Supporting Information

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

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Contents:

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 ((MH)+, (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.Me_2S** (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 l 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.

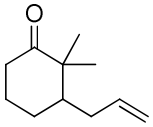
Modified general procedure A : 1,4 addition of organocuprate

To a solution of **CuBr.Me_2S** (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

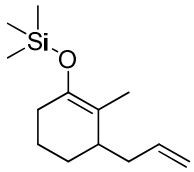
To a solution of the above **silyl enol ether** (n mmol) in **THF** (6.5n mL) and cooled at 0 ºC was rapidly added a solution of **methyllithium** (1.2n mmol). The resulting solution was stirred for 15 min, then cooled at -78 ºC. A solution of **methyl iodide** (5n mmol) in **HMPA** (n mL) was then quickly 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



$C_{11}H_{18}O$
M = 166.26 g.mol^{-1}
Colorless oil

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 %).



RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz):

144.3 (C=***C***OTMS), 137.8 (***C***H=CH_2), 115.5 (CH=***C***H_2), 114.8 (***C***=COTMS), 38.6 (***C***H-C=C), 37.6, 30.4, 27.0, 20.2 (4 x ***C***H_2), 14.4 (***C***H_3C=C), 0.61 (Si(***C***H_3)$_3$)

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 %

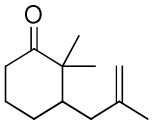
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 5.70 (dddd, J=5.7 Hz, J=8.5 Hz, J=10.1 Hz, J=16.9 Hz, 1H, CH_2=C***H***), 4.95 – 5.2 (m, 2H, C***H$_2$***=CH), 2.46 (ddd, J=6.0 Hz, J=11.7 Hz, J=14.0, 1H, C***H$_{2(ax)}$***-C=O), 2.32 – 2.32 (m, 2H, C***H$_{2(eq)}$***-C=O, C***H$_2$***-CH=CH_2), 1.90 – 1.98 (m, 1H, C***H$_2$***C***H$_2$***C***H***C***H$_2$***), 1.76 – 1.87 (m, 2H, C***H$_2$***C***H$_2$***C***H***C***H$_2$***), 1.38 – 1.62 (m, 3H, C***H$_2$***C***H$_2$***C***H***C***H$_2$***), 1.11 (s, 3H, C***H$_3$***), 1.01 (s, 3H, C***H$_3$***).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 215.7 (***C***=O), 137.5 (***C***H=CH_2), 115.9 (CH=***C***H_2), 48.7 (***C***$(CH_3)_2$), 47.3 (***C***H-C$(Me)_2$), 37.9, 34.4, 25.7, 24.8 (4 x ***C***H_2), 22.9 (***C***H_3), 19.9 (***C***H_3).

IR ν (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 7b



$C_{12}H_{20}O$
M = 180.29 $g.mol^{-1}$
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 %

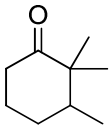
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.69 (s, 1H, C=C***H*****$_2$**), 4.61 (s, 1H, C=C***H*****$_2$**), 2.42 (ddd, J=6.2Hz, J=11.9Hz, J=13.9Hz, 1H, C***H*****$_{2(ax)}$**-C=O), 2.23 (dtd, J=1.3Hz, J=4.8Hz, J=13.9Hz, 1H, C***H*****$_{2(eq)}$**-C=O), 2.1 (m, 1H,C***H*****$_2$**-C***H*****$_2$**-C***H***-C***H*****$_2$**), 1.84 – 1.94 (m, 1H,C***H*****$_2$**-C***H*****$_2$**-C***H***-C***H*****$_2$**), 1.79 (dd, J=11.3Hz, J=13.5Hz, 1H, C***H*****$_2$**-C***H*****$_2$**-C***H***-C***H*****$_2$**), 1.69 – 1.76 (m, 1H,C***H*****$_2$**-C***H*****$_2$**-C***H***-C***H*****$_2$**), 1.60 (s, 3H, C***H*****$_3$**-C=CH_2), 1.44 – 1.58 (m, 2H,C***H*****$_2$**-C***H*****$_2$**-C***H***-C***H*****$_2$**), 1.29 – 1.41 (m, 1H,C***H*****$_2$**-C***H*****$_2$**-C***H***-C***H*****$_2$**), 1.06 (s, 3H, C***H*****$_3$**), 0.96 (s, 3H, C***H*****$_3$**).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 215.6 (***C***=O), 143.6 (***C*****$_q$**=CH_2), 112.0 (CH=***C***H_2), 48.5 (***C***$(CH_3)_2$), 44.9 (***C***H-$C_q(Me)_2$), 38.3, 37.7 (***C***H_2CO, ***C***H_2-C=CH_2), 25.4, 24.8 (***C***H_2-***C***H_2-CH), 22.7 (C(***C***$H_3)_2$), 21.7 (***C***H_3C=CH_2), 19.7 (C(***C***$H_3)_2$).

IR ν (cm^{-1}) (CCl_4): 1709 (C=O).

HRMS (EI+): calcd for $C_{12}H_{20}O$ 180.1514, found: 180.1521.

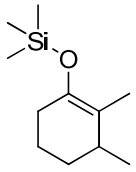
2,2,3-Trimethyl-cyclohexanone 7c



$C_9H_{16}O$
$M = 140.22\ g.mol^{-1}$
Colorless oil

Reference: Chapuis, C.; Brauchli, R.; Thommen, W. *Helv. Chim. Acta* **1993**, *76*, 535.

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}C (δ, ppm) ($CDCl_3$, 100.6 MHz):

143.2 (C=***C***OTMS), 116.4 (***C***=COTMS), 35.6 (***C***H-C=C), 31.3, 30.5, 20.4 (3 x ***C***H_2), 19.9 (***C***H_3CH) 14.2 (***C***H_3C=C), 0.64 (Si(***C***H_3)$_3$)

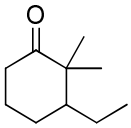
The **silyl enol ether** (1.22 g, 6.2 mmol) was then transformed following general procedure B, yielding compound **7c**.

Purification: None

Yield: 59 %

Product described in the literature.

3-Ethyl-2,2-dimethyl-cyclohexanone 7d



$C_{10}H_{18}O$
M = 154.25 g.mol^{-1}
Colorless oil

Reference: Chapuis, C.; Brauchli, R.; Thommen, W. *Helv. Chim. Acta* **1993**, *76*, 535.

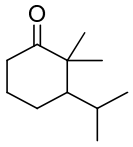
Reaction: Following general procedure A, the reaction was carried out using **2-methyl-2-cyclohexenone (**1.1 mL, 10 mmol), and **ethylmagnesium bromide (1M in THF)**, giving crude silyl enol ether.
The **silyl enol ether** (10 mmol) was then transformed following general procedure B, yielding compound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

Purification: None

Yield: 75 %

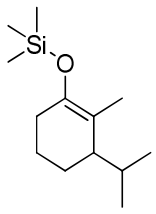
Product described in the literature.

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



$C_{11}H_{20}O$
M = 168.28 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 **isopropylmagnesium bromide (2M in THF)**, giving crude silyl enol ether.



RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz):

145.0 (C=***C***OTMS), 114.9 (***C***=COTMS), 44.4 (***C***H-C=C), 30.8, 28.3, 21.0 (3 x ***C***H_2), 22.3, 22.2 (CH(***C***H_3)$_2$), 16.1 (***C***H(CH_3)$_2$), 13.8 (***C***H_3C=C), 0.63 (Si(***C***H_3)$_3$)

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 %

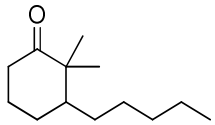
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 2.5 (dt, J=6.3Hz, J=13.4Hz, 1H, C***H***$_2$CO), 2.22 – 2.28 (m, 1H, C***H***$_2$CO), 2.00 – 2.07 (m, 1H, C***H***$_2$-C***H***$_2$), 1.95 (dtd, J=1.0Hz, J=7.0Hz, J=13.8Hz, 1H, C***H***$_2$-C***H***$_2$), 1.44 – 1.68 (m, 3H, C***H***$_2$-C***H***$_2$-C***H***-C***H***), 1.27 – 1.32 (m, 1H, C***H***$_2$-C***H***$_2$-C***H***-C***H***),1.09 (s, 3H, C(C***H*****$_3$**$)_2$), 1.07 (s, 3H, C(C***H*****$_3$**$)_2$), 0.92 (d, J=7.0Hz, 3H, CH(C***H*****$_3$**$)_2$), 0.89 (d, J=6.9Hz, 3H, CH(C***H*****$_3$**$)_2$).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 216.0 (***C***=O), 52.7 (***C***HCH$(CH_3)_2$), 50.0 (***C*****$_q$**$(Me)_2$), 38.2 (***C***H_2CO), 26.8 (***C***H$(CH_3)_2$), 25.8 (***C***H_2-CH_2), 24.8 (CH_3), 22.7 (CH_3), 21.3 (***C***H_2-CH_2), 20.7 (CH_3), 19.1 (CH_3).

IR ν (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 7f



$C_{13}H_{24}O$
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 %

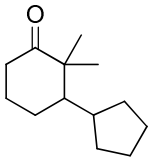
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 2.49 (ddd, J=6.1Hz, J=12.0Hz, J=13.9Hz, 1H, C***H***$_2$CO), 2.26 – 2.33 (m, 1H, C***H***$_2$CO), 1.93 – 2.02 (m, 1H, C***H***$_2$-C***H***$_2$), 1.84 – 1.90 (m, 1H, C***H***$_2$-C***H***$_2$), 1.53 – 1.65 (m, 1H, C***H***$_2$-C***H***$_2$-C***H***-pentyl), 1.52 – 1.35 (m, 4H, C***H***$_2$-C***H***$_2$-C***H***-(C***H*****$_2$**$)_4$), 1.10 – 1.35 (m, 6H, C***H***$_2$-C***H***$_2$-C***H***-(C***H*****$_2$**$)_4$), 1.10 (s, 3H, C(C***H*****$_3$**$)_2$), 1.01 (s, 3H, C(C***H*****$_3$**$)_2$), 0.88 (t, J=7.0Hz, 3H, $(CH_2)_4$C***H*****$_3$**).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 216.6 (***C***=O), 49.0 (***C*****$_q$**$(Me)_2$), 47.8 (***C***H-pentyl), 38.0 (***C***H_2CO), 32.0, 29.6, 27.9, 26.1, 25.2, 22.6 ((***C***H_2**$)_2$**-CH-(***C***H_2**$)_4$**), 22.8, (C(***C***$H_3)_2$), 19.9 (C(***C***$H_3)_2$), 14.0 (($CH_2)_4$***C***H_3).

IR ν (cm^{-1}) (CCl_4) 1708 (C=O).

HRMS (EI+) calcd for $C_{13}H_{24}O$ 196.1827, found: 196.1822.

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



$C_{13}H_{22}O$
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 %

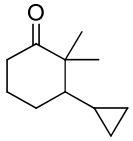
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz) 2.45 – 2.55 (m, 1H, C***H*****$_{2(ax)}$**-C=O), 2.23 – 2.32 (m, 1H, C***H*****$_{2(eq)}$**-C=O), 1.90 – 2.08 (m, 2H), 1.24 – 1.80 (m, 10H), 1.18 – 1.35 (m, 2H) (C***H*****$_2$**C***H*****$_2$**C***H*****C***H*****(C***H*****$_2$)$_4$**), 1.06 (s, 3H, C***H*****$_3$**), 0.96 (s, 3H, C***H*****$_3$**).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz) 216.3 (***C***=O), 50.9 (***C***HC_q(Me)$_2$), 49.9 (***C*****$_q$**(Me)$_2$), 39.9 (***C***H$(CH_2)_4$), 38.0 (***C***H_2CO), 33.7, 29.2, 25.9, 25.6, 24.6, 23.1 (***C***H_2-***C***H_2CH-***C***H(***C***$H_2)_4$), 23.3 (CH_3), 21.0 (CH_3).

IR ν (cm^{-1}) (CCl_4) 1706 (C=O).

HRMS (EI+) calcd for $C_{13}H_{22}O$ 194.1671, found: 194.1662.

3-Cyclopropyl-2,2-dimethyl-cyclohexanone 7h



$C_{11}H_{18}O$
M = 166.26 $g.mol^{-1}$
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 ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 2.38 (ddd, J=6.0Hz, J=10.7Hz, J=14.0Hz, 1H, C***H*****$_{2(ax)}$**-C=O), 2.23 (dtd, J=0.9Hz, J=5.5Hz, J=14.0Hz, 1H, C***H*****$_{2(eq)}$**-C=O), 1.87 – 1.96 (m, 1H, $COCH_2$-C***H*****$_2$**-C***H*****$_2$**), 1.73 – 1.82 (m, 1H, $COCH_2$-C***H*****$_2$**-C***H*****$_2$**), 1.48 – 1.70 (m, 2H, $COCH_2$-C***H*****$_2$**-C***H*****$_2$**), 1.12 (s, 3H, C***H*****$_3$**), 1.09 (s, 3H, C***H*****$_3$**), 0.67 (dt, J=3.8Hz, J=9.5Hz, C***H***$(CH_2)_2$), 0.46 – 0.62 (m, 2H, C***H***-CH(C***H***$_2)_2$), 0.31 – 0.39 (m, 1H, CH(C***H***$_2)_2$), 0.13 (td, J=4.6Hz, J=9.6Hz, 1H, CH(C***H***$_2)_2$), -0.10 (td, J=4.9Hz, J=14.8Hz, 1H, CH(C***H***$_2)_2$).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 216.0 (***C***=O), 53.1 (***C***$HC_q(Me)_2$), 49.8 (***C*****$_q$**$(Me)_2$), 37.5 (***C***H_2CO), 27.0, 24.8 ($COCH_2$-***C***H_2-***C***H_2), 23.8 (CH_3), 20.7 (CH_3), 11.8 (***C***$H(CH_2)_2$), 7.19 (CH(***C***$H_2)_2$), 2.14 (CH(***C***$H_2)_2$).

IR ν (cm^{-1}) (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

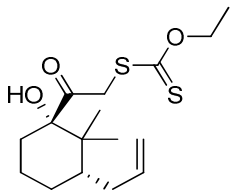
To a stirred solution of **ethyl vinyl ether** (5n mmol) in freshly **distilled THF** (2n ml) under nitrogen and at – 78°C, was added dropwise over 10 minutes ***tert*-butyl lithium** (~1.35 M in pentane, 2n mmol). After 15 more minutes, the acetone/dry ice bath was replaced by a water/ice bath, and 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 $MgSO_4$. 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 $MgSO_4$, 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 **10a**



$C_{16}H_{26}O_3S_2$
M = 330.51 g.mol^{-1}
White solid

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

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

Yield: 58 % (over 3 steps)

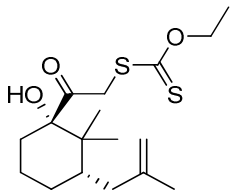
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 5.70 (m, 1H, CH_2=C***H***), 4.98 (m, 2H, C***H*****$_2$**=CH), 4.64 (q, J= 7.1 Hz, 2H, OC***H*****$_2$**CH_3), 4.58 (d, J=18.0 Hz, 1H, SC***H*****$_2$**), 4.25 (d, J=18.0 Hz, 1H, SC***H*****$_2$**), 2.27 (m, 1H, C***H*****$_2$**$CH=CH_2$), 2.12 (m, 1H, C***H***$C(Me)_2$), 2.00 (s, 1H, OH), 1.86 – 1.93 (m, 1H, C***H*****$_2$**COH), 1.61 – 1.72 (m, 2H, C***H*****$_2$**$CH=CH_2$ and CH_2C***H*****$_2$**CH), 1.52 – 1.61 (m, 3H, C***H*****$_2$**COH and C***H*****$_2$**CH_2CH), 1.42 (t, J=7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.02 – 1.15 (m, 1H, CH_2C***H*****$_2$**CH), 0.97 (s, 3H, $C(CH_3)_2$), 0.91 (s, 3H, $C(CH_3)_2$).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 214.1 (***C***=S), 206.7 (***C***=O), 138.7 (***C***$H=CH_2$), 115.3 ($CH=CH_2$), 83.4 (***C***OH), 70.5 (O***C***H_2), 45.3 (S***C***H_2), 41.5 (***C***$(CH_3)_2$), 41.3 (***C***H), 34.9 (***C***H_2-$CH=CH_2$), 33.6 (***C***H_2COH), 25.8 (CH_2***C***H_2CH), 22.4 (C(***C***$H_3)_2$), 20.8 (***C***H_2CH_2CH), 16.1 (C(***C***$H_3)_2$),13.8 (CH_2***C***H3).

IR ν (cm^{-1}) (CCl_4): 3623 (OH), 1714 (C=O), 1224, 1053 (C=S, C-O).

HRMS (EI+): calcd for $C_{16}H_{26}O_3S_2$ 330.1324, found: 330.1317.

Dithiocarbonic acid ethyl ester {2-[1-hydroxy-2,2-dimethyl-3-(2-methyl-allyl)-cyclohexyl]-2-oxo-ethyl} ester **10b**



$C_{17}H_{28}O_3S_2$
M = 344.53 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 %

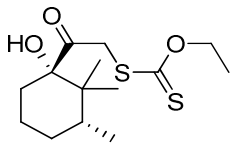
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.70 (s, 1H, C=C***H₂***), 4.63 (s, 1H, C=C***H₂***), 4.62 (q, J= 6.9 Hz, 2H, OC***H₂***CH_3), 4.58 (d, J=18.2 Hz, 1H, SC***H***$_2$), 4.24 (d, J=18.0 Hz, 1H, SC***H***$_2$), 2.21 – 2.29 (m, 1H, C***H₂***C***H₂***C***H₂***C***H***C***H₂***), 2.09 – 2.15 (m, 1H, C***H₂***C***H₂***C***H₂***C***H***C***H₂***), 2.12 (s, 1H, O***H***), 1.87 – 1.92 (m, 1H, C***H₂***C***H₂***C***H₂***C***H***C***H₂***), 1.65 – 1.70 (m, 1H, C***H₂***C***H₂***C***H₂***C***H***C***H₂***), 1.67 (s, 3H, C***H₃***-C=CH_2), 1.50 – 1.63 (m, 4H, C***H₂***C***H₂***C***H₂***C***H***C***H₂***), 1.40 (t, J=7.1 Hz, 3H, OCH_2C***H₃***), 0.98 – 1.08 (m, 1H, C***H₂***C***H₂***C***H₂***C***H***C***H₂***), 0.94 (s, 3H, C(C***H₃***)$_2$), 0.89 (s, 3H, C(C***H₃***)$_2$).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 214.0 (***C***=S), 206.7 (***C***=O), 144.9 (***Cq***=CH_2), 111.5 (CH=***C***H_2), 83.4 (***C***OH), 70.4 (O***C***H_2), 45.3 (S***C***H_2), 41.4 (***C***$(CH_3)_2$), 39.0 (***C***H_2C_q=CH_2), 38.7 (***C***H), 33.5 (***C***H_2-COH), 25.7 (CH_2***C***H_2CH), 22.12, 22.07 (C(***C***$H_3)_2$, ***C***H_3C=CH_2), 20.8 (***C***H_2CH_2CH), 15.9 (C(***C***$H_3)_2$),13.7 (CH_2***C***H3).

IR ν (cm^{-1}) (CCl_4): 3623, 3495 (OH), 1715 (C=O), 1223, 1053 (C=S, C-O).

HRMS (EI+): calcd for $C_{17}H_{28}O_3S_2$ 344.1480, found: 344.1474.

Dithiocarbonic acid ethyl ester [2-(1-hydroxy-2,2,3-trimethyl-cyclohexyl)-2-oxo-ethyl] ester **10c**



$C_{14}H_{24}O_3S_2$
M = 304.47 g.mol^{-1}
White solid

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 %

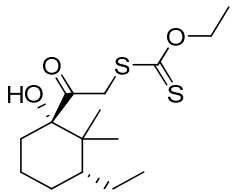
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.63 (q, J= 7.1 Hz, 2H, OC***H*₂**CH_3), 4.58 (d, J=18.0 Hz, 1H, SC***H*₂**), 4.25 (d, J=18.0 Hz, 1H, SC***H*₂**), 2.22 (m, 1H, C***H***C(Me)$_2$), 2.00 (s, 1H, OH), 1.84 – 1.91 (m, 1H, C***H*₂**C***H*₂**C***H*₂**), 1.50 – 1.72 (m, 3H, C***H*₂**C***H*₂**C***H*₂**), 1.42 – 1.50 (m, 1H, C***H*₂**C***H*₂**C***H*₂**), 1.42 (t, J=7.1 Hz, 3H, OCH_2C***H*₃**), 1.16 – 1.26 (m, 1H, C***H*₂**C***H*₂**C***H*₂**), 0.92 (s, 3H, C(C***H*₃**)$_2$), 0.90 (s, 3H, C(C***H*₃**)$_2$), 0.83 (d, J=6.9Hz, 3H, CHC***H*₃**).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 214.1 (***C***=S), 206.9 (***C***=O), 83.4 (***C***OH), 70.4 (O***C***H_2), 45.3 (S***C***H_2), 41.4 (***C***$(CH_3)_2$), 35.7 (***C***H), 33.6 (***C***H_2COH), 29.4 (CH_2***C***H_2CH), 22.4 (C(***C***$H_3)_2$), 21.1 (***C***H_2CH_2CH), 16.0 (C(***C***$H_3)_2$), 15.1 (***C***H_3-CH), 13.8 (CH_2***C***H3).

IR ν (cm^{-1}) (CCl_4): 3624, 3494 (OH), 1716 (C=O), 1224, 1053 (C=S, C-O).

HRMS (EI+): calcd for $C_{14}H_{24}O_3S_2$ 304.1167, found: 304.1168.

Dithiocarbonic acid ethyl ester [2-(3-ethyl-1-hydroxy-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester **10d**



$C_{15}H_{26}O_3S_2$
M = 318.50 g.mol^{-1}
White solid

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 %

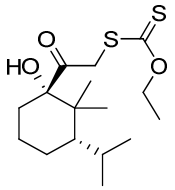
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.63 (q, J= 7.1 Hz, 2H, OC***H*****$_2$**CH_3), 4.58 (d, J=18.1 Hz, 1H, SC***H*****$_2$**), 4.24 (d, J=18.1 Hz, 1H, SC***H*****$_2$**), 2.02 (s, 1H, OH), 1.83 – 1.91 (m, 2H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.68 – 1.76 (m, 1H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.45 – 1.68 (m, 4H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.41 (t, J=7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.16 – 1.26 (m, 1H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**), 1,00 – 1,10 (m, 1H, CHC***H*****$_2$**CH_3), 0.93 (s, 3H, C(C***H*****$_3$**)$_2$), 0.87 (s, 3H, C(C***H*****$_3$**)$_2$), 0.84 – 0.90 (m, 4H, CHC***H*****$_2$**C***H*****$_3$**).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 214.1 (***C***=S), 206.8 (***C***=O), 83.4 (***C***OH), 70.4 (O***C***H_2), 45.4 (S***C***H_2), 43.6 (***C***H), 41.7 (***C***$(CH_3)_2$), 33.5 (***C***H_2COH), 25.4 (CH_2***C***H_2CH), 22.7 (CH***C***H_2CH_3), 22.2 (C(***C***$H_3)_2$), 20.9 (***C***H_2CH_2CH), 15.9 (C(***C***$H_3)_2$), 13.7 (OCH_2***C***H_3), 13.3 ($CHCH_2$***C***H_3).

IR ν (cm^{-1}) (CCl_4): 3623, 3496 (OH), 1716 (C=O), 1224, 1053 (C=S, C-O).

HRMS (EI+): calcd for $C_{15}H_{26}O_3S_2$ 318.1324, found: 318.1314.

Dithiocarbonic acid ethyl ester [2-(1-hydroxy-3-isopropyl-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester — 10e



$C_{16}H_{28}O_3S_2$
M = 332.52 $g.mol^{-1}$
White solid

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 %

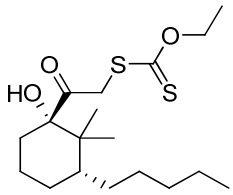
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.63 (q, J= 7.1 Hz, 2H, OC***H*****$_2$**CH_3), 4.58 (d, J=18.3 Hz, 1H, SC***H*****$_2$**), 4.24 (d, J=18.1 Hz, 1H, SC***H*****$_2$**), 2.06 (dd, J=2.8Hz, J=13.0Hz, 1H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.91 (s, 1H, OH), 1.80 – 1.90 (m, 2H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.68 – 1.76 (m, 1H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.44 – 1.65 (m, 4H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.42 (t, J=7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.15 – 1.28 (m, 1H, C***H***(C***H*****$_3$**)$_2$), 0.94 (s, 6H, C(C***H*****$_3$**)$_2$), 0.91 (d, J=6.9Hz, 3H, CH(C***H*****$_3$**)$_2$), 0.82 (d, J=6.9Hz, 3H, CH(C***H*****$_3$**)$_2$).

RMN ^{13}C (δ, ppm) (CDCl$_3$, 100.6 MHz) 214.1 (***C***=S), 206.7 (***C***=O), 83.5 (***C***OH), 70.4 (O***C***H$_2$), 45.53 (***C***H), 45.48 (S***C***H$_2$), 42.8 (***C***(CH$_3$)$_2$), 33.9 (***C***H$_2$COH), 25.5, 25.3, 22.2 (C(***C***H$_3$)$_2$, ***C***H(***C***H$_3$)$_2$), 21.35, 21.30 (***C***H$_2$***C***H$_2$), 19.2, 16.6 (C(***C***H$_3$)$_2$, ***C***H(***C***H$_3$)$_2$), 13.8 (CH$_2$***C***H$_3$).

IR ν (cm^{-1}) (CCl$_4$) 3623, 3424 (OH), 1718 (C=O), 1223, 1053 (C=S, C-O).

HRMS (EI+) calcd for $C_{16}H_{28}O_3S_2$ 332.1480, found: 332.1476.

Dithiocarbonic acid ethyl ester [2-(1-hydroxy-2,2-dimethyl-3-pentyl-cyclohexyl)-2-oxo-ethyl] ester — 10f



$C_{18}H_{32}O_3S_2$
M = 360.57 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 %

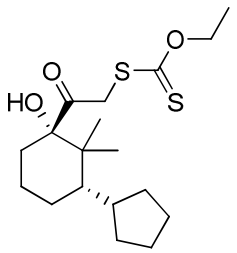
RMN ^{1}H (δ, ppm) (CDCl$_3$, 400 MHz) 4.64 (q, J= 7.1 Hz, 2H, OC***H*****$_2$**CH$_3$), 4.59 (d, J=18.3 Hz, 1H, SC***H*****$_2$**), 4.24 (d, J=18.0 Hz, 1H, SC***H*****$_2$**), 1.99 (s, 1H, OH), 1.92 – 2.02 (m, 1H, C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**C***H***), 1.86 – 1.92 (m, 1H, (C***H*****$_2$**)$_3$**C***H***),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

RMN ^{13}C (δ, ppm) (CDCl$_3$, 100.6 MHz) 214.0 (***C***=S), 206.8 (***C***=O), 83.4 (***C***OH), 70.4 (O***C***H$_2$), 45.4 (S***C***H$_2$), 41.6 (***C***H), 41.5 (***C***(CH$_3$)$_2$), 33.5 (***C***H$_2$COH), 32.2, 30.0, 28.3, 26.2, 22.6, 20.9 (***C***H$_2$***C***H$_2$CH(***C***H$_2$)$_4$), 22.1 (C(***C***H$_3$)$_2$), 15.9 (C(***C***H$_3$)$_2$), 14.0 ((CH$_2$)$_4$***C***H$_3$), 13.7 (OCH$_2$***C***H$_3$).

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

HRMS (EI+) calcd for $C_{18}H_{32}O_3S_2$ 360.1793, found: 360.1802.

Dithiocarbonic acid [2-(3-cyclopentyl-1-hydroxy-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester ethyl ester **10g**



$C_{18}H_{30}O_3S_2$
M = 358.56 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 %

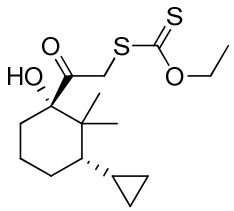
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.64 (q, J=7.2 Hz, 2H, OC***H*₂**CH_3), 4.58 (d, J=18.1 Hz, 1H, SC***H*₂**), 4.26 (d, J=18.0 Hz, 1H, SC***H*₂**), 2.21 (td, J=3.5Hz, J=12.7Hz, 1H, C***H*₂**COH), 1.91 (s, 1H, O***H***), 1.84 – 1.92 (m, 2H, C***H*₂**COH, (C***H*₂**)$_2$C***H***C***H***(C***H*₂**)$_4$), 1.67 – 1.76 (m, 1H, (C***H*₂**)$_2$C***H***C***H***(C***H*₂**)$_4$), 1.45 – 1.64 (m, 8H, (C***H*₂**)$_2$C***H***C***H***(C***H*₂**)$_4$), 1.42 (t, J=7.1 Hz, 3H, OCH$_2$C***H*₃**), 1.17 – 1.32 (m, 4H, (C***H*₂**)$_2$C***H***C***H***(C***H*₂**)$_4$), 0.96 (s, 3H, C(C***H*₃**)$_2$), 0. 93 (s, 3H, C(C***H*₃**)$_2$).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 214.0 (***C***=S), 206.7 (***C***=O), 83.6 (***C***OH), 70.4 (O***C***H$_2$), 45.5 (S***C***H$_2$), 44.1 (***C***HC(Me)$_2$), 42.6 (***C***(CH$_3$)$_2$), 39.5 (***C***H(CH$_2$)$_4$), 33.9 (***C***H$_2$), 33.8 (***C***H$_2$), 29.2 (***C***H$_2$), 25.9 (***C***H$_2$), 24.7 (***C***H$_2$), 23.0 (C(***C***H$_3$)$_2$), 22.9 (***C***H$_2$), 21.4 (***C***H$_2$), 17.0 (C(***C***H$_3$)$_2$), 13.7 (CH$_2$***C***H3).

IR ν (cm^{-1}) (CCl_4): 3624 (OH), 1715 (C=O), 1223, 1052 (C=S, C-O).

HRMS (EI+): calcd for $C_{18}H_{30}O_3S_2$ 358.1637, found: 358.1639.

Dithiocarbonic acid [2-(3-cyclopropyl-1-hydroxy-2,2-dimethyl-cyclohexyl)-2-oxo-ethyl] ester ethyl ester **10h**



$C_{16}H_{26}O_3S_2$
M = 330.51 g.mol^{-1}
White solid

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}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.62 (q, J=7.1 Hz, 2H, OC***H₂***CH_3), 4.56 (d, J=18.0 Hz, 1H, SC***H***$_2$), 4.22 (d, J=18.0 Hz, 1H, SC***H***$_2$), 2.09 (s, 1H, O***H***), 1.87 (dd, J=2.6Hz, J=9.2Hz, 1H, C***H₂***C***H₂***C***H₂***), 1.51 – 1.66 (m, 4H, C***H₂***C***H₂***C***H₂***), 1.3 – 1.4 (m, 1H, C***H₂***C***H₂***C***H₂***), 1.40 (t, J=7.1Hz, 3H, OCH_2C***H₃***), 1.18 – 1.28 (m, 1H, $C(Me)_2$***C***H), 1.04 (s, 3H, $C(C$***H₃***$)_2$), 1.02 (s, 3H, $C(C$***H₃***$)_2$), 0.52 – 0.60 (m, 1H, $C(Me)_2CH$***C***H), 0.44 – 0.52 (m, 1H, $C(Me)_2CHCH(C$***H***$_2)_2$), 0.29 – 0.37 (m, 1H, $C(Me)_2CHCH(C$***H***$_2)_2$), 0.17 (dt, J=5.1Hz, J=9.4Hz, 1H, $C(Me)_2CHCH(C$***H***$_2)_2$), -0.09 (dt, J=5.1Hz, J=9.3Hz, 1H, $C(Me)_2CHCH(C$***H***$_2)_2$).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 214.0 (***C***=S), 207.1 (***C***=O), 83.4 (***C***OH), 70.4 (O***C***H_2), 46.9 (***C***$HC(Me)_2$), 45.3 (S***C***H_2), 42.7 (***C***$(CH_3)_2$), 33.3 (***C***$H_2C(OH)$), 27.1 (***C***$H_2CH_2CH_2C(OH)$), 23.0 ($C($***C***$H_3)_2$), 20.9 (***C***$H_2CH_2C(OH)$), 16.8 ($C($***C***$H_3)_2$), 13.7 (CH_2***C***H3), 12.4 (***C***$HCHC(Me)_2$), 6.8 ((***C***$H_2)_2CHCHC(Me)_2$), 2.4 ((***C***$H_2)_2CHCHC(Me)_2$).

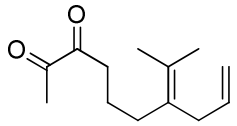
IR ν (cm^{-1}) (CCl_4): 3624 (OH), 3078 (C-H, cyclopropyl), 1714 (C=O), 1224, 1054 (C=S, C-O).

HRMS (EI+): calcd for $C_{16}H_{26}O_3S_2$ 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.

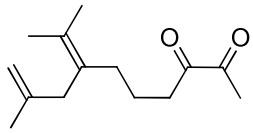
7-Isopropylidene-dec-9-ene-2,3-dione 11a



$C_{13}H_{20}O_2$
M = 208.30 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 ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz)	5.73 (tdd, J=6.4 Hz, J=10.0 Hz, J=16.6 Hz, 1H, C***H***=CH_2), 4.93 – 5.01 (m, 2H, CH=C***H₂***), 2.76 (d, J=6.3 Hz, 2H, C***H₂***-CH=CH_2), 2.71 (t, J=7.2 Hz, 2H, C***H₂***CO), 2.32 (s, 3H, C***H₃***CO), 2.04 (m, 2H, C***H₂***C=C$(Me)_2$), 1.65 (s, 3H, C=C(C***H₃***)$_2$), 1.67 (s, 3H, C=C(C***H₃***)$_2$), 1.62 – 1.70 (m, 2H, CH_2C***H₂***CH_2).
RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz)	199.4 (***C***=O), 197.6 (***C***=O), 136.5 (***C***H=CH_2), 128.9, 127.4 (***C*** $_q$=***C*** $_q$$(Me)_2$), 114.6 (CH=***C***$H_2$), 36.6, 35.4 (***C***$H_2$CO, ***C***$H_2$CH=$CH_2$), 31.5 ($CH_2$***C***$H_2$C=C$(Me)_2$), 23.8 (***C***$H_3$CO), 21.9 ($CH_2$***C***$H_2CH_2$), 20.5, 20.4 (C=C(***C***$H_3)_2$).
IR ν (cm^{-1}) (CCl_4)	1716 (C=O).
HRMS (EI+)	calcd for $C_{13}H_{20}O_2$ 208.1463, found: 208.1470.

7-Isopropylidene-9-methyl-dec-9-ene-2,3-dione 11b



$C_{14}H_{22}O_2$
M = 222.32 g.mol^{-1}
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 %

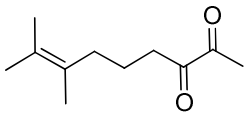
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 4.71 (s, 1H, C=C***H*****$_2$**), 4.62 (s, 1H, C=C***H*****$_2$**), 2.68 – 2.72 (m, 4H, C=C-C***H*****$_2$**-C=C, C***H*****$_2$**CO), 2.32 (s, C***H*****$_3$**CO), 2.02 (m, 2H, CH_2C***H*****$_2$**C=C), 1.69 (s, 3H, C***H*****$_3$**-C=C), 1.67 (s, 3H, C***H*****$_3$**-C=C), 1.64 (s, 3H, C***H*****$_3$**-C=C), 1.6 – 1.7 (m, 2H, C***H*****$_2$**CH_2C=C).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 199.4 (***C***=O), 197.5 (***C***=O), 144.1 (***C*****$_q$**=CH_2), 129.0, 127.8 (***C*****$_q$**=***C*****$_q$**(Me)$_2$), 110.4 (CH=***C***H_2), 40.2 (***C***H_2C_q=CH_2), 35.5 (***C***H_2CO,), 31.3 (CH_2***C***H_2C=C(Me)$_2$), 23.7, 22.5 (***C***H_3CO, ***C***H_3C_q=C), 22.0 (CH_2***C***H_2CH_2), 20.6, 20.4 (C=C(***C***H_3)$_2$).

IR ν (cm^{-1}) (CCl_4): 1716 (C=O).

HRMS (EI+): calcd for $C_{14}H_{22}O_2$ 222.1620, found: 222.1622.

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



$C_{11}H_{18}O_2$
M = 182.26 g.mol^{-1}
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 %

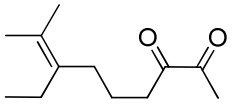
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 2.69 (t, J=7.2 Hz, 2H, C***H*****$_2$**CO), 2.32 (s, 3H, C***H*****$_3$**CO), 2.05 (t, J=7.5Hz, 2H, C***H*****$_2$**C=C(Me)$_2$), 1.68 (quint, J=7.5Hz, CH_2-C***H*****$_2$**-CH_2), 1.59 – 1.63 (m, 9H, C***H*****$_3$**C=C(C***H*****$_3$**)$_2$).

RMN ^{13}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 (***C***H_2CO), 33.5 (***C***H_2-C=C), 23.7 (***C***H_3CO), 21.6 (CH_2***C***H_2CH_2), 20.6 (C=C(***C***$H_3)_2$), 20.2 (C=C(***C***$H_3)_2$), 18.1 (***C***H_3C=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-non-7-ene-2,3-dione 11d



$C_{12}H_{20}O_2$
M = 196.29 $g.mol^{-1}$
Yellow oil

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 %

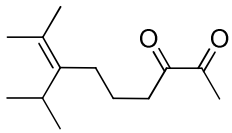
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz) 2.71 (t, J=7.2 Hz, 2H, C***H*****$_2$**CO), 2.33 (s, 3H, C***H*****$_3$**CO), 1.96 – 2.06 (m, 4H, C***H*****$_2$**C(=C)C***H*****$_2$**), 1.63 – 1.70 (m, 2H, CH_2-C***H*****$_2$**-CH_2), 1.63 (s, 3H, C=C(C***H*****$_3$**$)_2$), 1.62 (s, 3H, C=C(C***H*****$_3$**$)_2$), 0.92 (t, J=7.5Hz, CH_2C***H*****$_3$**).

RMN ^{13}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 (***C***H_2CO), 31.0 (CH_2***C***H_2-C=C), 25.0 (CH_3***C***H_2-C=C), 23.7 (***C***H_3CO), 22.1 (CH_2***C***H_2CH_2), 20.3 (C=C(***C***$H_3)_2$), 20.0 (C=C(***C***$H_3)_2$), 13.1 (***C***H_3CH_2C=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-non-7-ene-2,3-dione 11e



$C_{13}H_{22}O_2$
M = 210.31 $g.mol^{-1}$
Yellow oil

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 %

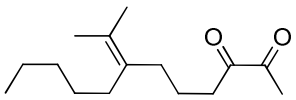
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 2.85 (sept., J=7.0Hz, 1H, C***H***$(CH_3)_2$), 2.76 (t, J=7.2 Hz, 2H, C***H*****$_2$**CO), 2.35 (s, 3H, C***H*****$_3$**CO), 1.92 – 1.98 (m, 2H, C***H*****$_2$**-C***H*****$_2$**-C=C), 1.66 (s, 3H, (C***H*****$_3$**$)_2$C=C), 1.65 (s, 3H, (C***H*****$_3$**$)_2$C=C), 1.58 – 1.66 (m, 2H, C***H*****$_2$**-C***H*****$_2$**-C=C), 0.96 (d, J=6.9Hz, 6H, CH(C***H*****$_3$**$)_2$).

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*****$_q$**$(Me)_2$), 36.1 (***C***H_2CO), 30.1 (***C***$H(CH_3)_2$), 27.2 (***C***H_2-C=C), 23.8 (***C***H_3CO), 23.8 (CH_2***C***H_2CH_2), 21.3 (CH(***C***$H_3)_2$), 20.9 (C=C(***C***$H_3)_2$), 19.7 (C=C(***C***$H_3)_2$).

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 %

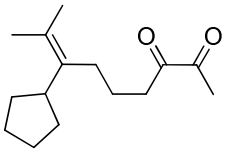
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 2.76 (t, J=7.2 Hz, 2H, C***H*****$_2$**CO), 2.33 (s, 3H, C***H*****$_3$**CO), 2.00 – 2.06 (m, 2H, C***H*****$_2$**C=C$(Me)_2$), 1.93 – 1.98 (m, 2H, C***H*****$_2$**C=C$(Me)_2$), 1.62 – 1.70 (m, 2H, CH_2C***H*****$_2$**CH_2), 1.63 (s, 6H, (C***H*****$_3$**$)_2$C=C), 1.22 – 1.36 (m, 6H, (C***H*****$_2$**$)_3CH_3$), 0.89 (t, J=7.0Hz, 3H, CH_2C***H*****$_3$**).

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*****$_q$**$(Me)_2$), 35.4 (***C***H_2CO), 32.09 (***C***H_2-C=C$(Me)_2$), 32.07 (***C***H_2-C=C$(Me)_2$), 31.4 (***C***$H_2CH_2CH_3$), 28.4 (***C***$H_2CH_2CH_2CH_3$), 23.7 (***C***H_3CO), 22.6, 22.1 (***C***H_2CH_3, ***C***H_2CH_2CO), 20.3 (C=C(***C***$H_3)_2$), 20.2 (C=C(***C***$H_3)_2$), 14.1 (CH_2***C***H_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**



$C_{15}H_{24}O_2$
M = 236.35 g.mol^{-1}
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 %

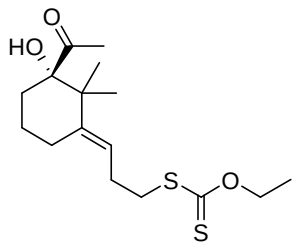
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz): 2.78 – 2.87 (m, 1H, C***H***$(CH_2)_4$), 2.75 (t, J=7.2Hz, 2H, C***H*****$_2$**CO), 2.34 (s, 3H, C***H*****$_3$**CO), 1.90 – 1.96 (m, 2H, C***H*****$_2$**C***H*****$_2$**C=C), 1.673 (s, 3H, C***H*****$_3$**C=C), 1.668 (s, 3H, C***H*****$_3$**C=C), 1.50 – 1.70 (m, 8H, C***H*****$_2$**C***H*****$_2$**C=C, CH(C***H*****$_2$$)_4$**), 1.22 – 1.34 (m, 2H, CH(C***H*****$_2$$)_4$**).

RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz): 199.4 (***C***=O), 197.6 (***C***=O), 133.5, 125.8 (***C*****$_q$**=***C*****$_q$**$(Me)_2$), 42.9 (***C***H$(CH_2)_4$), 36.0 (***C***H_2CO), 30.8 (CH(***C***$H_2)_4$), 28.1 (***C***H_2-C=C$(Me)_2$), 25.1 (CH(***C***$H_2)_4$), 23.8 (***C***H_3CO), 23.7 (***C***H_2CH_2CO), 20.9 (C=C(***C***$H_3)_2$), 20.0 (C=C(***C***$H_3)_2$).

IR ν (cm^{-1}) (CCl_4): 1716 (C=O).

HRMS (EI+): calcd for $C_{15}H_{24}O_2$ 236.1776, found: 236.1777.

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



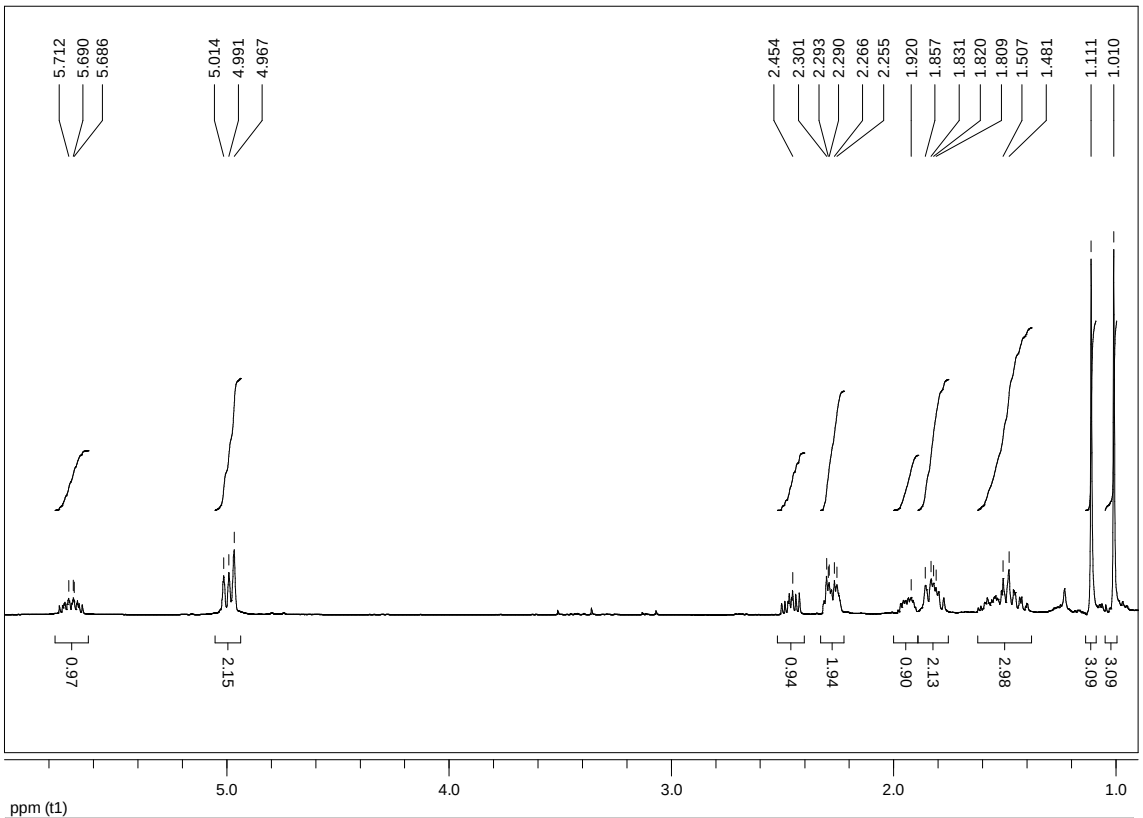
$C_{16}H_{26}O_3S_2$
M = 330.51 g.mol^{-1}
Colorless oil

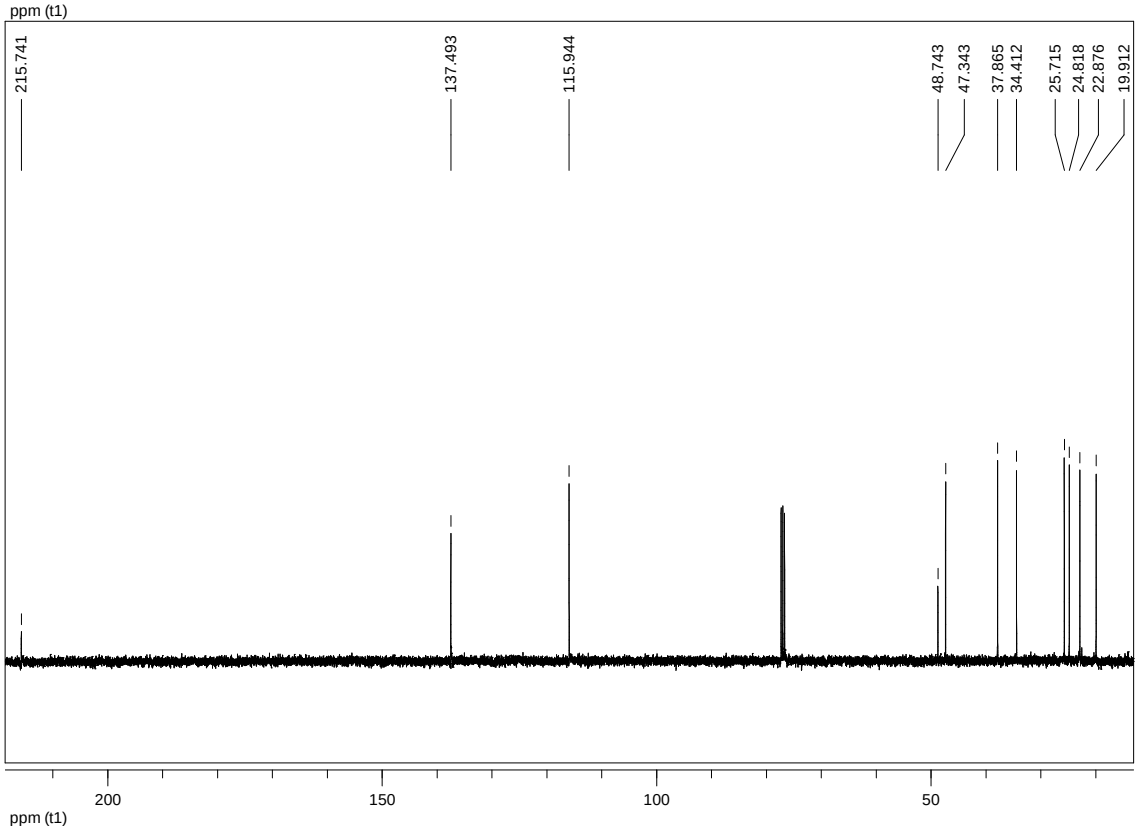
Reaction: A solution of xanthate **10h** (142 mg, 0.43 mmol) in **chlorobenzene** (1 mL), was refluxed under nitrogen for 15 minutes. **Dilauroyl peroxide** was then added by portion of 5 to 10% every 20 minutes. After addition of 45 % of DLP, the solvent was then removed *in vacuo*, giving crude compound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

Purification:	Column chromatography, elution with petroleum ether/ethyl acetate (9/1).
Yield:	45 %
RMN ^{1}H (δ, ppm) ($CDCl_3$, 400 MHz)	5.27 (t, J=7.3Hz, 1H, C=C***H***), 4.65 (q, J=7.1 Hz, 2H, OC***H₂***), 3.10 – 3.25 (m, 2H, SC***H₂***), 3.04 (s, 1H, O***H***), 2.44 – 2.58 (m, 2H, C=CHC***H₂***), 2.35 – 2.44 (m, 1H, C***H₂***C***H₂***C***H₂***), 2.25 (s, 3H, C***H₃***CO), 2.17 – 2.25 (m, 1H, C***H₂***C***H₂***C***H₂***), 2.11 (ddd, J=4.7Hz, J=10.8Hz, J=13.3Hz, 1H, C***H₂***C***H₂***C***H₂***), 1.67 – 1.77 (m, 1H, C***H₂***C***H₂***C***H₂***), 1.52 – 1.62 (m, 2H, C***H₂***C***H₂***C***H₂***), 1.42 (t, J=7.1Hz, 3H, OCH_2C***H₃***), 1.14 (s, 3H, $C(C$***H₃***$)_2$), 1.05 (s, 3H, $C(C$***H₃***$)_2$).
RMN ^{13}C (δ, ppm) ($CDCl_3$, 100.6 MHz)	214.8, 212.8 (***C***=S, ***C***=O), 145.6 (***C*****$_q$**=CH), 120.7 (C_q=***C***H), 83.6 (***C***OH), 69.9 (O***C***H_2), 44.2 (***C***$(Me)_2$), 36.0 (S***C***H_2), 30.8 (***C***H_2***C***H_2***C***H_2), 28.3 (***C***H_3CO), 26.6 (C=CH-***C***H_2), 23.8 ($C($***C***$H_3)_2$), 23.5 (***C***H_2***C***H_2***C***H_2), 22.8 ($C($***C***$H_3)_2$), 21.8 (***C***H_2***C***H_2***C***H_2), 13.8 (OCH_2***C***H_3).
IR ν (cm^{-1}) (CCl_4)	3626, 3545 (OH), 1711 (C=O), 1647 (C=C), 1214, 1053 (C=S, C-O).
HRMS (EI+)	calcd for $C_{16}H_{26}O_3S_2$ 330.1324, found: 330.1323.

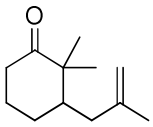
II. Copies of 1H and 13C NMR Spectra

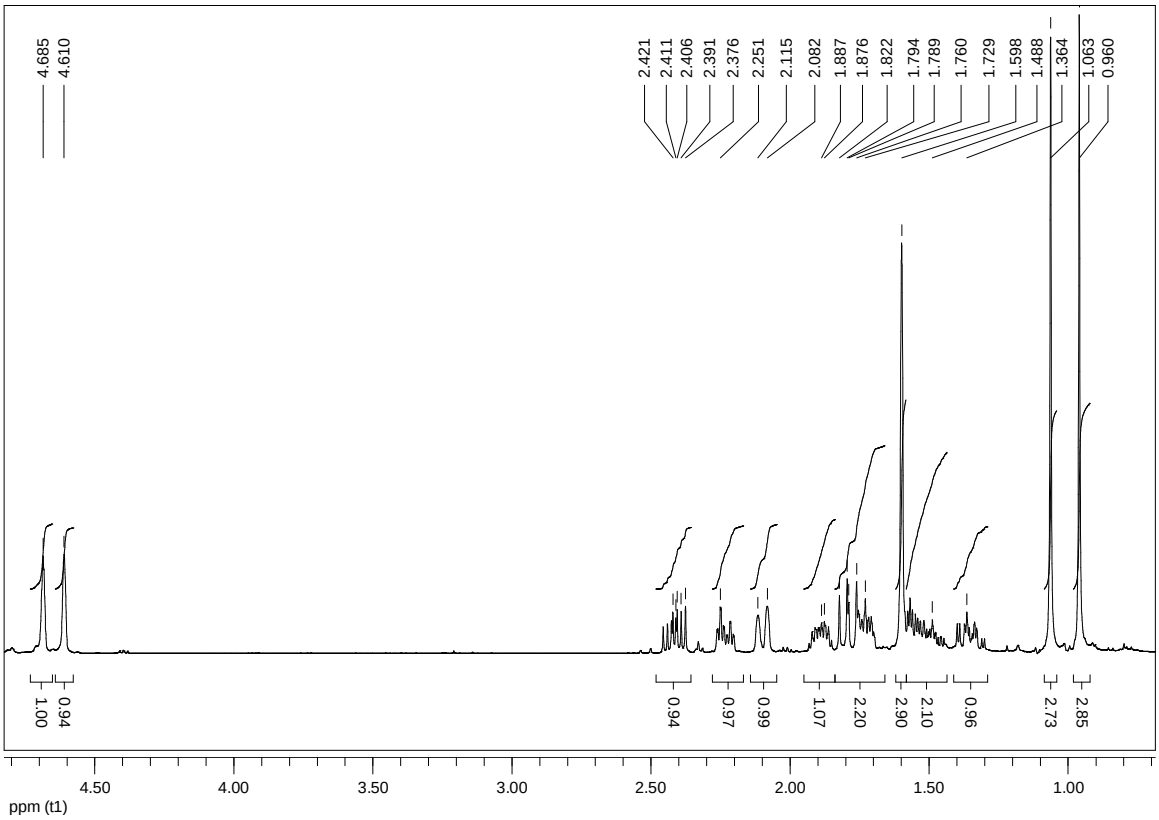
Compound 7a





Compound 7b

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1.794
1.789
1.760
1.729
1.598
1.488
1.364
1.063
0.960
1.00
0.94
0.94
0.97
0.99
1.07
2.20
2.06
2.10
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2.00
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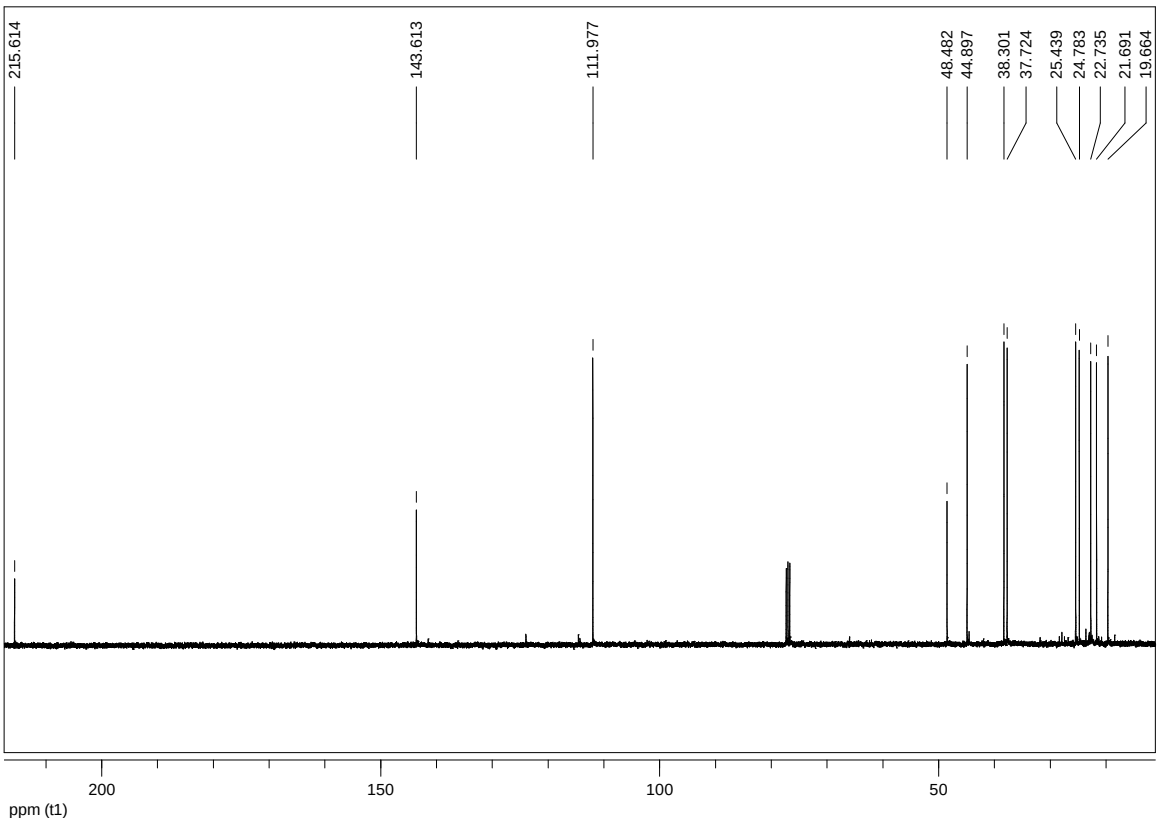
1.00
ppm (t1)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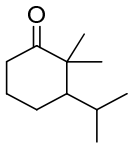
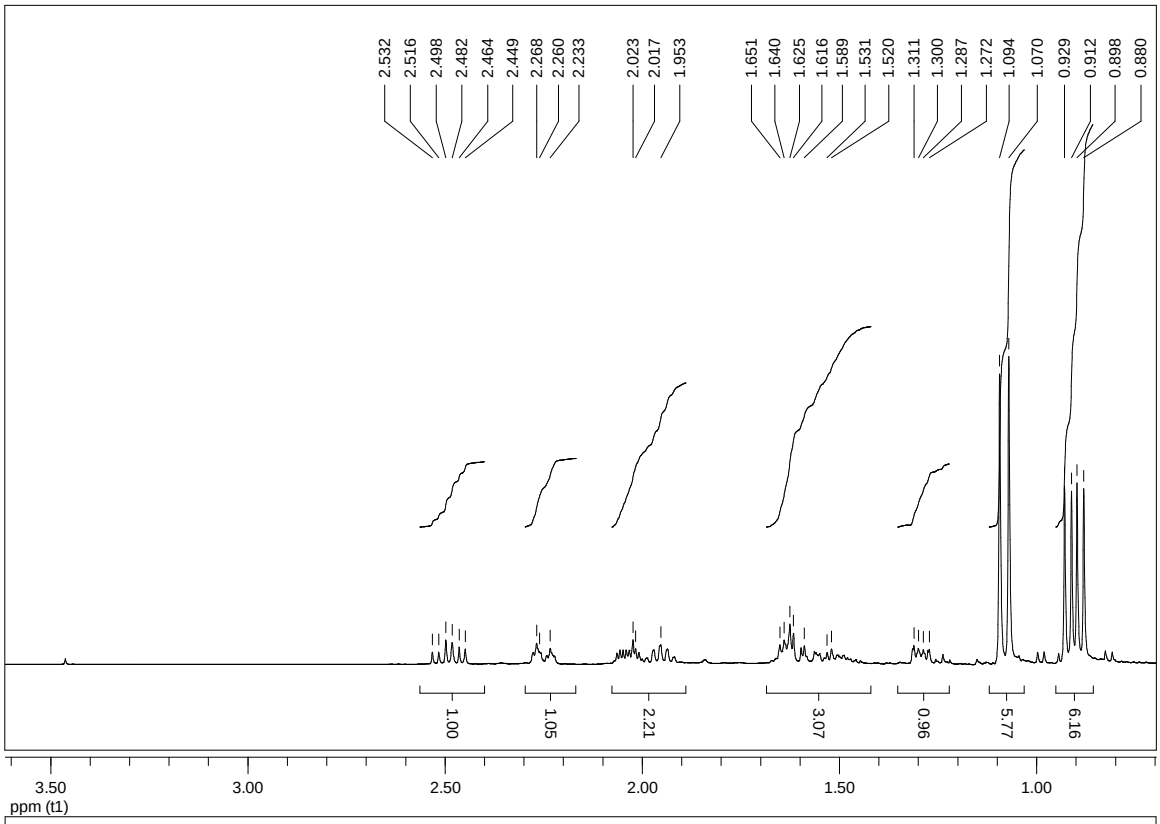
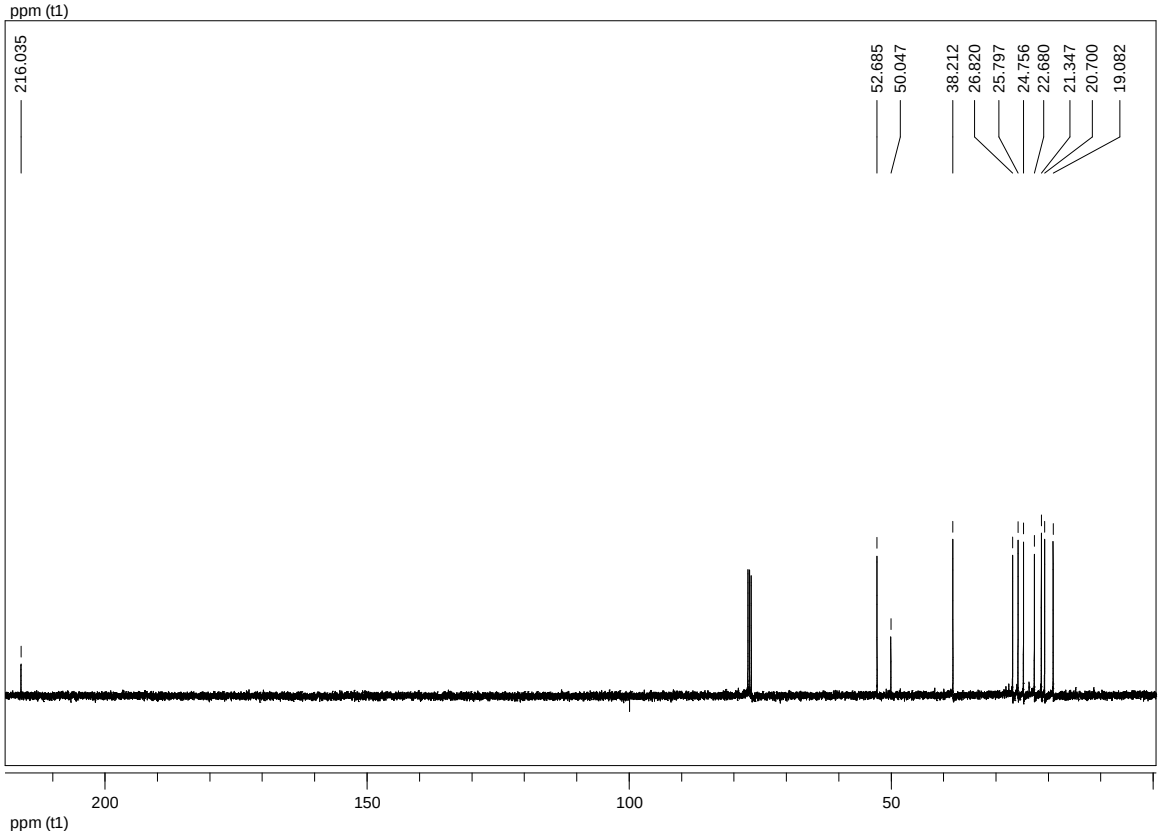
38.301
37.724
25.439
24.783
22.735
21.691
19.664
200
150
100
50
ppm (t1)

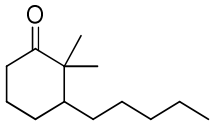
Compound 7e

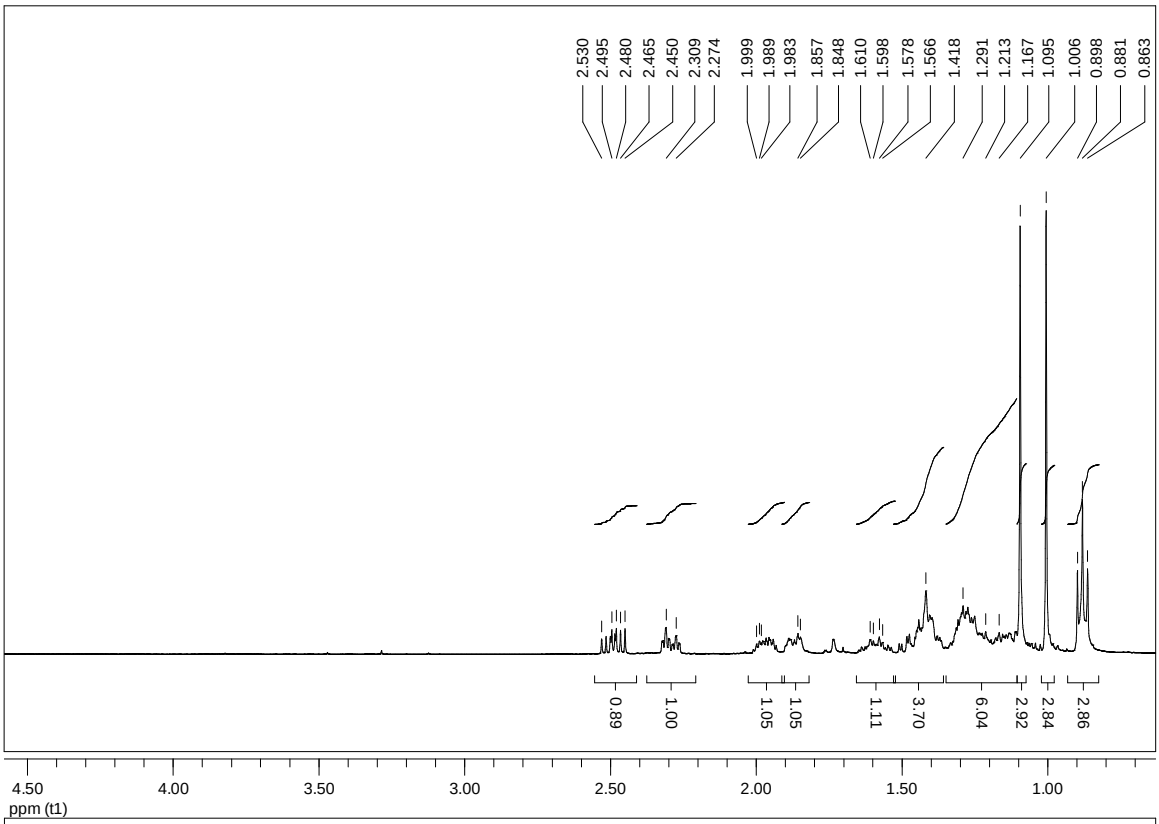



2.532
2.516
2.498
2.482
2.464
2.449
2.268
2.260
2.233
2.023
2.017
1.953
1.651
1.640
1.625
1.616
1.589
1.531
1.520
1.311
1.300
1.287
1.272
1.094
1.070
0.929
0.912
0.898
0.880
1.00
1.05
2.21
3.07
0.96
5.77
6.16
3.50
3.00
2.50
2.00
1.50
1.00
ppm (t1)


216.035
52.685
50.047
38.212
26.820
25.797
24.756
22.680
21.347
20.700
19.082
200
150
100
50
ppm (t1)

Compound 7f

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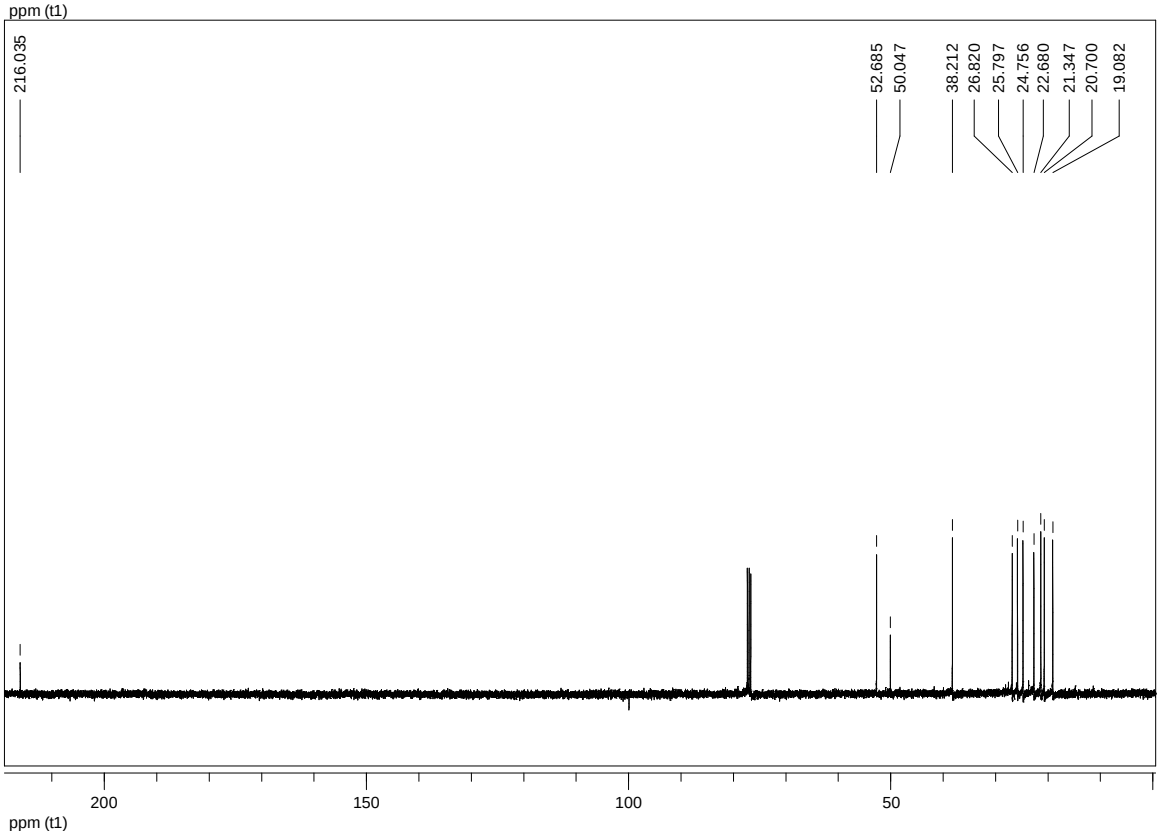
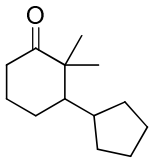
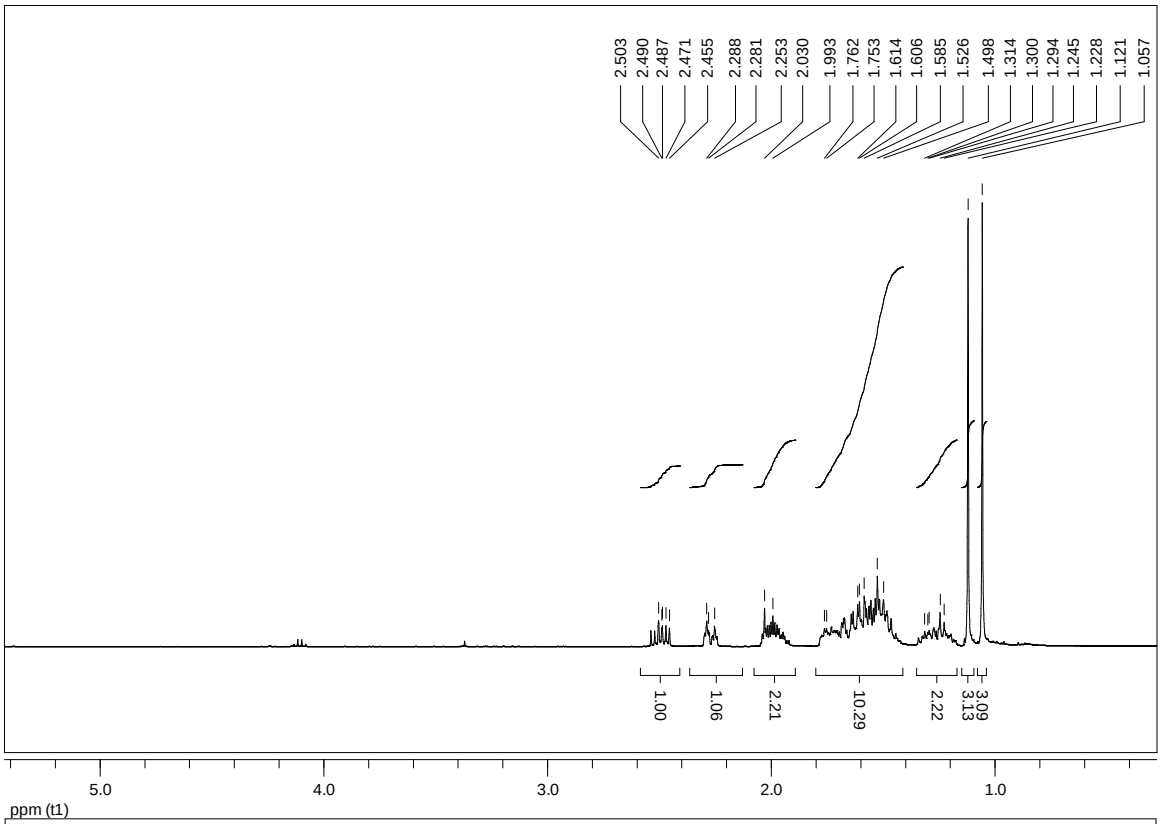
2.495
2.480
2.465
2.450
2.309
2.274
1.999
1.989
1.983
1.857
1.848
1.610
1.598
1.578
1.566
1.418
1.291
1.213
1.167
1.095
1.006
0.898
0.881
0.863
0.89
1.00
1.05
1.05
1.11
3.70
6.04
2.92
2.84
2.86
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (t1)


216.035
52.685
50.047
38.212
26.820
25.797
24.756
22.680
21.347
20.700
19.082
200
150
100
50
ppm (t1)

Compound 7g

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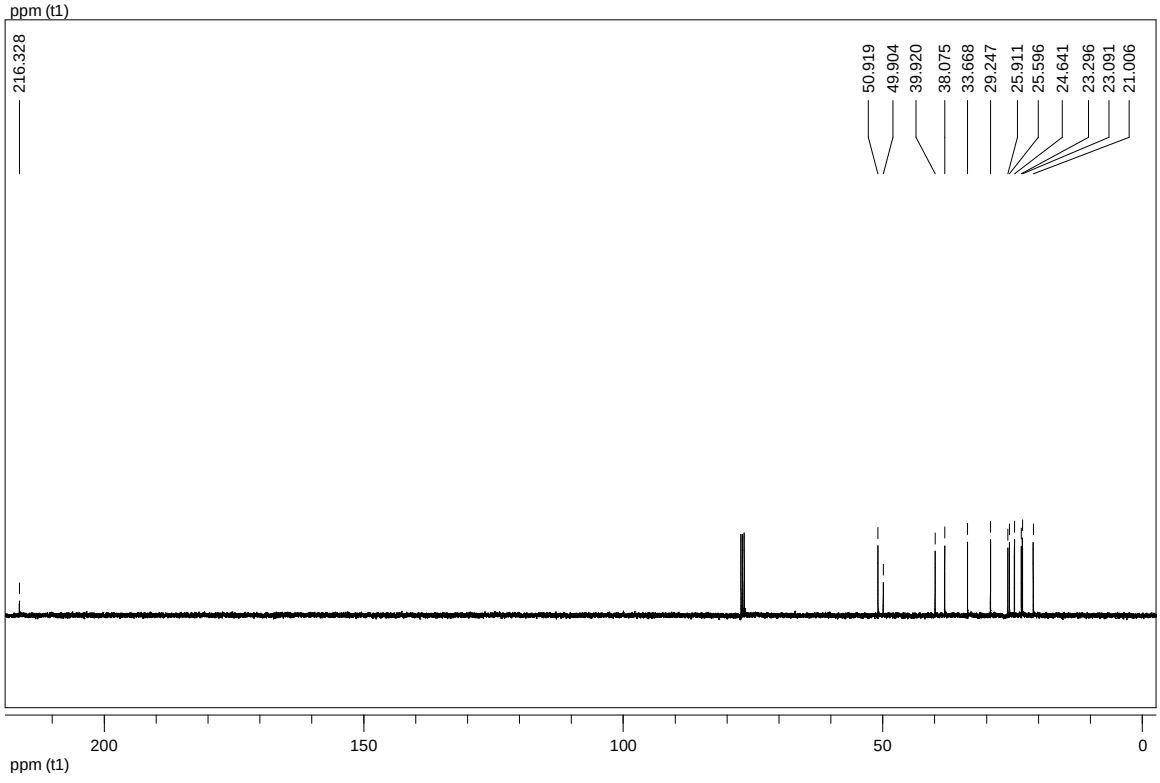
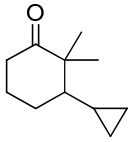
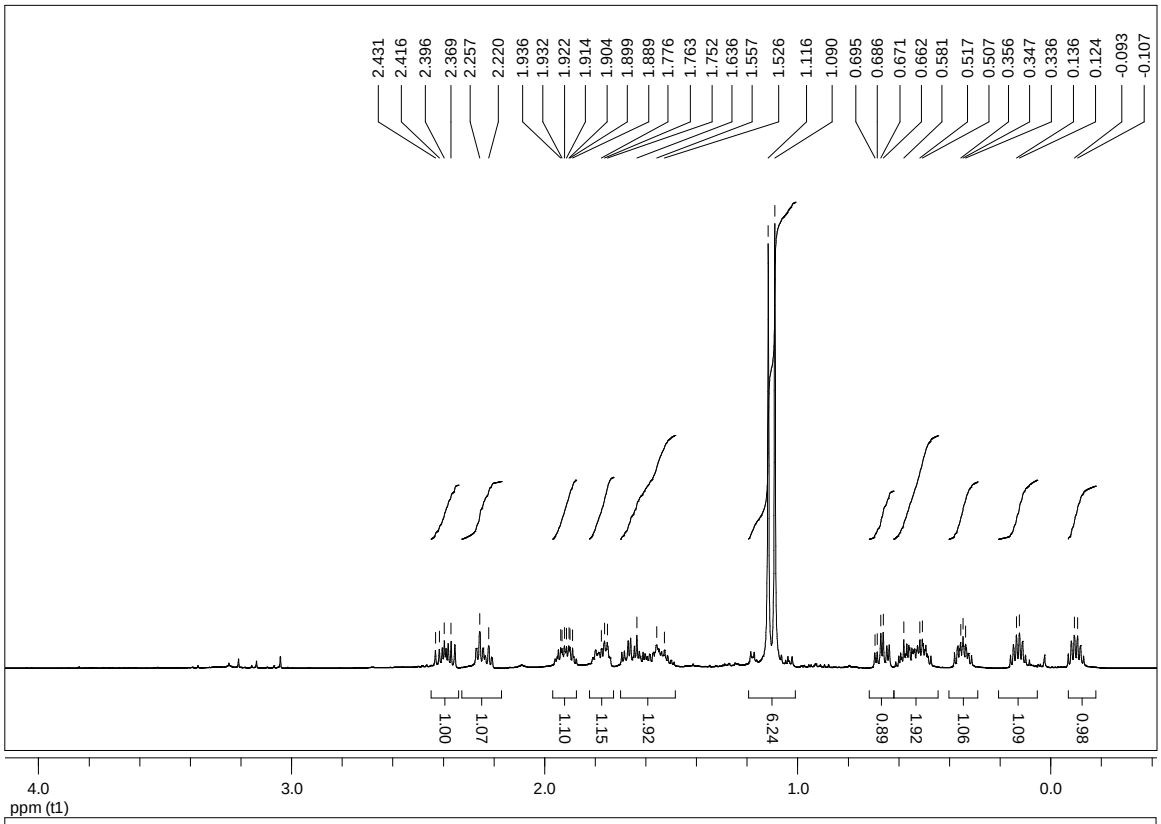
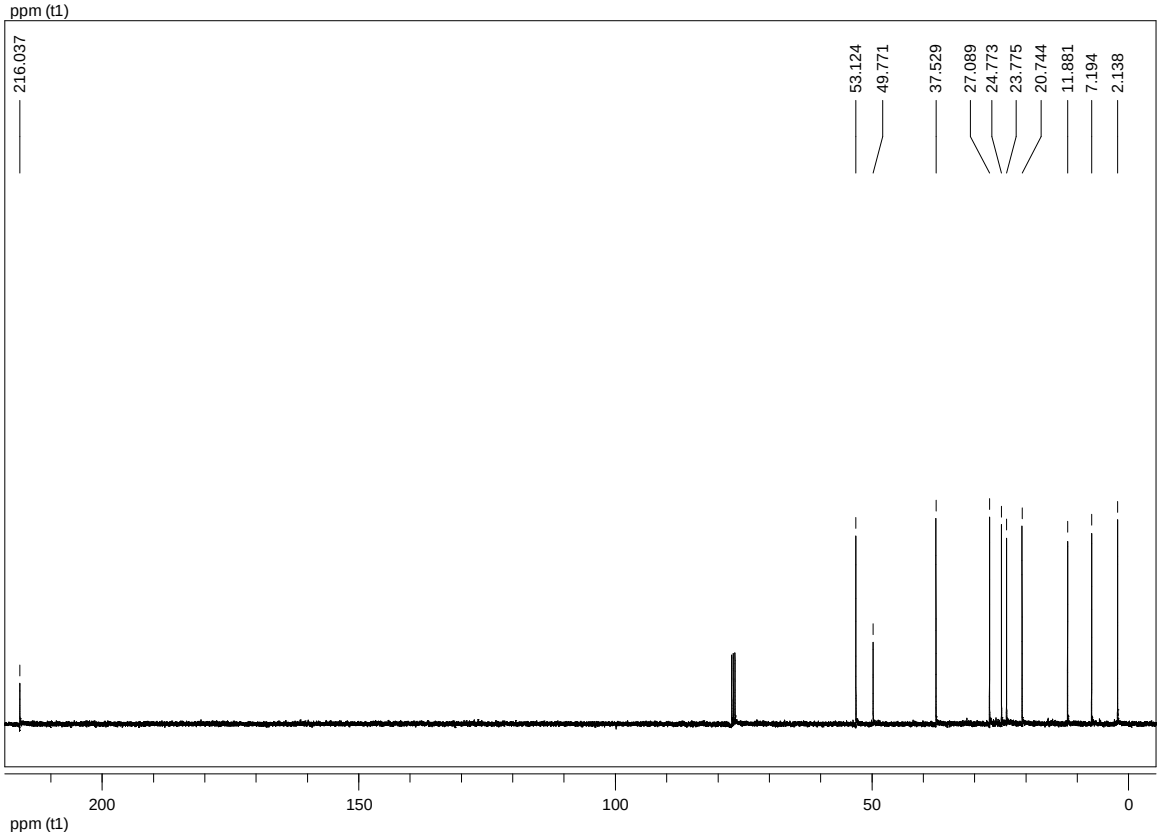
2.490
2.487
2.471
2.455
2.288
2.281
2.253
2.030
1.993
1.762
1.753
1.614
1.606
1.585
1.526
1.498
1.314
1.300
1.294
1.245
1.228
1.121
1.057
1.00
1.06
2.21
10.29
2.22
3.13
3.09
5.0
4.0
3.0
2.0
1.0
ppm (t1)


216.328
50.919
49.904
39.920
38.075
33.668
29.247
25.911
25.596
24.641
23.296
23.091
21.006
200
150
100
50
0
ppm (t1)

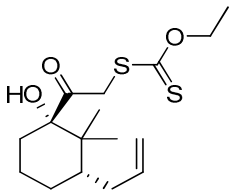
Compound 7h

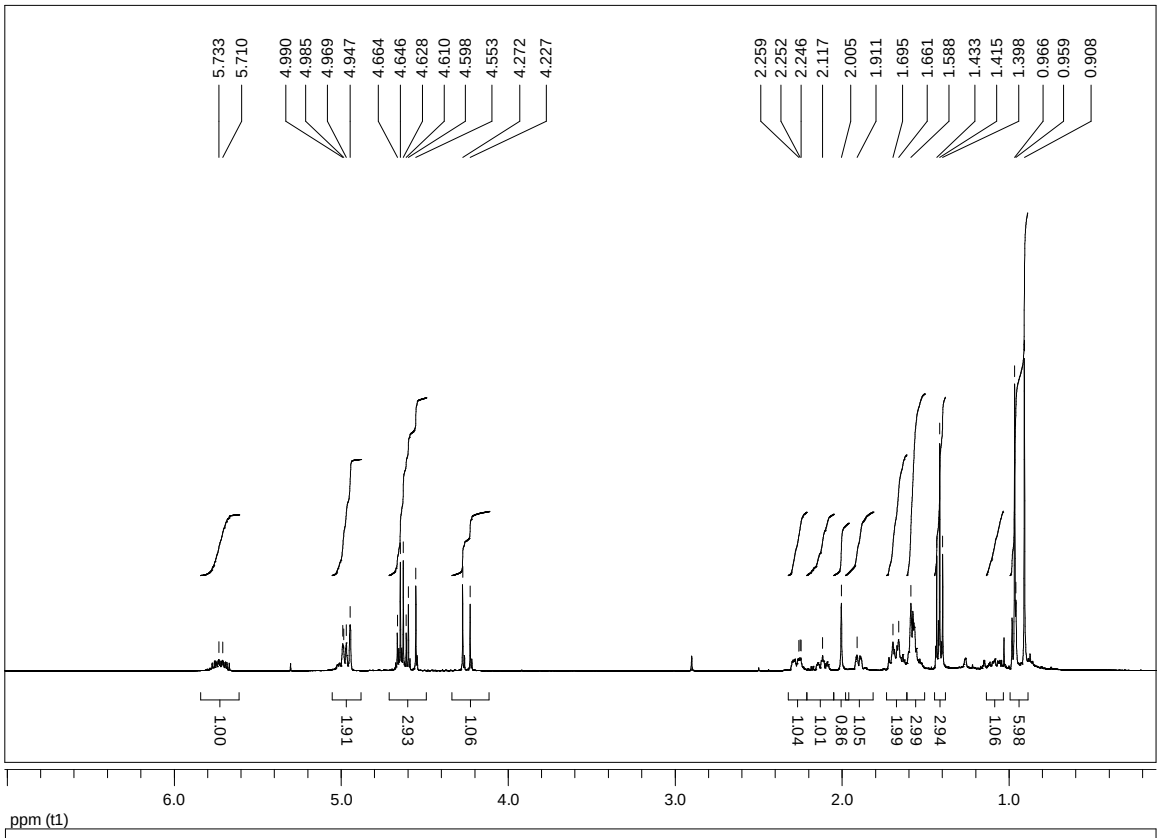


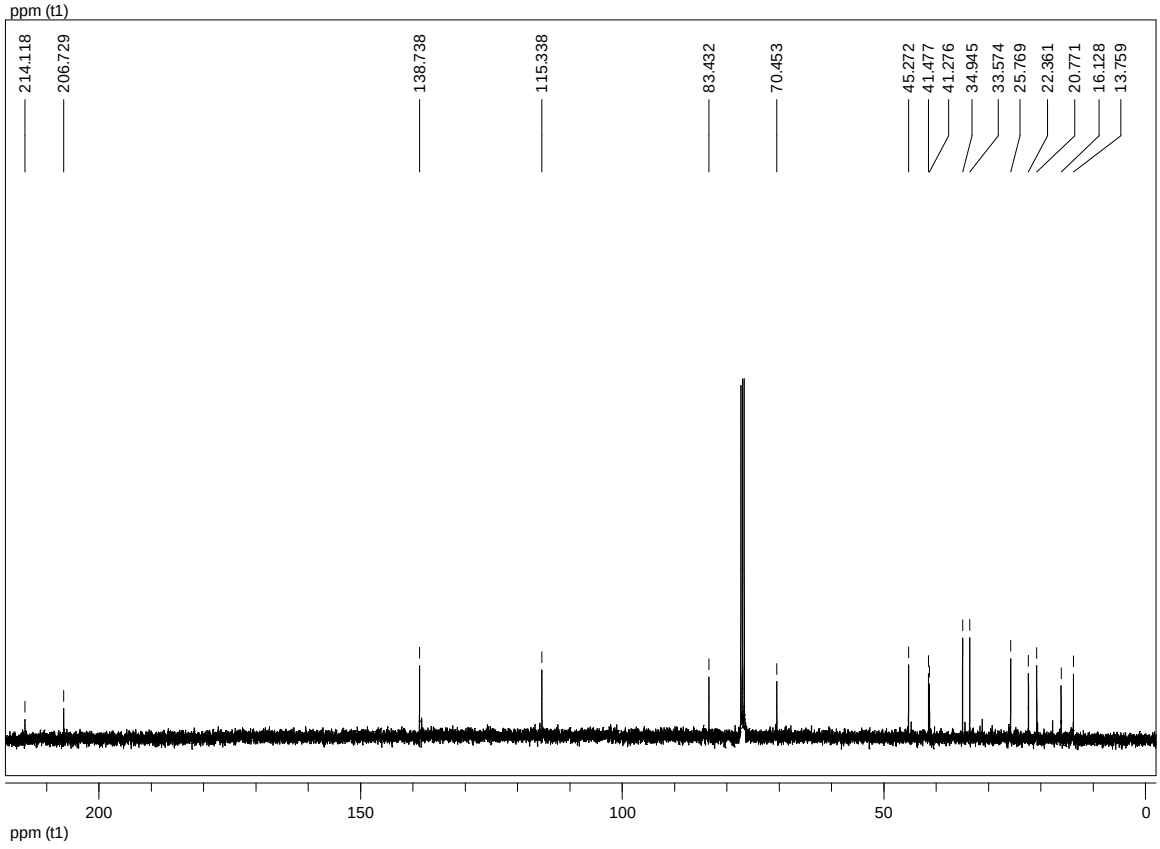

2.431
2.416
2.396
2.369
2.257
2.220
1.936
1.932
1.922
1.914
1.904
1.899
1.889
1.776
1.763
1.752
1.636
1.557
1.526
1.116
1.090
0.695
0.686
0.671
0.662
0.581
0.517
0.507
0.356
0.347
0.336
0.136
0.124
-0.093
-0.107
1.00
1.07
1.10
1.15
1.92
6.24
0.89
1.92
1.06
1.09
0.98
4.0
3.0
2.0
1.0
0.0
ppm (t1)


216.037
53.124
49.771
37.529
27.089
24.773
23.775
20.744
11.881
7.194
2.138
200
150
100
50
0
ppm (t1)

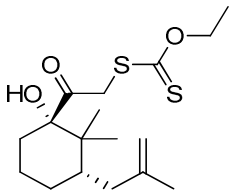
Compound 10a

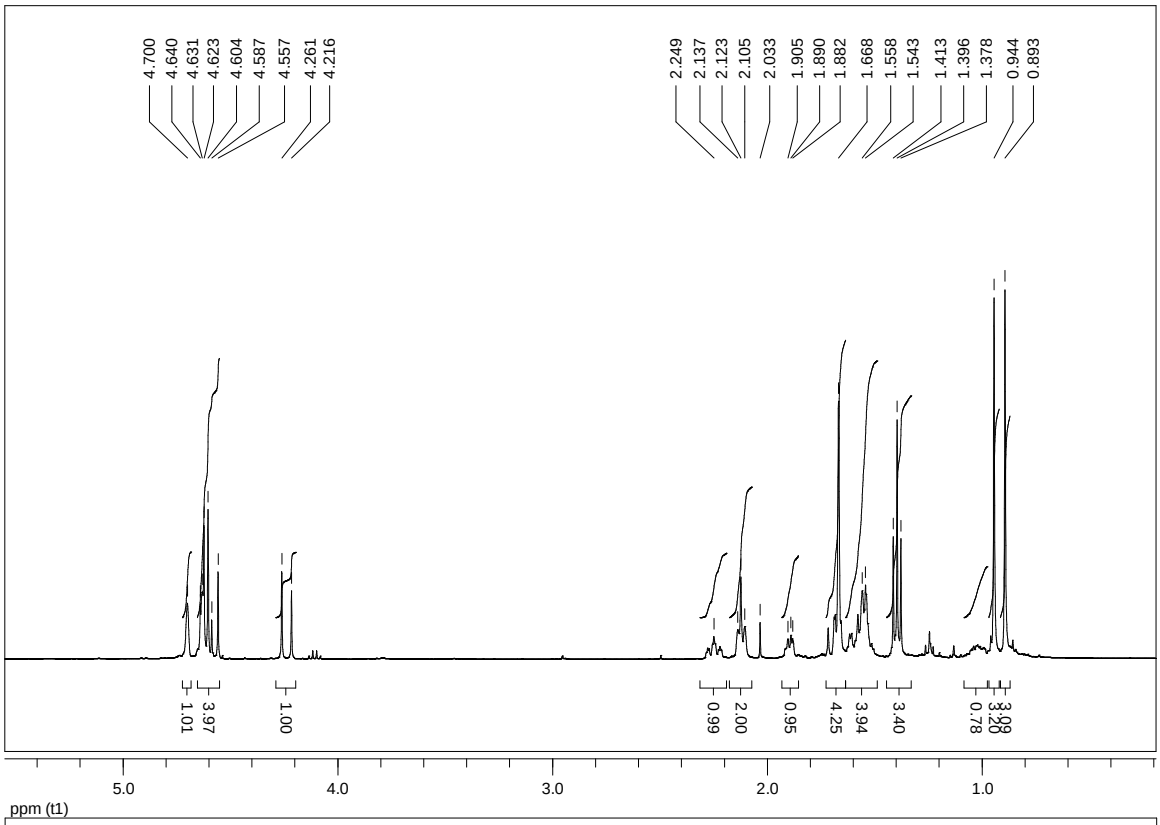


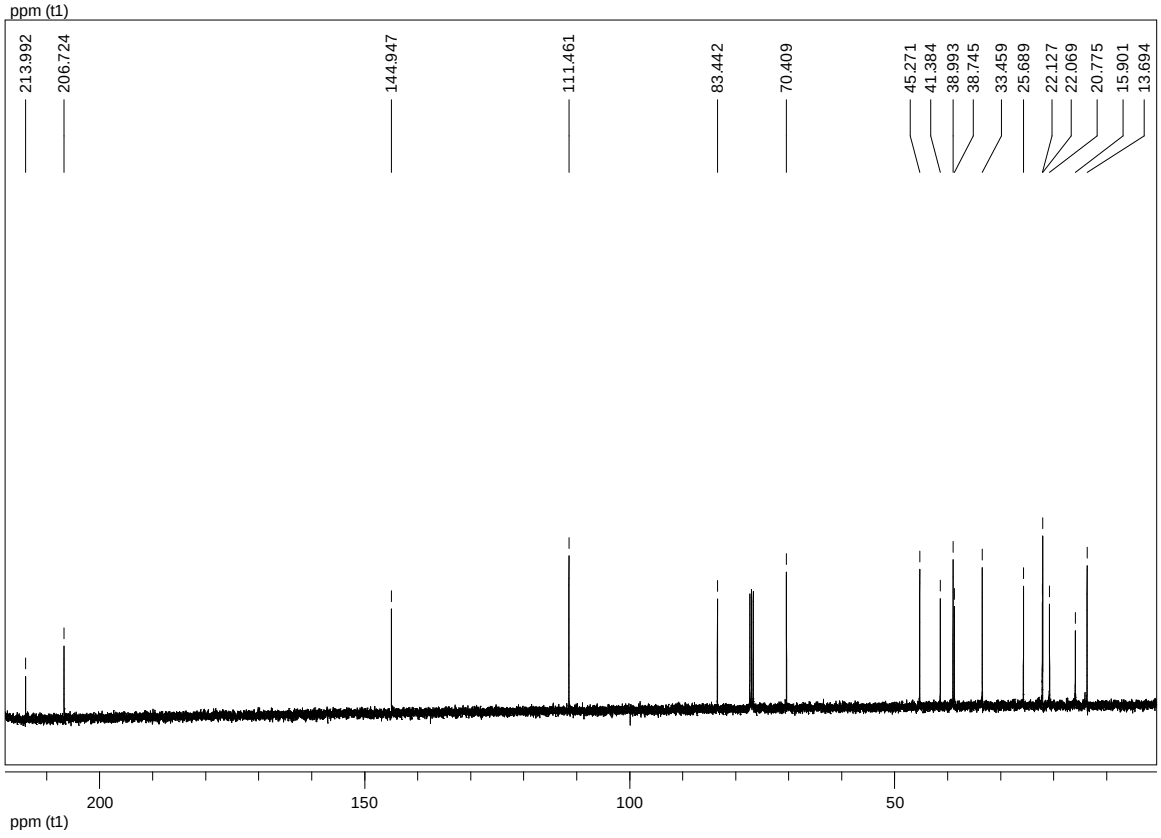




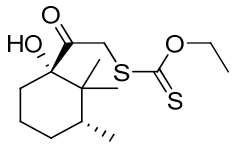
Compound 10b

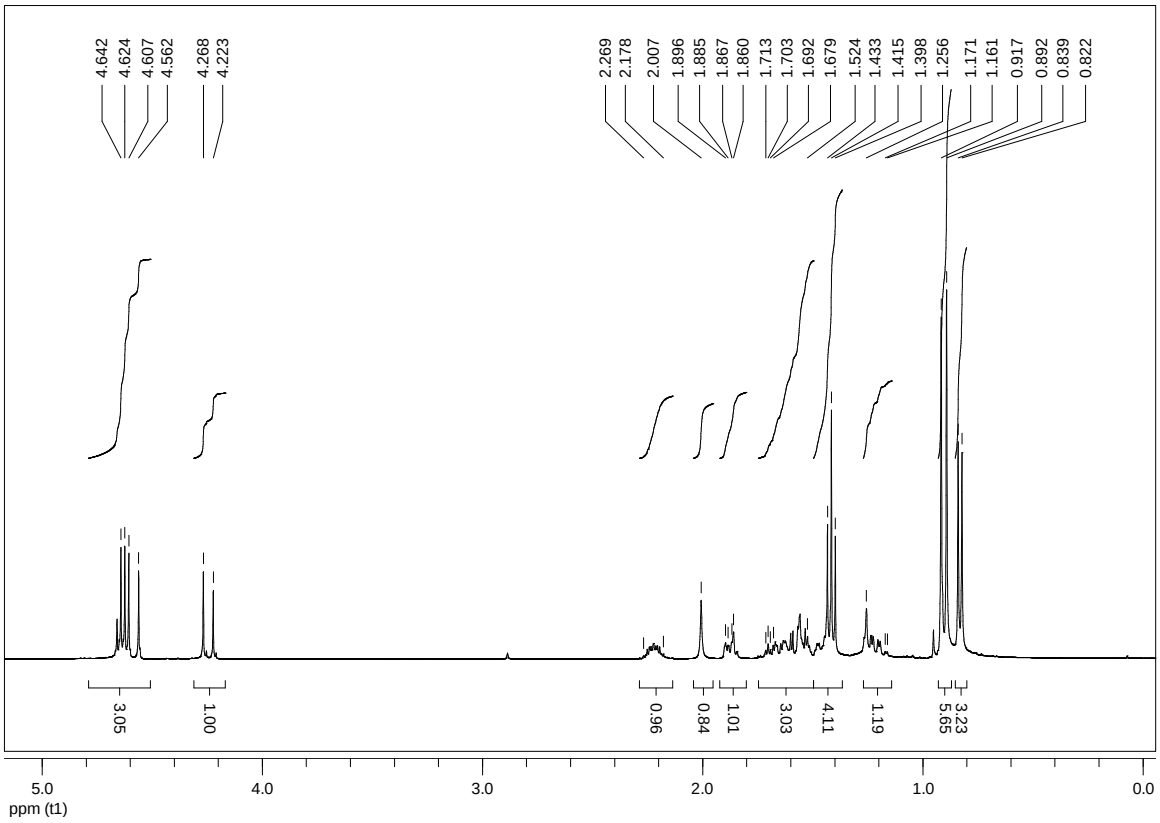


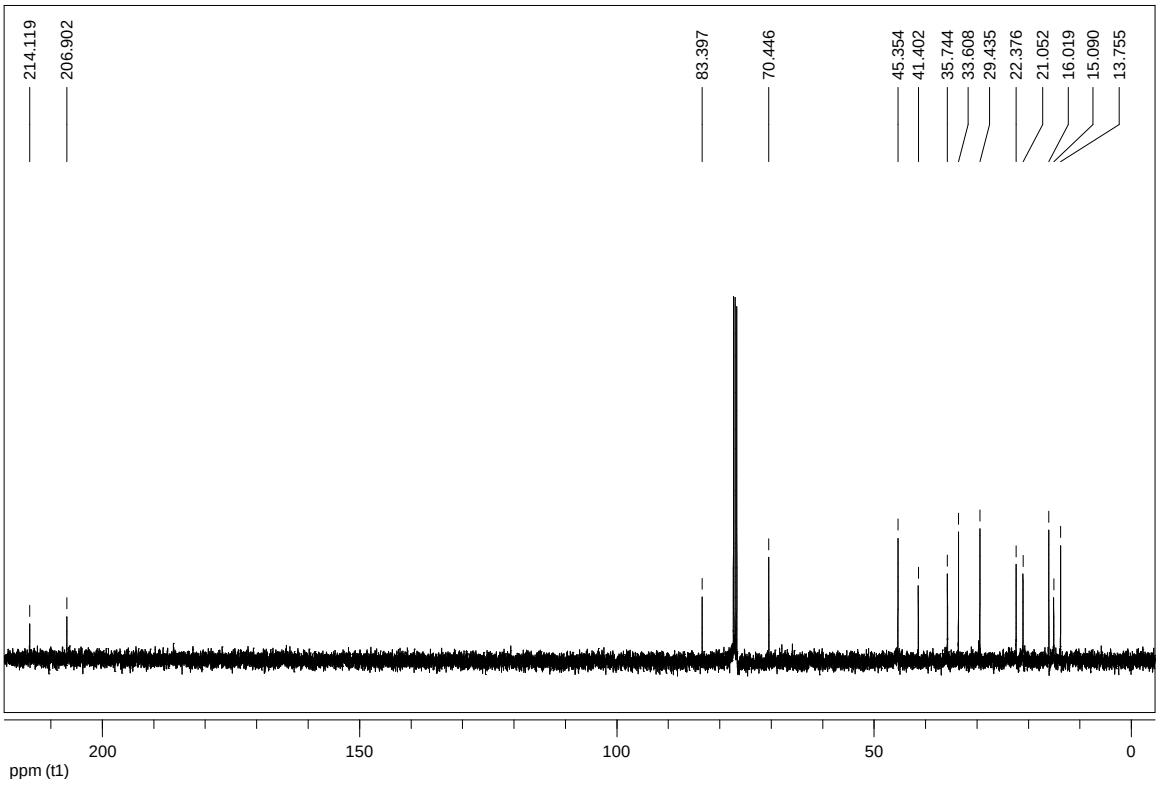




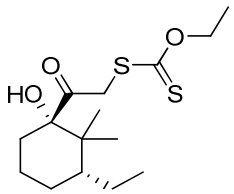
Compound 10c

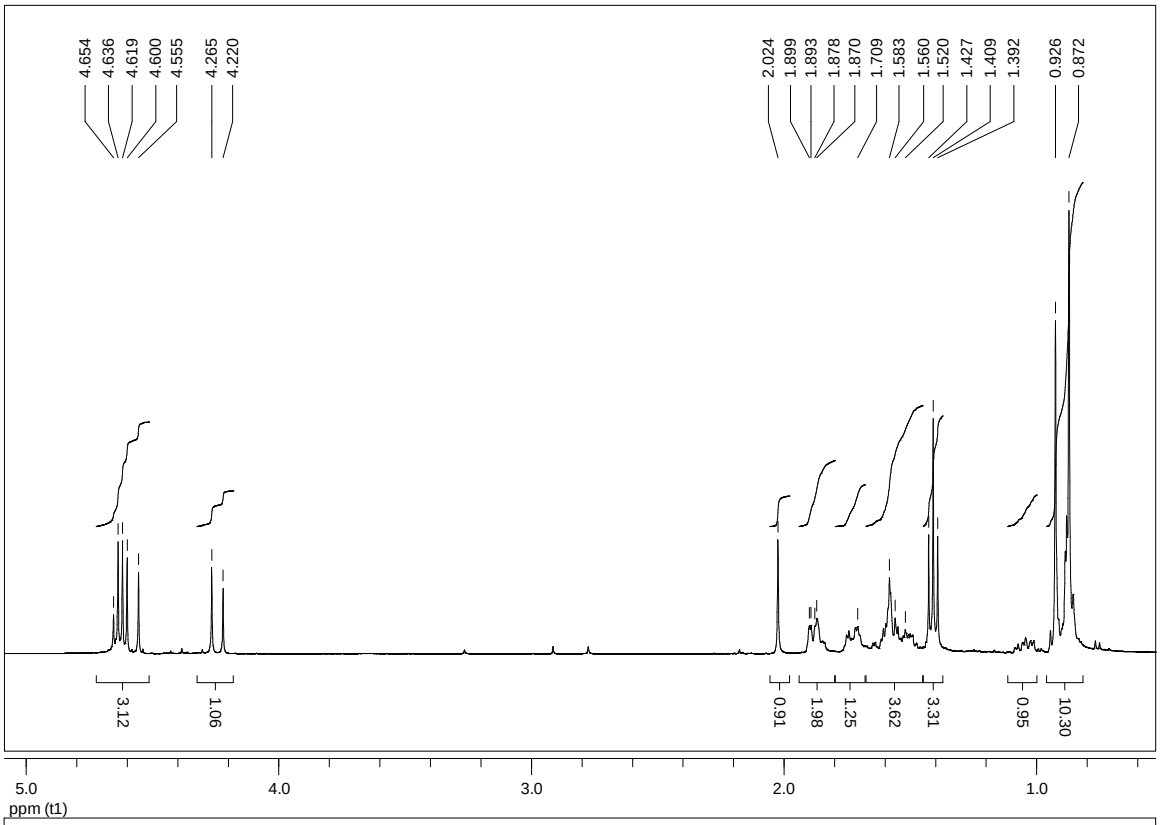


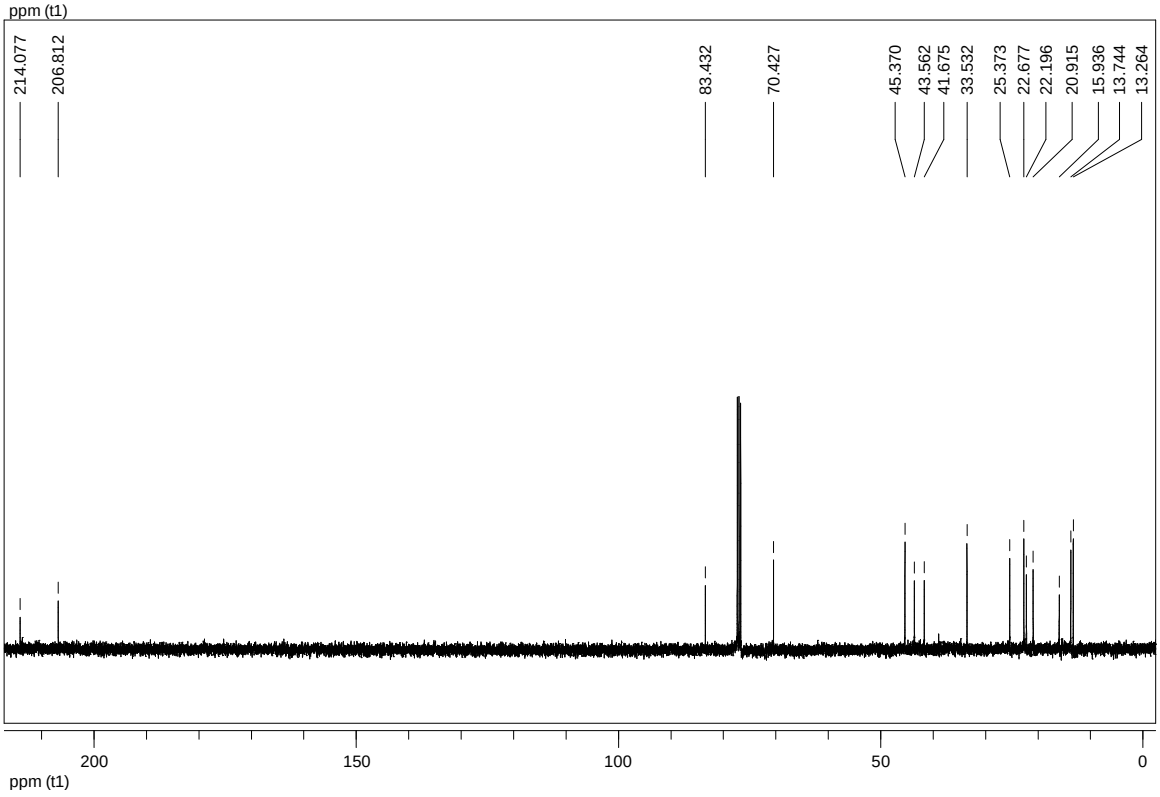




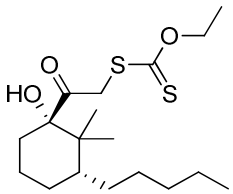
Compound 10d

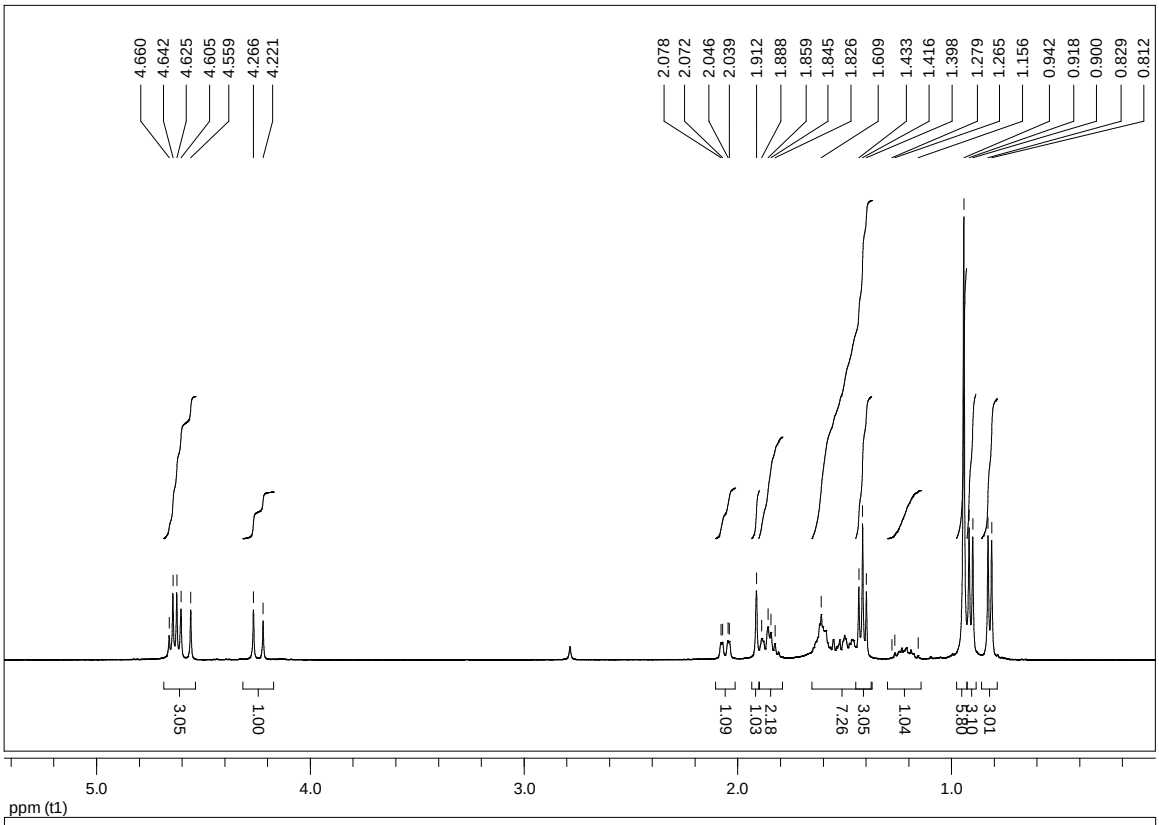


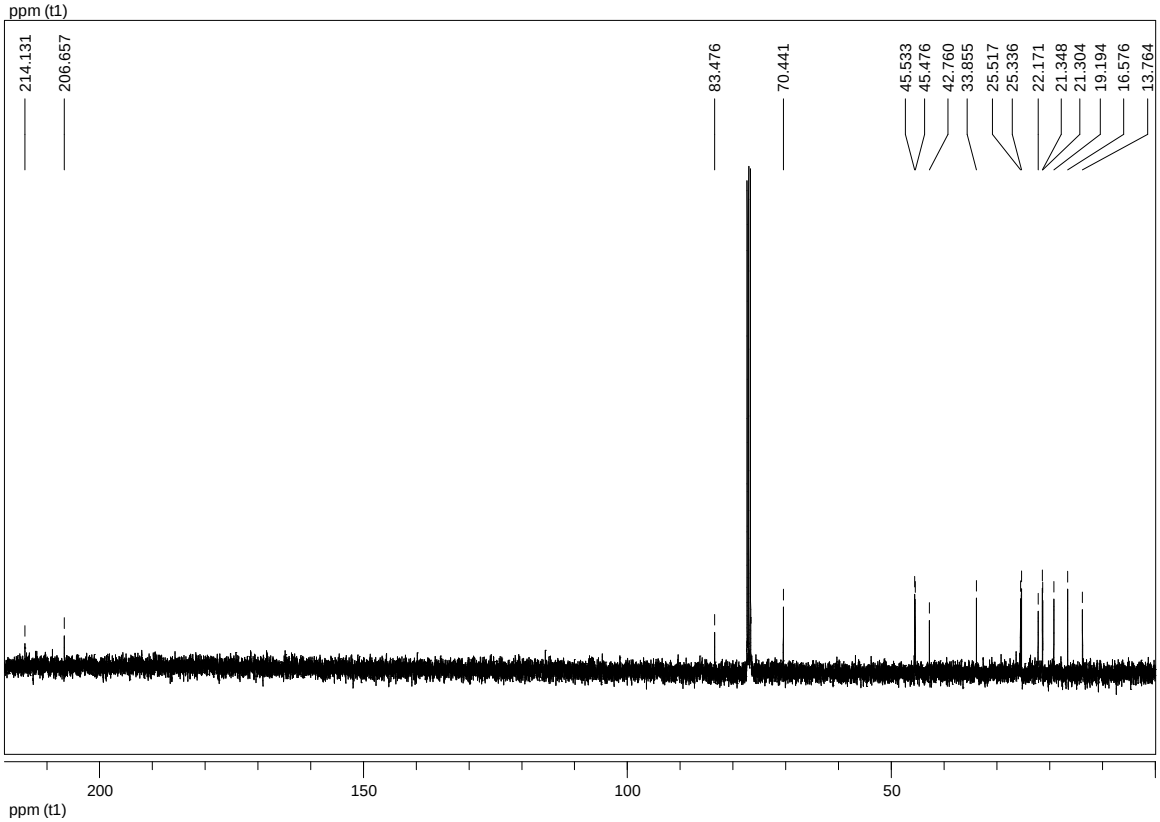




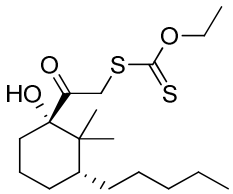
Compound 10e

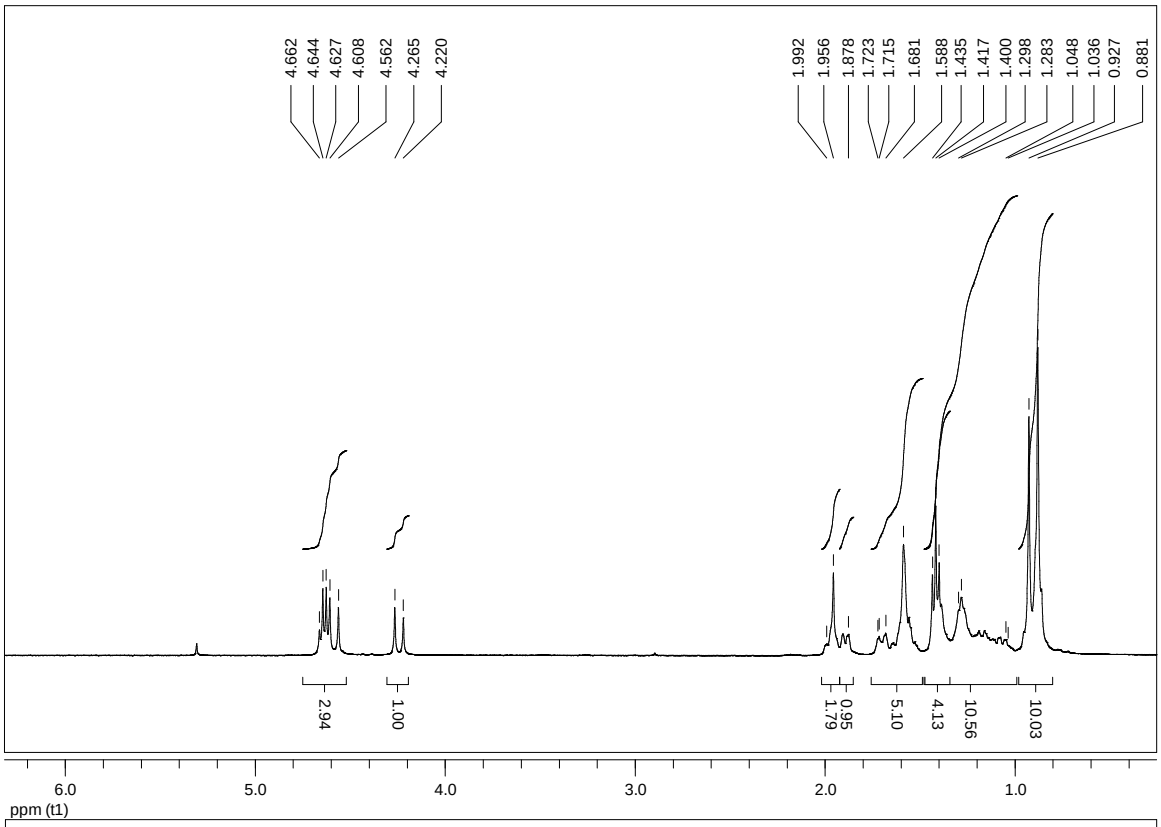


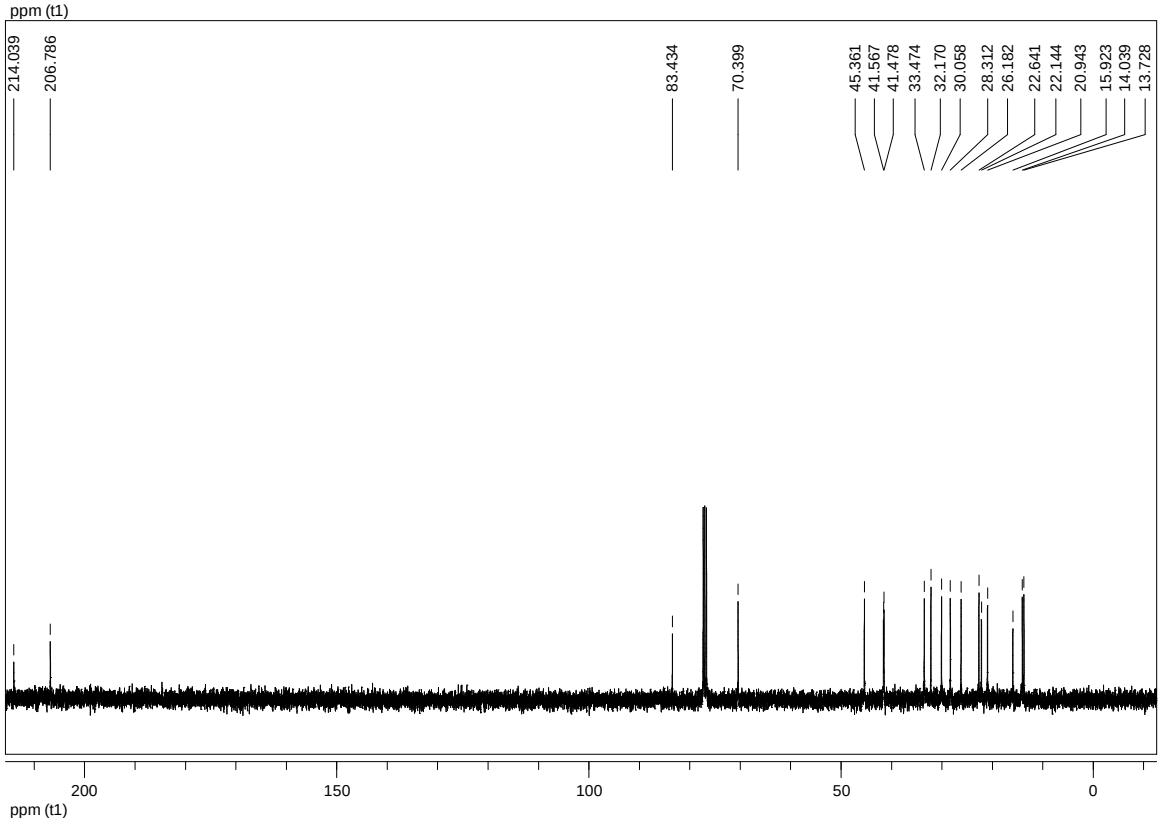




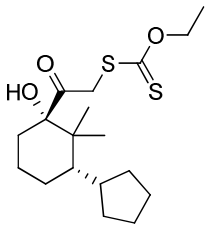
Compound 10f

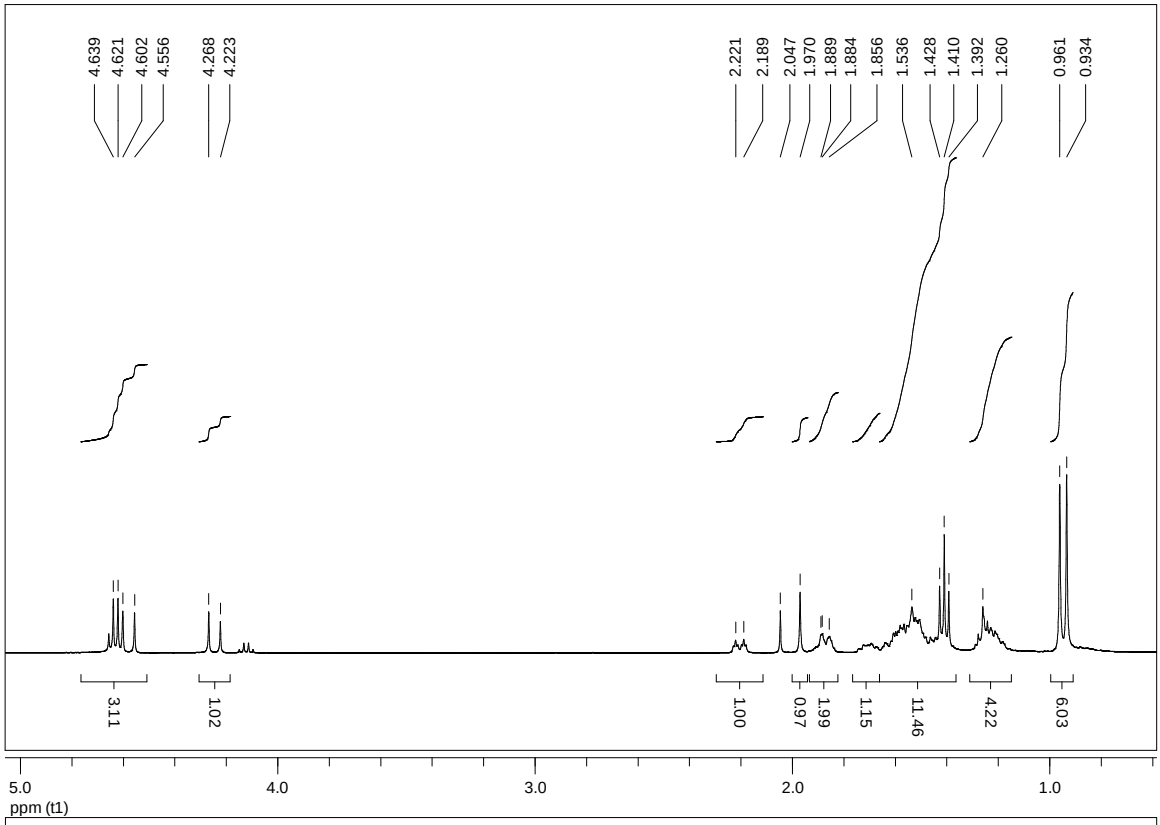


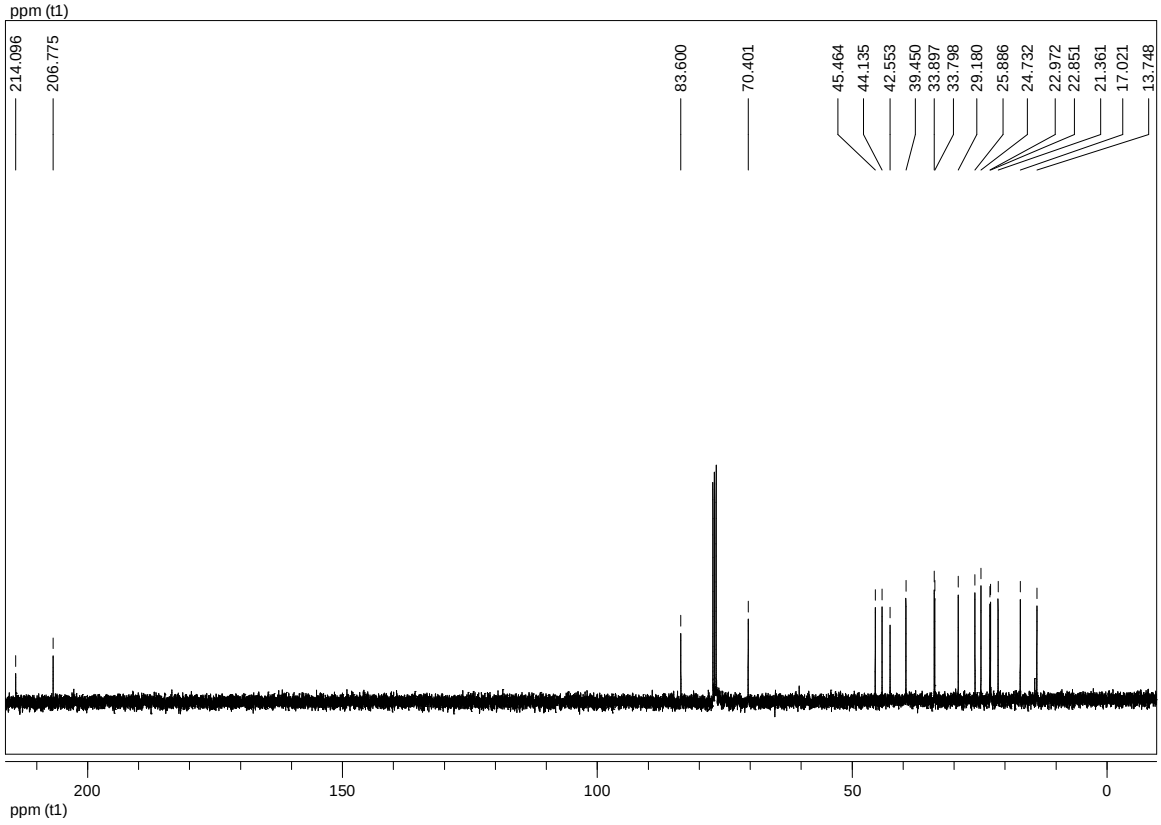




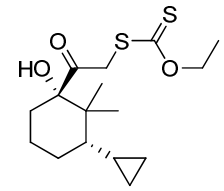
Compound 10g

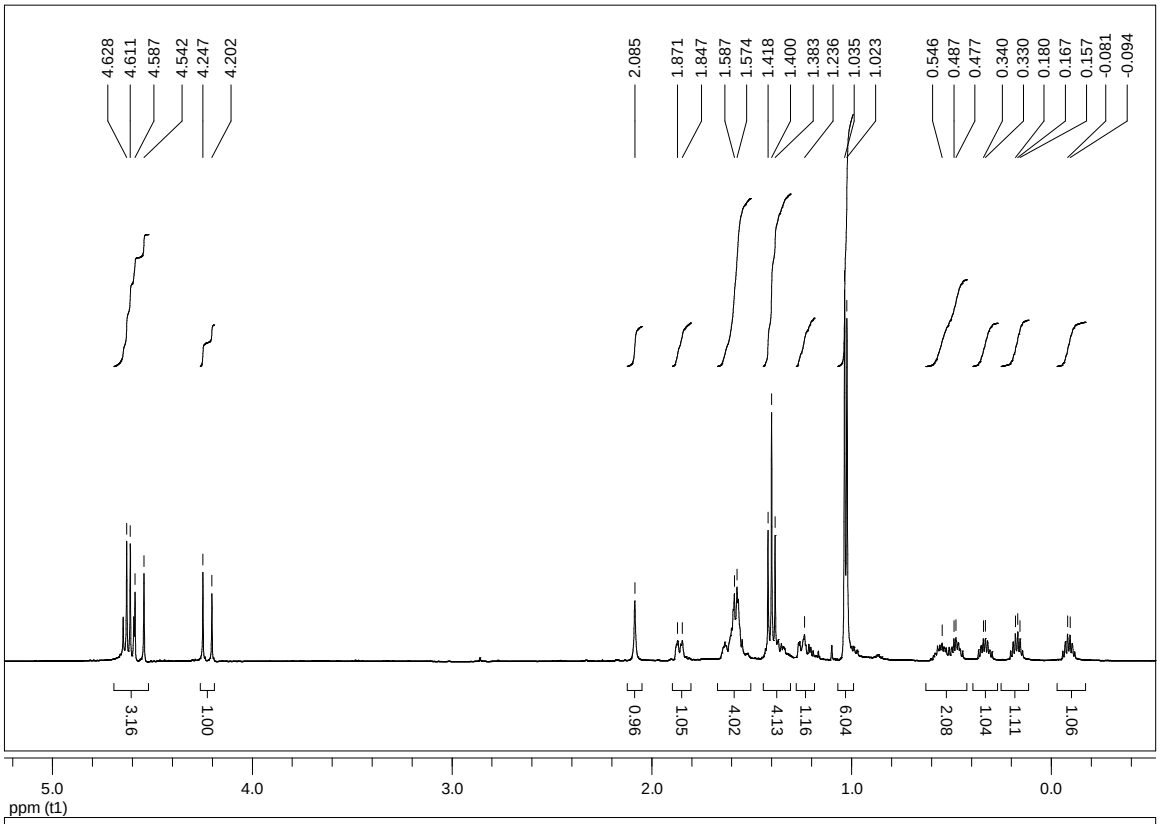


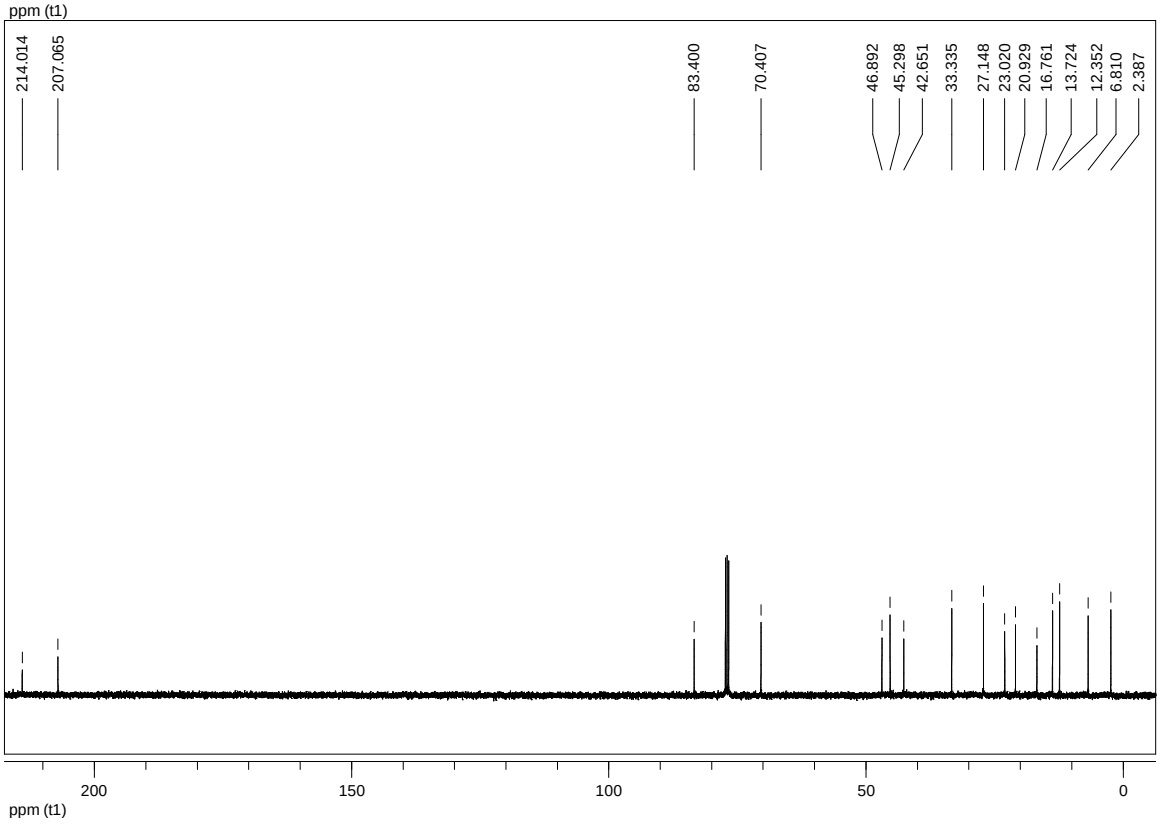




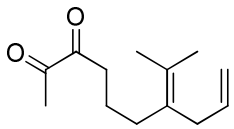
Compound 10h

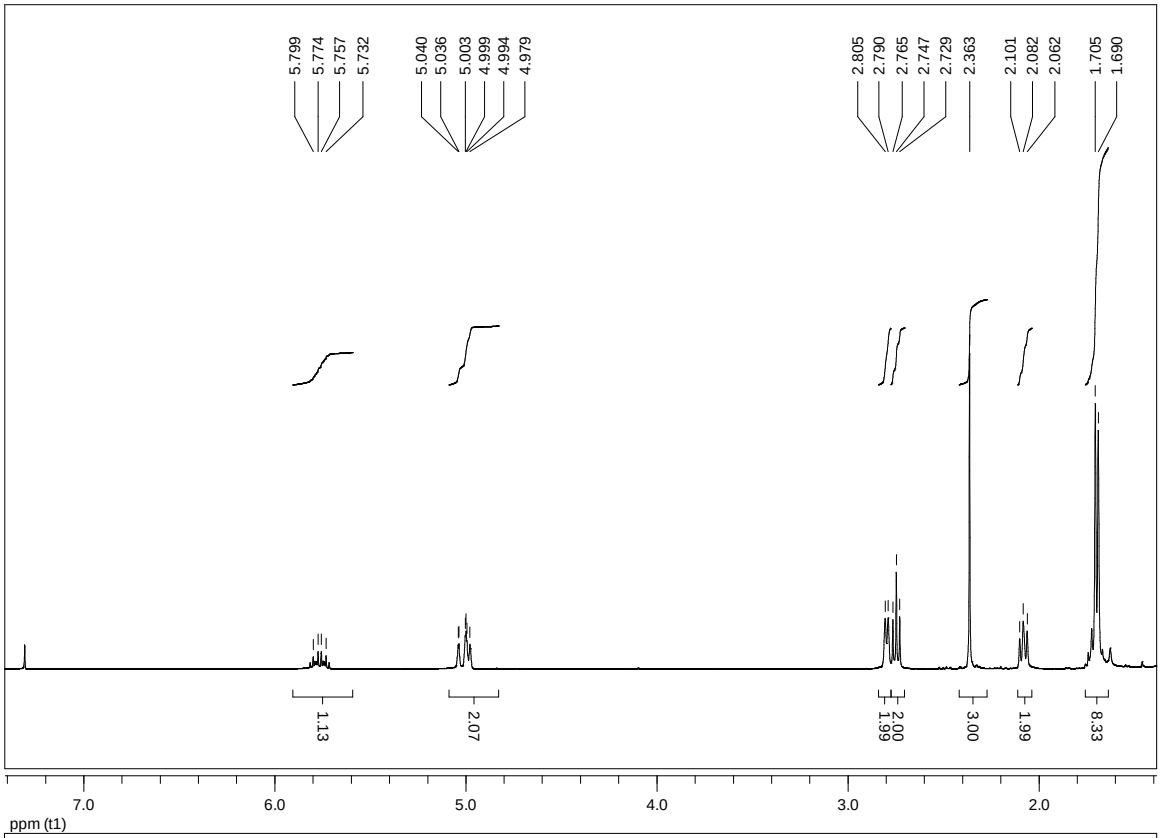


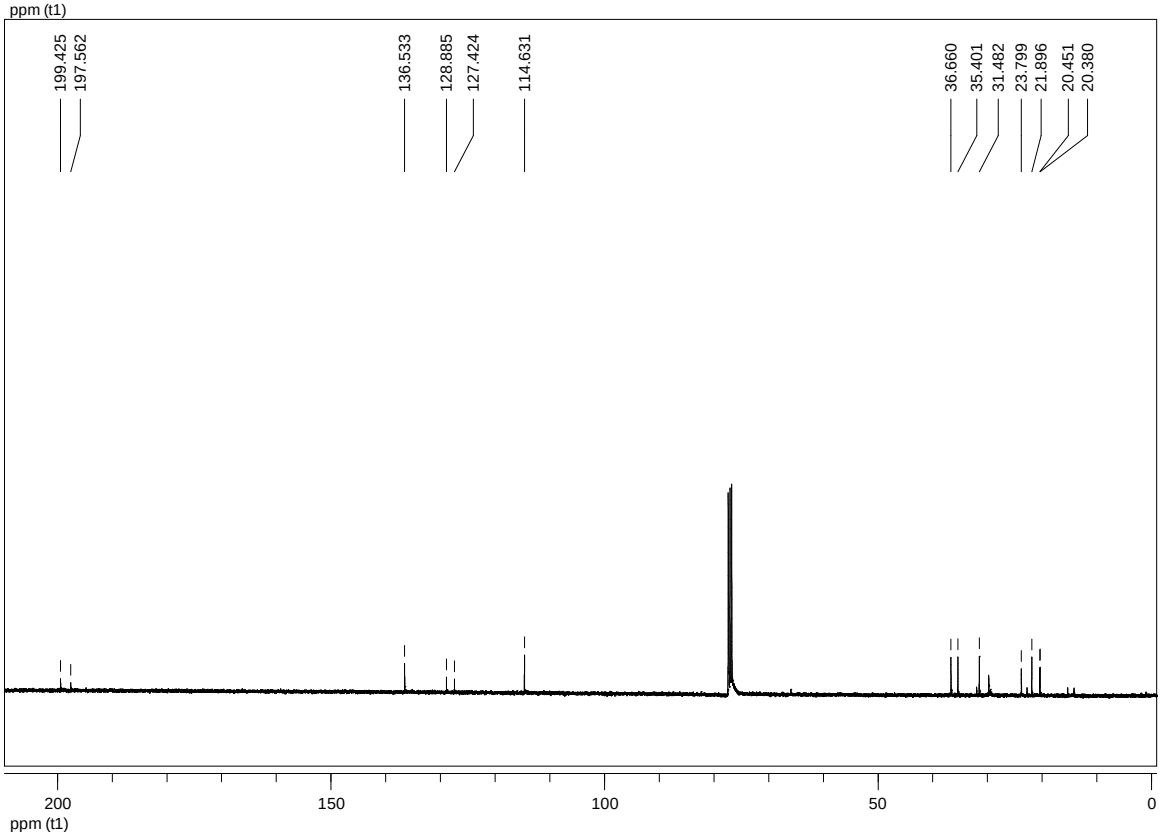




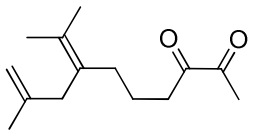
Compound 11a

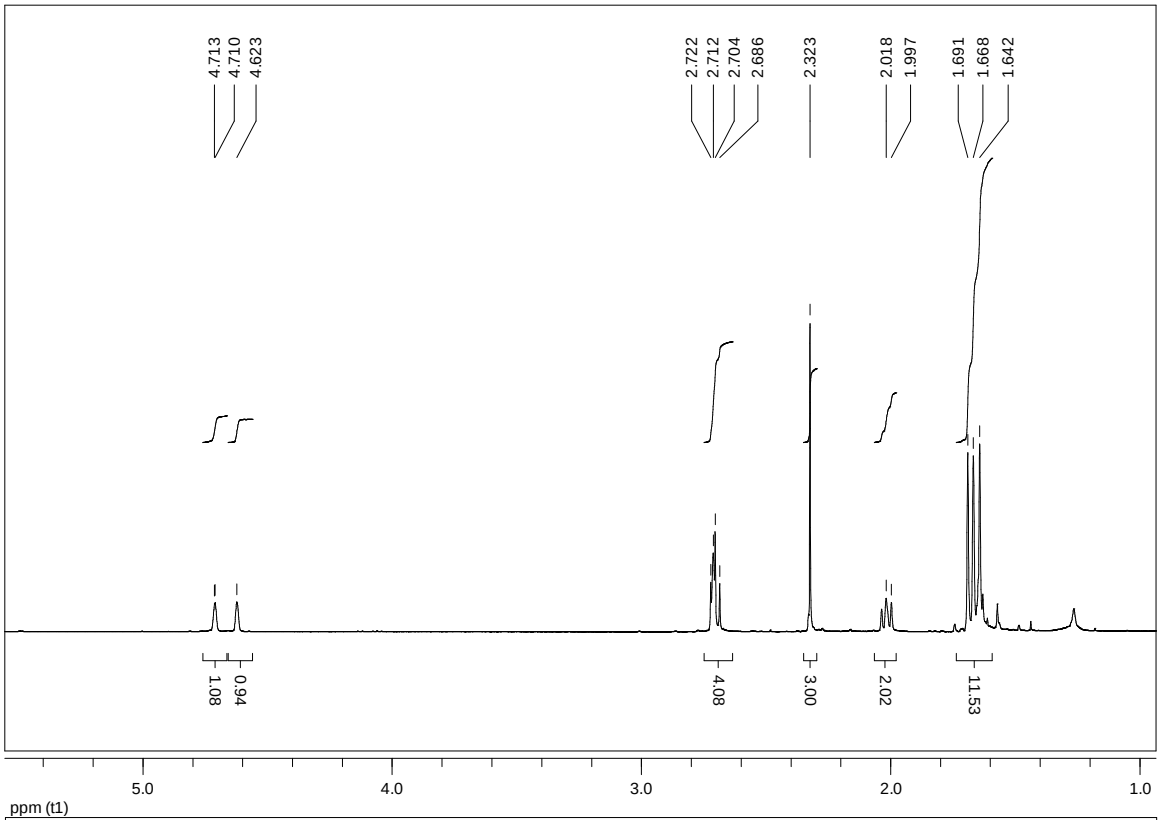


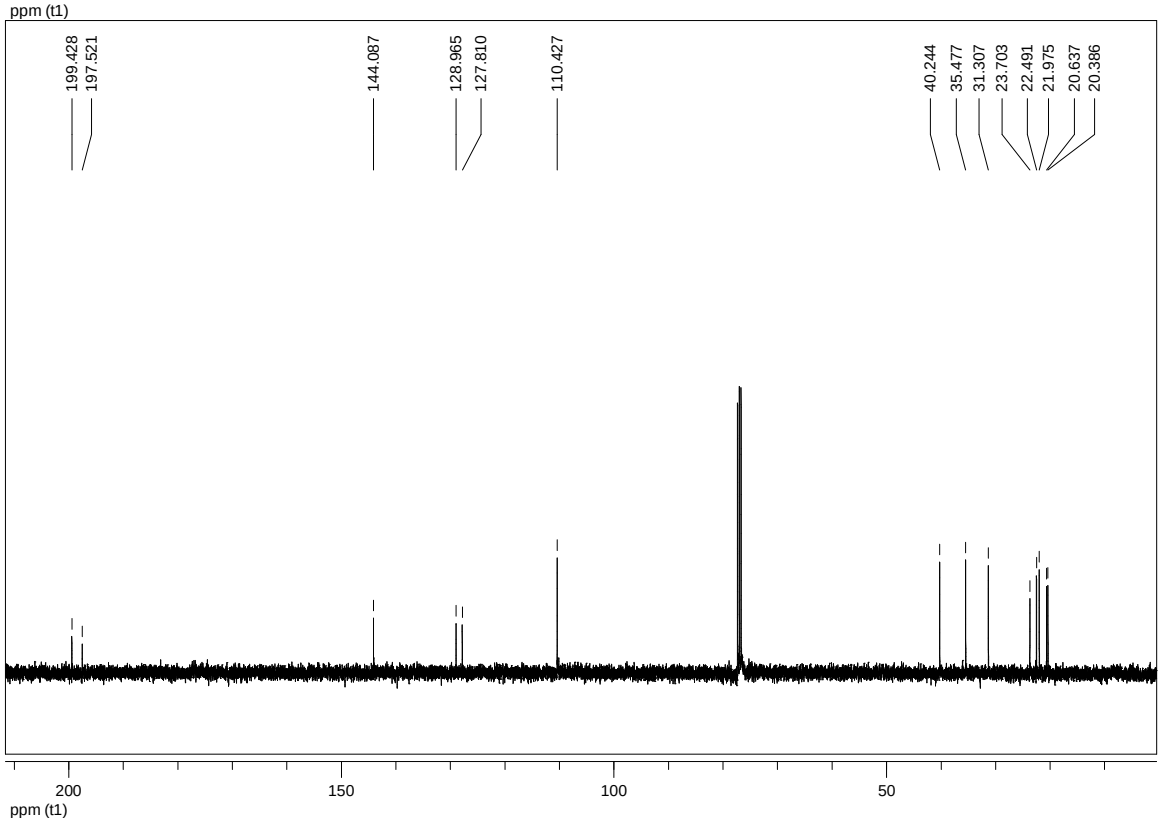




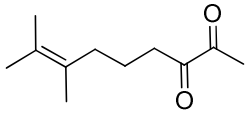
Compound 11b

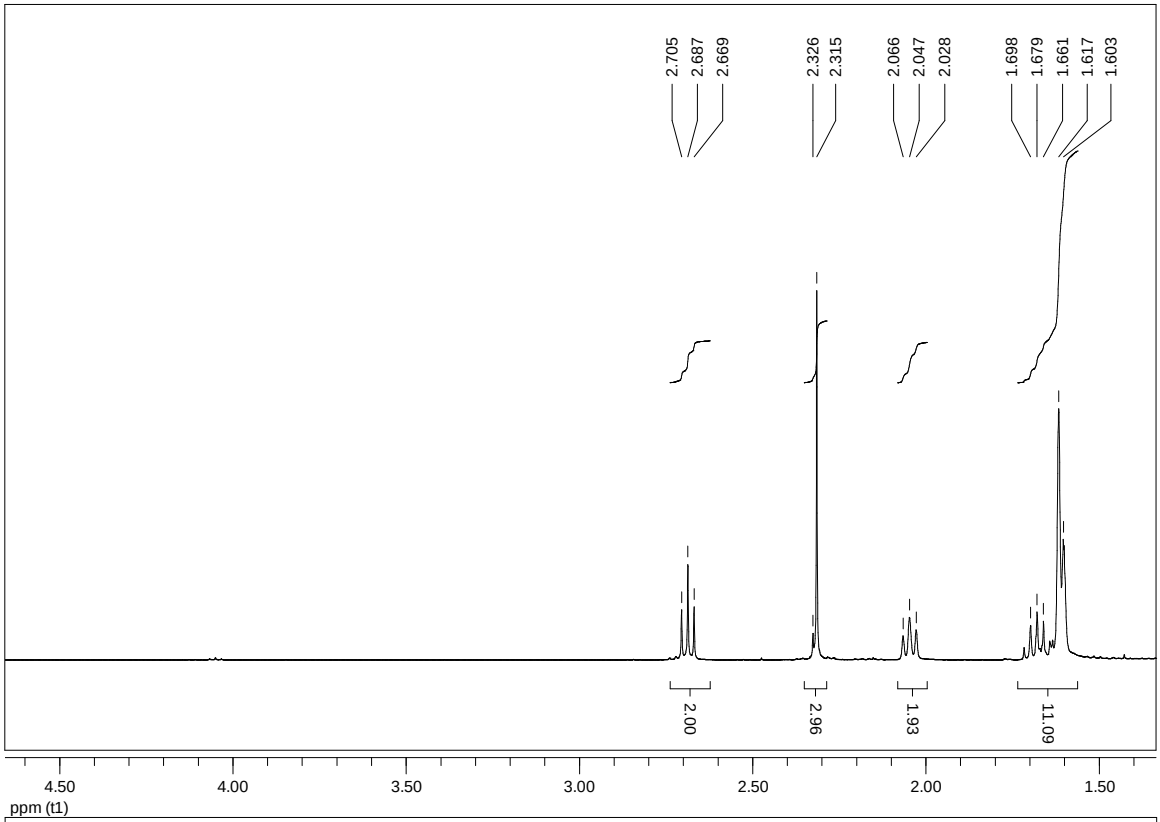


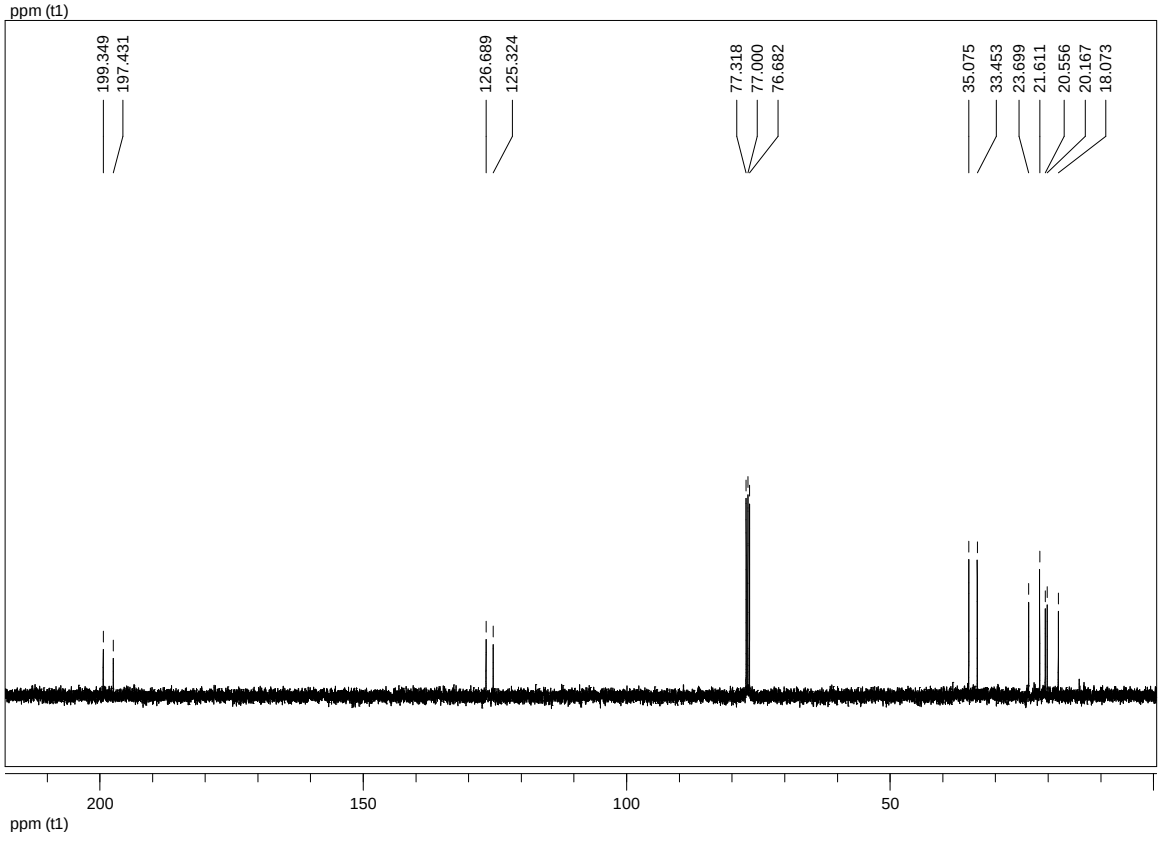




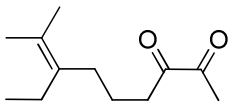
Compound 11c

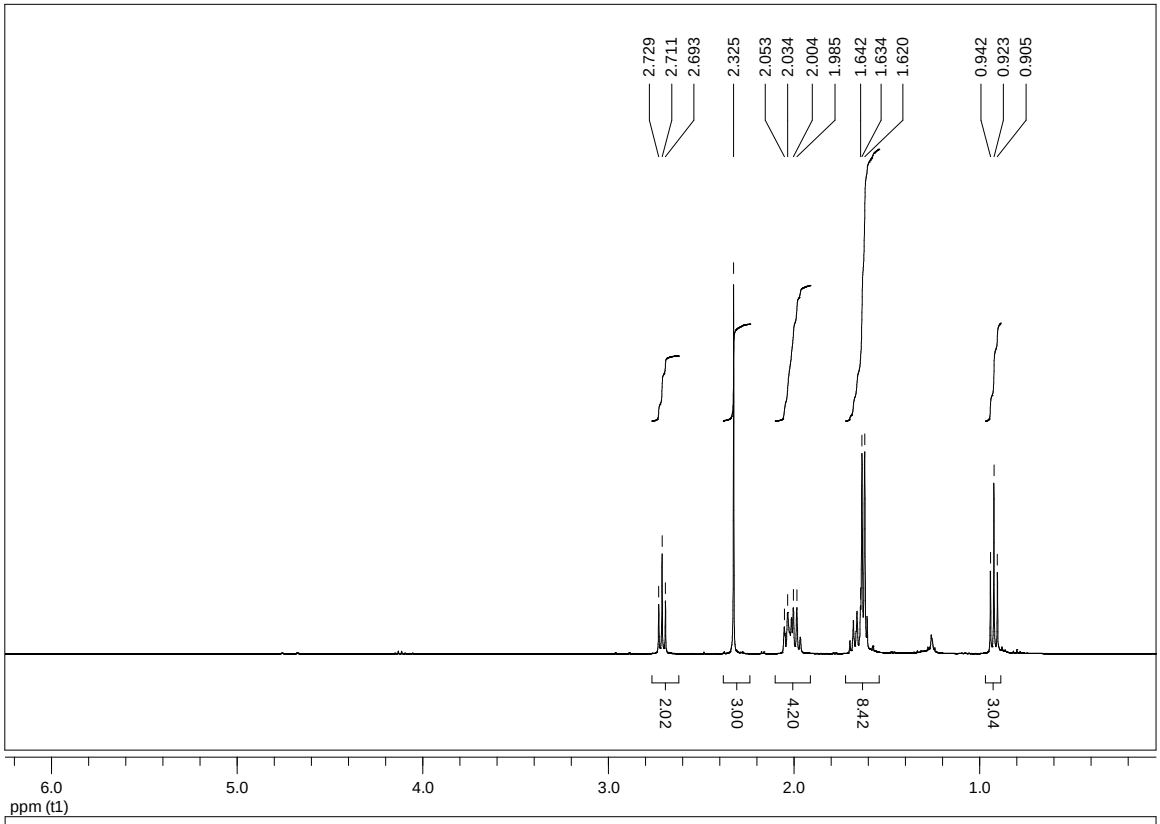


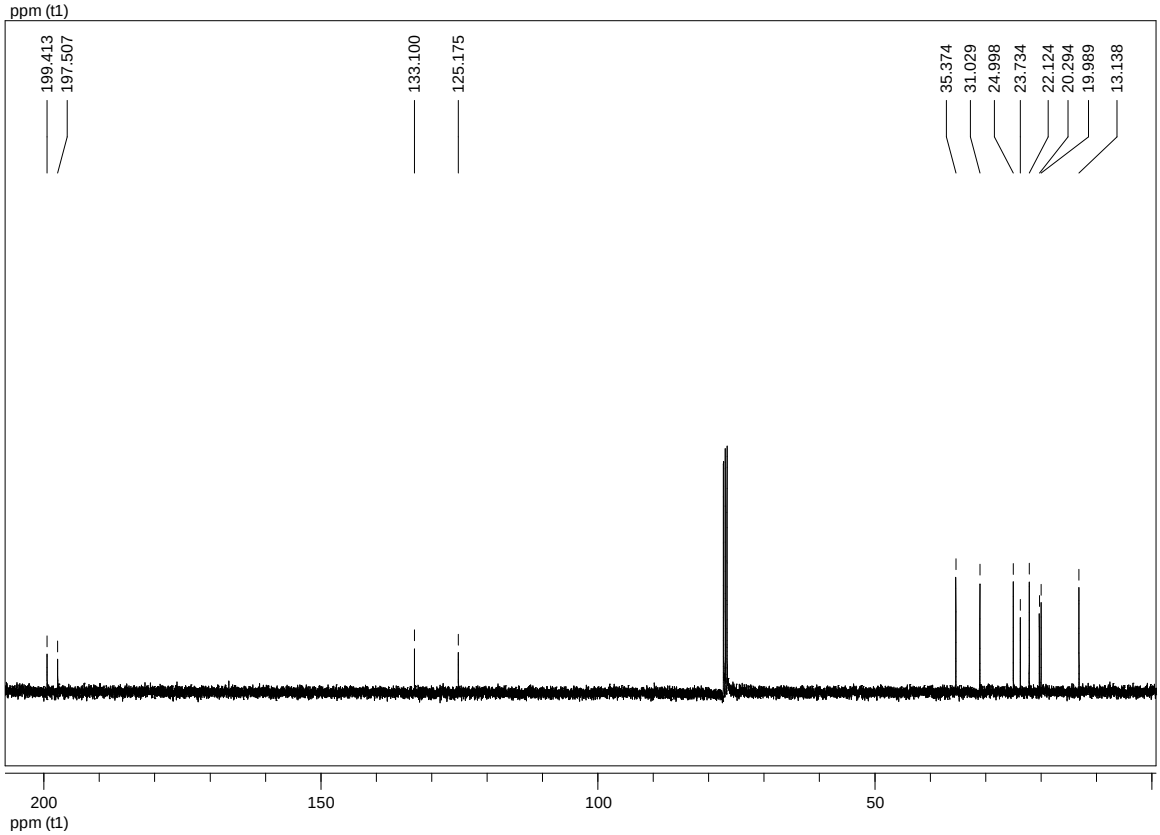




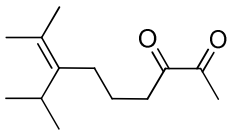
Compound 11d

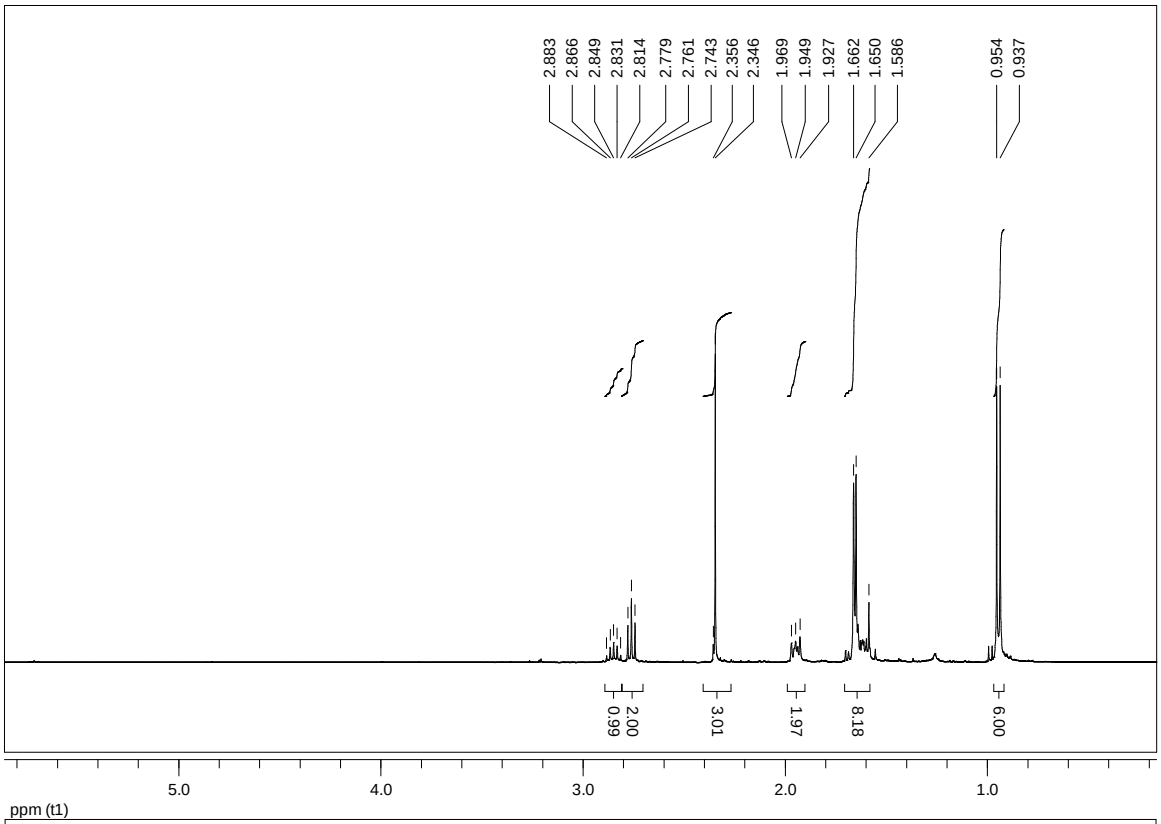


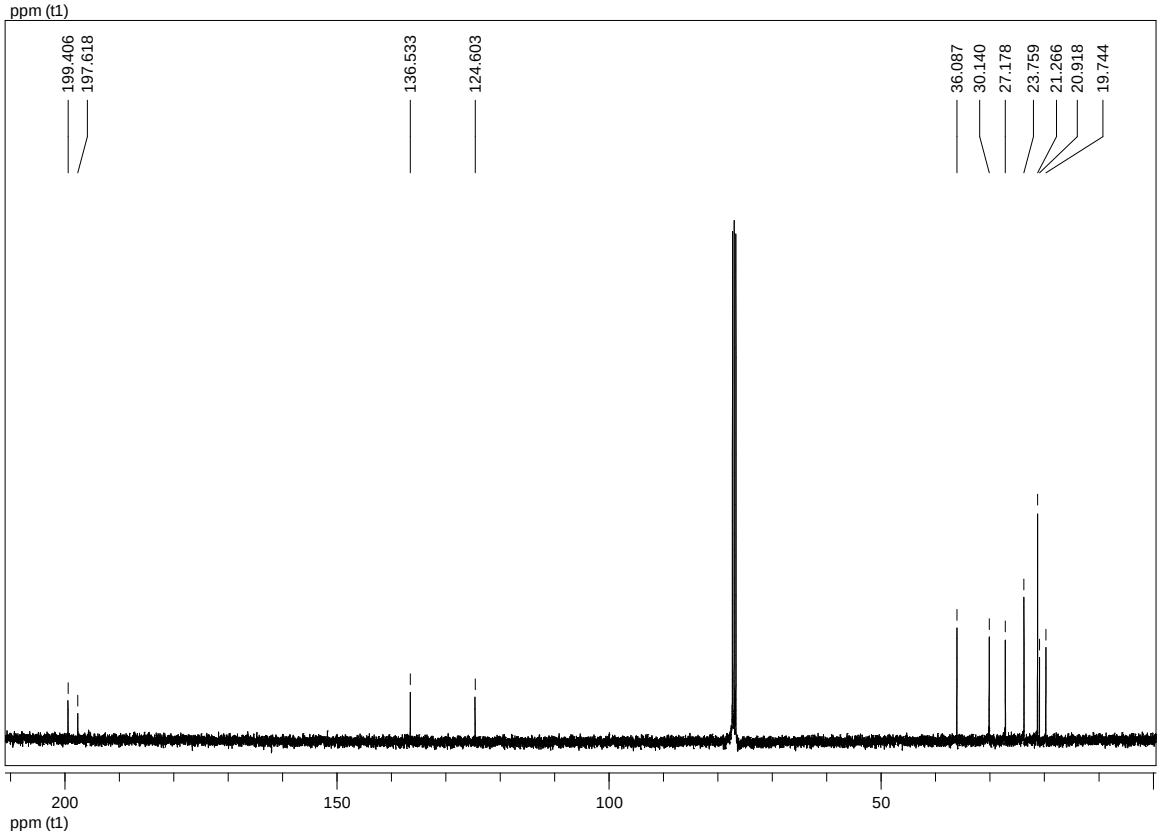




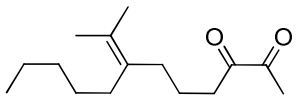
Compound 11e

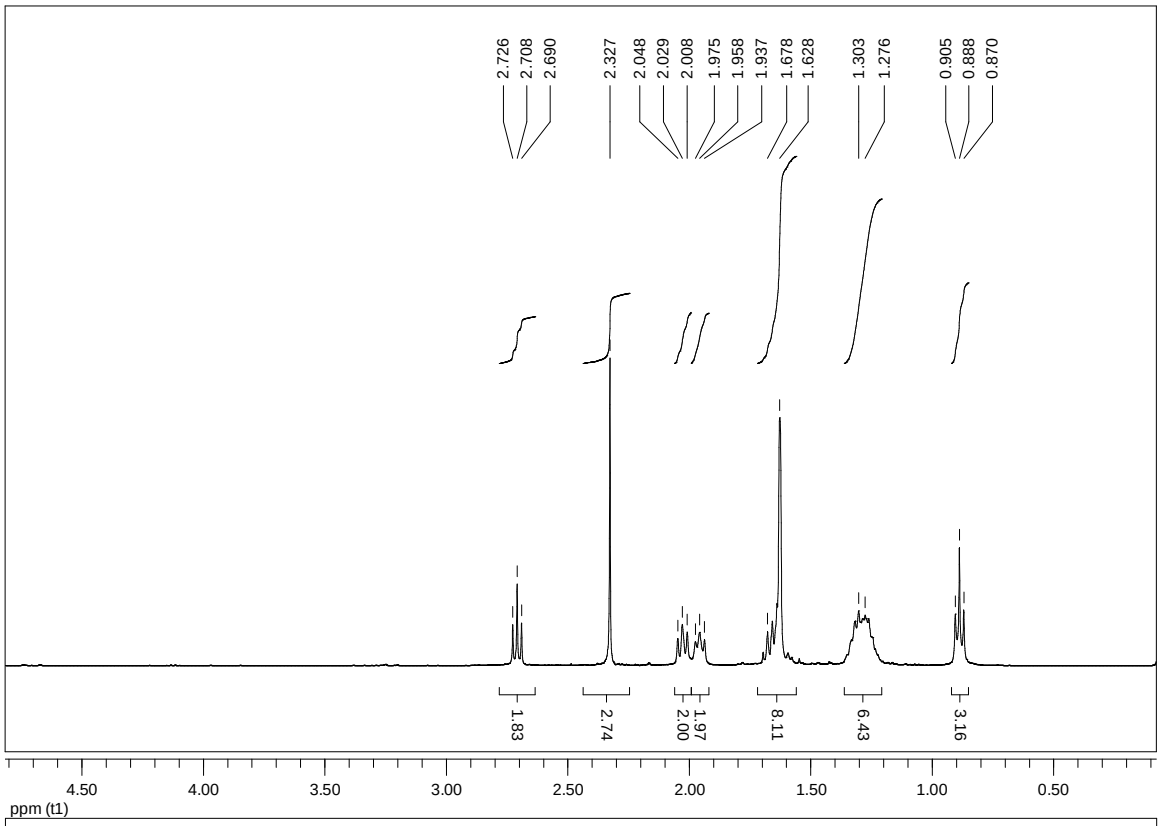


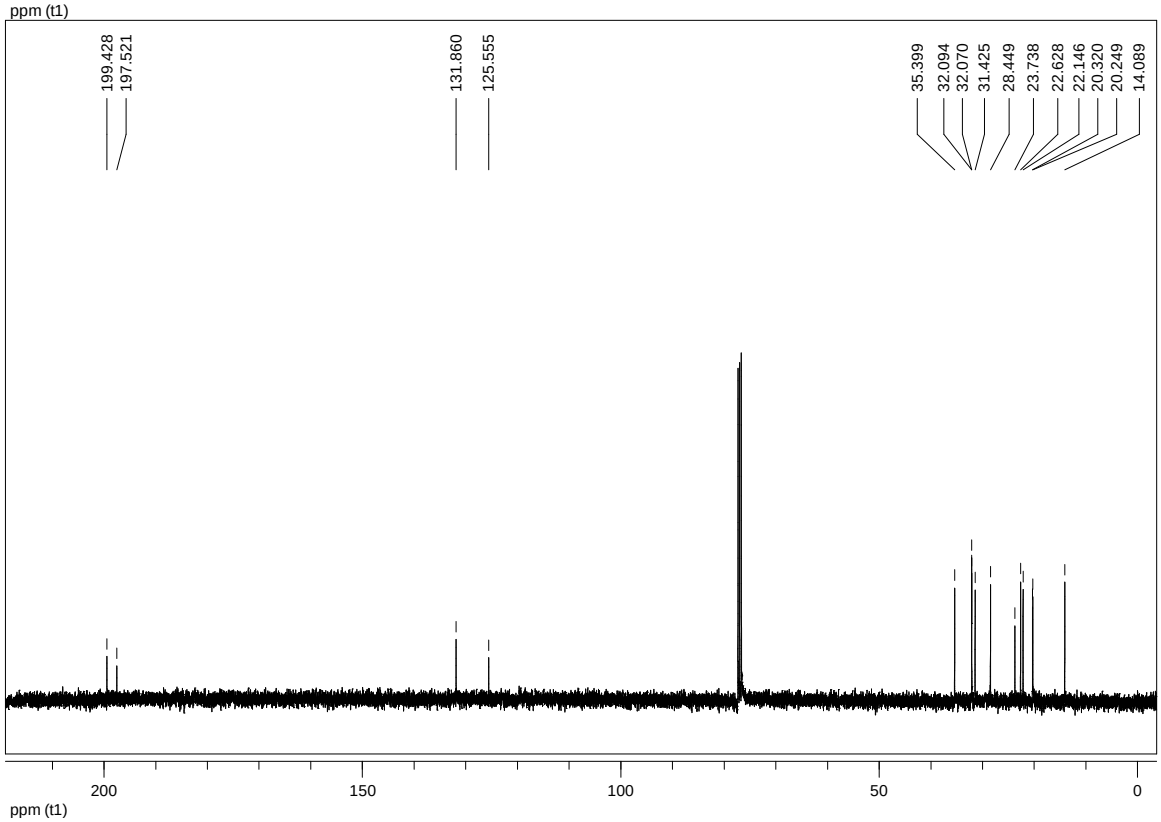




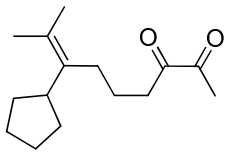
Compound 11f

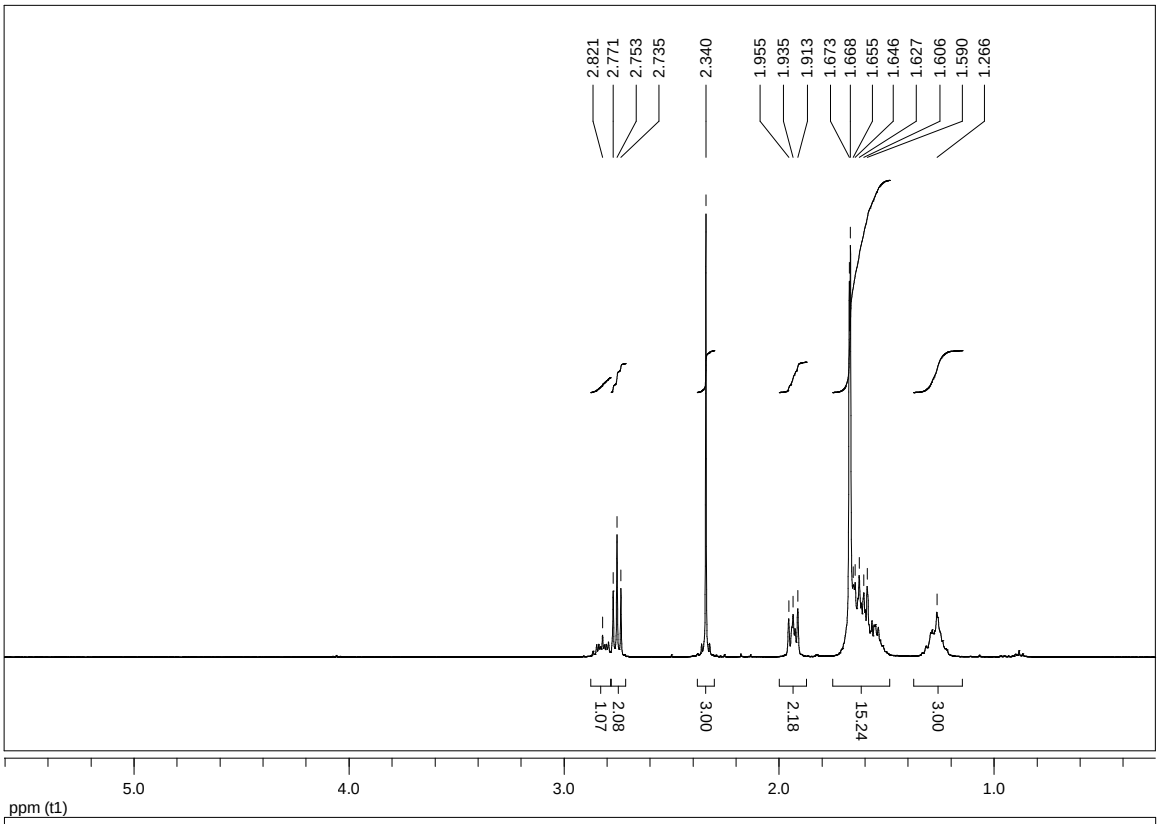


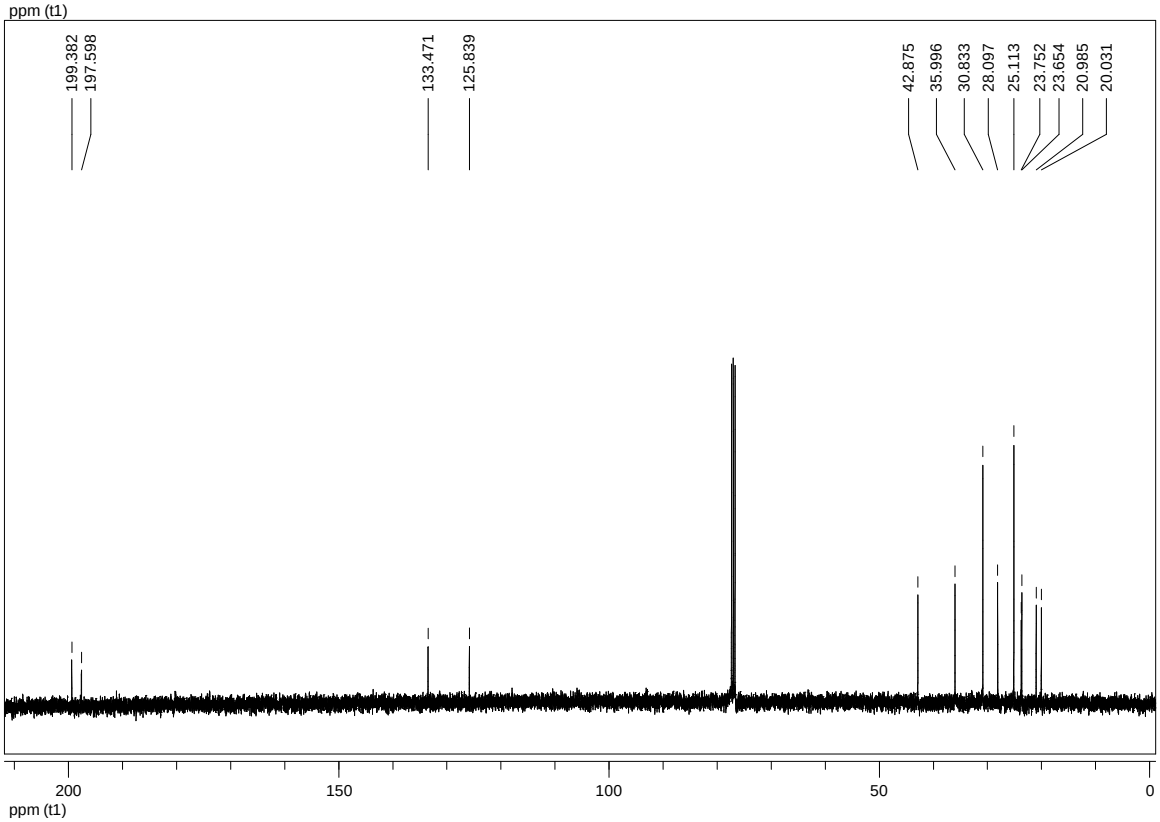




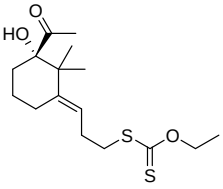
Compound 11g







Compound 17


O
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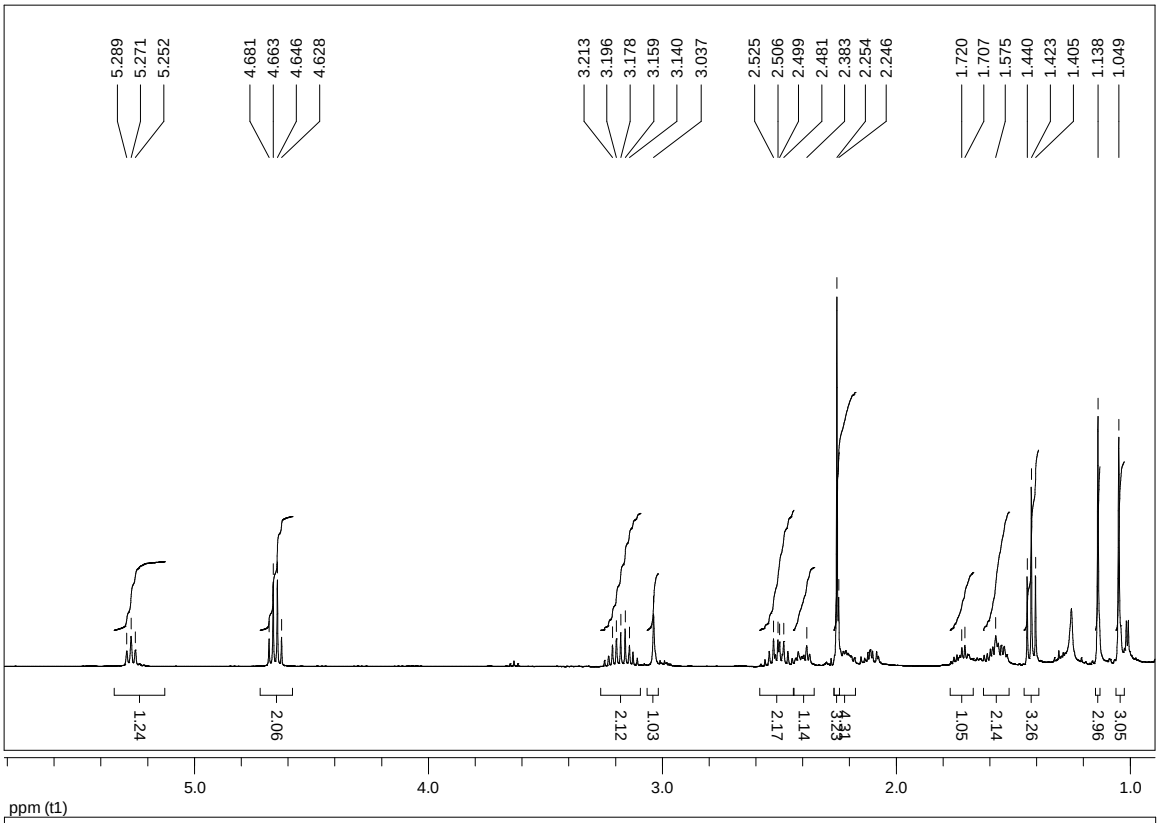
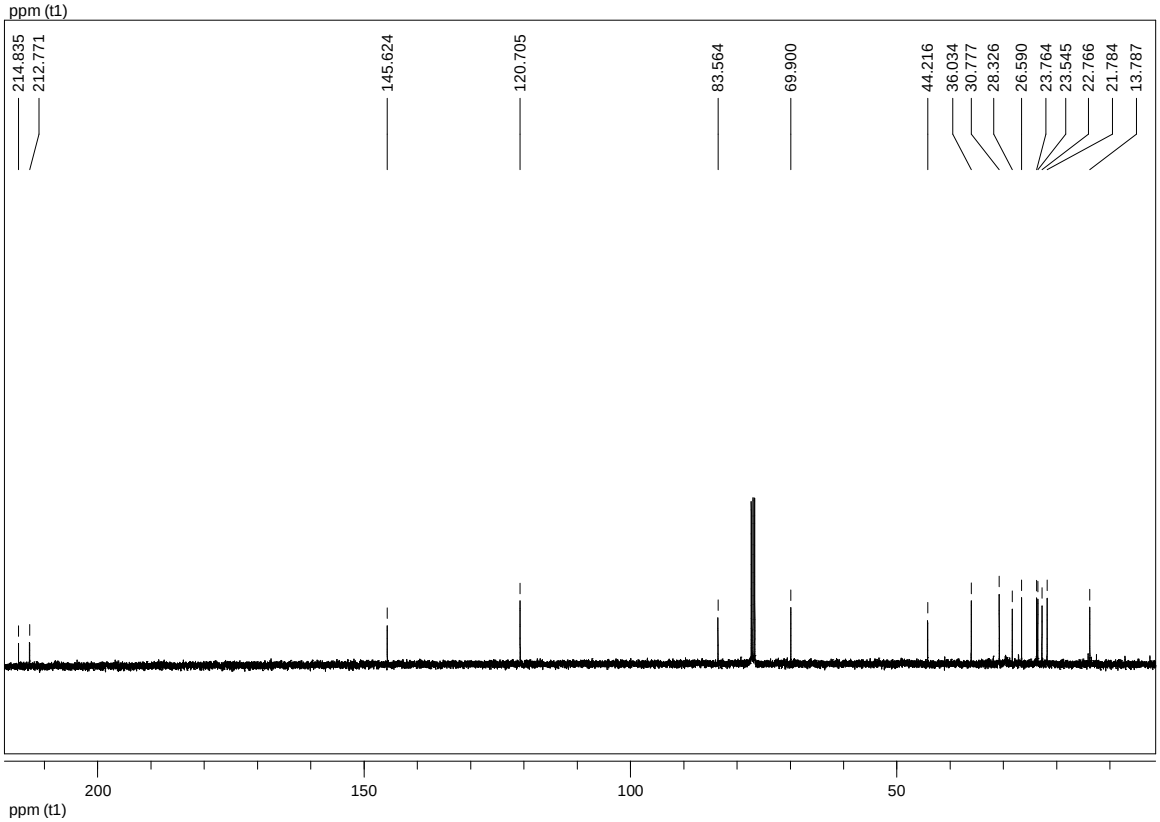

5.289
5.271
5.252
4.681
4.663
4.646
4.628
3.213
3.196
3.178
3.159
3.140
3.037
2.525
2.506
2.499
2.481
2.383
2.254
2.246
1.720
1.707
1.575
1.440
1.423
1.405
1.138
1.049
1.24
2.06
2.12
1.03
2.17
1.14
3.23
1.05
2.14
3.26
2.96
3.05
5.0
4.0
3.0
2.0
1.0
ppm (t1)


214.835
212.771
145.624
120.705
83.564
69.900
44.216
36.034
30.777
28.326
26.590
23.764
23.545
22.766
21.784
13.787
200
150
100
50
ppm (t1)