Supporting Information

Access to 1,2-diketones by an unusual radical cascade

Rama Heng* and Samir Z. Zard*

Laboratoire de Synthèse Organique, CNRS UMR 7652, Département de Chimie, Ecole Polytechnique,
91128 Palaiseau, France

* heng@dcso.polytechnique.fr ; zard@poly.polytechnique.fr

Contents:

General Experimental Methods ........................................................... 2
I. Experimental procedures and spectroscopic data......................... 3
   General procedure A: 1,4 addition of organocuprate ..................... 3
   Modified general procedure A: 1,4 addition of organocuprate .......... 3
   General procedure B: the cleavage of the silyl ether and alkylation .... 3
   General procedure C: addition of the ethyl vinyl ether .................. 11
   General procedure D: formation of the xanthate ............................ 11
   General procedure E: radical fragmentation of the cyclohexane ......... 19
II. Copies of 1H and 13C NMR Spectra ........................................... 25
General Experimental Methods

Anhydrous diethyl ether was obtained by distillation from sodium-benzophenone under nitrogen. Other solvents were used as supplied by commercial sources. Petroleum ether refers to the fraction of light petroleum ether, boiling between 40-60°C. All reagents were used as supplied by commercial sources unless otherwise stated. Purification procedures were in accordance with the instructions in D. D. Perrin and W. L. F. Armarego, “Purification of Laboratory Chemicals”, Fourth Edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40-63 μm) as the stationary phase. Thin Layer chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F254), which were visualized by the quenching of UV fluorescence (λmax = 254 nm) and/or by staining with vanillin in acidic ethanol followed by heating. Infrared spectra were recorded as solutions in CCl4 using CaF2 cells, on a Perkin-Elmer FT 1600. Absorption maxima (νmax) are reported in wavenumbers (cm⁻¹) and only selected peaks are reported. Magnetic resonance spectra were recorded at ambient temperature on either a Bruker AMX 400, or a Bruker Avance DPX 400 instruments. Proton magnetic resonance spectra (1H NMR) were recorded at 400 MHz and coupling constants (J) are reported to ± 0.5 Hz. Carbon magnetic resonance spectra (13C NMR) were recorded at 100.6 MHz. Chemical shifts (δH, δC) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. Low-resolution mass spectra (m/z) were recorded by chemical ionization (CI) on a Hewlett-Packard HP 5989B and only report molecular species ([M]+, ([MNH₄]+) and other major fragments. High-resolution mass spectra were recorded by positive electron impact ionization (EI+) at 70 eV on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ± 5 ppm.
I. Experimental procedures and spectroscopic data

*General procedure A: 1,4 addition of organocuprate*

To a solution of CuBr.Me₂S (0.1n mmol) and HMPA (2n mmol) in distilled THF (1.5n mL) was added dropwise, a solution of organomagnesium reagent (2n mmol) under a nitrogen atmosphere at -40 °C. After 30 min, 2-methyl-2-cyclohexenone (n mmol) and TMSCl (2n mmol) were added. After stirring for 1 h at -40 °C, triethylamine (1.9n mmol) was added, followed by water (2n mL). The mixture was extracted 3 times with diethyl ether. The combined organic layers were washed with water, dried and evaporated, giving crude silyl enol ether.

*Modified general procedure A: 1,4 addition of organocuprate*

To a solution of CuBr.Me₂S (1.6n mmol) in distilled THF (3n mL) was added under a nitrogen atmosphere a solution of organomagnesium reagent (1.5n mmol) at -100 °C. After 15 min at -100 °C a mixture of 2-methyl-2-cyclohexenone (n mmol) and TMSCl (2n mmol) in THF (0.75n mL) was added dropwise in 30 min. After 1.5 h HMPA (n mmol) and triethylamine (1.9n mmol) were added. Water was then added, and the mixture was extracted 3 times with petroleum ether. The combined organic layers were washed with water, dried and evaporate, giving crude silyl enol ether.

*General procedure B: the cleavage of the silyl ether and alkylation*

To a solution of the above silyl enol ether (n mmol) in THF (6.5n mL) and cooled at 0 °C was rapidly added a solution of methylolithium (1.2n mmol). The resulting solution was stirred for 15 min, then cooled at -78 °C. A solution of methyl iodide (5n mmol) in HMPA (n mL) was then quickly added. The resulting mixture was allowed to stir with gradual warming to room temperature (about 30 min), and was then diluted with diethyl ether and washed with water and brine. The organic layer was dried, and concentrated, to give crude 2,2-dimethyl-cyclohexanone.
3-Allyl-2,2-dimethyl-cyclohexanone 7a

\[
\begin{align*}
\text{C}_{11}\text{H}_{18}\text{O} \\
M = 166.26 \text{ g.mol}^{-1} \\
\text{Colorless oil}
\end{align*}
\]

Reaction: Following modified general procedure A, the reaction was carried out using 2-methyl-2-cyclohexenone (3.5 g, 31.8 mmol), and allylmagnesium bromide (1M in THF), giving crude silyl enol ether (5.8 g, 26 mmol, 82%).

\[
\begin{align*}
\text{RMN}^{13}\text{C} (\delta, \text{ ppm}) \text{ (CDCl}_3, \text{ 100.6 MHz):} \\
144.3 (\text{C=COTMS}), 137.8 (\text{CH=CH}_2), 115.5 (\text{CH=CH}_2), 114.8 (\text{C=COTMS}), 38.6 (\text{CH-C=C}), 37.6, 30.4, 27.0, 20.2 (4 \times \text{CH}_2), 14.4 (\text{CH=CH}_2), 0.61 (\text{Si(CH}_3)_3)
\end{align*}
\]

The silyl enol ether (5.8 g, 26 mmol) was then transformed following general procedure B, giving crude compound 7a.

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (95/5).

Yield: 55 %

\[
\begin{align*}
\text{RMN}^1\text{H} (\delta, \text{ ppm}) \text{ (CDCl}_3, \text{ 400 MHz):} \\
5.70 (\text{ddd}, J=5.7 \text{ Hz}, J=8.5 \text{ Hz}, J=10.1 \text{ Hz}, J=16.9 \text{ Hz}, 1\text{H}, \text{CH}_2=\text{CH}_2), 4.95 – 5.2 (\text{m}, 2\text{H}, \text{CH}_2=\text{CH}_2), 2.46 (\text{ddd}, J=6.0 \text{ Hz}, J=11.7 \text{ Hz}, J=14.0 \text{ Hz}, \text{CH}_2(\text{eq})=\text{C=C}), 2.32 – 2.32 (\text{m}, 2\text{H}, \text{CH}_2(\text{eq})=\text{C=O}, \text{CH}_2=\text{CH-CH}_2), 1.90 – 1.98 (\text{m}, 1\text{H}, \text{CH}_2\text{CH}_2\text{CH}_2\text{H}), 1.76 – 1.87 (\text{m}, 2\text{H}, \text{CH}_2\text{CH}_2\text{CH}_2\text{H}), 1.38 – 1.62 (\text{m}, 3\text{H}, \text{CH}_2\text{CH}_2\text{CH}_2\text{H}), 1.11 (\text{s}, 3\text{H}, \text{CH}_3), 1.01 (\text{s}, 2\text{H}, \text{CH}_3).
\end{align*}
\]

\[
\begin{align*}
\text{RMN}^{13}\text{C} (\delta, \text{ ppm}) \text{ (CDCl}_3, \text{ 100.6 MHz):} \\
215.7 (\text{C=O}), 137.5 (\text{CH=CH}_2), 115.9 (\text{CH=CH}_2), 48.7 (\text{C(CH}_3)_2), 47.3 (\text{CH-C(Me})_2), 37.9, 34.4, 25.7, 24.8 (4 \times \text{CH}_2), 22.9 (\text{CH}_3), 19.9 (\text{CH}_3).
\end{align*}
\]

IR \(\nu (\text{cm}^{-1})\) (CCl\(_4\)) 1709 (C=O).

HRMS (EI+) calcd for C\(_{11}\)H\(_{18}\)O 166.1358, found: 166.1364.
2,2-Dimethyl-3-(2-methyl-allyl)-cyclohexanone

\[
\text{C}_{12}\text{H}_{20}\text{O}
\]

\[M = 180.29 \text{ g.mol}^{-1}\]

Colorless oil

Reaction: Following general procedure A, the reaction was carried out using 2-methyl-2-cyclohexenone (1.1 mL, 10 mmol), and methallylmagnesium bromide (0.5M in THF), giving crude silyl enol ether.

The silyl enol ether was then transformed following general procedure B, yielding compound 7b.

Purification: Column chromatography, elution with petroleum ether/diethyl ether (95/5).

Yield: 19 %

\textbf{RMN} \textsuperscript{1}H (δ, ppm)

\begin{align*}
\text{(CDCl}_3, 400 \text{ MHz}) & \quad 4.69 \text{ (s, 1H, C}=\text{CH}_2), \quad 4.61 \text{ (s, 1H, C}=\text{CH}_2), \quad 2.42 \text{ (ddd, J=6.2Hz, J=11.9Hz, J=13.9Hz, 1H, CH}_2\text{ax}=\text{O}), \quad 2.23 \text{ (dt, J=1.3Hz, J=4.8Hz, J=13.9Hz, 1H, CH}_2\text{eq}=\text{O}), \quad 2.1 \text{ (m, 1H, CH}_2\text{ax}-\text{C}=\text{O}), \quad 1.84 \text{ – 1.94 (m, 1H, CH}_2\text{ax}-\text{CH}_2) \quad 1.79 \text{ (dd, J=11.3Hz, J=13.5Hz, 1H, CH}_2\text{eq}-\text{CH}_2) \quad 1.69 \text{ – 1.76 (m, 1H, CH}_2\text{eq}-\text{CH}_2) \quad 1.5 \text{ (s, 3H, CH}_3) \quad 0.96 \text{ (s, 3H, CH}_3).
\end{align*}

\textbf{RMN} \textsuperscript{13}C (δ, ppm)

\begin{align*}
\text{(CDCl}_3, 100.6 \text{ MHz}) & \quad 215.6 \text{ (C}=\text{O)}, \quad 143.6 \text{ (C}=\text{eq}=\text{C}), \quad 112.0 \text{ (CH}=\text{CH}_2), \quad 48.5 \text{ (CH}(\text{Me})_2), \quad 44.9 \text{ (CH}=\text{C}(\text{Me})_2), \quad 38.3, 37.7 \text{ (CH}_2\text{O}, \text{CH}_2\text{C}=\text{CH}_2), \quad 25.4, 24.8 \text{ (CH}_2\text{CH}_2\text{CH}), \quad 22.7 \text{ (C(CH}_3)_2), \quad 21.7 \text{ (CH}_3\text{C}=\text{CH}_2) \quad 19.7 \text{ (C(CH}_3)_2).
\end{align*}

\textbf{IR} ν (cm\textsuperscript{-1}) (CCl\textsubscript{4})

1709 (C=O).

\textbf{HRMS} (EI+) calcd for C\textsubscript{12}H\textsubscript{20}O 180.1514, found: 180.1521.
2,2,3-Trimethyl-cyclohexanone

\[
\begin{align*}
\text{C}_9\text{H}_{16}\text{O} \\
M &= 140.22 \text{ g.mol}^{-1} \\
\text{Colorless oil}
\end{align*}
\]


Reaction: Following general procedure A, the reaction was carried out using 2-methyl-2-cyclohexenone (1.1 mL, 10 mmol), and methylmagnesium bromide (1.4M in THF), giving crude silyl enol ether (1.22 g, 6.2 mmol).

RMN \(^{13}\text{C} (\delta, \text{ppm}) (\text{CDCl}_3, 100.6 \text{ MHz}):\)

143.2 (C=COTMS), 116.4 (C=COTMS), 35.6 (CH=CH=CH), 31.3, 30.5, 20.4 (3 x CH\(_2\)), 19.9 (CH\(_3\)CH) 14.2 (CH\(_3\)C=CH), 0.64 (Si(CH\(_3\))\(_3\))

The **silyl enol ether** (1.22 g, 6.2 mmol) was then transformed following general procedure B, yielding compound 7c.

Purification: None

Yield: 59 %

Product described in the literature.
3-Ethyl-2,2-dimethyl-cyclohexanone 7d

![Chemical Structure](image)

C\textsubscript{10}H\textsubscript{18}O  
M = 154.25 g.mol\textsuperscript{-1}  
Colorless oil


Reaction: Following general procedure A, the reaction was carried out using 2-methyl-2-cyclohexenone (1.1 mL, 10 mmol), and ethylmagnesium bromide (1M in THF), giving crude silyl enol ether. The silyl enol ether (10 mmol) was then transformed following general procedure B, yielding compound 7d.

Purification: None

Yield: 75%

Product described in the literature.

3-Isopropyl-2,2-dimethyl-cyclohexanone 7e

![Chemical Structure](image)

C\textsubscript{11}H\textsubscript{20}O  
M = 168.28 g.mol\textsuperscript{-1}  
Colorless oil

RMN \textsuperscript{13}C (δ, ppm) (CDCl\textsubscript{3}, 100.6 MHz):

145.0 (C=COTMS), 114.9 (C=COTMS), 44.4 (CH-C=C), 30.8, 28.3, 21.0 (3 x CH\textsubscript{2}), 22.3, 22.2 (CH(CH\textsubscript{3})\textsubscript{2}), 16.1 (CH(CH\textsubscript{3})\textsubscript{2}), 13.8 (CH\textsubscript{3}C=C), 0.63 (Si(CH\textsubscript{3})\textsubscript{3})

The silyl enol ether was then transformed following general procedure B, yielding compound 7e.
Purification: Column chromatography, elution with petroleum ether/ethyl acetate (95/5).

Yield: 80 %

RMN $^1$H ($\delta$, ppm) (CDCl$_3$, 400 MHz) 2.5 (dt, J=6.3Hz, J=13.4Hz, 1H, CH$_2$CO), 2.00 – 2.07 (m, 1H, CH$_2$-CH$_2$), 1.95 (dd, J=1.0Hz, J=7.0Hz, 1H, C(CH$_3$)$_2$), 1.09 (s, 3H, C(CH$_3$)$_2$).

RMN $^{13}$C ($\delta$, ppm) (CDCl$_3$, 100.6 MHz) 216.0 (C=O), 52.7 (Cq(Me)$_2$), 50.0 (CH$_2$CO), 26.8 (CH$_2$(CH$_3$)$_2$), 25.8 (CH$_2$-CH$_2$), 24.8 (CH$_3$), 22.7 (CH$_3$), 21.3 (CH$_2$-CH$_2$), 20.7 (CH$_3$), 19.1 (CH$_3$).

IR $\nu$ (cm$^{-1}$) (CCl$_4$) 1709 (C=O).

HRMS (EI+) calcd for C$_{11}$H$_{20}$O 168.1514, found: 168.1518.

2,2-Dimethyl-3-pentyl-cyclohexanone

![Chemical structure](image)

C$_{13}$H$_{24}$O

M = 196.33 g mol$^{-1}$

Colorless oil

Reaction: Following general procedure A, the reaction was carried out using 2-methyl-2-cyclohexenone (1.1 mL, 10 mmol), and pentylmagnesium bromide (2M in THF), giving crude silyl enol ether.

The silyl enol ether was then transformed following general procedure B, yielding compound 7f.

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (95/5).

Yield: 65 %

RMN $^1$H ($\delta$, ppm) (CDCl$_3$, 400 MHz) 2.49 (ddd, J=6.1Hz, J=12.0Hz, J=13.9Hz, 1H, CH$_2$CO), 2.26 – 2.33 (m, 1H, CH$_2$CO), 1.93 – 2.02 (m, 1H, CH$_2$-CH$_2$), 1.84 – 1.90 (m, 1H, CH$_2$-CH$_2$), 1.53 – 1.65 (m, 1H, CH$_2$-CH$_2$-pentyl), 1.52 – 1.35 (m, 4H, CH$_2$-CH$_2$-CH-(CH$_2$)$_4$), 1.10 – 1.35 (m, 6H, CH$_2$-CH$_2$-CH-(CH$_2$)$_4$), 1.10 (s, 3H, C(CH$_3$)$_2$), 1.01 (s, 3H, C(CH$_3$)$_2$), 0.88 (t, J=7.0Hz, 3H, (CH$_2$)$_4$CH$_3$).

RMN $^{13}$C ($\delta$, ppm) (CDCl$_3$, 100.6 MHz) 216.6 (C=O), 49.0 (Cq(Me)$_2$), 47.8 (CH-pentyl), 38.0 (CH$_2$CO), 32.0, 29.6, 27.9, 26.1, 25.2, 22.6 ((CH$_2$)$_2$-CH-(CH$_2$)$_4$), 22.8, (C(CH$_3$)$_2$), 19.9 (C(CH$_3$)$_2$), 14.0 ((CH$_2$)$_4$CH$_3$).
IR ν (cm⁻¹) (CCl₄) 1708 (C=O).

HRMS (EI+) calcld for C₁₃H₂₉O 196.1827, found: 196.1822.

**3-Cyclopentyl-2,2-dimethyl-cyclohexanone 7g**

![Chemical Structure](image)

C₁₃H₂₂O  
M = 194.31 g.mol⁻¹  
Colorless oil

Reaction: Following general procedure A, the reaction was carried out using 2-methyl-2-cyclohexenone (1.1 mL, 10 mmol), and cyclopentylmagnesium bromide (2M in THF), giving crude silyl enol ether.

The silyl enol ether was then transformed following general procedure B, yielding compound 7g.

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (97/3).

Yield: 55 %

**RMN **¹H (δ, ppm)  
(CDCl₃, 400 MHz)  
2.45 – 2.55 (m, 1H, CH₂(ax)-C=O), 2.23 – 2.32 (m, 1H, CH₂(eq)-C=O), 1.90 – 2.08 (m, 2H), 1.24 – 1.80 (m, 10H), 1.18 – 1.35 (m, 2H) (CH₂CH₂CH₂CHCH(CH₃)₄), 1.06 (s, 3H, CH₃), 0.96 (s, 3H, CH₃).

**RMN **¹³C (δ, ppm)  
(CDCl₃, 100.6 MHz)  
216.3 (C=O), 50.9 (CH₂(Me)₂), 49.9 (C₂(Me)₂), 39.9 (CH(CH₂)₄), 38.0 (CH₂CO), 33.7, 29.2, 25.9, 25.6, 24.6, 23.1 (CH₂CH₂CH₂CH(CH₃)₄), 23.3 (CH₃), 21.0 (CH₃).

**IR** ν (cm⁻¹) (CCl₄) 1706 (C=O).

**HRMS (EI+)** calcld for C₁₃H₂₉O 194.1671, found: 194.1662.
3-Cyclopropyl-2,2-dimethyl-cyclohexanone

\[ \text{C}_{11}\text{H}_{18}\text{O} \]
\[ M = 166.26 \text{ g.mol}^{-1} \]
Colorless oil

Reaction: Following general procedure A, the reaction was carried out using 2-methyl-2-cyclohexenone (1.1 mL, 10 mmol), and cyclopropylmagnesium bromide (0.5M in THF), giving crude silyl enol ether. The silyl enol ether was then transformed following general procedure B, yielding compound 7h.

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (97/3).

Yield: 26 %

**RMN**

\[ ^1H (\delta, \text{ ppm}) \]
\( (\text{CDCl}_3, 400 \text{ MHz}) \)

- 2.38 (ddd, J=6.0Hz, J=10.7Hz, J=14.0Hz, 1H, \( CH_{2(ax)}\)C=O)
- 2.23 (dt, J=0.9Hz, J=5.5Hz, J=14.0Hz, 1H, \( CH_{2(eq)}\)C=O)
- 1.87 – 1.96 (m, 1H, COCH\(_2\)CH\(_2\)CH\(_2\))
- 1.73 – 1.82 (m, 1H, COCH\(_2\)CH\(_2\)CH\(_2\))
- 1.48 – 1.70 (m, 2H, COCH\(_2\)CH\(_2\)CH\(_2\))
- 1.09 (s, 3H, CH\(_3\))
- 0.67 (dt, J=3.8Hz, J=9.5Hz, 1H, CH(CH\(_2\)_2)
- 0.46 – 0.62 (m, 2H, CH-CH(CH\(_2\)_2)
- 0.31 – 0.39 (m, 1H, CH(CH\(_2\)_2)
- 0.13 (td, J=4.6Hz, J=9.6Hz, 1H, CH(CH\(_2\)_2)
- -0.10 (td, J=4.9Hz, J=14.8Hz, 1H, CH(CH\(_2\)_2)

**RMN**

\[ ^{13}C (\delta, \text{ ppm}) \]
\( (\text{CDCl}_3, 100.6 \text{ MHz}) \)

- 216.0 (C=O)
- 53.1 (CHC\(_q\)(Me)\(_2\))
- 49.8 (C\(_q\)(Me)\(_2\))
- 37.5 (CH\(_2\)CO)
- 27.0, 24.8 (COCH\(_2\)CH\(_2\)CH\(_2\))
- 23.8 (CH\(_3\))
- 20.7 (CH\(_3\))
- 11.8 (CH(CH\(_2\)_2)
- 7.19 (CH(CH\(_2\)_2)
- 2.14 (CH(CH\(_2\)_2)

**IR** \( \nu (\text{cm}^{-1}) \) \( (\text{CCl}_4) \)

- 1709 (C=O)

**HRMS** (EI+)

Calcd for C\(_{11}\)H\(_{18}\)O 166.1358, found: 166.1358.
General procedure C: addition of the ethyl vinyl ether

To a stirred solution of ethyl vinyl ether (5n mmol) in freshly distilled THF (2n ml) under nitrogen and at –78°C, was added dropwise over 10 minutes tert-butyl lithium (~1.35 M in pentane, 2n mmol). After 15 more minutes, the acetone/dry ice bath was replaced by a water/ice bath, and stirring was kept for 15 minutes. The flask was cooled back to -78°C, and a solution of cyclobutanone (n mmol) in distilled THF (2n ml) was then added dropwise over 10 minutes. The mixture was then allowed to warm up to room temperature, and stirred for an additional 2 hours. Saturated ammonium chloride and diethyl ether were added to quench the reaction. The aqueous layer was then extracted with diethyl ether, and the combined organic layers were washed with brine, dried, and then concentrated under reduced pressure, yielding pure ethyl vinyl ether adduct.

General procedure D: formation of the xanthate

To a stirred solution of the ethyl vinyl ether adduct (n mmol) in a mixture of acetonitrile/water (9:1) (2n mL) under nitrogen in an ice water bath, was added a solution of N-bromosuccinimide (1.1n mmol) in acetonitrile/water (9:1) (2n mL). Stirring was kept for 20 more minutes, and the mixture was then partitioned between diethyl ether and water. The organic layer was then washed with brine, and dried over anhydrous MgSO₄. Filtration and removal of the solvent under reduced pressure, gave the α-bromo ketone. IR and ¹H NMR analysis could be used to see the formation of the carbonyl group.

The previous crude bromo ketone (n mmol) was then stirred in acetone (1.5n mL) under nitrogen at 0°C, and sodium O-neopentyl xanthate or potassium O-ethyl xanthate (1.2n mmol) was then added. After one hour at 0°C, the mixture was partitioned between diethyl ether and water. Brine was added to the aqueous layer, and extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered and the solvent were removed in vacuo to afford crude xanthate.
Dithiocarbonic acid [2-(3-allyl-1-hydroxy-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester ethyl ester

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{S} \\
\text{S} \\
\text{C} \\
\text{C} \\
\end{array}
\]

\[\text{C}_{16}\text{H}_{26}\text{O}_3\text{S}_2\]
\[M = 330.51 \text{ g.mol}^{-1}\]
White solid

Reaction: Following general procedure C, the reaction was carried out using \(7\text{a} (558 \text{ mg, 3.4 mmol})\). The adduct obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude xanthate \(10\text{a}\) as a 95 to 5 mixture of two diastereomers.

Purification: Column chromatography, elution with petroleum ether/dichloromethane (1/1).

Yield: 58 % (over 3 steps)

**RMN** \(\text{^1H (\(\delta\), ppm)}\) (CDCl\(_3\), 400 MHz)
- 5.70 (m, 1H, CH=CH), 4.98 (m, 2H, CH\(_2\)=CH), 4.64 (q, J= 7.1 Hz, 2H, OCH\(_2\)CH\(_3\)), 4.58 (d, J=18.0 Hz, 1H, SCH\(_2\)), 4.25 (d, J=18.0 Hz, 1H, SCH\(_2\)), 2.27 (m, 1H, CH\(_2\)CH=CH\(_2\)), 2.12 (m, 1H, CH\(_C(Me)\)\(_2\)), 2.00 (s, 1H, OH), 1.86 – 1.93 (m, 1H, CH\(_2\)COH), 1.61 – 1.72 (m, 2H, CH\(_2\)CH=CH\(_2\) and CH\(_2\)CH\(_2\)CH), 1.52 – 1.61 (m, 3H, CH\(_2\)COH and CH\(_2\)CH\(_2\)CH), 1.42 (t, J=7.1 Hz, 3H, OCH\(_3\)), 1.02 – 1.15 (m, 1H, CH\(_2\)CH\(_2\)CH), 0.97 (s, 3H, C(CH\(_3\))\(_2\)), 0.91 (s, 3H, C(CH\(_3\))\(_2\)).

**RMN** \(\text{^13C (\(\delta\), ppm)}\) (CDCl\(_3\), 100.6 MHz)
- 214.1 (C=S), 206.7 (C=O), 138.7 (CH=CH\(_2\)), 115.3 (CH=CH\(_2\)), 83.4 (COH), 70.5 (OCH\(_3\)), 45.3 (SCH\(_2\)), 41.5 (C(CH\(_3\))\(_2\)), 41.3 (CH), 34.9 (CH\(_2\)-CH=CH\(_2\)), 33.6 (CH\(_2\)COH), 25.8 (CH\(_2\)CH\(_2\)CH), 22.4 (C(CH\(_3\))\(_2\)), 20.8 (CH\(_2\)CH\(_2\)CH), 16.1 (C(CH\(_3\))\(_2\)), 13.8 (CH\(_2\)CH\(_3\)).

**IR** \(\text{\nu (cm}^{-1}\) (CCl\(_4\))
- 3623 (OH), 1714 (C=O), 1224, 1053 (C=S, C-O).

**HRMS (EI+)** calcd for C\(_{16}\)H\(_{26}\)O\(_3\)S\(_2\) 330.1324, found: 330.1317.
Dithiocarbonic acid ethyl ester \{2-[1-hydroxy-2,2-dimethyl-3-(2-methyl-allyl)-cyclohexyl]-2-oxo-ethyl\} ester

\[\text{C}_{17}\text{H}_{28}\text{O}_3\text{S}_2\]

\[M = 344.53 \text{ g.mol}^{-1}\]

White solid

Reaction: Following general procedure C, the reaction was carried out using 7b (328 mg, 1.8 mmol). The adduct thus obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude 10b.

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (93/7).

Yield: 37 %

**RMN**

\[^1\text{H}\] (δ, ppm) (CDCl\(_3\), 400 MHz)

4.70 (s, 1H, C=CH\(_2\)), 4.63 (s, 1H, C=CH\(_2\)), 4.62 (q, J= 6.9 Hz, 2H, OCH\(_2\)CH\(_3\)), 4.58 (d, J=18.2 Hz, 1H, SCH\(_2\)), 4.24 (d, J=18.0 Hz, 1H, SCH\(_2\)), 2.21 – 2.29 (m, 1H, CH\(_2\)CH\(_2\)CH\(_2\)CHCH\(_2\)), 2.09 – 2.15 (m, 1H, CH\(_2\)CH\(_2\)CH\(_2\)CHCH\(_2\)), 2.12 (s, 1H, OCH\(_3\)), 1.87 – 1.92 (m, 1H, CH\(_2\)CH\(_2\)CH\(_2\)CHCH\(_2\)), 1.65 – 1.70 (m, 1H, CH\(_2\)CH\(_2\)CH\(_2\)CHCH\(_2\)), 1.67 (s, 3H, CH\(_3\)-C=CH\(_2\)), 1.50 – 1.63 (m, 4H, CH\(_2\)CH\(_2\)CH\(_2\)CHCH\(_2\)), 1.40 (t, J=7.1 Hz, 3H, OCH\(_3\)CH\(_3\)), 0.98 – 1.08 (m, 1H, CH\(_2\)CH\(_2\)CH\(_2\)CHCH\(_2\)), 0.94 (s, 3H, C(CH\(_3\))\(_2\)), 0.89 (s, 3H, C(CH\(_3\))\(_2\)).

**RMN** \[^{13}\text{C}\] (δ, ppm) (CDCl\(_3\), 100.6 MHz)

214.0 (C=S), 206.7 (C=O), 144.9 (Cq=CH\(_2\)), 111.5 (CH=CH\(_2\)), 83.4 (COH), 70.4 (OCH\(_3\)), 45.3 (SCH\(_2\)), 41.4 (C(CH\(_3\))\(_2\)), 39.0 (CH\(_2\)Cq=CH\(_2\)), 38.7 (CH), 33.5 (CH\(_2\)-COH), 25.7 (CH\(_2\)CH\(_2\)CH), 22.12, 22.07 (C(CH\(_3\))\(_2\), CH\(_3\)C=CH\(_2\)), 20.8 (CH\(_2\)CH\(_2\)CH), 15.9 (C(CH\(_3\))\(_2\)), 13.7 (CH\(_2\)CH\(_3\)).

**IR** ν (cm\(^{-1}\)) (CCl\(_4\))

3623, 3495 (OH), 1715 (C=O), 1223, 1053 (C=S, C-O).

**HRMS** (EI+)

calcld for C\(_{17}\)H\(_{28}\)O\(_3\)S\(_2\) 344.1480, found: 344.1474.
Dithiocarbonic acid ethyl ester \[2-(1-hydroxy-2,2,3-trimethyl-cyclohexyl)-2-oxo-ethyl\] ester

\[
\begin{align*}
\text{C}_{14}\text{H}_{24}\text{O}_{3}\text{S}_{2} \\
M = 304.47 \text{ g.mol}^{-1} \\
	ext{White solid}
\end{align*}
\]

Reaction: Following general procedure C, the reaction was carried out using 7c (420 mg, 3 mmol). The adduct thus obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude 10c.

Purification: Crude washed with cold petroleum ether/diethyl ether

Yield: 70 %

\text{RMN} \, ^1\text{H} \, (\delta, \text{ppm}) \quad \text{(CDCl}_3, \, 400 \text{ MHz})
\begin{align*}
4.63 & \, (q, \, J= 7.1 \text{ Hz}, \, 2\text{H}, \, \text{OCH}_2\text{CH}_3), \\
4.58 & \, (d, \, J=18.0 \text{ Hz}, \, 1\text{H}, \, \text{SCCH}_2), \\
4.25 & \, (d, \, J=18.0 \text{ Hz}, \, 1\text{H}, \, \text{SCCH}_2), \\
2.22 & \, (m, \, 1\text{H}, \, \text{CH(CMe)}_2), \\
2.00 & \, (s, \, 1\text{H}, \, \text{OH}), \\
1.84 - 1.91 & \, (m, \, 1\text{H}, \, \text{CH}_2\text{CH}_2\text{CH}_2), \\
1.50 - 1.72 & \, (m, \, 3\text{H}, \, \text{CH}_2\text{CH}_2\text{CH}_2), \\
1.42 - 1.50 & \, (m, \, 1\text{H}, \, \text{CH}_2\text{CH}_2\text{CH}_2), \\
1.42 & \, (t, \, J=6.9 \text{Hz}, \, 3\text{H}, \, \text{OCH}_2\text{CH}_3), \\
1.16 - 1.26 & \, (m, \, 1\text{H}, \, \text{CH}_2\text{CH}_2\text{CH}_2), \\
0.92 & \, (s, \, 3\text{H}, \, \text{C(CCH}_3)_2), \\
0.90 & \, (s, \, 3\text{H}, \, \text{C(CH}_3)_2), \\
0.83 & \, (d, \, J=6.9 \text{Hz}, \, 3\text{H}, \, \text{CHCH}_3).
\end{align*}

\text{RMN} \, ^{13}\text{C} \, (\delta, \text{ppm}) \quad \text{(CDCl}_3, \, 100.6 \text{ MHz})
\begin{align*}
214.1 & \, (\text{C=S}), \\
206.9 & \, (\text{C=O}), \\
83.4 & \, (\text{COH}), \\
70.4 & \, (\text{OCH}_2), \\
45.3 & \, (\text{SCCH}_2), \\
41.4 & \, (\text{C(CH}_3)_2), \\
35.7 & \, (\text{CH}), \\
33.6 & \, (\text{CH}_2\text{COH}), \\
29.4 & \, (\text{CH}_2\text{CH}_2\text{CH}), \\
22.4 & \, (\text{C(CH}_3)_2), \\
21.1 & \, (\text{CH}_2\text{CH}_2\text{CH}), \\
16.0 & \, (\text{C(CH}_3)_2), \\
15.1 & \, (\text{CH}_3\text{-CH}), \\
13.8 & \, (\text{CH}_2\text{CH}_3).
\end{align*}

\text{IR} \, \nu \, (\text{cm}^{-1}) \quad (\text{CCl}_4)
\begin{align*}
3624, & \, 3494 \, (\text{OH}), \\
1716 & \, (\text{C=O}), \\
1224 & \, 1053 \, (\text{C=S, C-O}).
\end{align*}

\text{HRMS} \, (\text{EI}+)
\begin{align*}
calcld \, \text{for} \, \text{C}_{14}\text{H}_{24}\text{O}_{3}\text{S}_{2} & \, 304.1167, \, \text{found:} \, 304.1168.
\end{align*}

Dithiocarbonic acid ethyl ester \[2-(3-ethyl-1-hydroxy-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl\] ester

\[
\begin{align*}
\text{C}_{15}\text{H}_{26}\text{O}_{3}\text{S}_{2} \\
M = 318.50 \text{ g.mol}^{-1} \\
	ext{White solid}
\end{align*}
\]

Reaction: Following general procedure C, the reaction was carried out using 7d (1.13 g, 7.3 mmol). The adduct thus obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude 10d.
Purification: Crude washed with cold petroleum ether/diethyl ether

Yield: 70 %

**RMN **<sup>1</sup>H (δ, ppm)  
(CDCl<sub>3</sub>, 400 MHz)  
4.63 (q, J= 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 4.58 (d, J=18.1 Hz, 1H, SCH<sub>2</sub>), 4.24 (d, J=18.1 Hz, 1H, SCH<sub>2</sub>), 2.02 (s, 1H, OH), 1.83 – 1.91 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.68 – 1.76 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.45 – 1.68 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.41 (t, J=7.1 Hz, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.00 – 1.10 (m, 1H, CHCH<sub>2</sub>CH<sub>3</sub>), 0.93 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 0.87 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 0.84 – 0.90 (m, 4H, CHCH<sub>2</sub>CH<sub>3</sub>), 1.00 – 1.10 (m, 1H, CHCH<sub>2</sub>CH<sub>3</sub>), 0.93 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 0.87 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 0.84 – 0.90 (m, 4H, CHCH<sub>2</sub>CH<sub>3</sub>).

**RMN **<sup>13</sup>C (δ, ppm)  
(CDCl<sub>3</sub>, 100.6 MHz)  
214.1 (C=S), 206.8 (C=O), 83.4 (COH), 70.4 (OCH<sub>2</sub>), 45.4 (SCH<sub>2</sub>), 43.6 (CH), 41.7 (C(CH<sub>3</sub>)<sub>2</sub>), 33.5 (C<sub>6</sub>H<sub>2</sub>COH), 25.4 (CH<sub>2</sub>CH<sub>2</sub>CH), 22.7 (CHCH<sub>2</sub>CH<sub>3</sub>), 22.2 (C(CH<sub>3</sub>)<sub>2</sub>), 20.9 (CH<sub>2</sub>CH<sub>2</sub>CH), 15.9 (C(CH<sub>3</sub>)<sub>2</sub>), 13.7 (OCH<sub>2</sub>CH<sub>3</sub>), 13.3 (CHCH<sub>2</sub>CH<sub>3</sub>).

**IR** ν (cm<sup>-1</sup>) (CCl<sub>4</sub>)  
3623, 3496 (OH), 1716 (C=O), 1224, 1053 (C=S, C-O).

**HRMS** (EI+)  
calcld for C<sub>15</sub>H<sub>26</sub>O<sub>3</sub>S<sub>2</sub> 318.1324, found: 318.1314.

**Dithiocarbonic acid ethyl ester [2-(1-hydroxy-3-isopropyl-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester**

![Chemical structure](image)

**Reaction:** Following general procedure C, the reaction was carried out using **7e** (723 mg, 4.3 mmol). The adduct thus obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude **10e**.

**Purification:** Crude washed with cold petroleum ether/diethyl ether

**Yield:** 74 %

**RMN **<sup>1</sup>H (δ, ppm)  
(CDCl<sub>3</sub>, 400 MHz)  
4.63 (q, J= 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 4.58 (d, J=18.3 Hz, 1H, SCH<sub>2</sub>), 4.24 (d, J=18.1 Hz, 1H, SCH<sub>2</sub>), 2.06 (dd, J=2.8Hz, J=13.0Hz, 1H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.91 (s, 1H, OH), 1.80 – 1.90 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.68 – 1.76 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.44 – 1.65 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.42 (t, J=7.1 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.15 – 1.28 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.94 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 0.91 (d, J=6.9Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.82 (d, J=6.9Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>).
Dithiocarbonic acid ethyl ester [2-(1-hydroxy-2,2-dimethyl-3-pentyl-cyclohexyl)-2-oxo-ethyl] ester

\[
\text{C}_{18}H_{32}O_3S_2 \\
M = 360.57 \text{ g.mol}^{-1}
\]

White solid

Reaction: Following general procedure C, the reaction was carried out using 7f (809 mg, 4.1 mmol). The adduct thus obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude 10f.

Purification: Crude washed with cold petroleum ether

Yield: 72 %

RMN $^1H$ (δ, ppm) (CDCl$_3$, 400 MHz) 4.64 (q, J= 7.1 Hz, 2H, OCH$_2$CH$_3$), 4.59 (d, J=18.3 Hz, 1H, SCH$_2$), 4.24 (d, J=18.0 Hz, 1H, SCH$_2$), 1.99 (s, 1H, OH), 1.92 – 2.02 (m, 1H, CH$_2$CH$_2$CH$_2$CH), 1.86 – 1.92 (m, 1H, (CH$_2$)$_3$CH), 1.50 – 1.74 (m, 5H, (CH$_2$)$_3$CH(CH$_2$)$_2$), 1.35 – 1.44 (m, 1H, (CH$_2$)$_3$CH(CH$_2$)$_2$), 1.42 (t, J=7.1 Hz, 3H, OCH$_2$CH$_3$), 1.00 – 1.32 (m, 6H, (CH$_2$)$_3$CH(CH$_2$)$_2$), 0.93 (s, 3H, C(CH$_3$)$_2$), 0.88 (s, 3H, C(CH$_3$)$_2$), 0.84 – 0.96 (m, 4H, (CH$_2$)$_4$CH$_3$).

RMN $^{13}C$ (δ, ppm) (CDCl$_3$, 100.6 MHz) 214.0 (C=S), 206.7 (C=O), 83.4 (COH), 70.4 (OCH$_2$), 45.4 (SCH$_2$), 41.6 (CH), 41.5 (C(CH$_3$)$_2$), 33.5 (CH$_2$COH), 32.2, 30.0, 28.3, 26.2, 22.6, 20.9 (CH$_2$CH$_2$CH(CH$_2$)$_2$), 22.1 (C(CH$_3$)$_2$), 15.9 (C(CH$_3$)$_2$), 14.0 ((CH$_2$)$_4$CH$_3$), 13.7 (OCH$_2$CH$_3$).

IR ν (cm$^{-1}$) (CCl$_4$) 3624 (OH), 1715 (C=O), 1224, 1053 (C=S, C-O).

HRMS (EI+) calcd for C$_{18}$H$_{32}$O$_3$S$_2$ 360.1793, found: 360.1802.
Dithiocarbonic acid [2-(3-cyclopentyl-1-hydroxy-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester ethyl ester

\[
\text{C}_{18}\text{H}_{30}\text{O}_{3}\text{S}_{2}
\]
\[M = 358.56 \text{ g.mol}^{-1}\]
White solid

Reaction: Following general procedure C, the reaction was carried out using 7g (742 mg, 3.8 mmol). The adduct thus obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude 10g.

Purification: Brominated compound was simply filtered.

Yield: 65 %

**RMN** \(^1\text{H}\) (δ, ppm) (CDCl\(_3\), 400 MHz)

<table>
<thead>
<tr>
<th>Chemical Shift (δ, ppm)</th>
<th>Multiplicity</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.64</td>
<td>q</td>
<td>2H, OCH(_2)CH(_3)</td>
</tr>
<tr>
<td>4.58</td>
<td>d</td>
<td>1H, SCH(_2)</td>
</tr>
<tr>
<td>4.26</td>
<td>d</td>
<td>1H, SCH(_2)</td>
</tr>
<tr>
<td>2.21</td>
<td>td</td>
<td>3.5Hz, J=12.7Hz, 1H, CH(_2)CHOH</td>
</tr>
<tr>
<td>1.84 – 1.92</td>
<td>m</td>
<td>2H, CH(_2)COH, (CH(_2)(_2))CHCH(CH(_2)(_4)), 1.67 – 1.76 (m, 1H, (CH(_2)(_2))CHCH(CH(_2)(_4)), 1.45 – 1.64 (m, 8H, (CH(_2)(_2))CHCH(CH(_2)(_4)), 1.42 (t, J=7.1 Hz, 3H, OCH(_2)CH(_3)), 1.17 – 1.32 (m, 4H, (CH(_2)(_2))CHCH(CH(_2)(_4)), 0.96 (s, 3H, C(CH(_3)(_2)), 0.93 (s, 3H, C(CH(_3)(_2))</td>
</tr>
</tbody>
</table>

**RMN** \(^{13}\text{C}\) (δ, ppm) (CDCl\(_3\), 100.6 MHz)

<table>
<thead>
<tr>
<th>Chemical Shift (δ, ppm)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>214.0</td>
<td>C=S</td>
</tr>
<tr>
<td>206.7</td>
<td>C=O</td>
</tr>
<tr>
<td>83.6</td>
<td>COH</td>
</tr>
<tr>
<td>70.4</td>
<td>OCH(_2)</td>
</tr>
<tr>
<td>45.5</td>
<td>(SCH(_2))</td>
</tr>
<tr>
<td>44.1</td>
<td>(CH(_3)(Me)(_2))</td>
</tr>
<tr>
<td>42.6</td>
<td>(C(CH(_3)(_2))</td>
</tr>
<tr>
<td>39.5</td>
<td>C(CH(_2)(_4))</td>
</tr>
<tr>
<td>33.9</td>
<td>(CH(_2))</td>
</tr>
<tr>
<td>33.8</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>29.2</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>25.9</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>24.7</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>23.0</td>
<td>C(CH(_3)(_2))</td>
</tr>
<tr>
<td>22.9</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>21.4</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>17.0</td>
<td>C(CH(_3)(_2))</td>
</tr>
<tr>
<td>13.7</td>
<td>CH(_2)CH(_3)</td>
</tr>
</tbody>
</table>

**IR** \(\nu\) (cm\(^{-1}\)) (CCl\(_4\))

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3624</td>
<td>(OH)</td>
</tr>
<tr>
<td>1715</td>
<td>(C=O)</td>
</tr>
<tr>
<td>1223</td>
<td></td>
</tr>
<tr>
<td>1052</td>
<td>(C=S, C-O)</td>
</tr>
</tbody>
</table>

**HRMS** (EI+)

calcd for C\(_{18}\)H\(_{30}\)O\(_3\)S\(_2\) 358.1637, found: 358.1639.
Dithiocarbonic acid [2-(3-cyclopropyl-1-hydroxy-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester ethyl ester

\[
\begin{align*}
\text{C}_{16}\text{H}_{26}\text{O}_3\text{S}_2 \\
\text{M} = 330.51 \text{ g.mol}^{-1} \\
\text{White solid}
\end{align*}
\]

Reaction: Following general procedure C, the reaction was carried out using 7h (158 mg, 0.95 mmol). The adduct thus obtained was then transformed following general procedure D, using potassium O-ethylxanthate, to give crude 10h.

Purification: Crude washed with cold petroleum ether

Yield: 80%

**RMN** 
\[ ^1\text{H} (\delta, \text{ppm}) (\text{CDCl}_3, 400 \text{MHz}) \]
4.62 (q, J=7.1 Hz, 2H, OCH\textsubscript{2}CH\textsubscript{3}), 4.56 (d, J=18.0 Hz, 1H, SCH\textsubscript{2}), 4.22 (d, J=18.0 Hz, 1H, SCH\textsubscript{2}), 2.09 (s, 1H, OH), 1.87 (dd, J=2.6Hz, J=9.2Hz, 1H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.51 – 1.66 (m, 4H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.18 – 1.28 (m, 1H, C(Me)\textsubscript{2}CH), 1.04 (s, 3H, C(CH\textsubscript{3})\textsubscript{2}), 1.02 (s, 3H, C(CH\textsubscript{3})\textsubscript{2}), 0.52 – 0.60 (m, 1H, C(Me)\textsubscript{2}CHCH), 0.44 – 0.52 (m, 1H, C(Me)CCH(CH\textsubscript{2})\textsubscript{2}), 0.29 – 0.37 (m, 1H, C(Me)CCH(CH\textsubscript{2})\textsubscript{2}), 0.17 (dt, J=5.1Hz, J=9.4Hz, 1H, C(Me)CCH(CH\textsubscript{2})\textsubscript{2}), -0.09 (dt, J=5.1Hz, J=9.3Hz, 1H, C(Me)CCH(CH\textsubscript{2})\textsubscript{2}).

**RMN** 
\[ ^{13}\text{C} (\delta, \text{ppm}) (\text{CDCl}_3, 100.6 \text{MHz}) \]
214.0 (C=S), 207.1 (C=O), 83.4 (COH), 70.4 (OCH\textsubscript{2}), 46.9 (C(CH\textsubscript{2})\textsubscript{2}), 45.3 (SCH\textsubscript{2}), 42.7 (C(CH\textsubscript{3})\textsubscript{2}), 33.3 (CH\textsubscript{2}C(OH)), 27.1 (CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}C(OH)), 23.0 (C(CH\textsubscript{3})\textsubscript{2}), 20.9 (CH\textsubscript{2}CH\textsubscript{2}C(OH)), 16.8 (C(CH\textsubscript{3})\textsubscript{2}), 13.7 (CH\textsubscript{2}CH\textsubscript{3}), 12.4 (CCHC(Me)\textsubscript{2}), 6.8 (CH\textsubscript{2}CCHC(Me)\textsubscript{2}), 2.4 (CH\textsubscript{2}CHC(Me)\textsubscript{2}).

**IR** \( \nu (\text{cm}^{-1}) (\text{CCl}_4) \)
3624 (OH), 3078 (C-H, cyclopropyl), 1714 (C=O), 1224, 1054 (C=S, C-O).

**HRMS** (EI+) calcd for C\textsubscript{16}H\textsubscript{26}O\textsubscript{3}S\textsubscript{2} 330.1323, found: 330.1316.
General procedure E: radical fragmentation of the cyclohexane.

A solution of xanthate (n mmol) in chlorobenzene (10n ml), was refluxed under nitrogen for 15 minutes. Dilauroyl peroxide was then added by portion of 10% every 20 minutes, until the reaction is over. The solvent was then removed in vacuo, giving crude vicinal diketone.

7-Isopropylidene-dec-9-ene-2,3-dione

C\textsubscript{13}H\textsubscript{20}O\textsubscript{2}

\[ M = 208.30 \text{ g.mol}^{-1} \]

Yellow oil

Reaction: Following general procedure E, the reaction was carried out using xanthate 10a (165 mg, 0.5 mmol).

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (95/5).

Yield: 45 %

**RMN \textsuperscript{1}H (δ, ppm) (CDCl\textsubscript{3}, 400 MHz)**

5.73 (tdd, J=6.4 Hz, J=10.0 Hz, J=16.6 Hz, 1H, CH=CH\textsubscript{2}), 4.93 – 5.01 (m, 2H, CH=CH\textsubscript{2}), 2.76 (d, J=6.3 Hz, 2H, CH\textsubscript{2}-CH=CH\textsubscript{2}), 2.71 (t, J=7.2 Hz, 2H, CH\textsubscript{3}CO), 2.32 (s, 3H, CH\textsubscript{3}CO), 2.04 (m, 2H, CH\textsubscript{2}C=C(Me)\textsubscript{2}), 1.65 (s, 3H, C=C(CH\textsubscript{3})\textsubscript{2}), 1.67 (s, 3H, C=C(CH\textsubscript{3})\textsubscript{2}), 1.62 – 1.70 (m, 2H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}).

**RMN \textsuperscript{13}C (δ, ppm) (CDCl\textsubscript{3}, 100.6 MHz)**

199.4 (C=O), 197.6 (C=O), 136.5 (CH=CH\textsubscript{2}), 128.9, 127.4 (C\textsubscript{q}=C\textsubscript{q}(Me)\textsubscript{2}), 114.6 (CH=CH\textsubscript{2}), 36.6, 35.4 (CH\textsubscript{2}CO, CH\textsubscript{2}CH=CH\textsubscript{2}), 31.5 (CH\textsubscript{2}CH\textsubscript{2}C=C(Me)\textsubscript{2}), 23.8 (CH\textsubscript{3}CO), 21.9 (CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 20.5, 20.4 (C=C(CH\textsubscript{3})\textsubscript{2}).

**IR ν (cm\textsuperscript{-1}) (CCl\textsubscript{4})**

1716 (C=O).

**HRMS (EI+)**

calcd for C\textsubscript{13}H\textsubscript{20}O\textsubscript{2} 208.1463, found: 208.1470.
7-Isopropylidene-9-methyl-dec-9-ene-2,3-dione 11b

![Chemical structure of 7-Isopropylidene-9-methyl-dec-9-ene-2,3-dione](image)

\[
\text{C}_{14}\text{H}_{22}\text{O}_2 \\
M = 222.32 \text{ g.mol}^{-1} \\
\text{Yellow oil}
\]

Reaction: Following general procedure E, the reaction was carried out using xanthate 10b (86 mg, 0.25 mmol).

Purification: Column chromatography, elution with petroleum ether/diethyl ether (97/3).

Yield: 45%

\begin{itemize}
  \item **RMN** \textsuperscript{1}H (δ, ppm) (CDCl\textsubscript{3}, 400 MHz): 4.71 (s, 1H, C=C\textsubscript{2}H\textsubscript{2}), 4.62 (s, 1H, C=C\textsubscript{2}H\textsubscript{2}), 2.68 – 2.72 (m, 4H, C=C-C\textsubscript{2}H\textsubscript{2}-C=C, C\textsubscript{2}H\textsubscript{2}CO), 2.32 (s, CH\textsubscript{3}CO), 2.02 (m, 2H, CH\textsubscript{3}CH\textsubscript{2}C=C), 1.69 (s, 3H, CH\textsubscript{3}-C=C), 1.67 (s, 3H, CH\textsubscript{3}-C=C), 1.64 (s, 3H, CH\textsubscript{3}-C=C), 1.58 – 1.7 (m, 2H, C\textsubscript{2}H\textsubscript{2}CH\textsubscript{2}C=C).
  \item **RMN** \textsuperscript{13}C (δ, ppm) (CDCl\textsubscript{3}, 100.6 MHz): 199.4 (C=O), 197.5 (C=O), 144.1 (C\textsubscript{q}=CH\textsubscript{2}), 129.0, 127.8 (C\textsubscript{q}=C\textsubscript{q}(Me)\textsubscript{2}), 110.4 (CH=CH\textsubscript{2}), 40.2 (CH\textsubscript{2}C\textsubscript{q}=CH\textsubscript{2}), 35.5 (CH\textsubscript{2}CO\textsubscript{2}), 31.3 (CH\textsubscript{2}CH\textsubscript{2}C=CH\textsubscript{2}(Me)\textsubscript{2}), 23.7, 22.5 (CH\textsubscript{3}CO, CH\textsubscript{3}C\textsubscript{q}=C), 22.0 (CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 20.6, 20.4 (C=C(CH\textsubscript{3})\textsubscript{2}).
  \item **IR** ν (cm\textsuperscript{-1}) (CCl\textsubscript{4}): 1716 (C=O).
  \item **HRMS** (EI+) calcd for C\textsubscript{14}H\textsubscript{22}O\textsubscript{2} 222.1620, found: 222.1622.
\end{itemize}

7,8-Dimethyl-non-7-ene-2,3-dione 11c

![Chemical structure of 7,8-Dimethyl-non-7-ene-2,3-dione](image)

\[
\text{C}_{11}\text{H}_{18}\text{O}_2 \\
M = 182.26 \text{ g.mol}^{-1} \\
\text{Yellow oil}
\]

Reaction: Following general procedure E, the reaction was carried out using xanthate 10c (150 mg, 0.5 mmol).

Purification: Column chromatography, elution with petroleum ether/diethyl ether (97/3).

Yield: 74%

\begin{itemize}
  \item **RMN** \textsuperscript{1}H (δ, ppm) (CDCl\textsubscript{3}, 400 MHz): 2.69 (t, J=7.2 Hz, 2H, CH\textsubscript{2}CO), 2.32 (s, 3H, CH\textsubscript{3}CO), 2.05 (t, J=7.5Hz, 2H, CH\textsubscript{2}C=CH\textsubscript{2}(Me)\textsubscript{2}), 1.68 (quint, J=7.5Hz, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.59 – 1.63 (m, 9H, CH\textsubscript{3}C=CH\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}).
\end{itemize}
RMN $^1$C (δ, ppm) (CDCl$_3$, 100.6 MHz) 199.3 (C=O), 197.4 (C=O), 126.7, 125.3 (C$_q$=C$_q$(Me)$_2$), 35.1 (CH$_2$CO), 33.5 (CH$_2$-C=C), 23.7 (CH$_3$CO), 21.6 (CH$_2$CH$_2$CH$_2$), 20.6 (C=C(CH$_3$)$_2$), 20.2 (C=C(CH$_3$)$_2$), 18.1 (CH$_3$C=C(Me)$_2$).

IR ν (cm$^{-1}$) (CCl$_4$) 1716 (C=O).

HRMS (EI+) calcd for C$_{11}$H$_{18}$O$_2$ 182.1307, found: 182, 1308.

$7$-Ethyl-$8$-methyl-$9$-ene-$2,3$-dione $11d$

Reaction: Following general procedure E, the reaction was carried out using xanthate $10d$ (159 mg, 0.5 mmol).

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (97/3).

Yield: 73 %

RMN $^1$H (δ, ppm) (CDCl$_3$, 400 MHz) 2.71 (t, J=7.2 Hz, 2H, CH$_2$CO), 2.33 (s, 3H, CH$_3$CO), 1.96 – 2.06 (m, 4H, CH$_2$C(=C)CH$_2$), 1.63 – 1.70 (m, 2H, CH$_2$-CH$_2$-CH$_2$), 1.63 (s, 3H, C=C(C(H$_3$)$_2$)), 1.62 (s, 3H, C=C(C(H$_3$)$_2$)), 0.92 (t, J=7.5Hz, CH$_3$CH$_3$).

RMN $^1$C (δ, ppm) (CDCl$_3$, 100.6 MHz) 199.4 (C=O), 197.5 (C=O), 133.1, 125.2 (C$_q$=C$_q$(Me)$_2$), 35.4 (CH$_2$CO), 31.0 (CH$_2$CH$_2$-C=C), 25.0 (CH$_2$CH$_2$-C=C), 23.7 (CH$_3$CO), 22.1 (CH$_2$CH$_2$CH$_2$), 20.3 (C=C(CH$_3$)$_2$), 20.0 (C=C(CH$_3$)$_2$), 13.1 (CH$_3$CH$_2$C=C).

IR ν (cm$^{-1}$) (CCl$_4$) 1716 (C=O).

HRMS (EI+) calcd for C$_{12}$H$_{20}$O$_2$ 196.1463, found: 196.1462.

$7$-Isopropyl-$8$-methyl-$9$-ene-$2,3$-dione $11e$

Reaction: Following general procedure E, the reaction was carried out using xanthate $10e$ (166 mg, 0.5 mmol).
Purification: Column chromatography, elution with petroleum ether/ethyl acetate (97/3).

Yield: 73 %

**RMN $^1$H (δ, ppm)**
(CDCl$_3$, 400 MHz) 2.85 (sept., J=7.0 Hz, 1H, $CH(CH_3)_2$), 2.76 (t, J=7.2 Hz, 2H, $CH_2CO$), 2.35 (s, 3H, $CH_3CO$), 1.92 – 1.98 (m, 2H, $CH_2-CH_2-C=C$), 1.66 (s, 3H, (CH$_3)_2C=C$), 1.65 (s, 3H, (CH$_3)_2C=C$), 1.58 – 1.66 (m, 2H, $CH_2-CH_2-C=C$), 0.96 (d, J=6.9Hz, 6H, CH($CH_3)_2$).

**RMN $^{13}$C (δ, ppm)**
(CDCl$_3$, 100.6 MHz) 199.4 (C=O), 197.6 (C=O), 136.5, 124.6 ($C_q=C_q(\text{Me})_2$), 36.1 ($CH_2CO$), 30.1 (CH(CH$_3)_2$), 27.2 ($CH_2-C=C$), 23.8 ($CH_3CO$), 23.8 ($CH_2CH_2CH_2$), 21.3 (CH($CH_3)_2$), 20.9 (C=C(CH$_3)_2$), 19.7 (C=C($CH_3)_2$).

**IR ν (cm$^{-1}$) (CCl$_4$)** 1716 (C=O).

**HRMS (EI+)** calcd for C$_{13}$H$_{22}$O$_2$ 210.1620, found: 210.1610.

### 7-Isopropylidene-dodecane-2,3-dione 11f

- C$_{15}$H$_{26}$O$_2$
- M = 238.37 g mol$^{-1}$
- Yellow oil

**Reaction:** Following general procedure E, the reaction was carried out using xanthate 10f (180 mg, 0.5 mmol).

**Purification:** Column chromatography, elution with petroleum ether/diethyl ether (97/3).

**Yield:** 67 %

**RMN $^1$H (δ, ppm)**
(CDCl$_3$, 400 MHz) 2.76 (t, J=7.2 Hz, 2H, $CH_2CO$), 2.33 (s, 3H, $CH_3CO$), 2.00 – 2.06 (m, 2H, $CH_2C=C(\text{Me})_2$), 1.93 – 1.98 (m, 2H, $CH_2C=C(\text{Me})_2$), 1.62 – 1.70 (m, 2H, $CH_2CH_2CH_2$), 1.63 (s, 6H, (CH$_3)_2C=C$), 1.22 – 1.36 (m, 6H, (CH$_2)_2CH_3$), 0.89 (t, J=7.0Hz, 3H, CH$_2CH_3$).

**RMN $^{13}$C (δ, ppm)**
(CDCl$_3$, 100.6 MHz) 199.4 (C=O), 197.5 (C=O), 131.9, 125.6 ($C_q=C_q(\text{Me})_2$), 35.4 ($CH_2CO$), 32.09 ($CH_2-C=C(\text{Me})_2$), 32.07 ($CH_2-C=C(\text{Me})_2$), 31.4 ($CH_2CH_2CH_3$), 28.4 ($CH_2CH_2CH_2CH_3$), 23.7 ($CH_3CO$), 22.6, 22.1 ($CH_2CH_3$, $CH_2CH_2CO$), 20.3 (C=C(CH$_3)_2$), 20.2 (C=C(CH$_3)_2$), 14.1 (CH$_2CH_3$).

**IR ν (cm$^{-1}$) (CCl$_4$)** 1716 (C=O).

**HRMS (EI+)** calcd for C$_{15}$H$_{26}$O$_2$ 238.1933, found: 238.1928.
7-Cyclopentyl-8-methyl-non-7-ene-2,3-dione 11g

![Chemical Structure](image)

C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>
M = 236.35 g.mol<sup>-1</sup>
Yellow oil

Reaction: Following general procedure E, the reaction was carried out using xanthate 10g (180 mg, 0.5 mmol).

Purification: Column chromatography, elution with petroleum ether/ethyl acetate (98/2).

Yield: 64%

RMN <sup>1</sup>H (δ, ppm) (CDCl<sub>3</sub>, 400 MHz)
- 2.78 – 2.87 (m, 1H, CH(CH<sub>2</sub>)<sub>4</sub>), 2.75 (t, J=7.2Hz, 2H, CH<sub>2</sub>CO), 2.34 (s, 3H, CH<sub>2</sub>CO), 1.90 – 1.96 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>C=C=C), 1.673 (s, 3H, CH<sub>3</sub>C=C), 1.668 (s, 3H, CH<sub>3</sub>C=C), 1.50 – 1.70 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>C=C, CH(CH<sub>2</sub>)<sub>4</sub>), 1.22 – 1.34 (m, 2H, CH(CH<sub>2</sub>)<sub>4</sub>).

RMN <sup>13</sup>C (δ, ppm) (CDCl<sub>3</sub>, 100.6 MHz)
- 199.4 (C=O), 197.6 (C=O), 133.5, 125.8 (C<sub>q</sub>=C<sub>q</sub>(Me)<sub>2</sub>), 42.9 (CH(CH<sub>2</sub>)<sub>4</sub>), 36.0 (CH<sub>2</sub>CO), 30.8 (CH(CH<sub>2</sub>)<sub>4</sub>), 28.1 (CH<sub>2</sub>-C=C(Me)<sub>2</sub>), 25.1 (CH(CH<sub>2</sub>)<sub>4</sub>), 23.8 (CH<sub>3</sub>CO), 23.7 (CH<sub>2</sub>CH<sub>2</sub>CO), 20.9 (C=C(CH<sub>3</sub>)<sub>2</sub>), 20.0 (C=C(CH<sub>3</sub>)<sub>2</sub>).

IR ν (cm<sup>-1</sup>) (CCl<sub>4</sub>) 1716 (C=O).

HRMS (EI+) calcd for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub> 236.1776, found: 236.1777.

Dithiocarbonic acid [3-(-3-acetyl-3-hydroxy-2,2-dimethyl-cyclohexylidene)-propyl] ester ethyl ester 17

![Chemical Structure](image)

C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>S<sub>2</sub>
M = 330.51 g.mol<sup>-1</sup>
Colorless oil

Reaction: A solution of xanthate 10h (142 mg, 0.43 mmol) in chlorobenzene (1 mL), was refluxed under nitrogen for 15 minutes. Dilauroyl peroxide was then added by portion of 5 to 10% every 20 minutes. After addition of 45% of DLP, the solvent was then removed in vacuo, giving crude compound 17.
Purification: Column chromatography, elution with petroleum ether/ethyl acetate (9/1).

Yield: 45 %

**RMN $^1$H ($\delta$, ppm)** (CDCl$_3$, 400 MHz)

5.27 (t, J=7.3 Hz, 1H, C=CH), 4.65 (q, J=7.1 Hz, 2H, OCH$_2$), 3.10 – 3.25 (m, 2H, SCH$_2$), 3.04 (s, 1H, OH), 2.44 – 2.58 (m, 2H, C=CHCH$_2$), 2.35 – 2.44 (m, 1H, CH$_2$CH$_2$CH$_2$), 2.25 (s, 3H, CH$_3$CO), 2.17 – 2.25 (m, 1H, CH$_2$CH$_2$CH$_2$), 2.11 (ddd, J=4.7Hz, J=10.8Hz, J=13.3Hz, 1H, CH$_2$CH$_2$CH$_2$), 1.67 – 1.77 (m, 1H, CH$_2$CH$_2$CH$_2$), 1.52 – 1.62 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.42 (t, J=7.1Hz, 3H, OCH$_2$CH$_3$), 1.14 (s, 3H, C(CH$_3$)$_2$), 1.05 (s, 3H, C(CH$_3$)$_2$).

**RMN $^{13}$C ($\delta$, ppm)** (CDCl$_3$, 100.6 MHz)

214.8, 212.8 (C=S, C=O), 145.6 (C$_q$=CH), 120.7 (C$_q$=CH), 83.6 (COH), 69.9 (OCH$_2$), 44.2 (C(Me)$_2$), 36.0 (SCH$_2$), 30.8 (CH$_2$CH$_2$CH$_2$), 28.3 (CH$_3$CO), 26.6 (C=CH-CH$_2$), 23.8 (C(CH$_3$)$_2$), 23.5 (CH$_2$CH$_2$CH$_2$), 22.8 (C(CH$_3$)$_2$), 21.8 (CH$_2$CH$_2$CH$_2$), 13.8 (OCH$_2$CH$_3$).

**IR $\nu$ (cm$^{-1}$)** (CCl$_4$)

3626, 3545 (OH), 1711 (C=O), 1647 (C=C), 1214, 1053 (C=S, C-O).

**HRMS (EI+)**

calcd for C$_{16}$H$_{26}$O$_3$S$_2$ 330.1324, found: 330.1323.
II. Copies of 1H and 13C NMR Spectra

Compound 7a

[Image of NMR spectra for compound 7a]
Compound 7e
Compound 7g

[Chemical structure diagram]

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011
<table>
<thead>
<tr>
<th>Compound 10b ppm (t1)</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.700</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.640</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.631</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.623</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.604</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.587</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.557</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.261</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.216</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ppm (t1)</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>213.992</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>206.724</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>144.947</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111.461</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>83.442</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.409</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45.271</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.384</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.993</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.745</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.459</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.689</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.127</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.069</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.775</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.901</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.694</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.748</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.018</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.089</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.173</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.973</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.265</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.732</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.466</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.031</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.769</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.403</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.227</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.203</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.008</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.958</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.833</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.685</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.489</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.390</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.118</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.944</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.893</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Compound 10c**

![NMR Spectrum of Compound 10c](image)

- *ppm (t1)*
  - 0.0
  - 1.0
  - 2.0
  - 3.0
  - 4.0
  - 5.0
  - 6.0

- *ppm (t2)*
  - 0.96
  - 1.01
  - 4.11
  - 3.03
  - 1.19
  - 0.84
Compound 10e

Supplementary Material (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2011
Compound 10f

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011
Compound 10h

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011
Compound 11a
Compound 11d
**Compound 11e**

![NMR Spectrogram](image)

**Supplementary Material (ESI) for Chemical Communications**

This journal is (c) The Royal Society of Chemistry 2011
Compound 11f

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011
Compound 11g

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011
Supplementary Material (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2011

Compound 17

-ppm (t1)

1.0 2.0 3.0 4.0 5.0

5.289 5.271 5.252
4.681 4.663 4.646 4.628
3.213 3.196 3.178 3.159 3.140
3.037 2.525 2.506 2.499 2.481 2.383 2.254 2.246
1.720 1.707 1.575 1.440 1.423 1.405 1.138 1.049

-ppm (t1)


-ppm (t1)

200 150 100 50

214.835 212.771