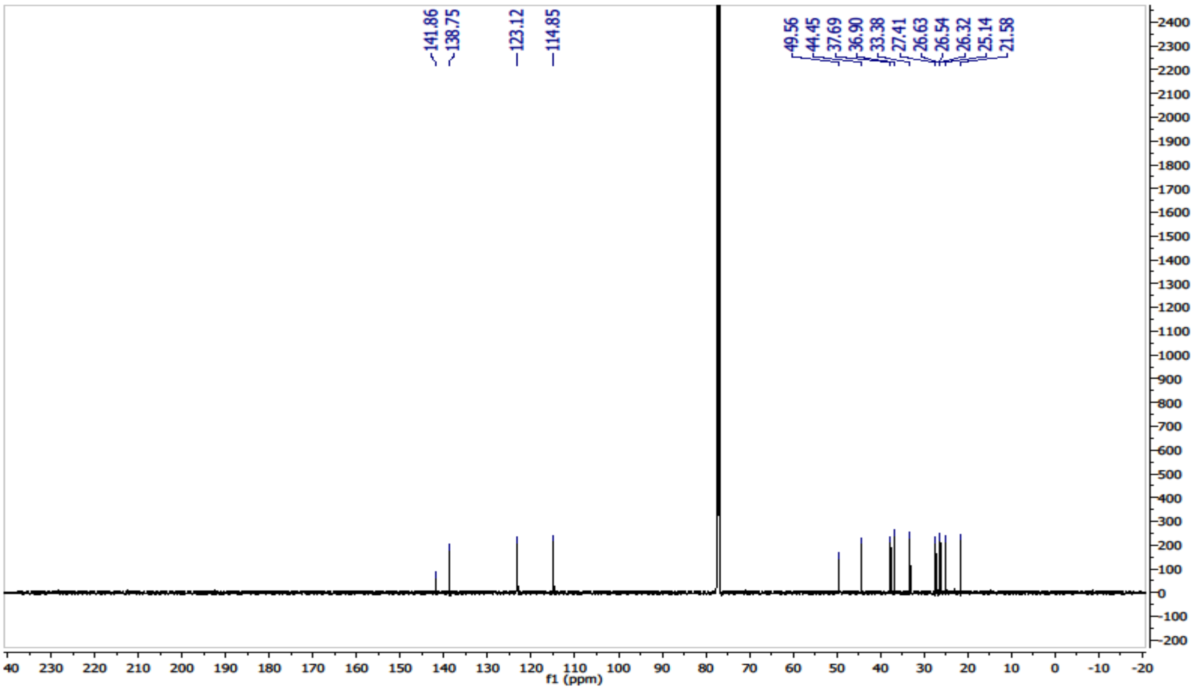
10-Methyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1f)



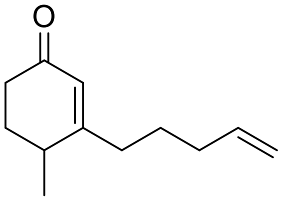
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



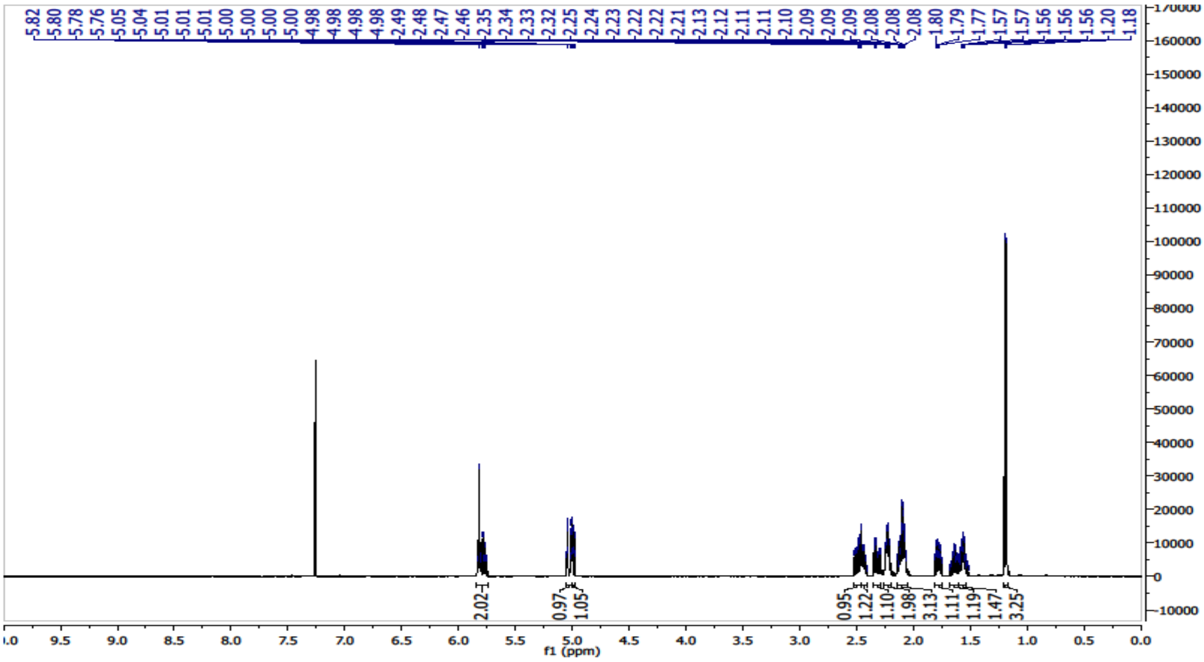
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



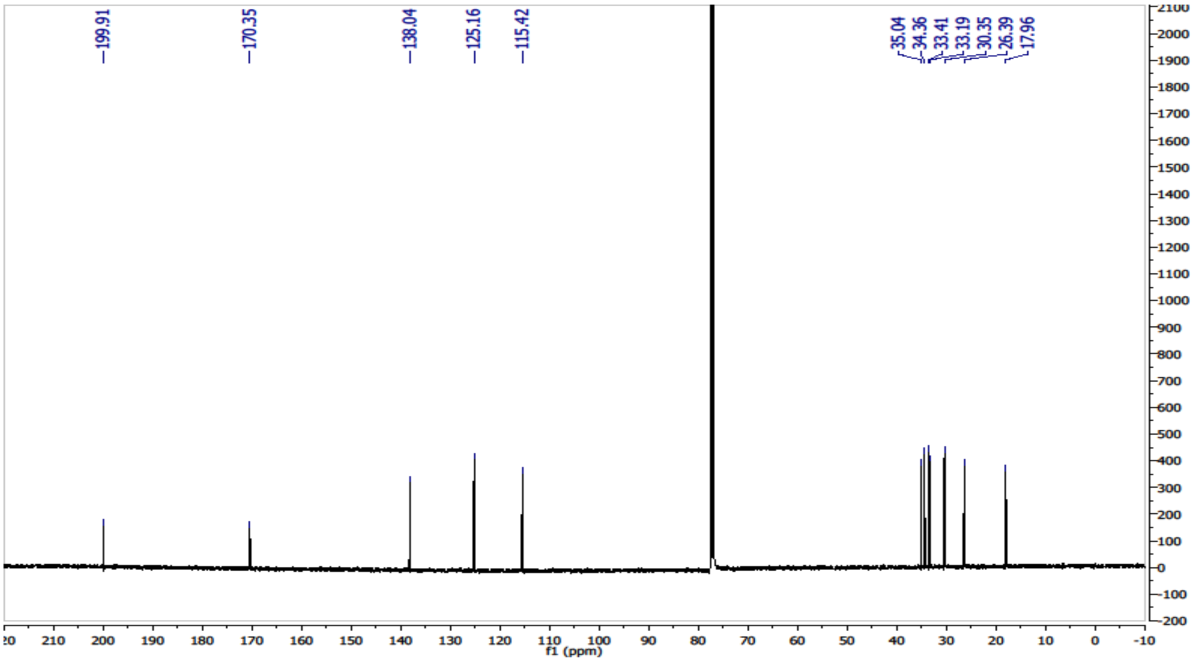
4-Methyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (9g)



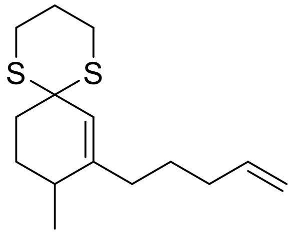
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



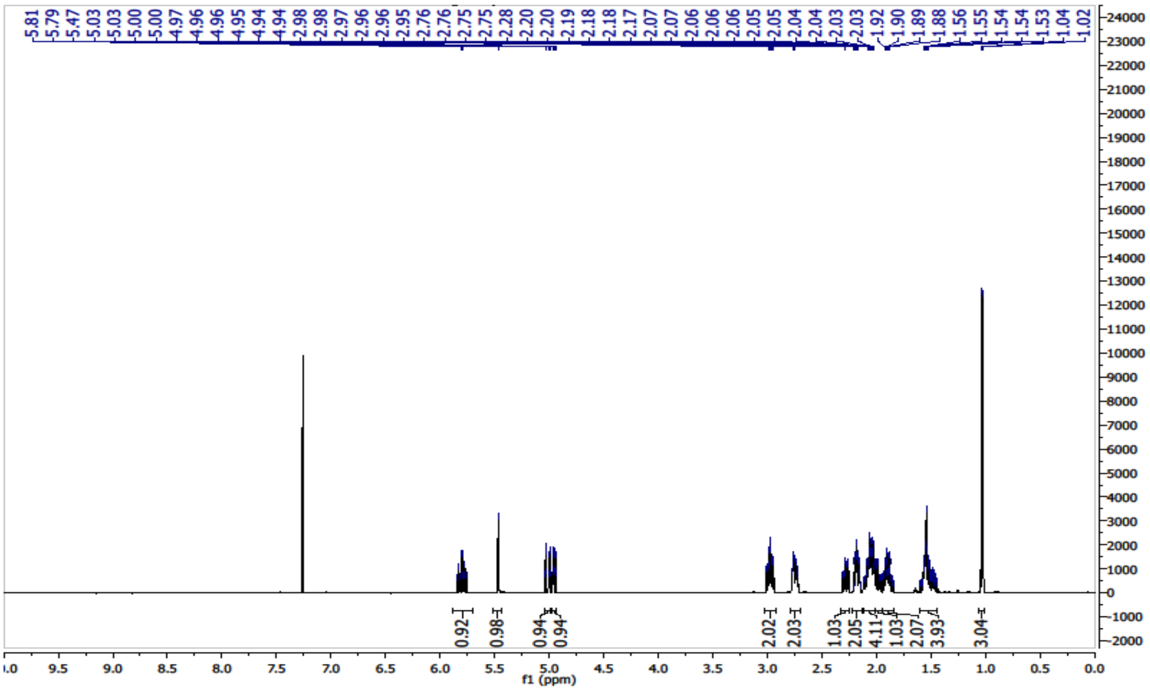
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



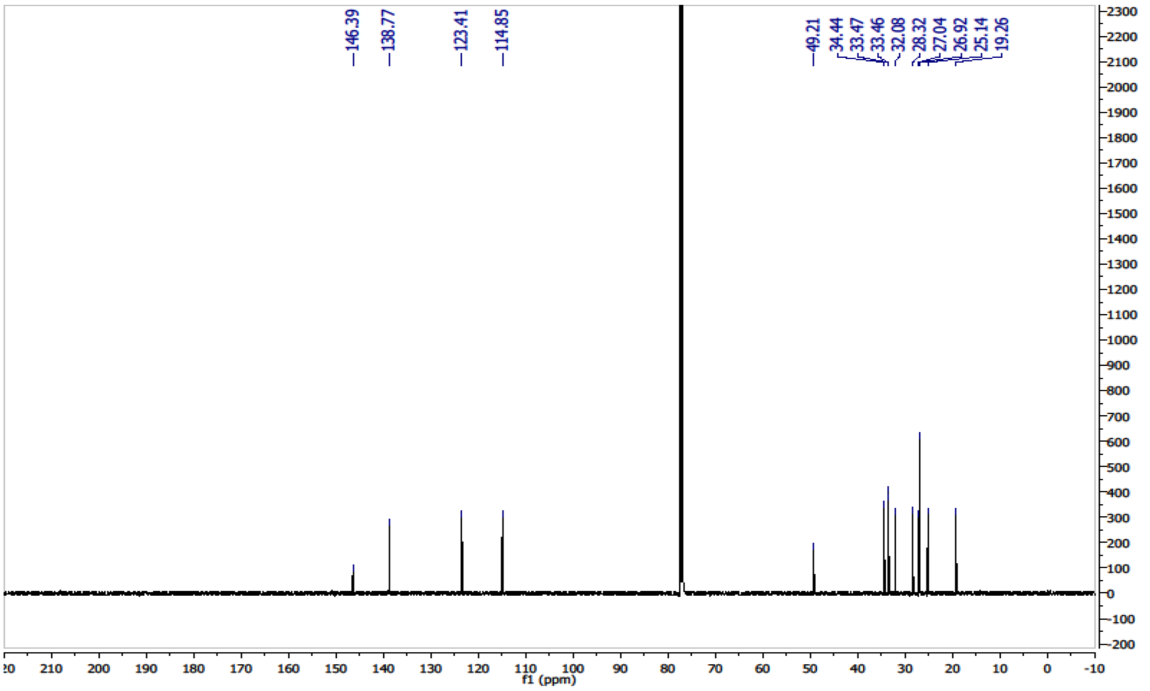
9-Methyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1g)



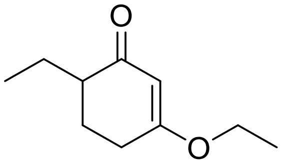
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



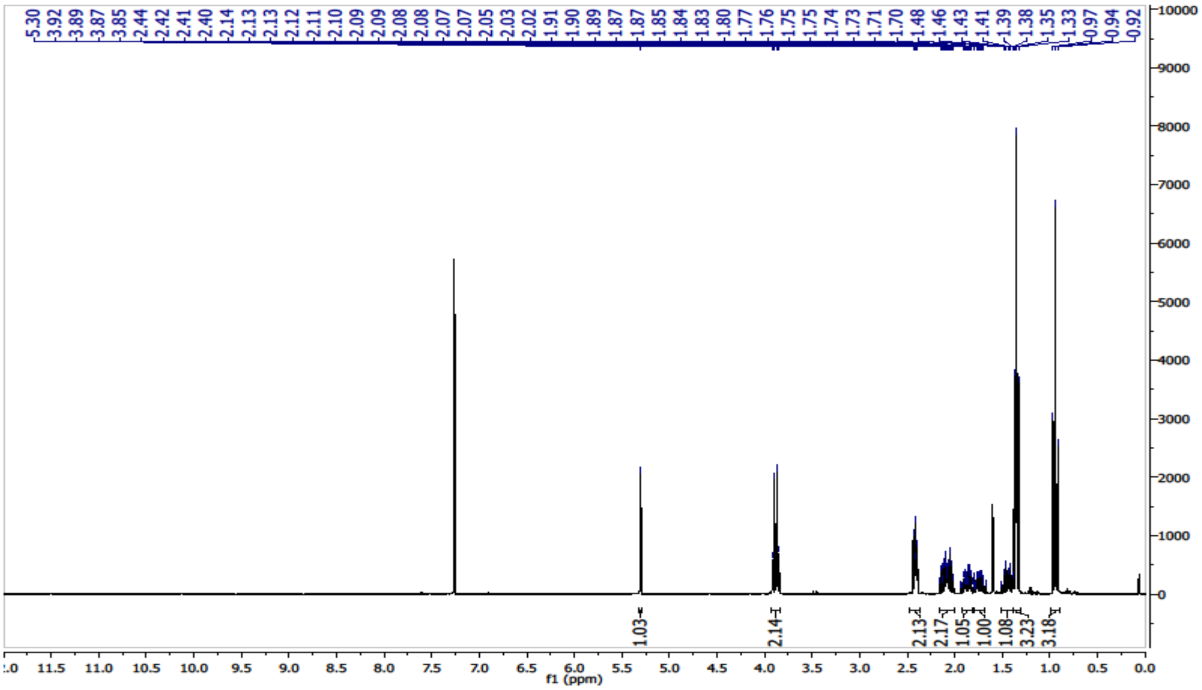
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



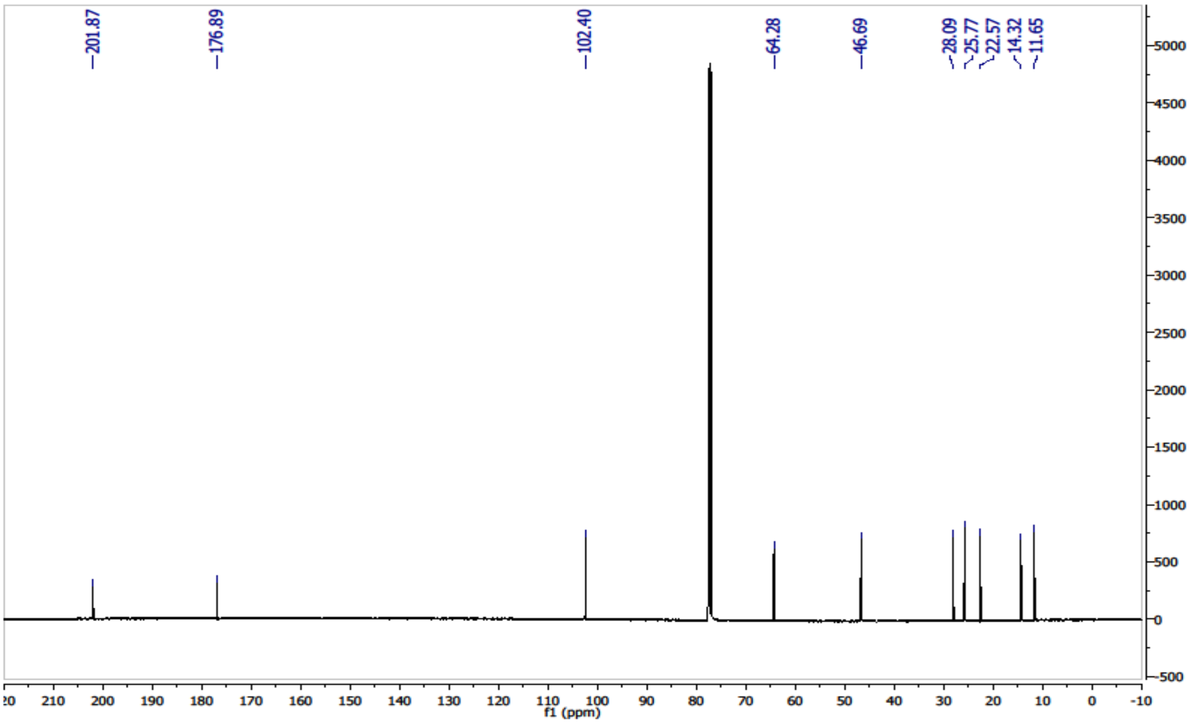
3-Ethoxy-6-ethylcyclohex-2-en-1-one (20)



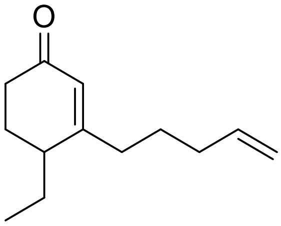
^{1}H-NMR (500 MHz, CDCl$_3$, 298 K)



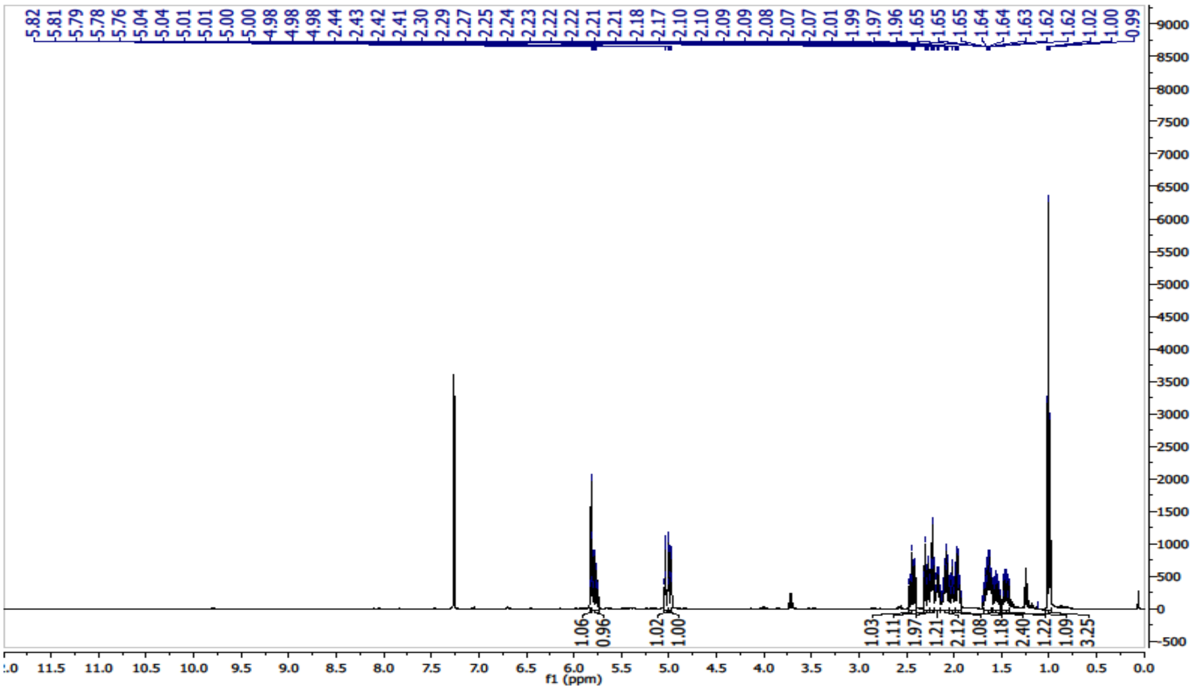
^{13}C-NMR (126 MHz, CDCl$_3$, 300 K)



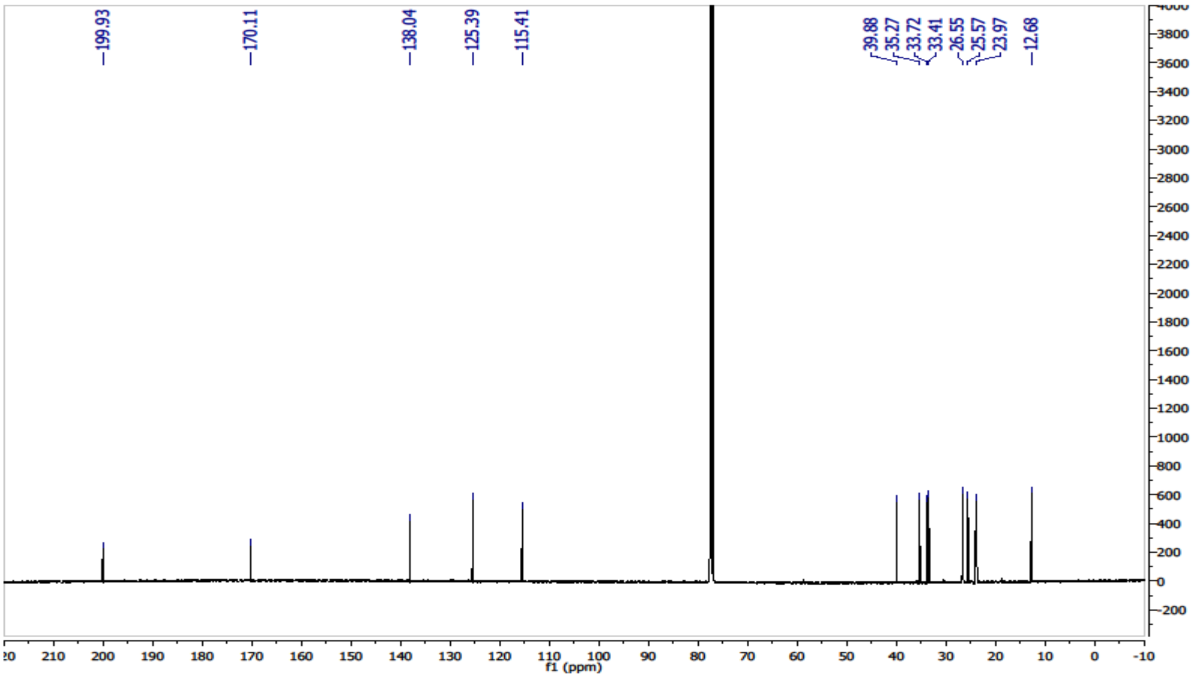
4-Ethyl-3-(pent-4-en-1-yl)cyclohex-2-en-1-one (9h)



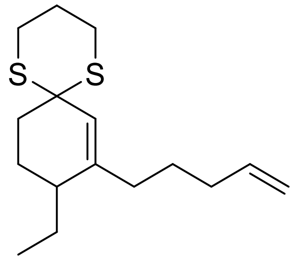
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



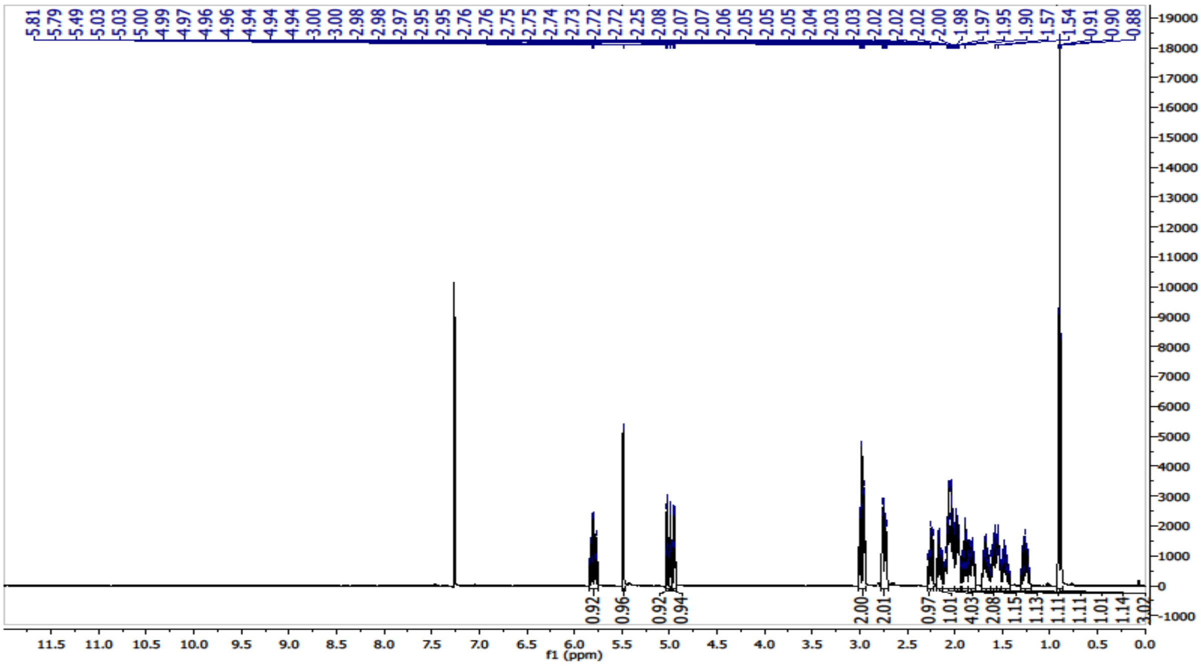
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



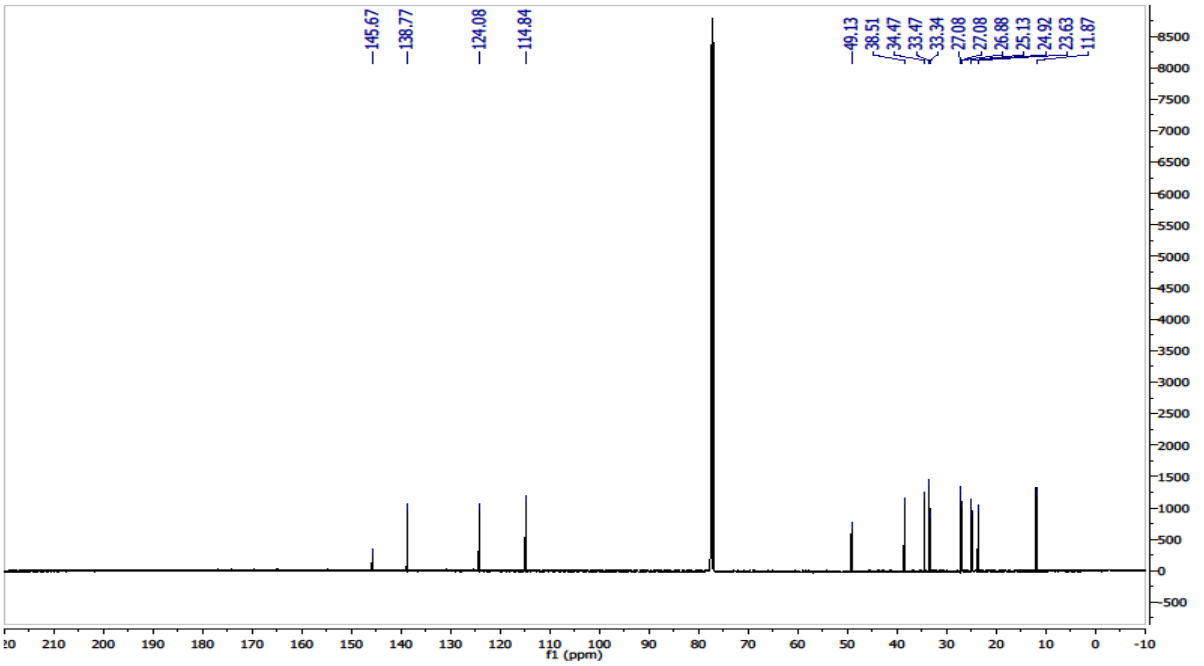
9-Ethyl-8-(pent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1h)



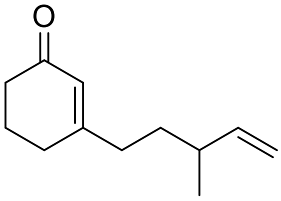
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



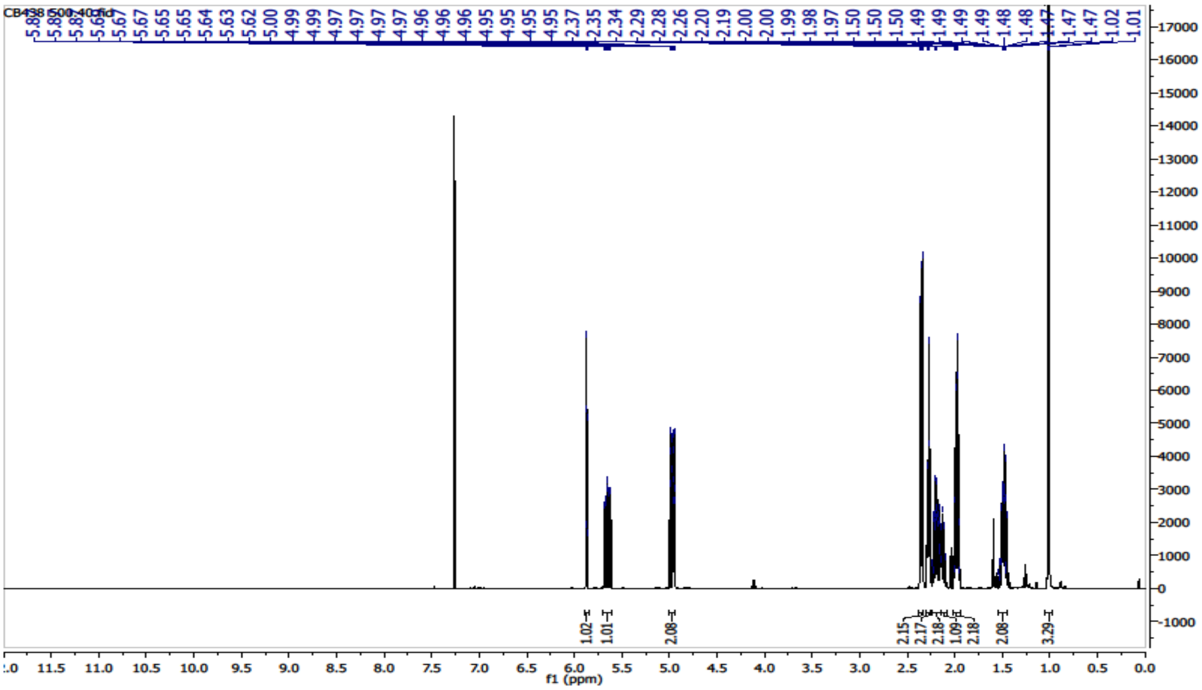
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



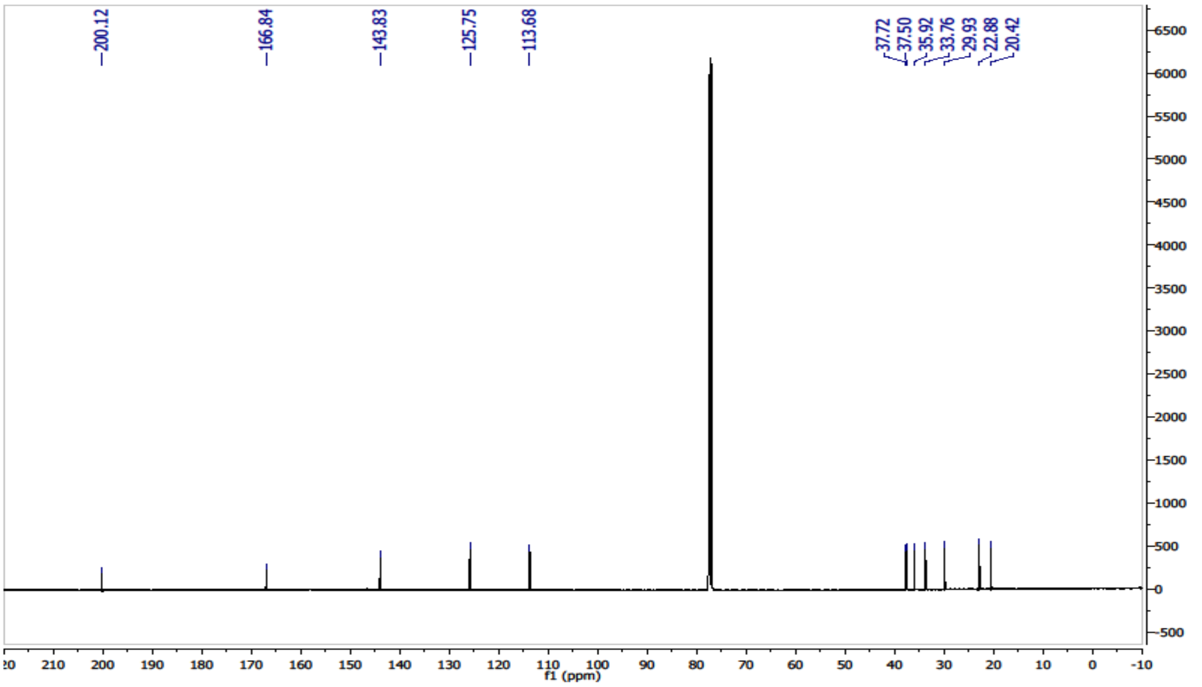
3-(3-Methylpent-4-en-1-yl)cyclohex-2-en-1-one (9i)



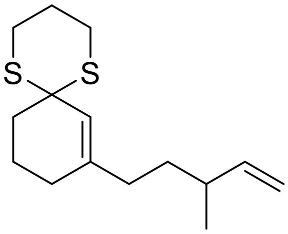
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



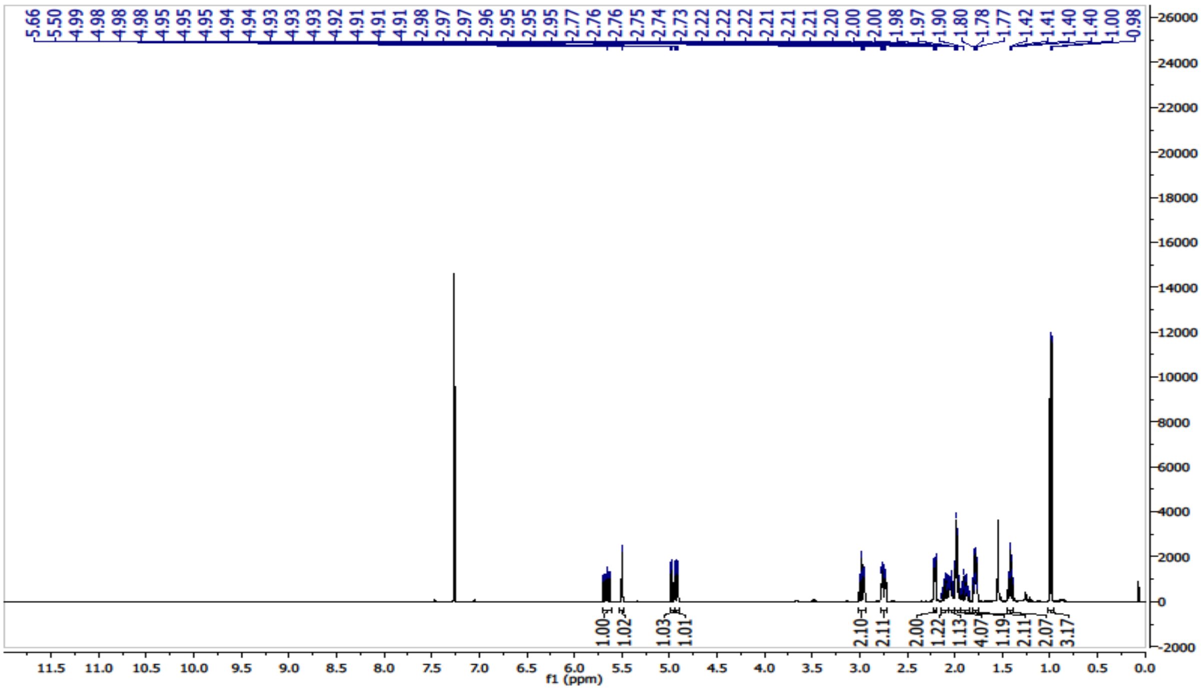
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



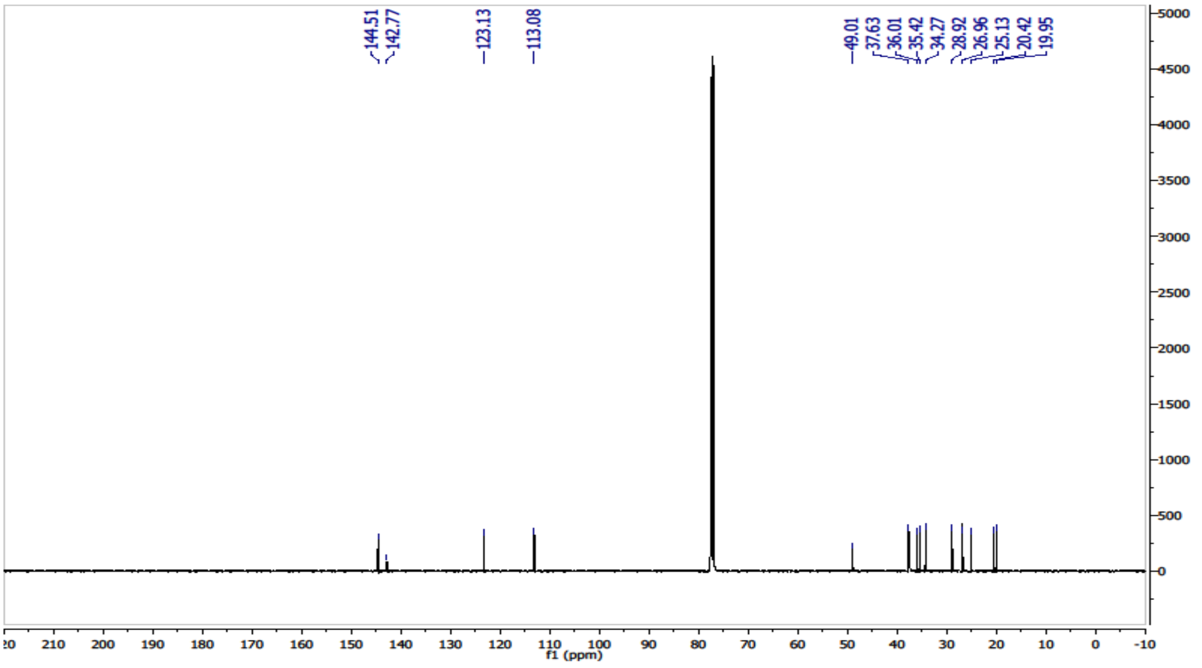
8-(3-Methylpent-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1i)



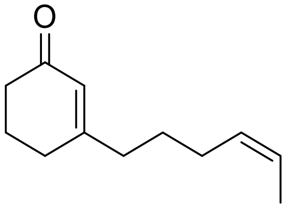
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



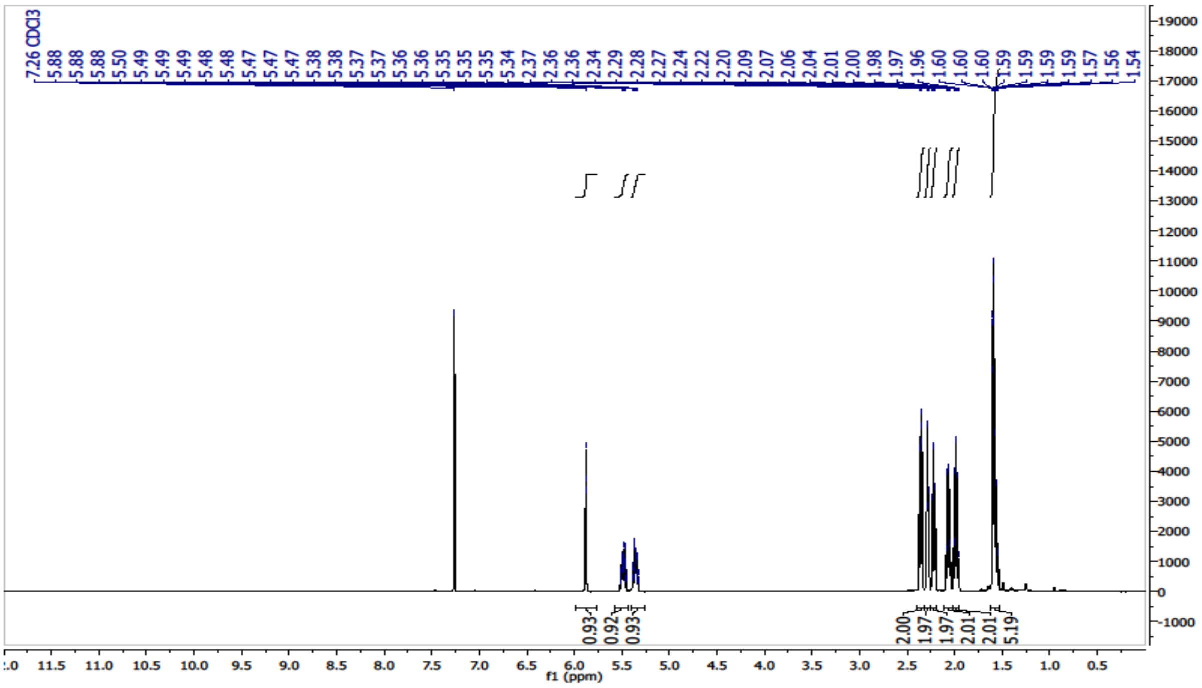
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



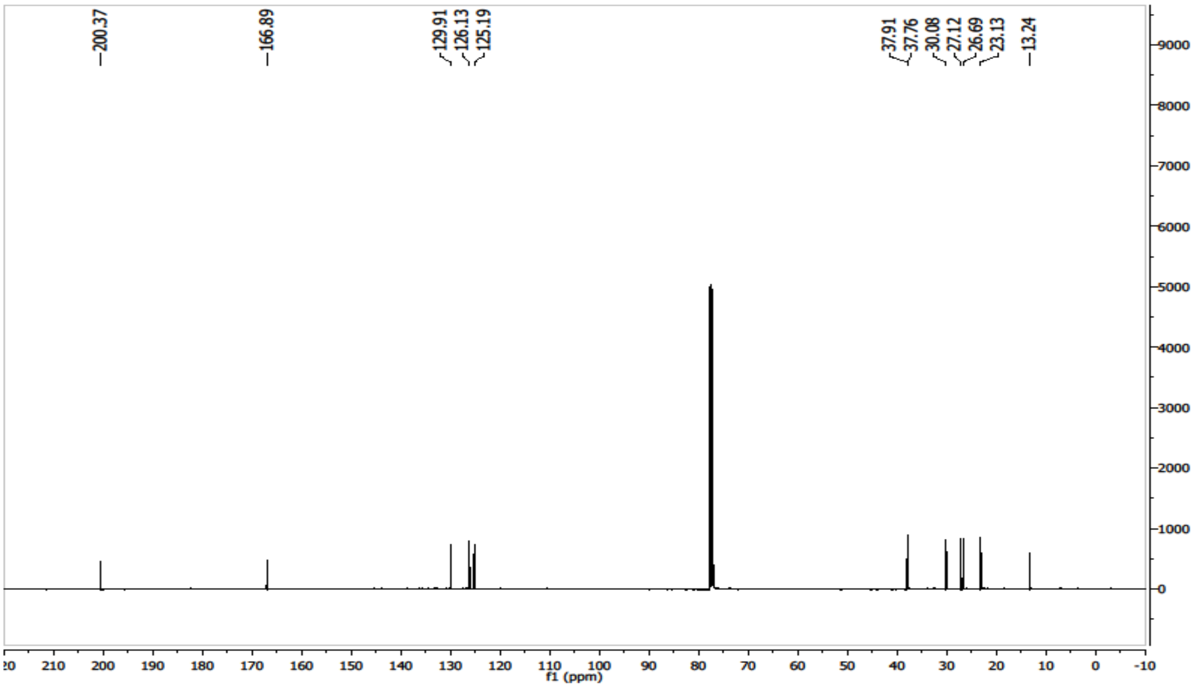
(*Z*)-3-(Hex-4-en-1-yl)cyclohex-2-en-1-one (9j)



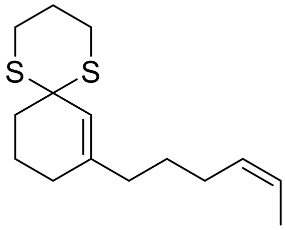
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



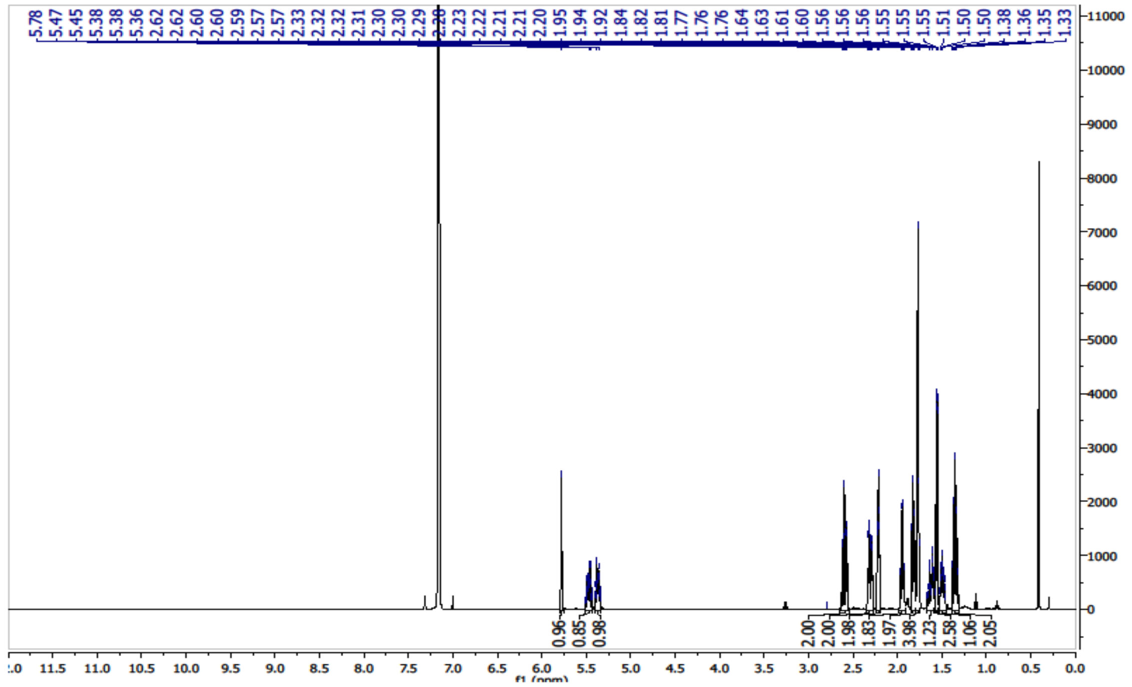
^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



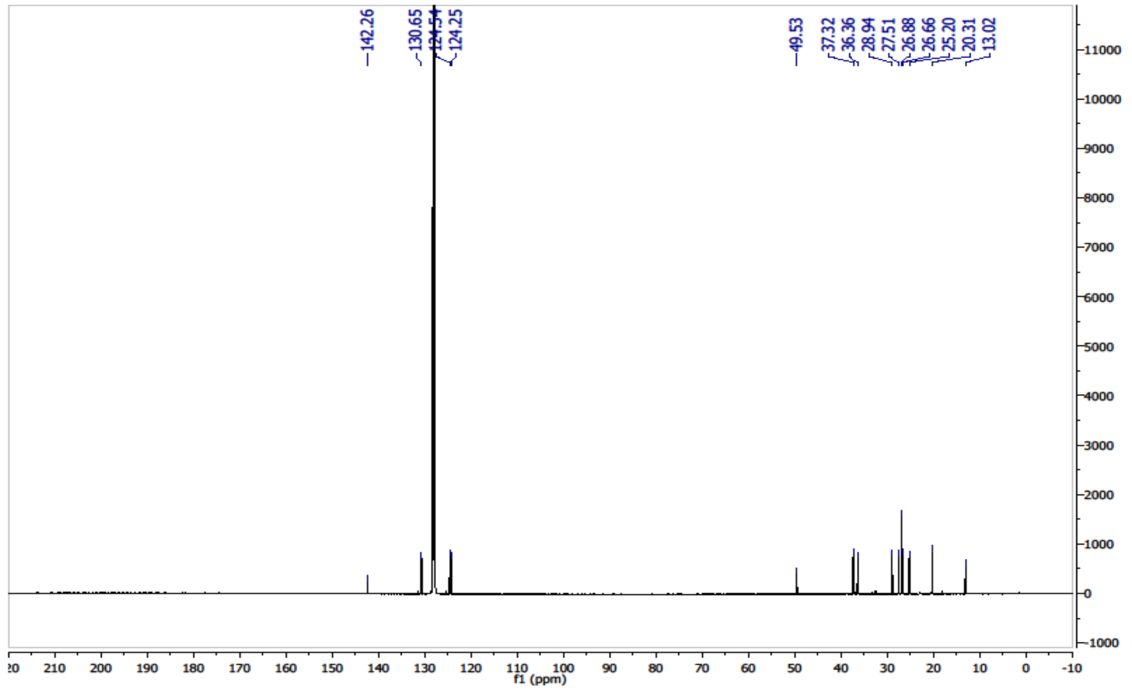
(*Z*)-8-(Hex-4-en-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (1j)



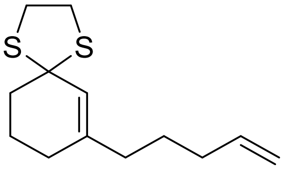
^{1}**H NMR** (500 MHz, CDCl$_3$, 298 K)



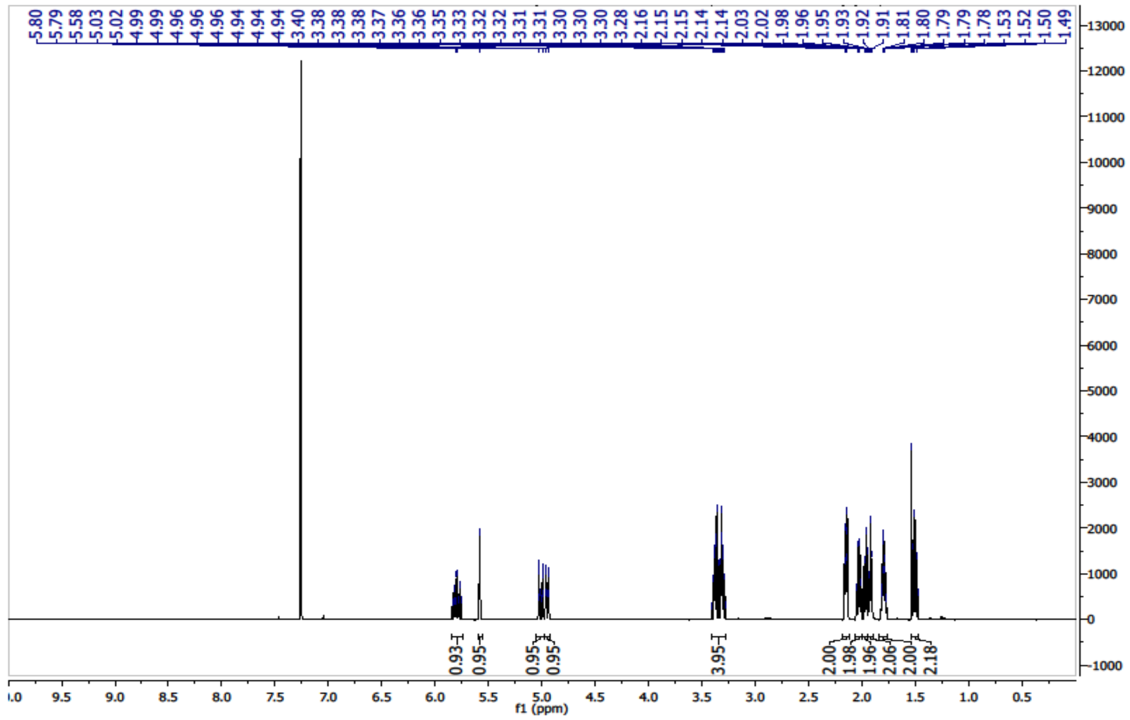
^{13}**C NMR** (126 MHz, CDCl$_3$, 300 K)



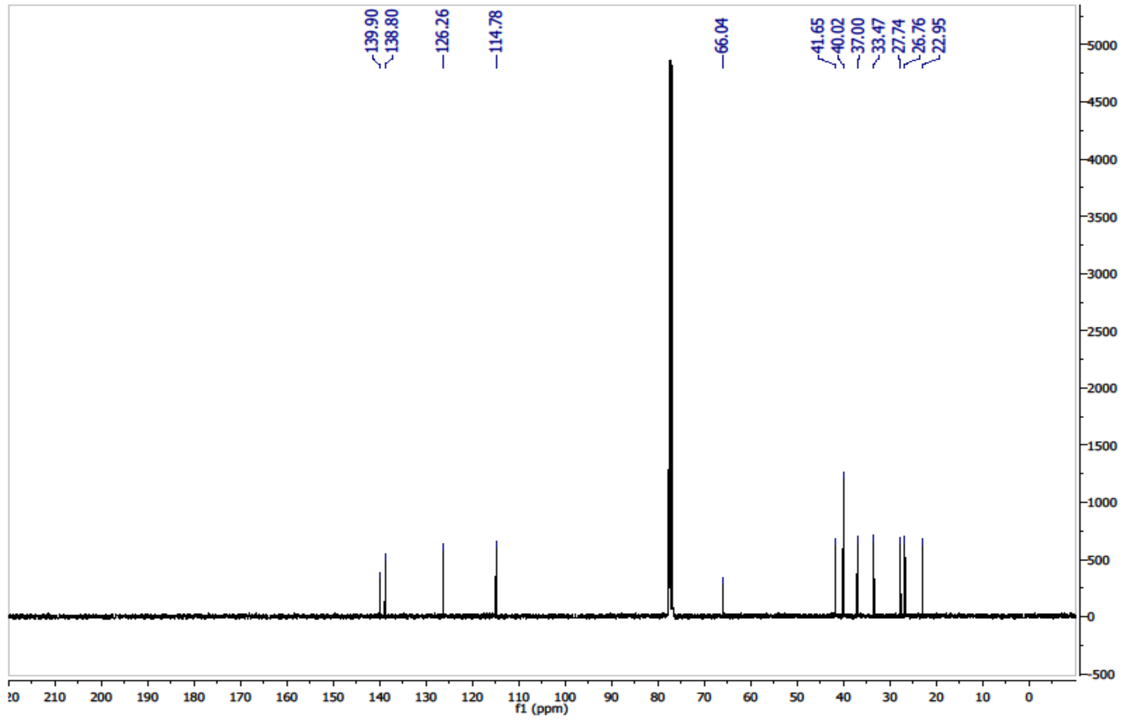
7-(Pent-4-en-1-yl)-1,4-dithiaspiro[4.5]dec-6-ene (25)



^{1}H-NMR (500 MHz, CDCl$_3$, 298 K)

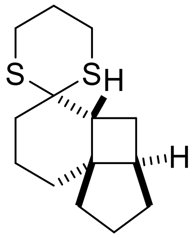


^{13}C-NMR (101 MHz, CDCl$_3$, 300 K)

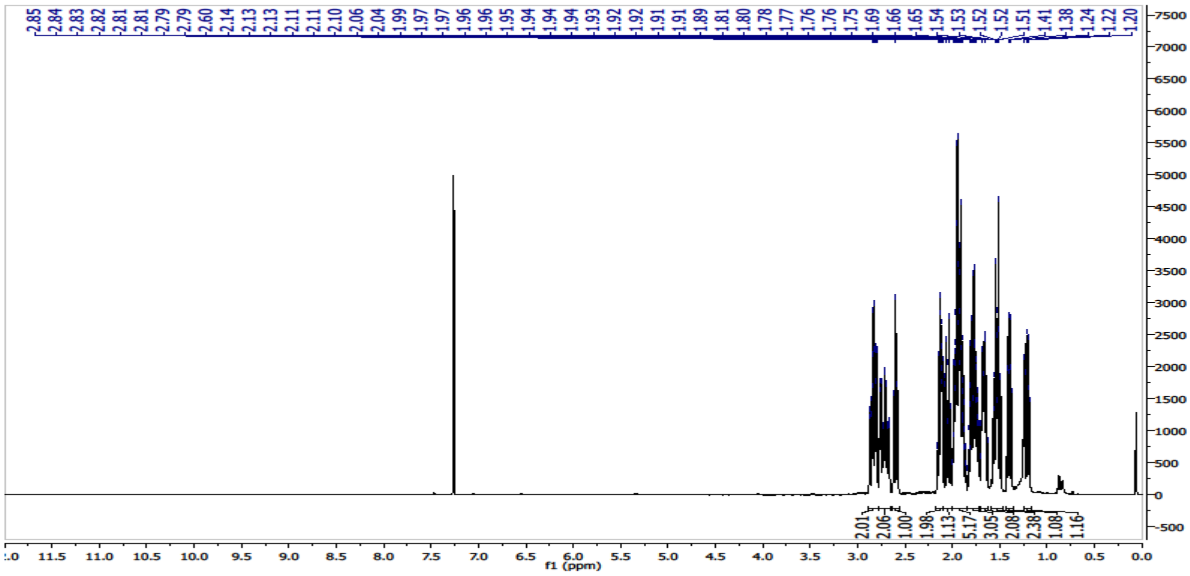


10.2 Cyclobutanes

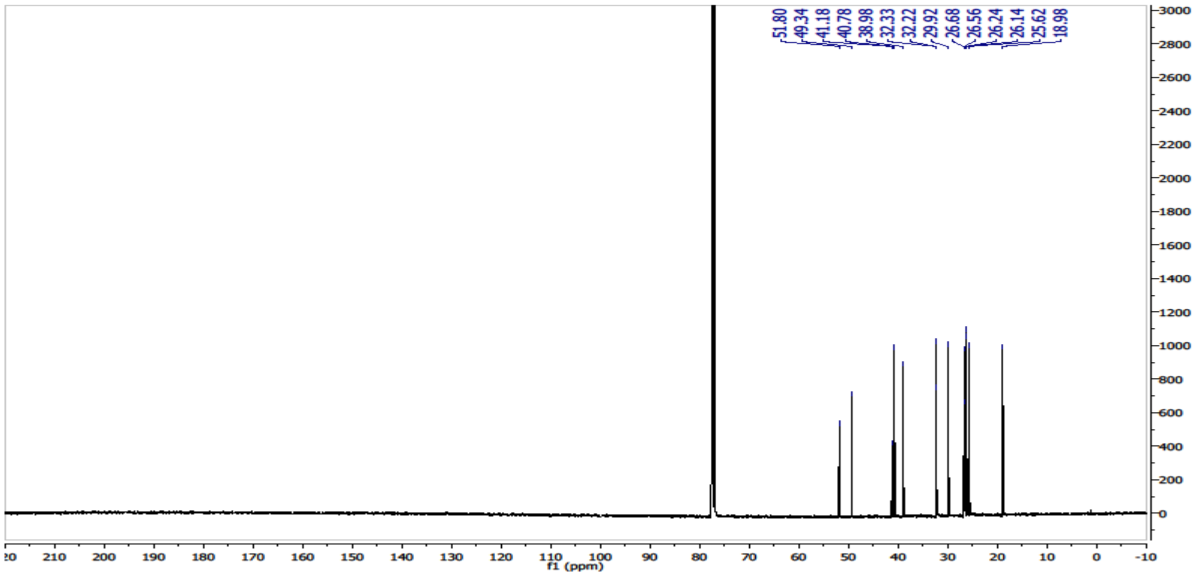
Octahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2a)



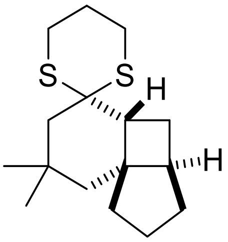
^{1}H NMR (500 MHz, CDCl$_3$, 298 K)



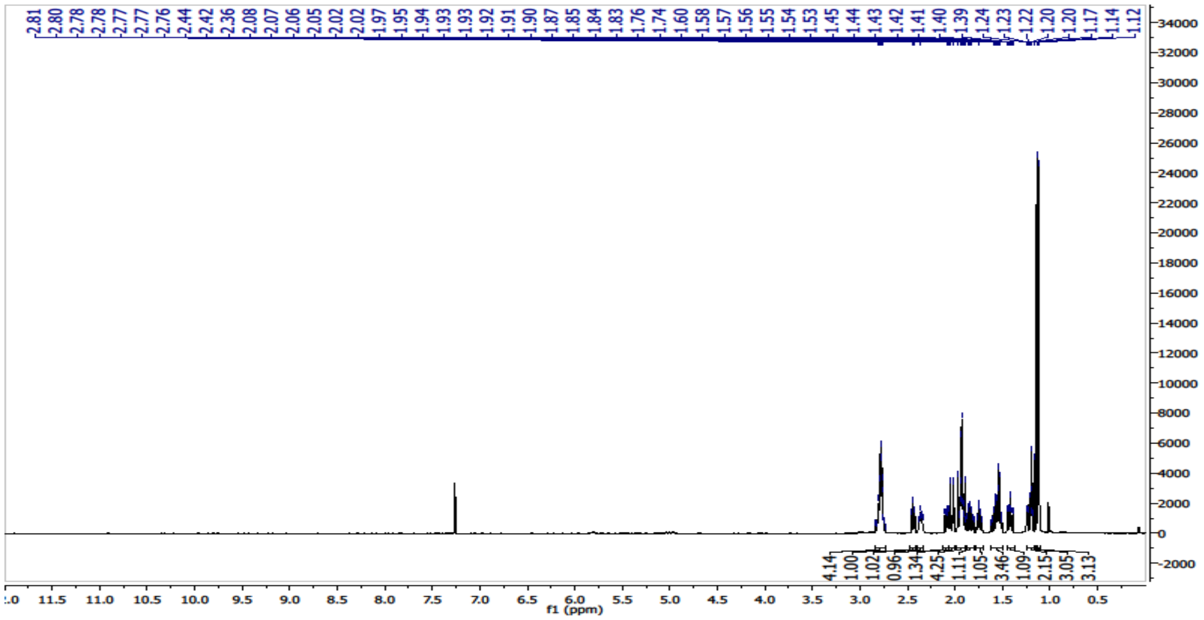
^{13}C NMR (126 MHz, CDCl$_3$, 300 K)



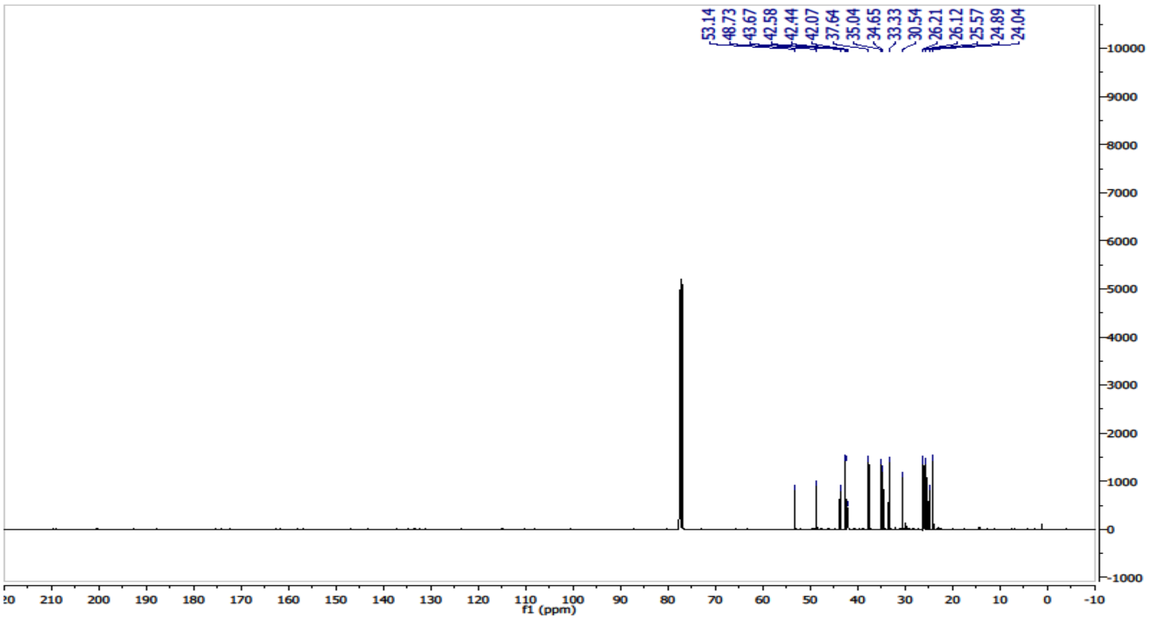
7,7-Dimethyloctahydro-6H-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2b)



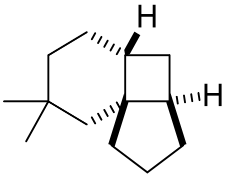
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



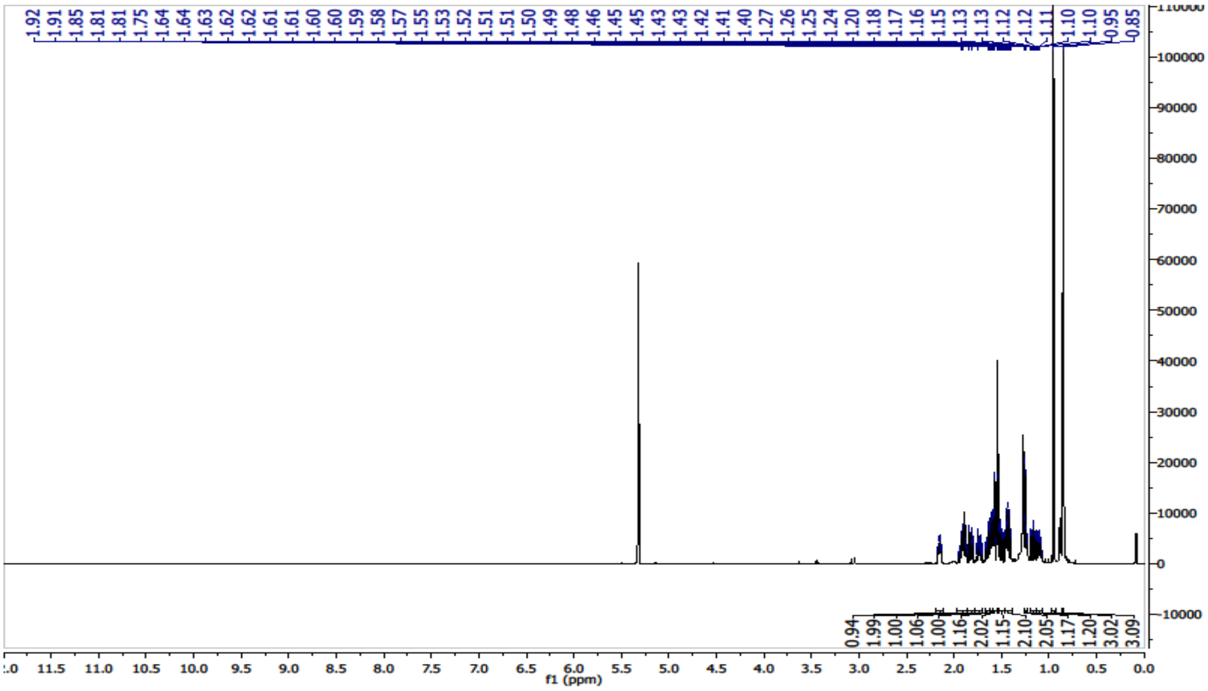
^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



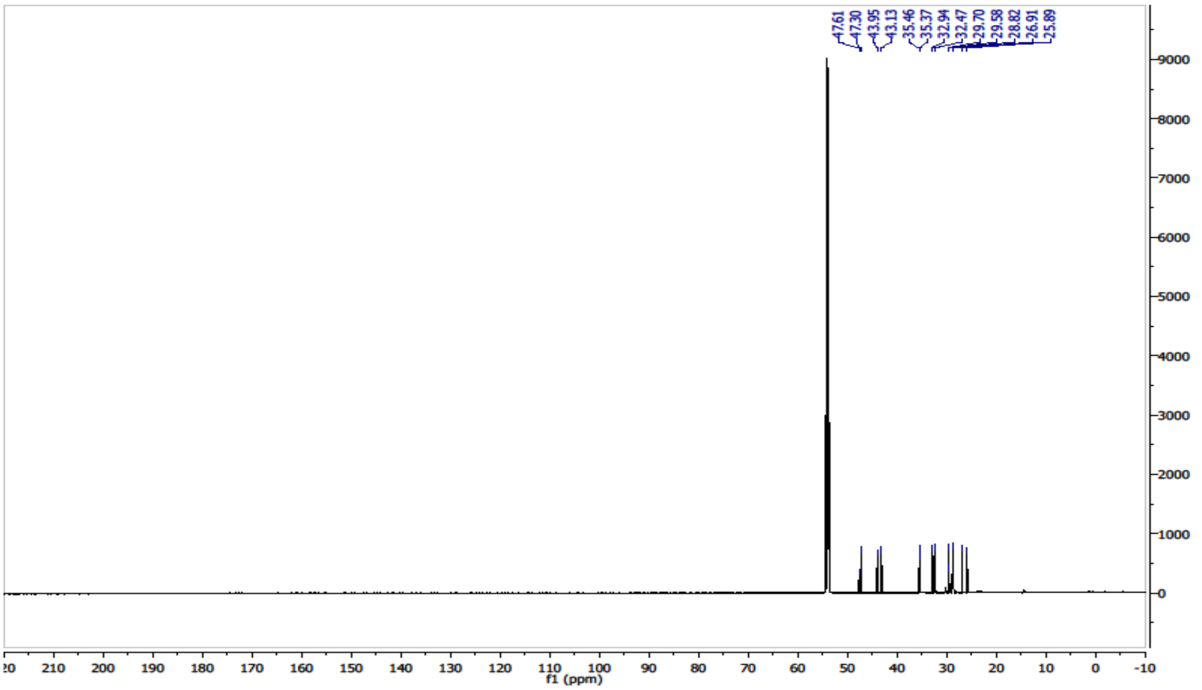
7,7-Dimethyldecahydrocyclopenta[1,4]cyclobuta[1,2]benzene (4)



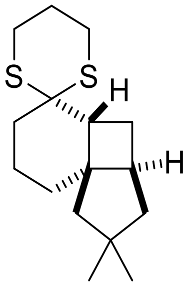
^{1}H NMR (500 MHz, CD_2Cl_2, 298 K)



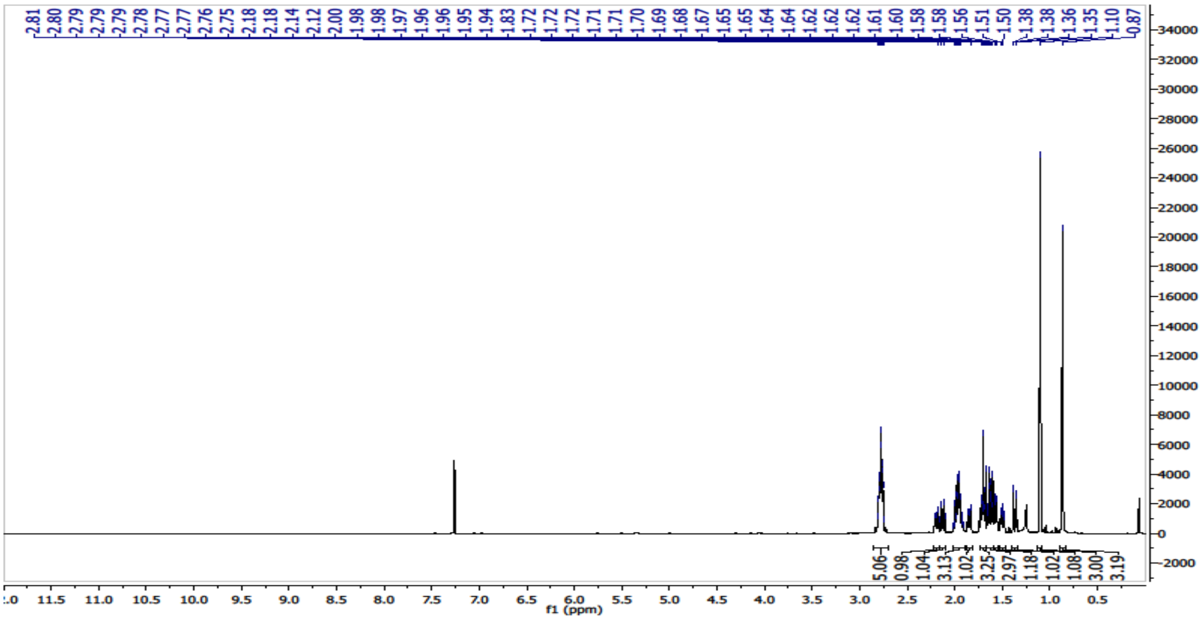
^{13}C NMR (126 MHz, CD_2Cl_2, 300 K)



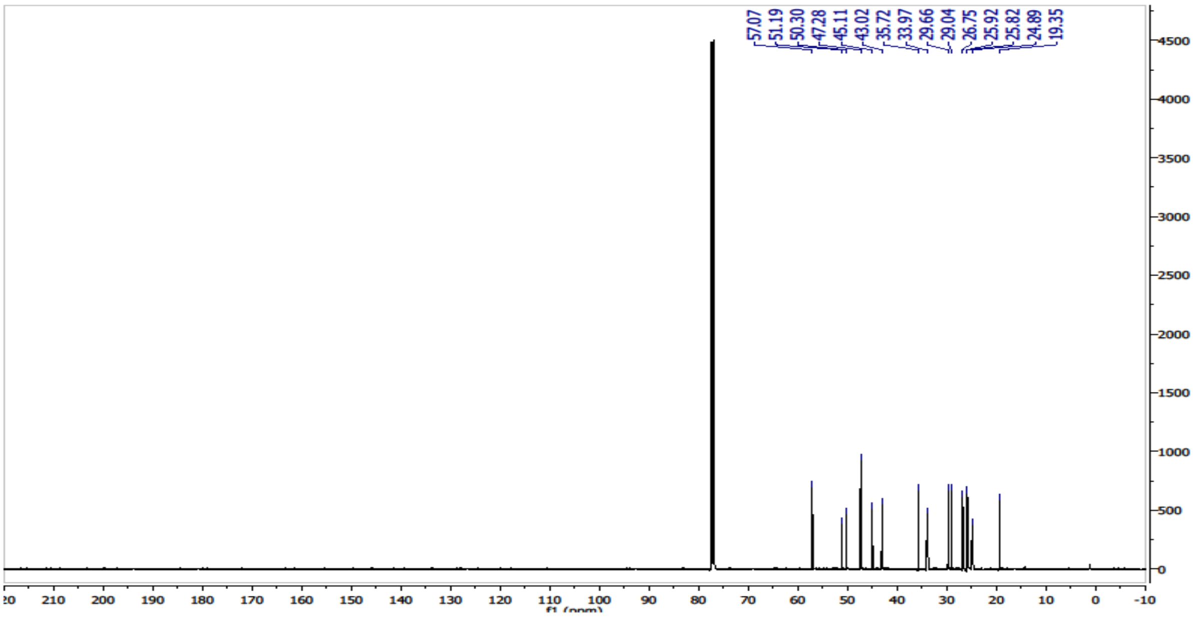
2,2-Dimethyloctahydro-6*H*-spiro[cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane] (2c)



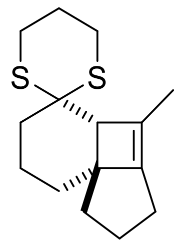
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



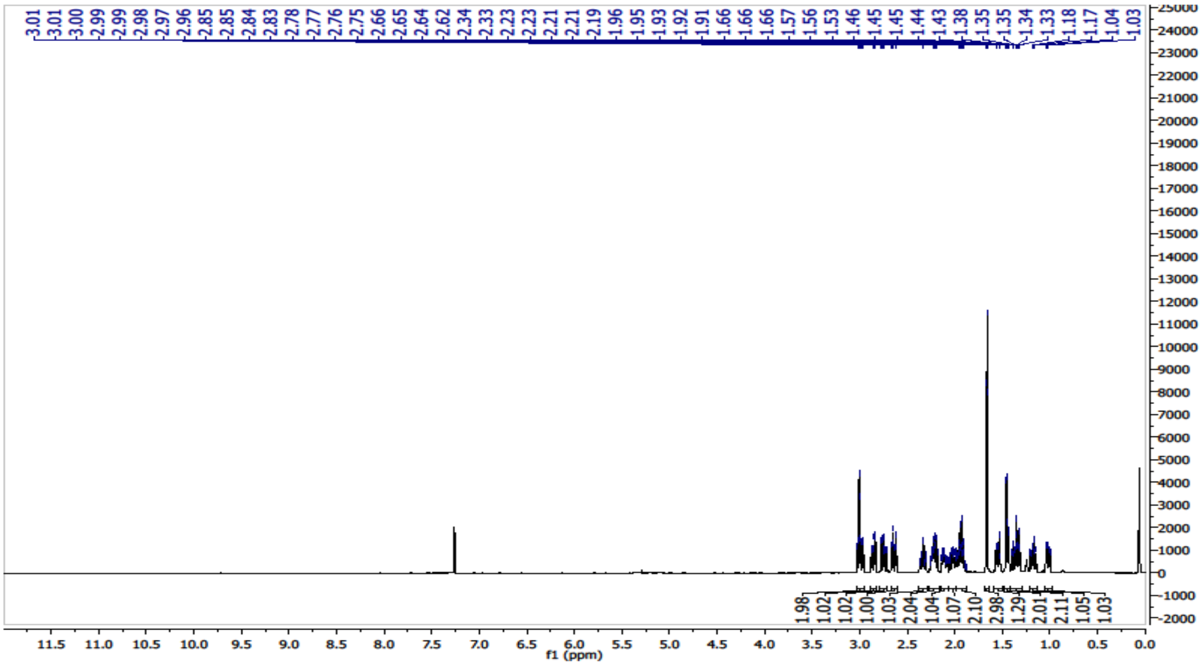
^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



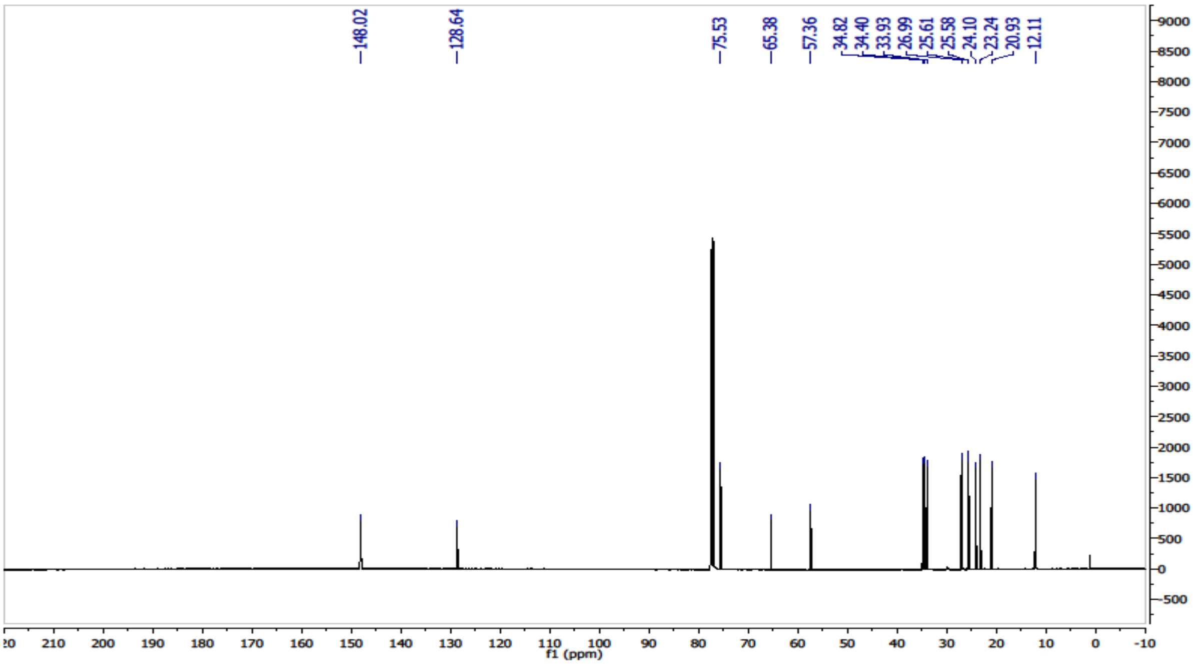
8-(Hex-4-yn-1-yl)-1,5-dithiaspiro[5.5]undec-7-ene (2d)



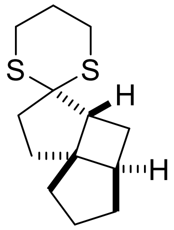
^{1}H NMR (500 MHz, CDCl$_3$, 298 K)



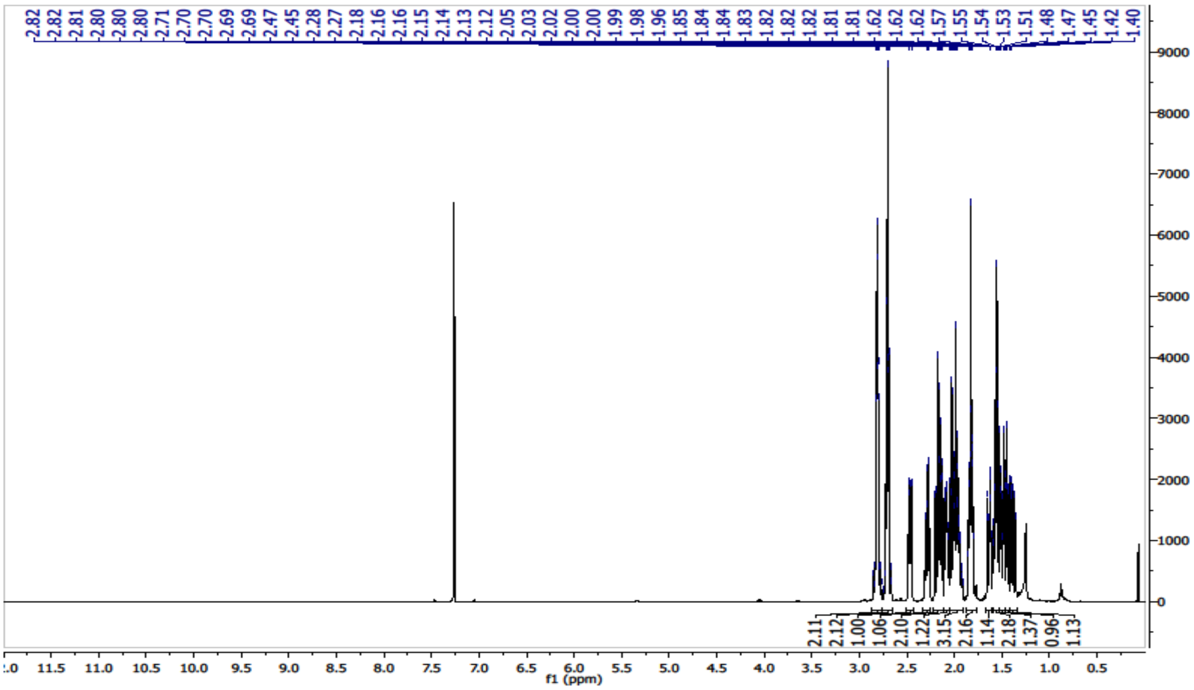
^{13}C NMR (126 MHz, CDCl$_3$, 300 K)



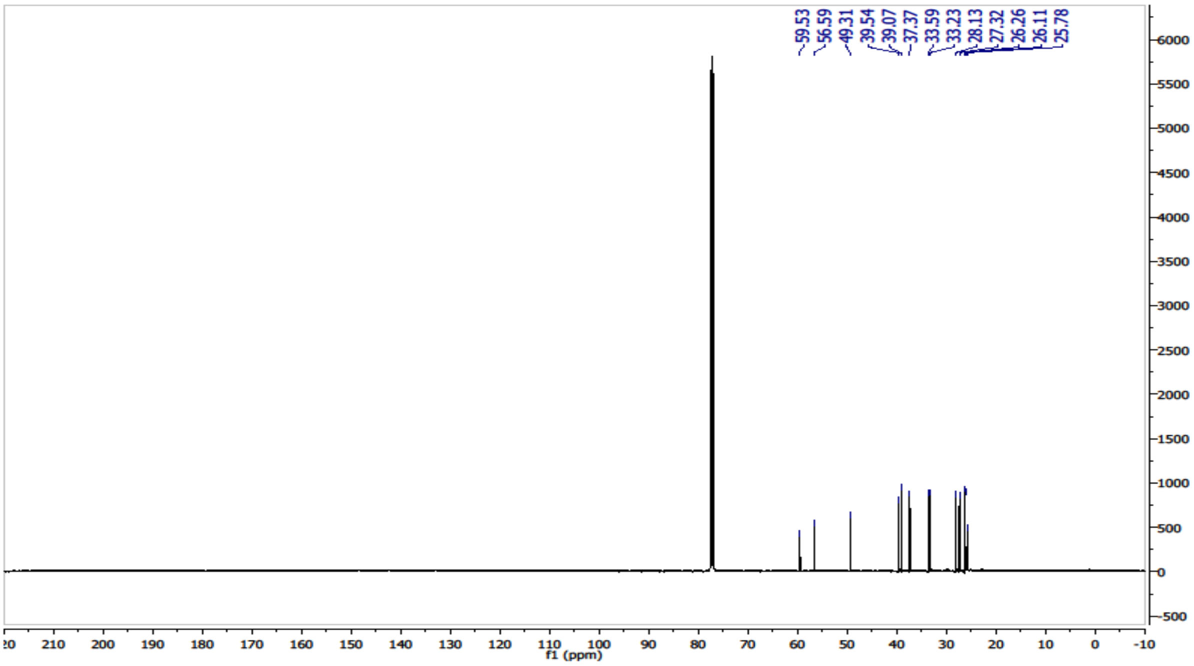
Octahydrospiro{cyclobuta[1,2:1,4]di[5]annulene-3,2'-[1,3]dithiane} (2e)



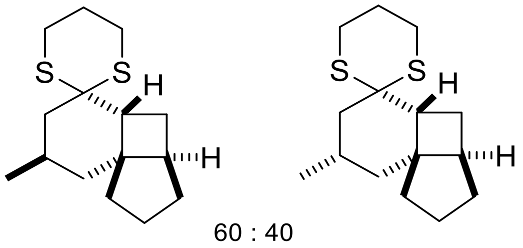
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



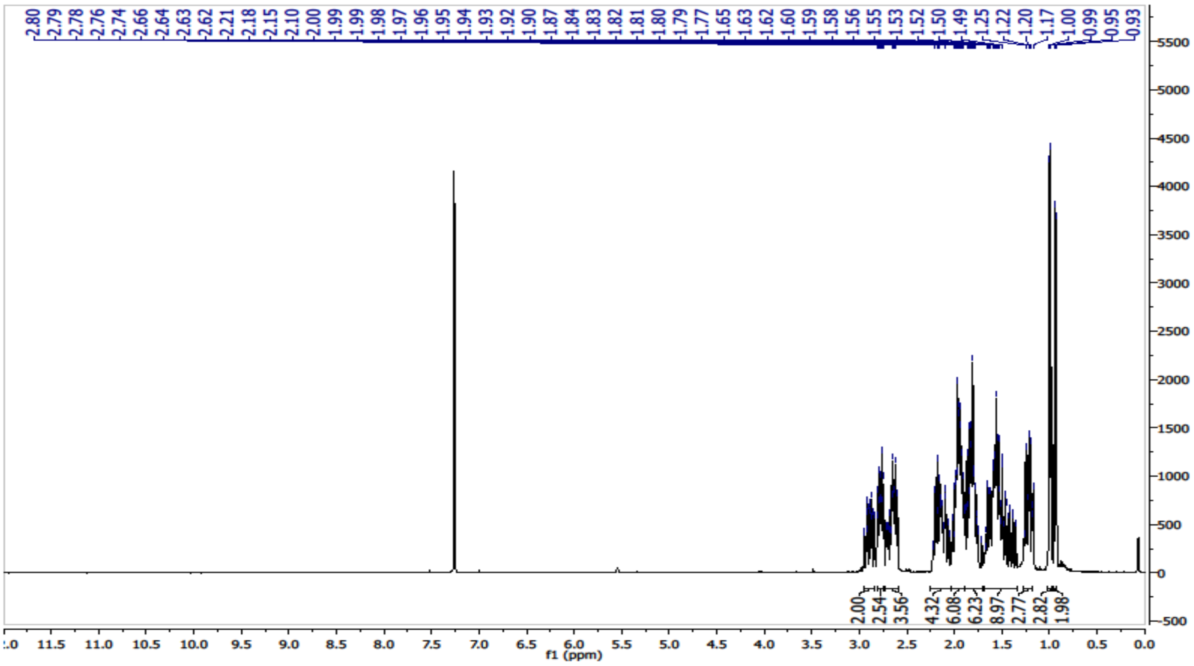
^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



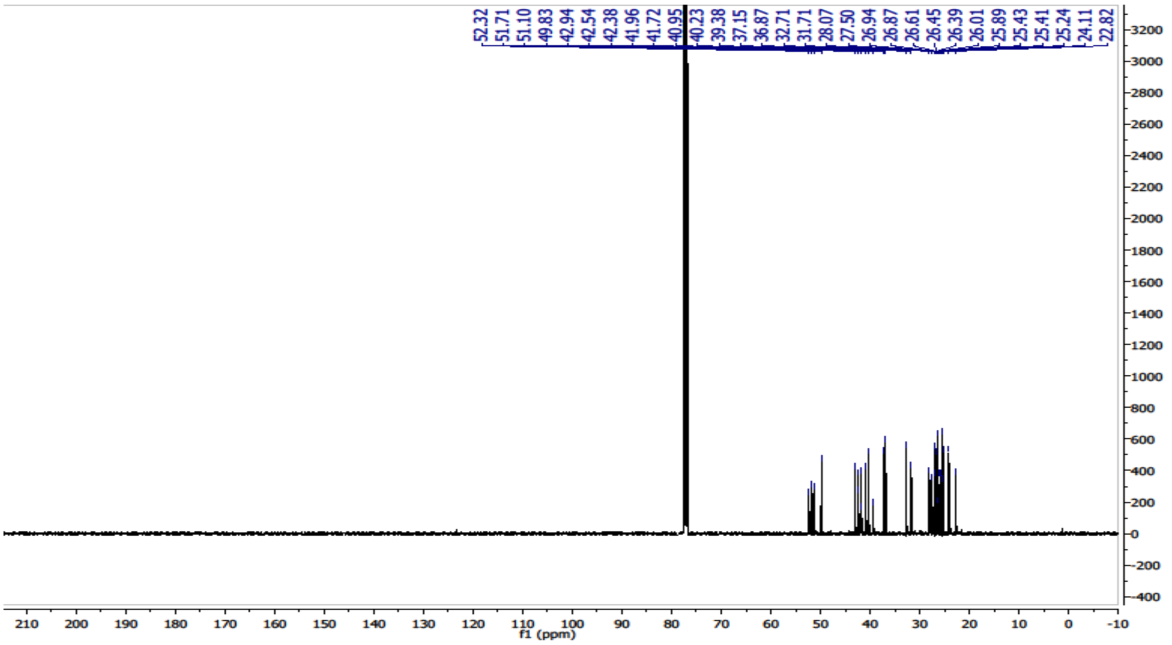
7-Methyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2f)



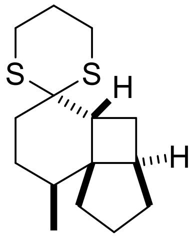
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



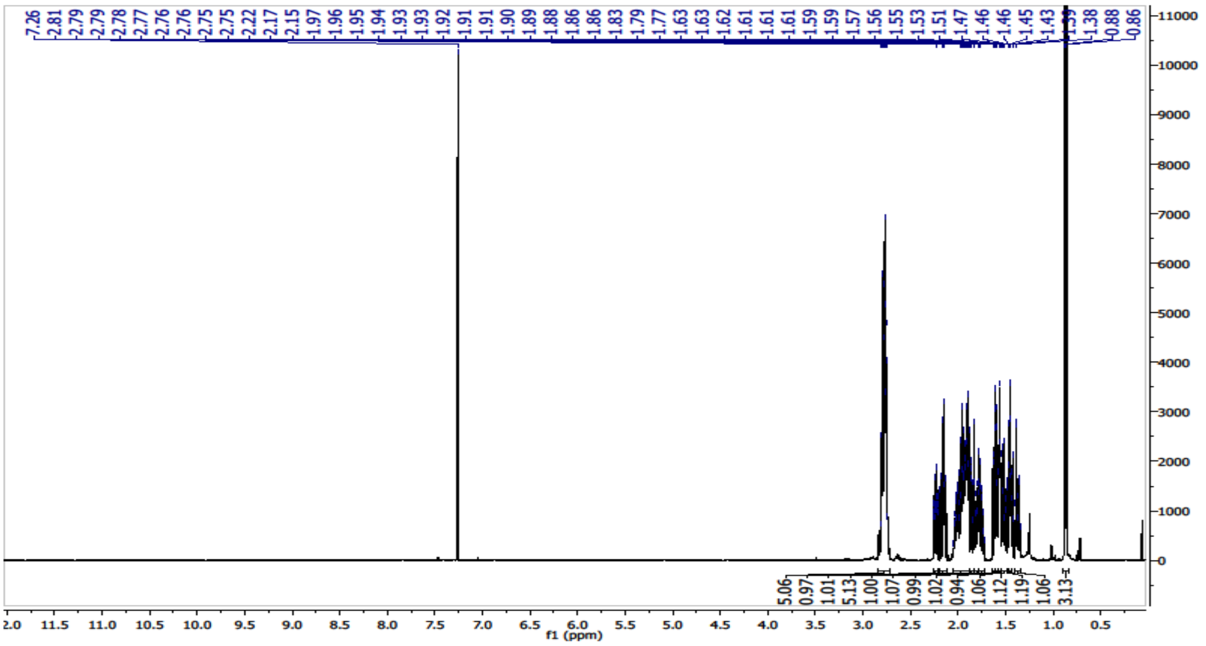
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



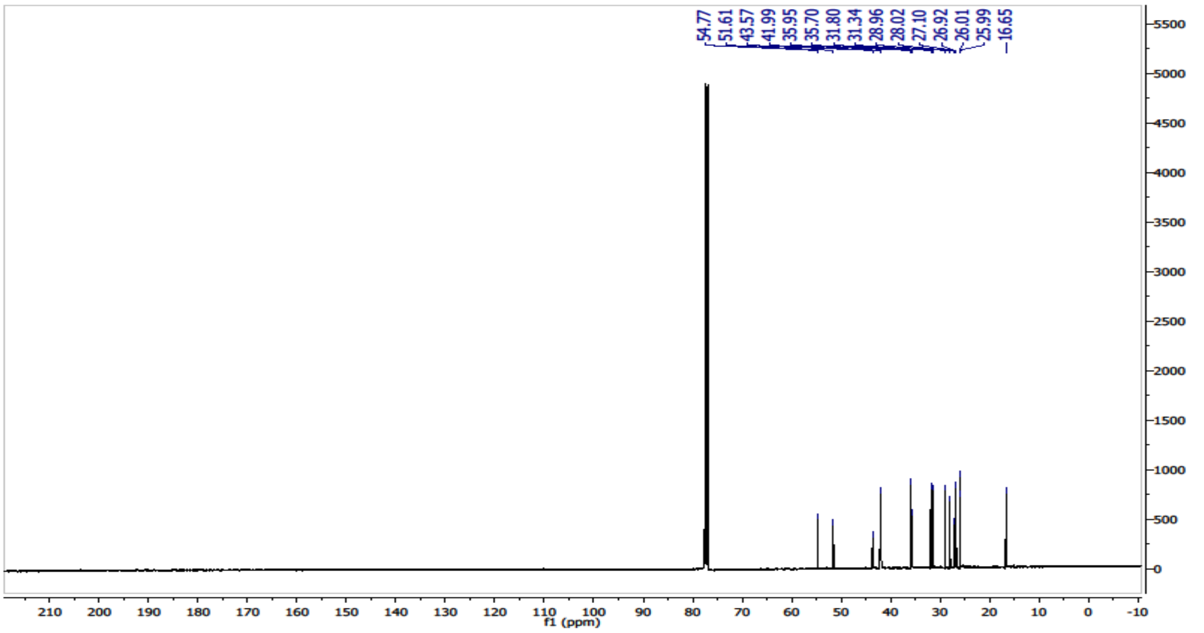
8-Methyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2g)



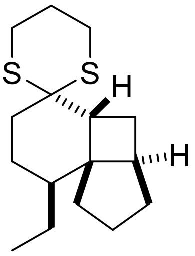
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



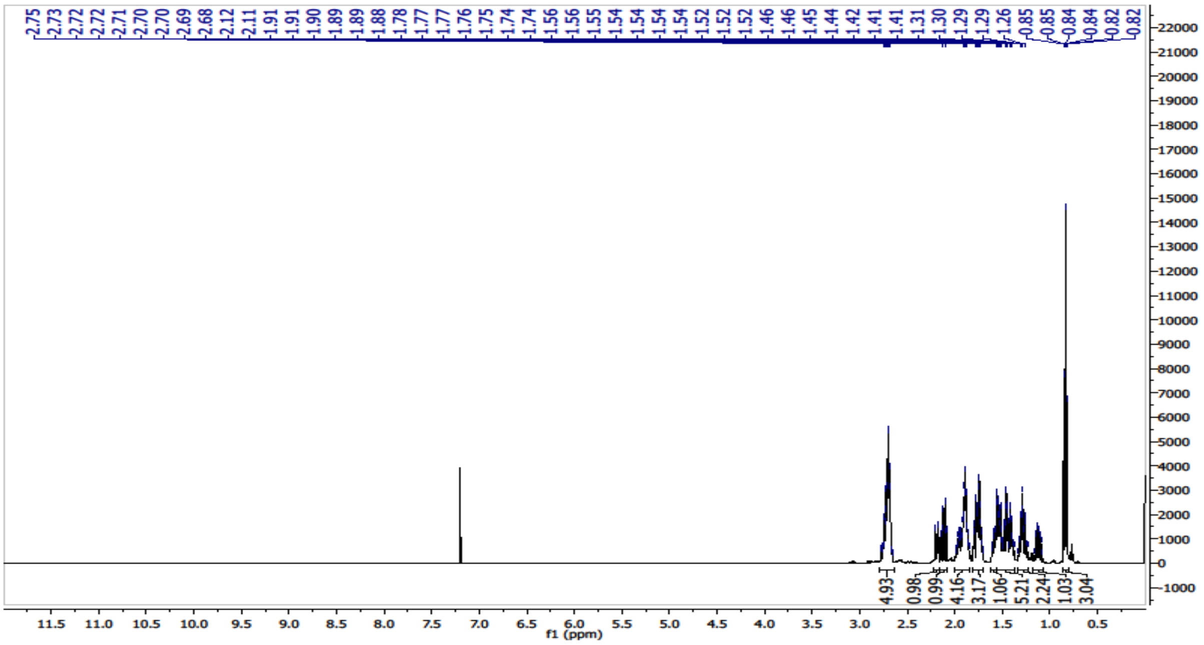
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



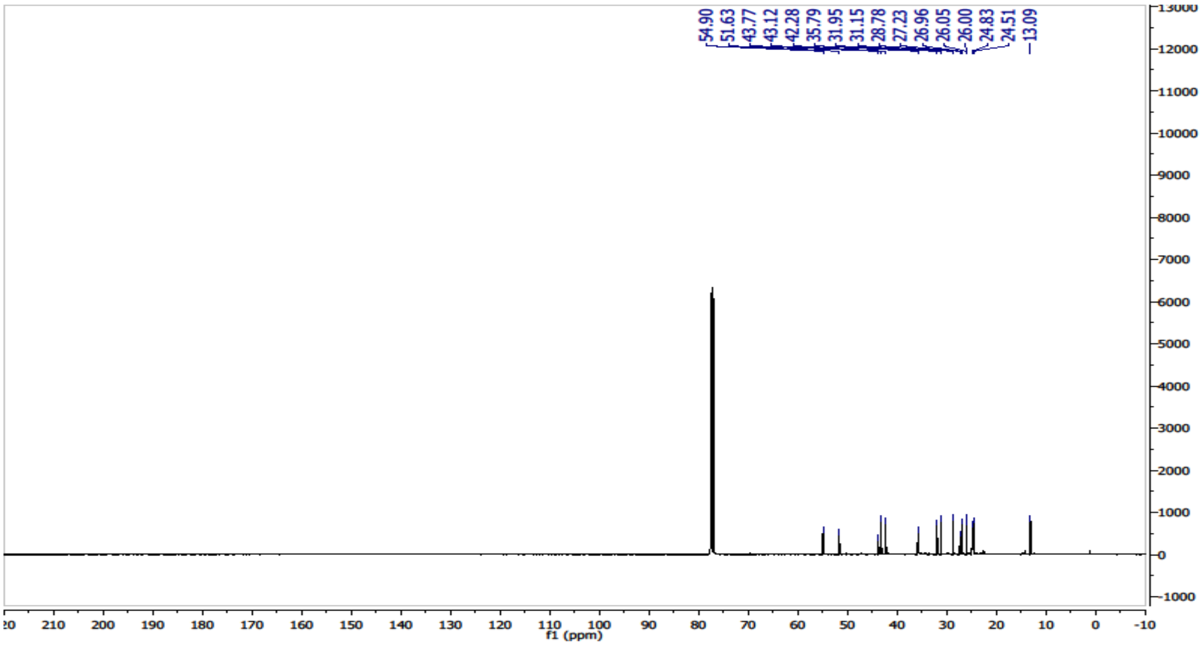
8-Ethyloctahydro-6H-spiro[cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane] (2h)



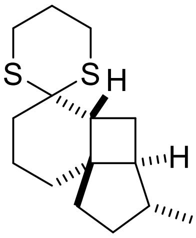
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)



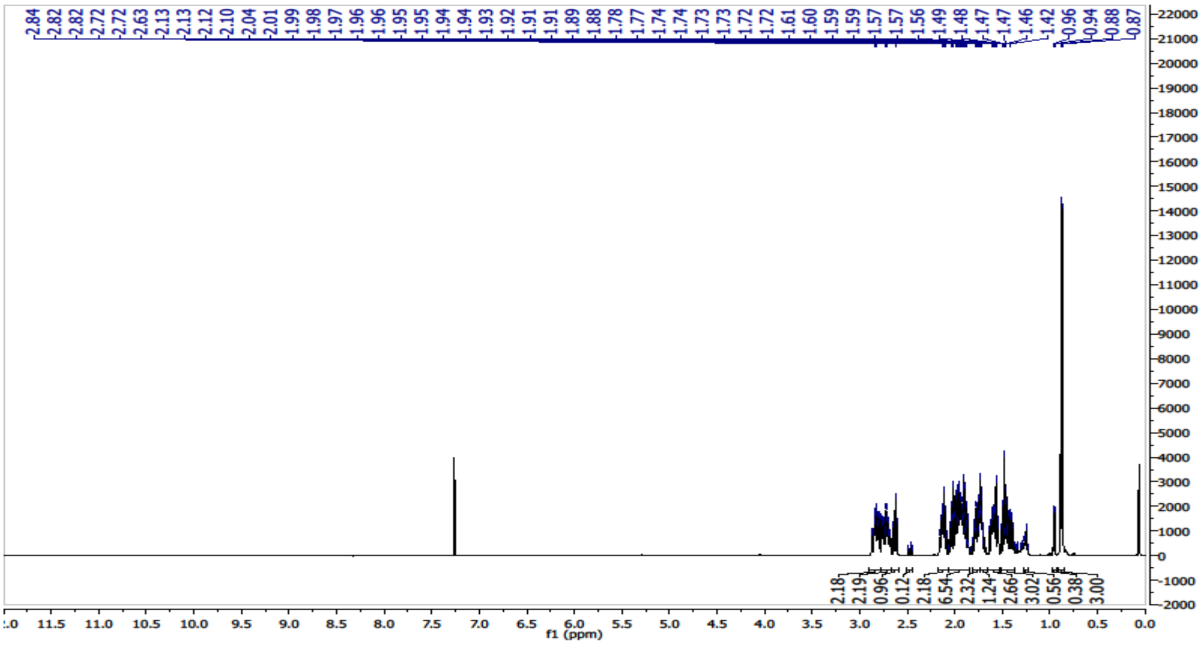
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K)



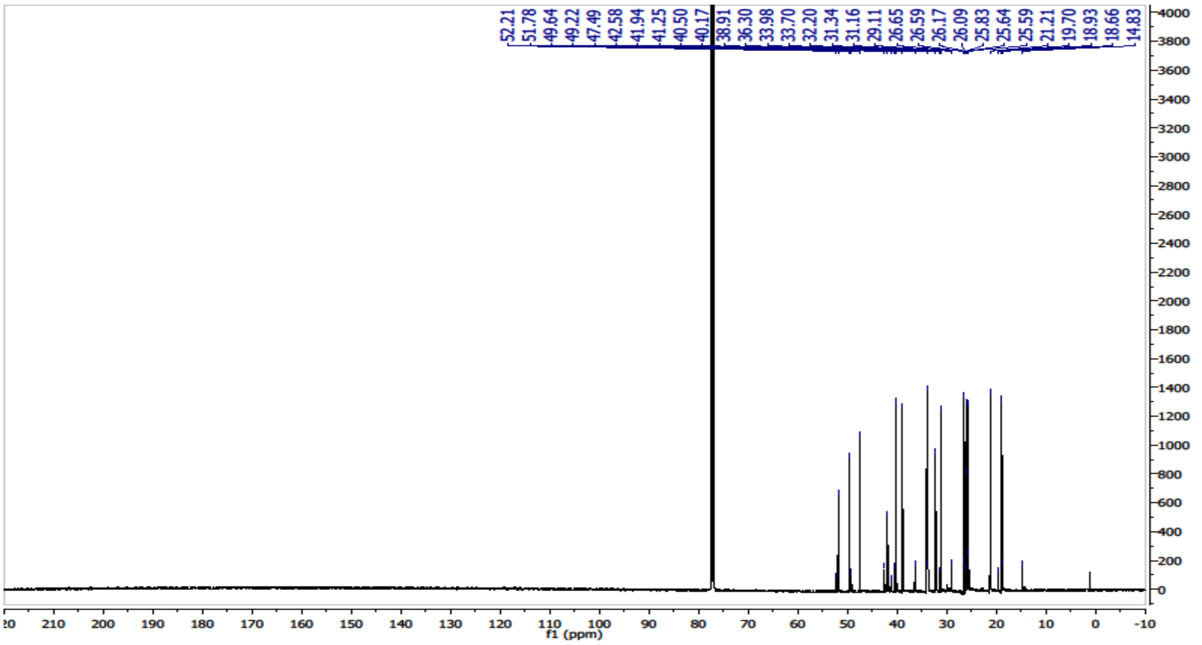
3-Methyloctahydro-6*H*-spiro{cyclopenta[1,4]cyclobuta[1,2]benzene-5,2'-[1,3]dithiane} (2i)



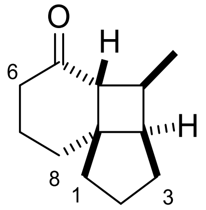
^{1}**H-NMR** (500 MHz, CDCl$_3$, 298 K)



^{13}**C-NMR** (126 MHz, CDCl$_3$, 300 K)

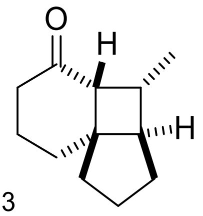


4-Methyloctahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (6)



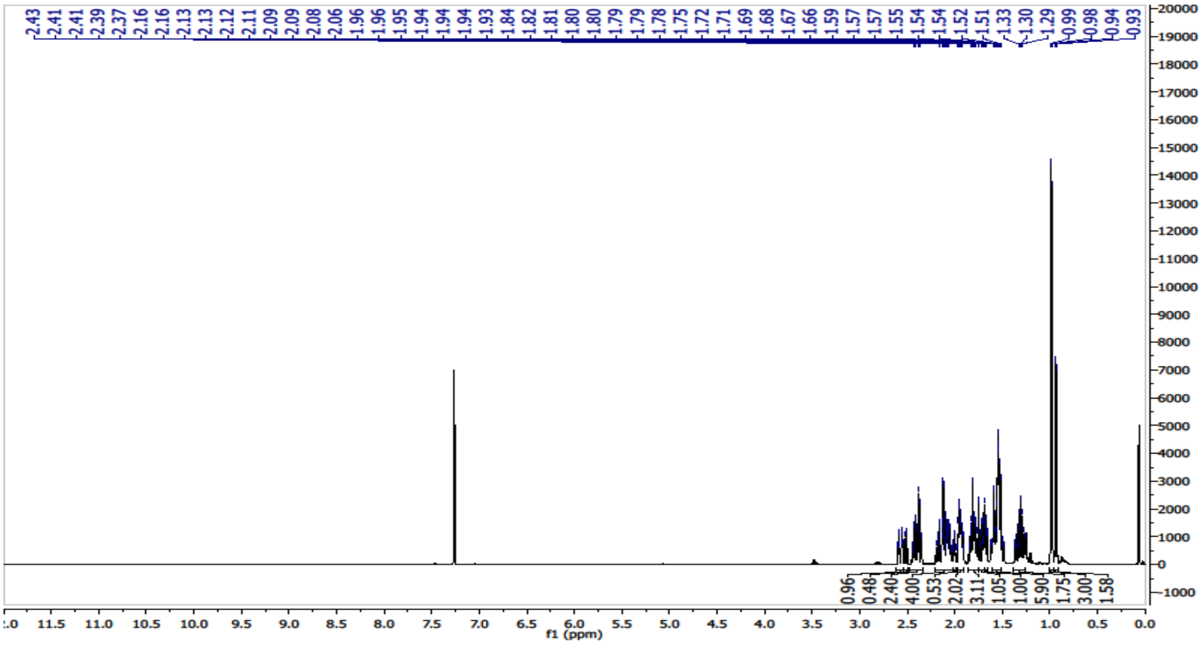
cis-**6**

67 : 33

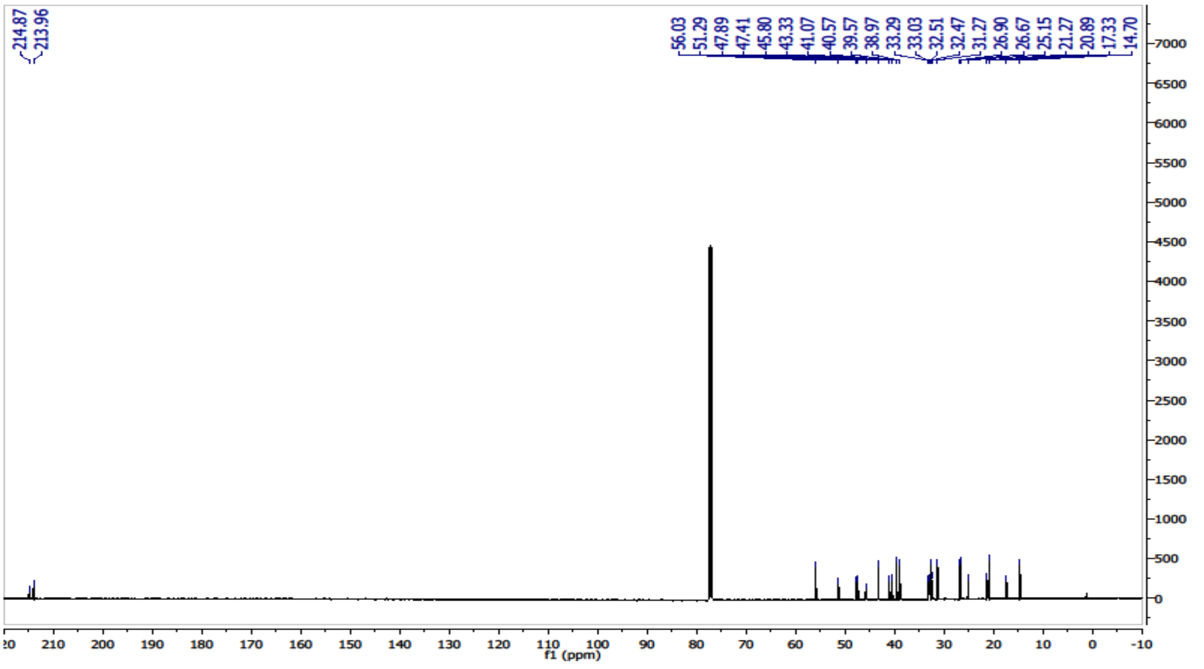


trans-**6**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



^{13}C NMR (126 MHz, $CDCl_3$, 300 K)



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