Supporting Information

Transfer of Chirality by the Use of an All Carbon Tether

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General procedure **A** for the addition of the vinyl ethyl ether:

To a stirred solution of ethyl vinyl ether (5.0 equiv) in freshly distilled THF (2 mL/ mmol of ketone) under nitrogen and at – 78°C, was added dropwise over 10 minutes *tert*-butyl lithium (~1.35 M in pentane, 2.0 equiv). After 15 more minutes, the acetone/dry ice bath was replaced by a water/ice bath, and stirring was kept for 15 min. The flask was cooled back to -78°C, and a solution of the ketone (1.0 equiv) in distilled THF (2 ml/mmol) was then added dropwise over 10 min. The mixture was then allowed to warm up to 20°C, and stirred for an additional 2 hours. Saturated NH_4Cl and ether were added to quench the reaction. The aqueous layer was then extracted with ether, and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo* to afford the corresponding ethyl vinyl ether adduct.

General procedure **B** for the xanthate formation from the vinyl ethyl ether adduct:

To a stirred solution of the ethyl vinyl ether adduct (1.0 equiv) in a mixture of acetonitrile/water (9:1) (2 mL/mmol) under nitrogen in an ice water bath, was added a solution of *N*-bromosuccinimide (1.1 equiv) in acetonitrile/water (9:1) (2 mL/mmol). Stirring was kept for 20 more minutes, and the mixture was then partitioned between 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 ^{1}H NMR analysis could be used to see the formation of the carbonyl group.

The previous crude bromo ketone (1.0 equiv) was then stirred in acetone (1.5 mL/mmol) under nitrogen at 0°C, and potassium *O*-ethyl xanthate (1.2 equiv) was then added. After one hour at 0°C, the mixture was partitioned between ether and water. Brine was added to the aqueous layer, and extracted with 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.

General procedure **C** for radical addition:

A stirred solution of xanthate (1.0 equiv) in ethyl acetate (AcOEt) (1 mL/mmol of xanthate) was refluxed for 15 min under a nitrogen flow. Dilauroyl peroxide (DLP) (5 mol %) was then added and additional DLP (5 mol %) was added every 90 min until total consumption of the starting material or until no evolution could be detected by TLC analysis. The reaction mixture was then cooled to 20°C and evaporated to dryness under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

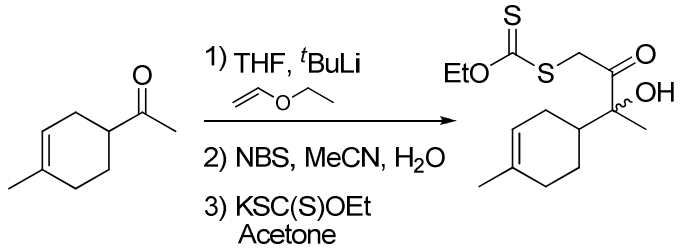
General procedure **D** for reduction of xanthate with hydrophosphorous acid:

A solution of xanthate (1.0 equiv), triethylamine (5.5 equiv) and hypophosphorous acid (50% in water) (5.0 equiv) in dioxane (12.5 mL/mmol of xanthate) was refluxed under nitrogen for 15 minutes. AIBN (0.15 mL/mmol of xanthate) in dioxane (0.4 mL/mmol) was then added to the solution, and reflux was kept for an additional one hour under nitrogen. The resulting mixture was partitioned between ethyl acetate and water. The organic layer was then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*, giving crude reduced product.

General procedure **E** for the cleavage of α hydroxyketone:

To a stirred solution of the hydroxyketone (1.0 equiv) in ethanol (1.25 mL/mmol), was added water (225 μL/ mmol), hydroxylamine hydrochloride (3.0 equiv), and sodium hydroxide (8.0 equiv). After being refluxed for 3 hours, the mixture was then partitioned between ethyl acetate and water. The aqueous layer was then extracted with ethyl acetate, and the combined organic layers were washed with water, brine, dried over $MgSO_4$ and the solvent were removed *in vacuo*, giving the oxime.
The crude product was then dissolved in pyridine (1.2 mL/mmol), and methanesulfonyl chloride (2.0 equiv) was added. Stirring was kept overnight at 20°C. Water was then added, and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding nitrile.

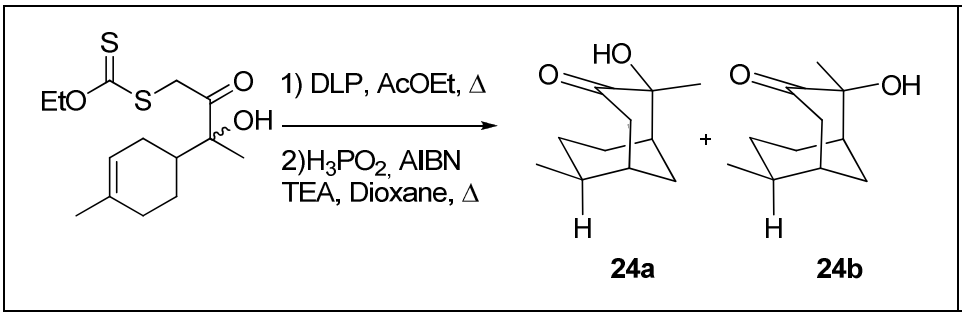
***O*-Ethyl *S*-3-hydroxy-3-(4-methylcyclohex-3-enyl)-2-oxobutyl carbonodithioate**	**6b**

	$C_{14}H_{22}O_3S_2$ M= 302.5 g.mol^{-1}

Following general procedure **A**, the reaction was carried out using 1-(4-Methyl-cyclohex-3-enyl)-ethanone (2.2 mL, 15.0 mmol). The adduct obtained was transformed following general procedure **B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford the xanthate **6b** (2.77 g, 61% over 3 steps) as a yellow oil as a mixture of diastereomers in a 1:1 ratio of the 2 epimers at C-3.

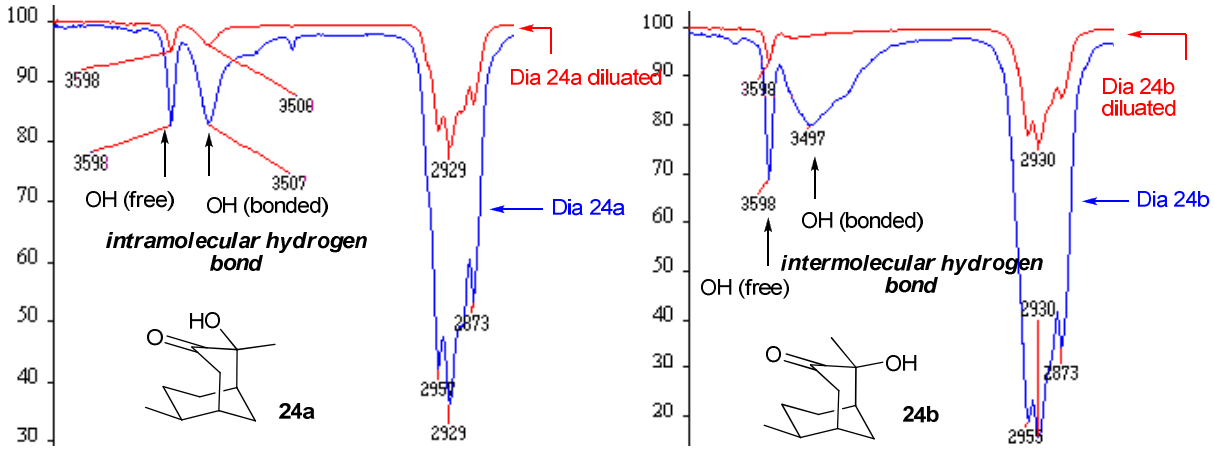
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	5.27-5.41 (m, 1H), 4.63 (q, *J*= 7.1 Hz, 2H), 4.27-4.40 (m, 2H), 3.28, 3.29 (sbr, 1H), 1.80-2.15 (m, 6H), 1.56-1.66 (m, 1H), 1.63 (s, 3H), 1.45, 1.40 (2s, 3H), 1.41 (t, *J*= 7.1 Hz, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	213.3, 213.1, 207.4, 207.1, 133.8, 133.7, 119.9, 119.5, 81.2, 80.8, 70.8, 70.8, 42.0, 41.1, 40.8, 30.2, 30.2, 25.8, 24.9, 23.6, 22.1, 23.2, 23.2, 23.2, 23.1, 13.7.
IR (ν, cm^{-1}, CCl_4)	3618, 3503, 1715, 1227, 1055.
HRMS (EI)	Calcd. for $C_{14}H_{22}O_3S_2$: 302.1011 Found: 302.1009

2-Hydroxy-2,6-dimethylbicyclo[3.3.1]nonan-3-one **24a,b**



$C_{11}H_{18}O_2$
M= 182.3 g.mol^{-1}

Following general procedure **C**, the reaction was carried out using the xanthate **6b** (150 mg, 0.5 mmol) and needed 10 mol % of DLP to go to completion. Crude xanthate **23** was then transformed following general procedure **D**. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford the α-hydroxyketone **24a,b** (73 mg, 80% over 2 steps) as a mixture of diastereomers in a 1:1 ratio of the 2 epimers at C-3 as two colorless oils. The diastereomers **24a** and **24b** were separated at this step and mixed together after characterization for the next step. By analyzing the infrared data, we can determine the structure of the diastereomer **24a** which has an intramolecular hydrogen bond and the structure of the diastereomer **24b** which has an intermolecular hydrogen bond.



Diastereomer **24a**:

^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz) 2.77 (dd, *J*= 16.2Hz, 6.1 Hz, 1H), 2.52 (ddd, *J*= 13.1, 6.0, 3.2 Hz, 1H), 2.40 (dt, *J*= 16.2, 2.1 Hz, 1H), 2.22-2.30 (m, 1H), 2.05-2.11 (m, 1H), 2.01-2.05 (m, 1H), 1.66-1.80 (m, 2H), 1.45-1.60 (m, 2H), 1.34-1.44 (m, 1H), 1.30 (s, 3H), 0.87 (d, *J*= 6.9 Hz, 3H), 0.74 -0.87 (m, 1H).

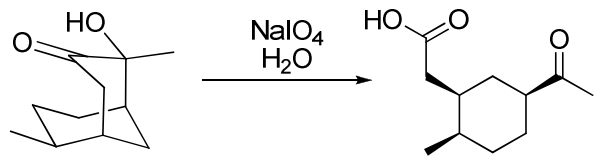
^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz) 212.4, 76.6, 41.8, 38.0, 37.4, 35.7, 30.8, 27.8, 27.0, 21.9, 19.7.

IR (ν, cm^{-1}, CCl$_4$) 3598, 3497, 1712.

HRMS (EI)	Calcd. for $C_{11}H_{18}O_2$: 182.1307	Found: 182.1315

Diastereomer **24b :** **^{1}H NMR** (δ, ppm) ($CDCl_3$, 400 MHz)	2.56 -2.62 (m, 1H), 2.49 (dd, *J*= 16.2, 6.0 Hz, 1H), 2.10- 2.25 (m, 4H), 1.60-1.82 (m, 2H), 1.71 (s, 1H), 1.23-1.41 (m, 2H), 1.40 (s, 3H), 0.88 (d, *J*= 6.9Hz, 3H), 0.77-0.90 (m, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	217.1, 77.7, 42.2, 38.0, 37.9, 35.9, 33.4, 27.9, 26.9, 26.4, 19.6.
IR (ν, cm^{-1}, CCl_4)	3528, 1741, 1709.
HRMS (EI)	Calcd. for $C_{11}H_{18}O_2$: 182.1307 Found: 182.1315

5-Acetyl-1,2-dimethylcyclohexyl)acetonitrile 25

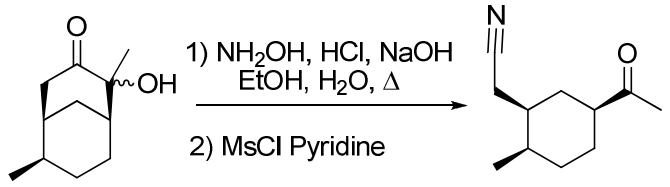


$C_{11}H_{18}O_3$
M= 198.3 g.mol^{-1}

A solution of the hydroxyl ketone **24a** (91 mg, 0.5 mmol) was stirred in water (17 mL) with sodium periodate (785 mg, 3.6 mmol) for 24 hours. A solution of sodium hydroxide (5%) has then been added, and the basic aqueous layer was extracted with diethyl ether. Chlorhydric acid (3M) was then added, until the pH of the solution reached 1, and the aqueous phase was then extracted with diethyl ether. The organic layer thus obtained was then washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure, giving pure acid **25** (72 mg, 73%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	7.7-10.1 (sbr, 1H), 2.32-2.43 (m, 1H), 2.14-2.30 (m, 2H), 2.12 (s, 3H), 1.98-2.09 (m, 1H), 1.85-1.97 (m, 1H), 1.52-1.68 (m, 3H), 1.34-1.46 (m, 1H), 1.18-1.33 (m, 2H), 0.82 (d, *J*= 7.0 Hz, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	212.0, 178.6, 51.3, 39.0, 36.4, 32.4, 30.3, 28.0, 27.6, 22.0, 11.7.
IR (ν, cm^{-1}, CCl_4)	3528, 1741, 1709.
HRMS (EI)	Calcd. for $C_{11}H_{18}O_3$: 198.1263 Found: 198.1256

5-Acetyl-1,2-dimethylcyclohexyl)acetonitrile 27

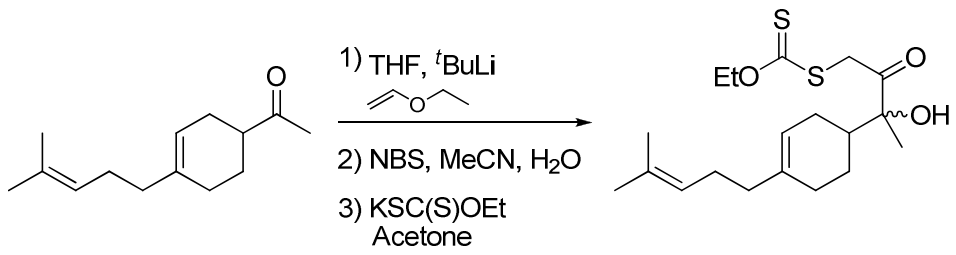


$C_{11}H_{17}NO$
M= 179.3 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **24a,b** (182 mg, 1.0 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford the nitrile **27** (1.63 g, 80% over 2 steps) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	2.55 (tt, *J*= 11.7, 4.0 Hz, 1H), 2.13-2.26 (m, 2H), 2.13 (s, 3H), 1.66-1.85 (m, 3H), 1.40-1.53 (m, 4H), 1.20 (s, 3H), 0.94 (d, *J*= 7.1 Hz, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	210.7, 118.7, 50.9, 37.1, 32.2, 29.9, 28.1, 27.4, 22.1, 22.0, 11.2.
IR (ν, cm^{-1}, CCl_4)	2249, 1714.
HRMS (EI)	Calcd. for $C_{11}H_{17}NO$: 179.1310 : Found: 179.1305

O-Ethyl S-3-hydroxy-3-(4-(4-methylpent-3-enyl)cyclohex-3-enyl)-2-oxobutyl carbonodithioate **30b**



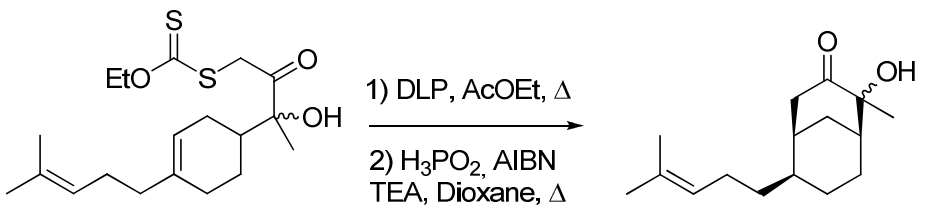
$C_{19}H_{30}O_3S_2$
M= 370.6 g.mol^{-1}

Following general procedure **A**, the reaction was carried out using 1-(4-(4-methylpent-3-enyl)cyclohex-3-enyl)ethanone[1] (7.5 mmol 1.55 g). The adduct obtained was transformed following general procedure **B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford the xanthate **30b** (2.14 g, 77% over 3 steps) as a yellow oil as a mixture of diastereomers in a 1:1 ratio of the 2 epimers at C-3.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	5.46-5.48 (m, 0.5H), 5.35-5.37 (m, 0.5H), 5.11, 5.35 (m, 1H), 4.70 (q, *J*= 7.1 Hz, 1H), 4.69 (q, *J*= 7.1 Hz, 1H), 4.31-4.44 (m, 2H), 3.31 (sbr, 1H), 1.94-2.11 (m, 9H), 1.72 (s, 3H), 1.64 (s, 3H), 1.35-1.40 (m, 2H), 1.52 (s, 3H), 1.47 (t, *J*= 7.1 Hz, 1.5H), 1.48 (t, *J*= 7.1 Hz, 1.5H)
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	213.4, 213.3, 207.5, 207.5, 137.7, 137.6, 131.3, 131.5, 124.2, 119.6, 119.3, 81.3, 81.0, 71.0, 70.9, 42.1, 41.4, 41.1, 37.5, 37.5, 28.7, 28.7, 26.5, 26.5, 25.9, 25.0, 25.8, 23.8, 22.3, 17.8, 13.8.
IR (ν, cm^{-1}, CCl_4)	3618, 3505, 3155, 2983, 2914, 1816, 1795, 1717, 1469, 1383, 1228, 1097, 1054.
HRMS (EI)	Calcd. for $C_{19}H_{30}O_3S_2$: 370.1637 Found: 370.1630

[1] The ketone was prepared from methylvinyl ketone and myrcene in one step according to literature procedures: Veselovsky, V. V.; Gybin, A. S.; Lozanova, A. M.; Moiseenkov, A. M.; Smit, W. A. *Tetrahedron Lett.* **1988**, *29*, 175.

2-Hydroxy-2-methyl-6-(4-methylpent-3-enyl)bicyclo[3.3.1]nonan-3-one **31a,b**

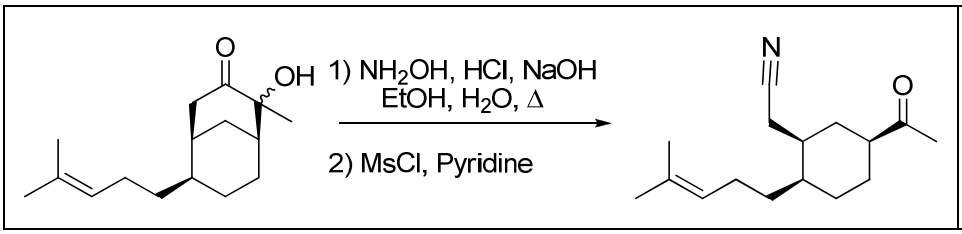


$C_{16}H_{26}O_2$
M= 250.4 g.mol^{-1}

Following general procedure **C**, the reaction was carried out using the xanthate **30b** (mg, 2.0 mmol) and needed 10 mol % of DLP to go to completion. Crude xanthate was then transformed following general procedure **D**. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford the α-hydroxyketone **31** (351 mg, 70% over 2 steps) as a mixture of diastereomers in a 1:1 ratio of the 2 epimers at C-3 as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	5.06 (t, *J*= 7.1 Hz, 1H), 3.83 (s, 0.5H), 2.78 (dd, *J*= 16.1, 6.1 Hz, 0.5H), 1.89-2.53 (m, 3.5H), 1.67 (s, 3H), 1.23-1.66 (m, 8H), 1.57 (s, 3H), 1.41 (s, 1.5H), 1.32 (s, 1.5H), 0.77-0.89 (m, 2H).
Diastereomer **31a**	
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	212.2, 131.6, 124.4, 77.3, 42.4, 40.3, 38.3, 35.5, 34.2, 30.8, 28.0, 25.8, 25.8, 25.4, 22.1, 17.7.
Diastereomer **31b**	
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	217.3, 131.5, 124.3, 77.8, 42.7, 40.5, 38.2, 36.2, 34.1, 33.4, 27.9, 26.4, 25.7, 25.3, 25.1, 17.6.
IR (ν, cm^{-1}, CCl_4)	3598, 3504, 2930, 2858, 1709, 1646, 1461, 1415, 1376, 1316, 1239, 1166, 1126.
HRMS (EI)	Calcd. for $C_{16}H_{26}O_2$: 250.1933 Found: 250.1933

2-(5-Acetyl-2-(4-methylpent-3-enyl)cyclohexyl)acetonitrile 32



$C_{16}H_{25}NO$
M= 247.4 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **31a,b** (87 mg, 0.35 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford the nitrile **32** (65 mg, 75% over 2 steps) as a colorless oil.

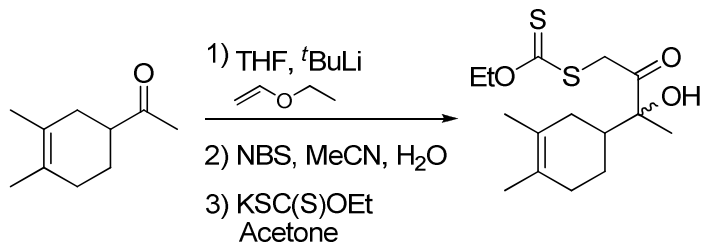
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.07 (t, *J*= 7.1 Hz, 1H), 2.37-2.45 (m, 1H), 2.28 (dd, *J*= 7.9, 2.4 Hz, 2H), 2.15 (s, 3H), 1.71-2.06 (m, 7H), 1.68 (s, 3H), 1.59 (s, 3H), 1.29-1.42 (m, 4H), 1.08-1.16 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 210.8, 132.2, 123.7, 118.8, 50.8, 37.2, 35.0, 28.2, 28.2, 27.8, 25.7, 25.7, 24.1, 22.0, 21.8, 17.7

IR (ν, cm^{-1}, CCl_4): 2936, 2863, 2248, 1713, 1451, 1427, 1376, 1353, 1162, 1176.

HRMS (EI): Calcd. for $C_{16}H_{25}NO$: 247.1936 Found: 247.1940

S-3-(3,4-Dimethylcyclohex-3-enyl)-3-hydroxy-2-oxobutyl O-ethyl carbonodithioate **35b**



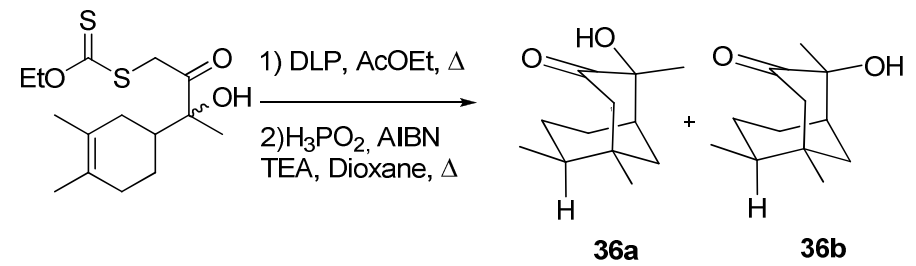
$C_{15}H_{24}O_3S_2$
M= 316.5 g.mol^{-1}

Following general procedure **A**, the reaction was carried out using 1-(3,4-dimethylcyclohex-3-enyl)ethanone[2] (6.09 g, 40 mmol). The adduct obtained was transformed following general procedure **B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford the xanthate **35b** (8.48 g, 67% over 3 steps) as a yellow oil as a mixture of diastereomers in a 1:1 ratio of the 2 epimers at C-3.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	4.65 (q, *J*= 7.1 Hz, 1H), 4.64 (q, *J*= 7.1 Hz, 2H), 4.28-4.38 (m, 2H), 3.24 (sbr, 1H), 1.89-2.06 (m, 5H), 1.63, 1.60, 1.56 (3s, 6H), 1.38-1.50 (m, 1H), 1.47, 1.40 (2s), 1.42 (t, *J*= 7.1 Hz).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	213.3, 213.2, 207.3, 207.3, 125.5, 125.4, 124.5, 124.2, 81.2, 80.9, 70.9, 70.9, 42.0, 41.9, 41.7, 32.1, 31.2, 31.9, 24.0, 22.5, 23.3, 23.1, 19.2, 19.1, 18.7 , 13.7
IR (ν, cm^{-1}, CCl_4)	3598, 3513, 2979, 2937, 1711, 1459, 1375, 1221, 1113, 1053.
HRMS (EI)	Calcd. for $C_{15}H_{24}O_3S_2$: 316.1167 Found: 316.1160

[2] The ketone was prepared from but-3-en-2-one and 2,3-dimethylbuta-1,3-diene in one step according to literature procedures: Kreiser, W.; Haumesser, W.; Thomas, A. F. . *Helvitica Chem. Acta* **1974**, *57*, 164.

4-Hydroxy-1,4,8-trimethylbicyclo[3.3.1]nonan-3-one **36a,b**



$C_{12}H_{20}O_2$
M= 196.3 g.mol^{-1}

Following general procedure **C**, the reaction was carried out using the xanthate **35b** (870 mg, 2.75 mmol) and needed 10 mol % of DLP to go to completion. Crude xanthate was then transformed following general procedure **D**. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford the α-hydroxyketone **36a,b** (372 mg, 69% over 2 steps) as a mixture of diastereomers in a 1:1 ratio of the 2 epimers at C-3 as two colorless oils. The diastereomers **36a** and **36b** were separated at this step and mixed together after characterization for the next step.

Diastereomer **36a**:

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 2.43 (d, *J*= 16.2 Hz, 1H), 2.27-2.35 (m, 2H), 2.07-2.10 (m, 1H), 1.77-1.71 (m, 1H), 1.49-1.56 (m, 1H), 1.33-1.42 (m, 3H), 1.31 (s, 3H), 0.96 (s, 3H), 0.83 (d, *J*= 6.6Hz, 3H), 0.80 -0.86 (m, 2H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 212.2, 75.5, 44.3, 42.8, 41.2, 38.6, 38.1, 28.8, 28.5, 28.0, 21.6, 15.6.

IR (ν, cm^{-1}, CCl_4): 3598, 3487, 2955, 928, 2870, 1711, 1456, 1443, 1375, 1318, 1215, 1157, 1123, 1073, 1025.

HRMS (EI): Calcd. for $C_{12}H_{20}O_2$: 196.1463 Found : 196.1460

Diastereomer **36b :**

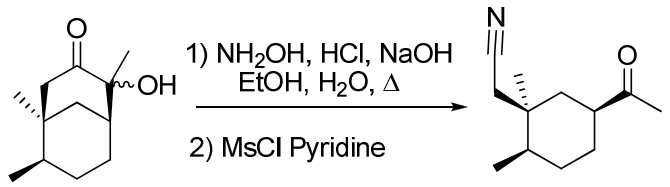
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 3.80 (s, 1H), 2.50 (dd, *J*= 16.1, 3.3 Hz, 1H), 2.20- 2.23 (m, 1H), 2.15 (d, *J*= 16.1 Hz, 1H), 1.96-2.01 (m, 1H), 1.62 (dt, *J*= 13.8, 3.2 Hz, 1H), 1.33-1.44 (m, 3H), 1.38 (s, 3H), 0.98 (s, 3H), 0.83 (d, *J*= 6.6 Hz, 3H), 0.80-0.86 (m, 2H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 216.8, 77.0, 44.1, 43.1, 41.5, 41.3, 39.1, 28.9, 28.4, 27.9, 26.7, 15.6.

IR (ν, cm^{-1}, CCl_4) 3507, 2959, 2927, 2873, 1707, 1462, 1453, 1373, 1241, 1162, 1147, 1125, 1106, 1024.

HRMS (EI) Calcd. for $C_{12}H_{20}O_2$: 196.1463 Found : 196.1460

5-Acetyl-1,2-dimethylcyclohexyl)acetonitrile 37

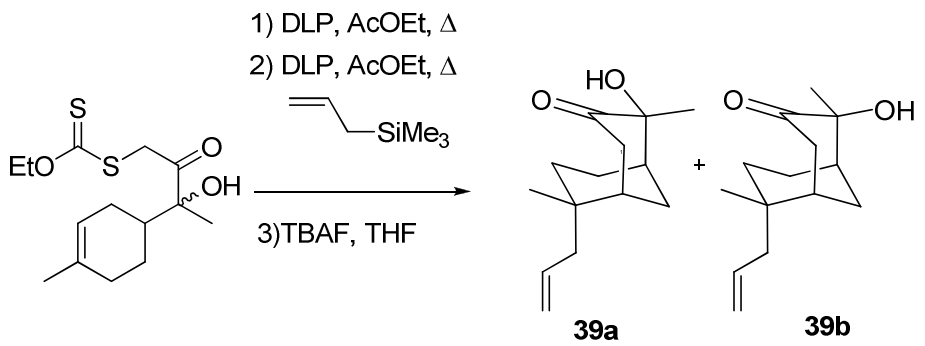


$C_{12}H_{19}NO$
M= 193.3 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **36a,b** (90 mg, 0.46 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford the nitrile **37** (1.63 g, 83% over 2 steps) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	2.55 (tt, *J*= 11.7, 4.0 Hz, 1H), 2.13-2.26 (m, 2H), 2.13 (s, 3H), 1.66-1.85 (m, 3H), 1.40-1.53 (m, 4H), 1.20 (s, 3H), 0.94 (d, *J*= 7.1 Hz, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	211.1, 117.9, 46.6, 35.6, 34.7, 33.3, 29.9, 28.1, 28.1, 24.5, 22.3, 14.6.
IR (ν, cm^{-1}, CCl_4)	2960, 2874, 2249, 1712, 1558, 1541, 1455, 1434, 1359, 1320, 1302, 1175, 1127.
HRMS (EI)	Calcd. for $C_{12}H_{19}NO$: 193.1467 Found: 193.1460

6-(3,3-Diethoxypropyl)-2-hydroxy-2,6-dimethylbicyclo[3.3.1]nonan-3-one 39a,b



$C_{14}H_{22}O_2$
M= 222.3 g.mol^{-1}

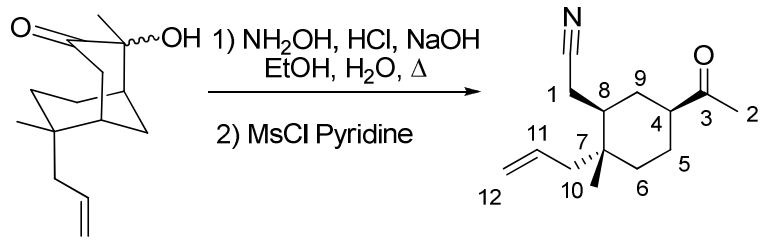
Following general procedure **C**, the reaction was carried out using the xanthate **6b** (303 mg, 2.0 mmol) and needed 10 mol % of DLP to go to completion. Allyltrimethylsilane (305 µL, 2.0 equiv) was added to the reaction mixture and needed 20 mol% to go to completion. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford the xanthate **38**. To a solution of xanthate **38** in THF (7 mL) was added TBAF (4 mL, 4.0 mmol). The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 85:15) to afford the α-hydroxyketone **39b** (144 mg, 32% over 3 steps) and a mixture of α-hydroxyketone **39a** and the α-hydroxyketone **24a** in a 7:3 ratio (190 mg, 32% over 3 steps for **39a**) as two colorless oils.

Diastereomer **39a**:

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	5.72-5.82 (m, 1H), 5.02-5.06 (m, 2H), 2.86 (dd, *J*= 15.9, 5.9 Hz, 1H), 2.47-2.53 (m, 1H), 2.25-2.31 (m, 1H), 2.22-2.30 (m, 1H), 1.90-1.93 (m, 1H), 1.86 (ddd, *J*= 13.9, 6.2, 3.1 Hz, 1H), 1.53-1.75 (m, 3H), 1.32 (s, 3H), 1.16-1.28 (m, 3H), 0.97 (td, *J*= 14.8, 4.8 Hz, 1H), 0.87 (s, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	212.0, 134.7, 117.4, 76.4, 42.4, 42.0, 40.7, 39.7, 35.7, 30.3, 25.6, 25.3, 23.5, 22.0.
IR (ν, cm^{-1}, CCl_4)	3595, 3503, 2975, 2931, 2874, 1711, 1455, 1444, 1376, 1264, 1238, 1125, 1063.
HRMS (EI)	Calcd. for $C_{14}H_{22}O_2$: 222.1620 Found: 222.1616

Diastereomer **39b:** **^{1}H NMR** (δ, ppm) ($CDCl_3$, 400 MHz)	5.76 (dddd, *J*= 17.0, 10.4, 8.0, 7.0 Hz, 1H), 5.01-5.06 (m, 2H), 3.83 (s, 1H), 2.65-2.71 (m, 1H), 2.51-2.58 (m, 2H), 2.31 (dd, *J*= 13.8, 8.1 Hz, 1H), 1.91-2.21 (m, 5H), 1.44-1.50 (m, 1H), 1.40 (s, 3H), 0.87 (s, 3H), 0.98-1.25 (m, 2H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	217.0, 134.6, 117.4, 77.4, 42.5, 42.3, 40.5, 40.2, 36.0, 30.3, 27.9, 27.9, 25.5, 22.1.
IR (ν, cm^{-1}, CCl_4)	3509, 2975, 2931, 2872, 1709, 1455, 1445 1378, 1264, 1238, 1125, 1065.
HRMS (EI)	Calcd. for $C_{14}H_{22}O_2$: 222.1620 Found: 222.1622

5-Acetyl-2-allyl-2-methylcyclohexyl)acetonitrile 40



$C_{14}H_{21}NO$
M= 219.3 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **39a,b** (233 mg, 1.0 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford the nitrile **40** (178 mg, 81% over 2 steps) as a colorless oil.

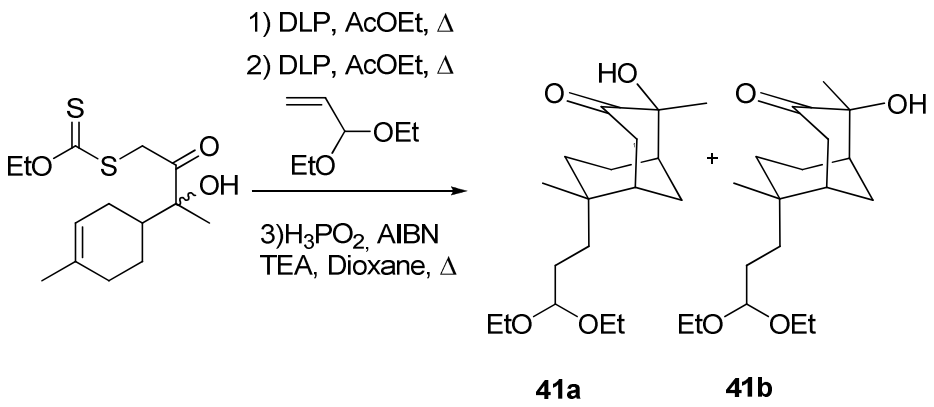
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.72-5.83 (m, 1H), 5.04-5.13 (m, 2H), 2.54 (tt, *J*= 11.6, 3.4 Hz, 1H), 2.32-2.41 (m, 2H), 2.16 (s, 3H), 1.97-2.09 (m, 3H), 1.69-1.81 (m, 2H), 1.37-1.51 (m, 4H), 0.81 (s, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 210.6, 133.1, 119.4, 118.6, 50.7, 46.0, 40.3, 36.6, 35.6, 29.0, 28.3, 23.8, 18.6, 17.8.

IR (ν, cm^{-1}, CCl_4): 3079, 2978, 2937, 2870, 2248, 1713, 1639, 1468, 1444, 1425, 1355, 1212, 1175, 1148.

HRMS (EI): Calcd. for $C_{14}H_{21}NO$: 219.1623 Found: 219.1625

6-(3,3-Diethoxypropyl)-2-hydroxy-2,6-dimethylbicyclo[3.3.1]nonan-3-one 41a,b



$C_{18}H_{32}O_4$
M= 312.4 g.mol^{-1}

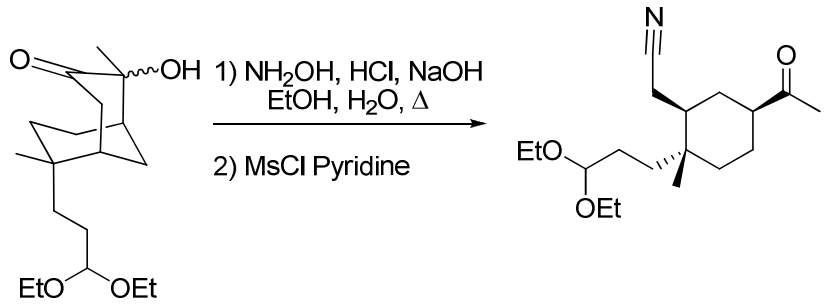
Following general procedure **C**, the reaction was carried out using the xanthate **6b** (605 mg, 2.0 mmol) and needed 10 mol % of DLP to go to completion. Acrolein diethyl acetal (475µL, 2.0 equiv) was added to the reaction mixture and needed 15 mol% to go to completion. Crude xanthate was then transformed following general procedure **D**. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford the α-hydroxyketone **41a,b** (312 mg, 50% over 3 steps) as a mixture of diastereomers in a 1:1 ratio of the 2 epimers at C-3 as two colorless oils. The diastereomers **41a** and **41b** were separated at this step and mixed together after characterization for the next step.

Diastereomer **41a**:

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	4.45 (t, *J*= 5.5 Hz, 1H), 3.59-3.68 (m, 2H), 3.39-3.45 (m, 2H), 2.85(dd, *J*= 15.9, 6.0 Hz, 1H), 2.48-2.53 (m, 1H), 2.24-2.28 (m, 1H), 1.81-2.04 (m, 4H), 1.49-1.59 (m, 4H), 1.32 (s, 3H), 1.20 (t, *J*= 7.3 Hz, 3H), 1.20 (t, *J*= 7.3 Hz, 3H), 1.18-1.39 (m, 3H), 0.84 (s, 3H), 0.74-0.87 (m, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	212.0, 103.4, 76.5, 61.0, 60.8, 42.1, 40.7, 39.7, 35.1, 32.5, 30.7, 27.8, 25.6, 25.5, 23.6, 22.0, 15.4.
IR (ν, cm^{-1}, CCl_4)	3598, 3502, 2976, 2931, 2876, 1710, 1465, 1455, 1444, 1417, 1375, 1343, 1238, 1126, 1063.
HRMS (EI)	Calcd. for $C_{18}H_{32}O_4$: 312.2301 Found: 312.2292

Diastereomer **41b :** **^{1}H NMR** (δ, ppm) ($CDCl_3$, 400 MHz)	4.45 (t, *J*= 5.5 Hz, 1H), 3.61-3.66 (m, 2H), 3.41-3.44 (m, 2H), 2.65-2.71 (m, 1H), 2.54 (dd, *J*= 16.0, 5.8 Hz, 1H), 2.16- 2.19 (m, 1H), 2.06-2.11 (m, 1H), 1.90-1.96 (m, 3H), 1.46-1.65 (m, 4H), 1.40 (s, 3H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.12-1.26 (m, 3H), 0.84 (s, 3H), 0.78-0.90 (m, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	217.0, 103.3, 77.4, 61.0, 60.8, 43.3, 40.4, 40.2, 35.2, 32.5, 30.5, 28.0, 27.9, 27.7, 25.4, 22.1, 15.3.
IR (ν, cm^{-1}, CCl_4)	3509, 2975, 2930, 2875, 1709, 1467, 1455, 1444, 1421, 1376, 1344, 1241, 1124, 1063.
HRMS (EI)	Calcd. for $C_{18}H_{31}O_3$: 295.2273 Found: 295.2275

5-Acetyl-2-allyl-2-methylcyclohexyl)acetonitrile 42

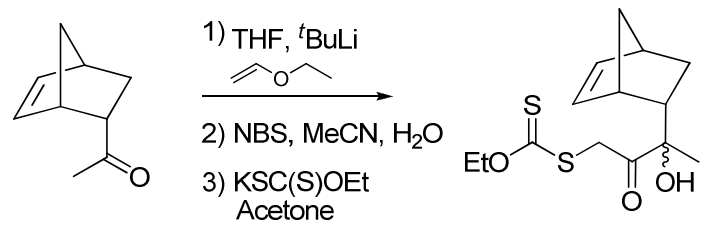


$C_{18}H_{31}NO_3$
M= 309.4 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **41a,b** (222 mg, 0.71 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 8:2) to afford the nitrile **42** (154 mg, 70% over 2 steps) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	4.42 (t, *J*= 5.4 Hz, 1H), 3.58-3.66 (m, 2H), 3.45-3.52 (m, 2H), 2.52 (dd, *J*= 16.7, 3.4 Hz, 1H), 2.32-2.40 (m, 1H), 2.16 (s, 3H), 1.97-2.09 (m, 2H), 1.65-1.74 (m, 4H), 1.48-1.58 (m, 2H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.18-1.29 (m, 4H), 0.78 (s, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	210.6, 119.5, 103.1, 61.4, 61.2, 50.7, 40.9, 36.3, 36.1, 34.7, 29.0, 28.2, 27.2, 23.8, 18.7, 17.6, 15.3.
IR (ν, cm^{-1}, CCl_4)	2976, 2931, 2873, 2249, 1714, 1467, 1444, 1375, 1354, 1127, 1062.
HRMS (EI)	Calcd. for $C_{18}H_{31}NO_3$: 309.2304 Found: 309.2300

***S*-(*S*)-3-((1*S*,2*S*,4*S*)-Bicyclo[2.2.1]hept-5-en-2-yl)-3-hydroxy-2-oxobutyl O-ethyl carbonodithioate**	**46b**



$C_{14}H_{20}O_3S_2$
M= 300.4 g.mol^{-1}

Following general procedure **A**, the reaction was carried out using endo-2-acetyl-5norbornene (5.4 mL, 40 mmol). The adduct obtained was transformed following general procedure **B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford the xanthate **46b** (7.57 g, 63% over 3 steps) as a yellow oil as a mixture of diastereomers in a 9:1 ratio of the 2 epimers at C-3.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 6.28-6.30 (m, 0.1H), 6.25-6.28 (m, 0.9H), 6.08-6.10 (m, 0.9H), 6.06-6.09 (m, 0.1H), 4.57-4.65 (m, 2H), 4.21-4.42 (m, 2H), 3.04 (sbr, 1H), 2.82 (sbr, 1H), 2.57-2.67 (m, 1H), 2.56 (s, 0.1H), 2.45 (s, 0.9H), 1.93 (ddd, *J*= 11.8, 9.6, 3.9 Hz, 0.1H), 1.76 (ddd, *J*= 11.7, 9.6, 3.9 Hz, 0.9H), 1.30-1.40 (m, 6H), 1.24-1.28 (m, 2H), 1.12 (ddd, *J*= 11.8, 5.1, 2.3 Hz, 0.1H), 0.92 (ddd, *J*= 11.7, 5.3, 2.4 Hz, 0.9H).

Major diastereomer

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.4, 207.3, 138.5, 132.2, 80.9, 70.4, 50.3, 45.6, 43.8, 43.1, 42.4, 27.6, 25.8, 13.7.

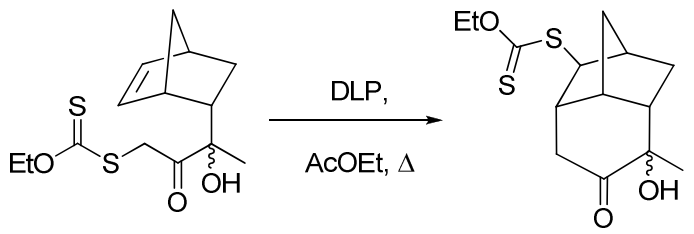
Minor diastereomer

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.4, 208.0, 139.2, 131.3, 81.1, 70.6, 51.4, 45.9, 44.4, 43.1, 42.2, 27.0, 26.3, 13.7.

IR (ν, cm^{-1}, CCl_4): 3558, 3311, 2980, 2901, 2873, 1716, 1445, 1367, 1263, 1227, 1114, 1053.

HRMS (EI): Calcd. for $C_{14}H_{20}O_3S_2$: 300.0854 Found: 300.0869

***O*-Ethyl *S*-(5-hydroxy-5-methyl-6-oxooctahydro-1*H*-2,4-methanoinden-1-yl) dithiocarbonate**	**47a,b**



$C_{14}H_{20}O_3S_2$
M= 300.4 g.mol^{-1}

Following general procedure **C**, the reaction was carried out using the xanthate **46b** (7.00 g, 23.3 mmol) and needed 10 mol% of DLP to go to completion The residue was purified by silica gel column chromatography (petroleum ether /ether) to afford the xanthate **47a,b** (6.30 g, 90%) as a mixture of diastereomers in a 9:1 ratio of the 2 epimers at C-3 as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.55-4.68 (m, 2H), 3.24 (dd, *J*= 13.8, 5.8 Hz, 0.9H), 3.05-3.08 (m, 1H, C***H***-7), 2.83 (dd, *J*= 14.7, 6.2 Hz, 0.1H) 2.76-2.78 (m, 1H) 2.30-2.40 (m, 4H), 1.87-1.95 (m, 1H), 1.64-1.73 (m, 1H), 1.68-1.71 (m, 1H), 1.41 (t, *J*= 7.1 Hz, 3H), 1.42, 1.27 (s, 3H), 1.20-1.25 (m, 1H), 1.03 (ddd, *J*= 14.1, 4.7, 2.7 Hz, 0.1H), 0.83 (ddd, *J*= 14.1, 4.7, 2.7, 0.9H).

Major diastereomer **47a**

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.6, 210.9, 76.9, 69.7, 55.7, 50.1, 44.7, 43.8, 39.0, 38.9, 38.0, 31.3, 22.4, 13.8.

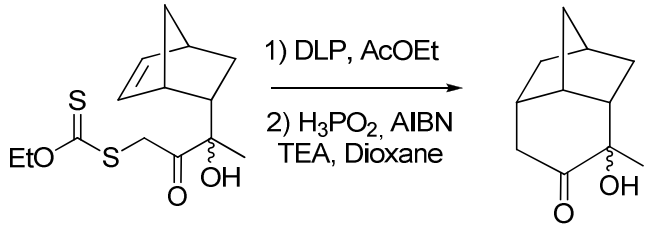
Minor diastereomer **47b**

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.2, 210.9, 76.9, 69.7, 55.7, 50.1, 44.7, 43.8, 39.0, 38.9, 38.0, 31.3, 22.4, 13.8.

IR (ν, cm^{-1}, CCl_4): 3603, 3503, 2978, 2958, 2900, 2877, 1722, 1453, 1421, 1377, 1294, 1215, 1113, 1061, 1018.

HRMS (EI): Calcd. for $C_{14}H_{20}O_3S_2$: 300.0854 Found: 300.0869

5-Hydroxy-5-methyloctahydro-6*H*-2,4-methanoinden-6-one 48a,b



$C_{11}H_{16}O_2$
M= 180.2 g.mol^{-1}

Following general procedure **C**, the reaction was carried out using the xanthate **46b** (901 mg, 3.0 mmol), and needed 10 mol % of DLP to go to completion. Crude xanthate was then transformed following general procedure **D**. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford the α-hydroxyketone **48a,b** (454 mg, 84%) as a mixture of diastereomers in a 9:1 ratio of the 2 epimers at C-3 as two colorless oils. The diastereomers **48a** and **48b** were separated at this step in order to characterize them and then combined for the next step.

Major diastereomer **48a**:

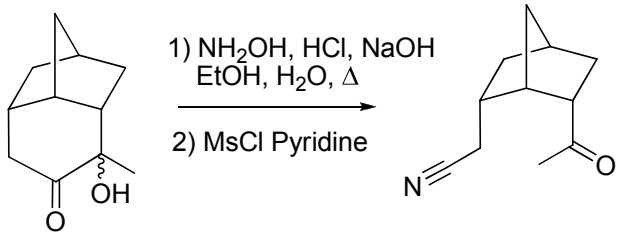
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	3.22 (dd, *J*= 13.4, 5.8 Hz, 1H), 2.63-2.66 (m, 1H), 2.41-2.46 (m, 1H), 2.24-2.30 (m, 1H), 2.10-2.14 (m, 2H), 1.67-1.81 (m, 2H), 1.37-1.47 (m, 2H), 1.23 (s, 3H), 0.73 (ddd, *J*= 12.5, 4.2, 2.5 Hz, 1H), 0.62 (ddd, *J*= 12.9, 5.1, 2.3 Hz, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	213.0, 76.7, 51.3, 40.5, 40.4, 38.9, 37.7, 37.3, 36.0, 32.2, 22.4.
IR (ν, cm^{-1}, CCl_4)	3604, 3494, 2949, 2873, 1720, 1453, 1421, 1376, 1353, 1309, 1198, 1114, 1098, 1047.
HRMS (EI)	Calcd. for $C_{11}H_{16}O_2$: 180.1150 Found: 180.1156

Minor diastereomer **48b** :

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	3.97 (s, 1H), 2.81 (dd, *J*= 14.2, 5.6 Hz, 1H), 2.36-2.51 (m, 4H) 2.14-2.16 (m, 1H), 1.79-1.87 (m, 1H), 1.64-1.73 (m, 1H), 1.46-1.49 (m, 2H), 1.45 (s, 3H), 0.81-0.86 (m, 1H), 0.72-0.76 (m, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	215.4, 77.3, 51.6, 41.1, 40.9, 40.5, 38.2, 36.7, 36.4, 31.8, 26.5.

IR (ν, cm^{-1}, CCl_4)	3499, 2953, 2874, 1714, 1558, 1541, 1454, 1377, 1366, 1323, 1197, 1174, 1098.
HRMS (EI)	Calcd. for $C_{11}H_{16}O_2$: 180.1150 Found: 180.1157

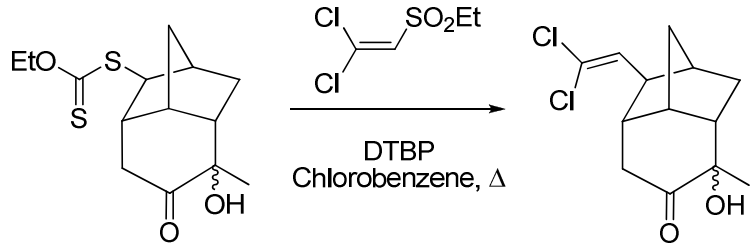
2-((1*S*,2*S*,4S,6*S*)-6-Acetylbicyclo[2.2.1]heptan-2-yl)acetonitrile 49

	$C_{11}H_{15}NO$ M= 177.2 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **48a,b** (220 mg, 1.22 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 8:2) to afford the nitrile **49** (195 g, 90% over 2 steps) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	2.88-2.95 (m, 2H), 2.23-2.36 (m, 4H), 2.30 (s, 3H), 1.95-2.03 (m, 1H), 1.79 (ddd, *J*= 12.8, 6.2, 1.7 Hz, 1H), 1.53-1.69 (m, 3H), 0.88-0.92 (m, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	211.1, 119.5, 54.7, 43.9, 42.8, 38.4, 37.5, 36.4, 30.2, 30.0, 19.9.
IR (ν, cm^{-1}, CCl_4)	2960, 2874, 2249, 1712, 1558, 1541, 1455, 1434, 1359, 1320, 1302, 1175, 1127.
HRMS (EI)	Calcd. for $C_{11}H_{15}NO$: 177.1154 Found: 177.1155

1-(2,2-Dichlorovinyl)-5-hydroxy-5-methyloctahydro-6*H*-2,4-methanoinden-6-one **50a,b**



$C_{13}H_{16}Cl_2O_2$
M= 275.2 g.mol^{-1}

A solution of xanthate **47a,b** (601 mg, 2.0 mmol) and dichlorovinyl ethyl sulfone (756 mg, 4.0 mmol, 2 equiv.) in chlorobenzene (2 mL) was heated to reflux under N_2 atmosphere for 10 min. To the solution 3 drops of DTBP was added at intervals of 4 hours. After refluxing for 12 hours, the reaction mixture was allowed to cool to 20°C. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ether 7:3) to afford the dichlorovinyl adduct **50a,b** (336 mg, 61%) as a mixture of diastereomers in a 9:1 ratio of the 2 epimers at C-3 as two colorless oils. The diastereomers **50a** and **50b** were separated at this step and mixed together after characterization for the next step.

Major diastereomer **50a**:

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.71 (d, *J*= 9.0 Hz, 1H), 3.22 (dd, *J*= 13.7, 5.9 Hz, 1H), 2.71-2.75 (m, 1H), 2.27-2.35 (m, 2H), 2.19-2.23 (m, 1H), 2.07 (d, *J*= 4.5 Hz, 1H), 2.00 (ddd, *J*= 9.0, 4.1, 1.5 Hz, 1H), 1.77-1.85 (m, 1H), 1.58-1.61 (m, 1H), 1.42-1.45 (m, 1H), 1.26 (s, 3H), 0.73 (ddd, *J*= 13.4, 5.1, 2.5 Hz, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 211.4, 133.6, 119.6, 76.8, 50.5, 48.6, 46.4, 42.7, 39.7, 39.0, 38.2, 31.8, 22.4.

IR (ν, cm^{-1}, CCl_4): 3604, 3497, 2958, 1716, 1646, 1615, 1455, 1421, 1377, 1114, 1068.

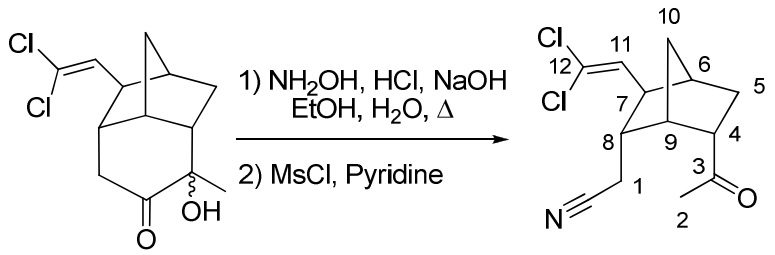
HRMS (EI): Calcd. for $C_{13}H_{16}Cl_2O_2$: 274.0527 Found: 274.0527

Minor diastereomer **50b**:

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.72 (d, *J*= 9.1 Hz, 1H), 3.96 (s, 1H), 2.84 (dd, *J*= 14.6, 6.0 Hz, 1H), 2.59-2.55 (m, 2H), 2.41-2.47 (m, 1H), 2.22-2.24 (m, 1H), 2.06 (d, *J*= 4.4 Hz, 1H), 1.99 (ddd, *J*= 9.0, 4.2, 1.4 Hz, 1H), 1.77 (ddd, *J*= 13.8, 2.6, 4.6 Hz, 1H), 1.58-1.62 (m, 1H), 1.50 (dd, *J*= 10.4, 1.3 Hz, 1H), 1.46 (s, 3H),

	0.95 (ddd, *J*= 13.8, 4.6, 2.6 Hz, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	214.5, 133.4, 119.9, 77.3, 50.8, 48.9, 46.8, 42.2, 41.2, 39.9, 38.6, 31.5, 26.6.
IR (ν, cm^{-1}, CCl_4)	3501, 2956, 2881, 1715, 1644, 1614, 1570, 1455, 1339, 1139.
HRMS (EI)	Calcd. for $C_{13}H_{16}Cl_2O_2$: 274.0527 Found: 274.0515

2-((1*S*,2S,3*S*,4*S*,6*S*)-6-Acetyl-3-(2,2-dichlorovinyl)bicyclo[2.2.1]heptan-2-yl)acetonitrile **51**

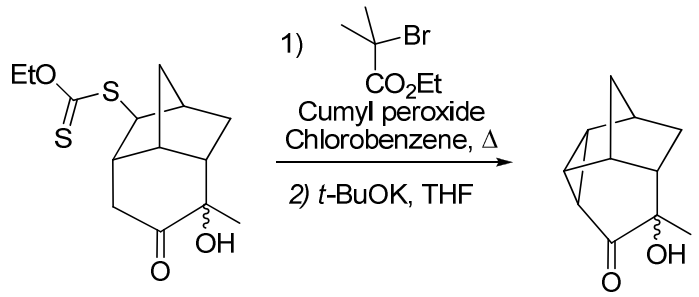


$C_{13}H_{15}Cl_2NO$
M= 272.2 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **50a,b** (210 mg, 0.81 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford the nitrile **51** (165 mg, 75% over 2 steps) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	5.63 (d, *J*= 9.5 Hz, 1H), 2.97-2.99 (m, 2H), 2.44 (dd, *J*= 17.4, 6.3 Hz, 1H), 2.35 (dd, *J*= 17.4, 10.7 Hz, 1H), 2.36 (s, 3H), 2.15-2.23 (m, 2H), 1.93-2.05 (m, 2H), 1.58-1.74 (m, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	210.8, 132.1, 120.9, 118.8, 53.6, 48.9, 46.7, 43.9, 43.4, 40.7, 30.3, 30.1, 18.6.
IR (ν, cm^{-1}, CCl_4)	2962, 2928, 2885, 2250, 1712, 1616, 1467, 1455, 1434, 1350, 1194, 1175, 1167.
HRMS (EI)	Calcd. for $C_{13}H_{15}Cl_2NO$: 271.0531 Found: 271.0527

O-Ethyl *S*-(5-hydroxy-5-methyl-6-oxooctahydro-1*H*-2,4-methanoinden-1-yl) dithiocarbonate **53a,b**



$C_{11}H_{14}O_2$
M= 178.2 g.mol^{-1}

Reference: Barbier, F.; Pautrat, F.; Quiclet-Sire, B.; Zard, S. Z. *Synlett* **2002**, 811.

A stirred solution of xanthate **47a,b** (601 mg, 2.0 mmol) and ethyl 2-bromo-2-methylpropionate (1.96 g, 10.0 mol, 5.0 equiv) in chlorobenzene (28 mL) was refluxed for 15 min under a nitrogen flow. Cumyl peroxide (272 mg, 20 mol%) was then added and additional cumul peroxide (20 mol %) was added every 2 hours. The reaction needed 140 mol% of cumyl peroxide to go to completion. The reaction mixture was then cooled to 20°C and evaporated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 8:2) to afford the corresponding bromide **52a,b** (368 mg, 71%).

To a stirred solution of bromide **52a,b** (50 mg, 0.14 mmol) in THF (1 mL) was added at 0°C *t*-BuOK (34 mg, 0.30 mmol, 2.2 equiv). The reaction mixture was allowed to warm to 20°C and stirred for 2 hours. Saturated NH_4Cl and ether were added to quench the reaction. The aqueous layer was then extracted with ether, and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo.* The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 7:3) to afford the corresponding tetracycle **53a,b** (21 mg, 85%). as a mixture of diastereomers in a 9:1 ratio of the 2 epimers at C-3 as a white solid for **53a** and a colorless oil for **53b**. The diastereomers **53a** and **53b** were separated at this step and mixed together after characterization for the next step.

Major diastereomer **53a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	2.64-2.67 (m 1H), 2.40-2.49 (m, 1H), 2.18-2.34 (m, 4H), 1.99-2.03 (m, 1H), 1.71-1.79 (m, 2H), 1.29 (s, 3H), 0.81-0.86 (m, 1H), 0.64 (td, *J*= 12.9, 3.0 Hz, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	209.7, 72.5, 54.4, 42.7, 38.9, 38.0, 37.8, 36.1, 35.9, 30.9, 22.3.
IR (ν, cm^{-1}, CCl_4)	3597, 3474, 3035, 2956, 2878, 1701, 1454, 1373, 1315, 1225, 1119,

1100, 1056.

HRMS (EI) Calcd. for $C_{11}H_{14}O_2$: 178.0994 Found: 178.0990

Tf =[98.6-99.9]

Minor diastereomer **53b**

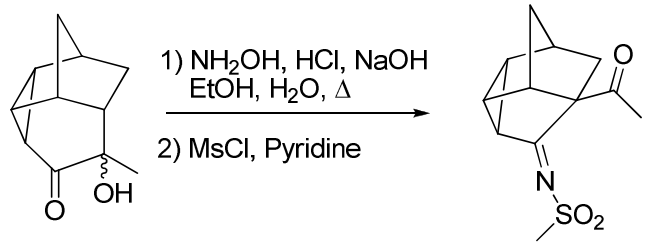
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 3.24 (dd, *J*= 13.4, 5.8 Hz, 1H), 2.65-2.67 (m 1H), 2.43-2.48 (m, 1H), 2.27-2.32 (m, 1H), 2.14-2.18 (m, 2H), 1.69-1.83 (m, 2H), 1.41-1.50 (m, 2H), 1.24 (s, 3H), 0.76 (ddd, *J*= 12.4, 4.1, 2.5 Hz, 1H), 0.65 (ddd, *J*= 12.9, 5.1, 2.3 Hz, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 212.6, 51.4, 40.6, 40.4, 38.9, 37.7, 37.3, 36.0, 32.3, 22.5. The quaternary carbon of the alcool cannot be seen because of the carbons of the chloroforme.

IR (ν, cm^{-1}, CCl_4) 3604, 2952, 2873, 1721, 1453, 1376, 1264, 1198, 114, 1088, 1046.

HRMS (EI) Calcd. for $C_{11}H_{14}O_2$: 178.0994 Found: 178.0999

6-Acetyltricyclo[3.2.1.0^{2,4}]octane-3-carbonitrile 54



$C_{12}H_{15}NO_3S$
M= 253.3 g.mol^{-1}

Following general procedure **E**, the reaction was carried out using the hydroxyl ketone **53a,b** (178 mg, 1.0 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 7:3) to afford the imine **54** (152 mg, 60% over 2 steps) as a yellow oil.

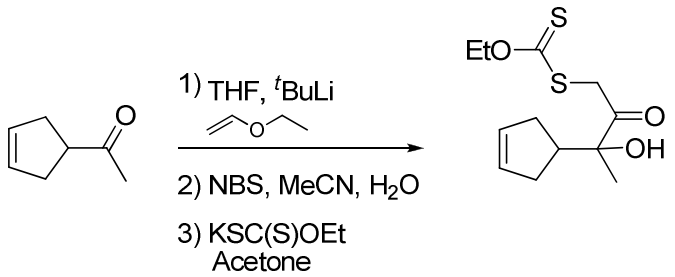
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 3.14 (ddd, *J*= 7.0, 4.9, 2.1 Hz, 1H), 3.08-3.10 (m, 1H), 3.06 (s, 3H), 2.88 (dt, *J*= 7.5, 4.5 Hz, 1H), 2.64-2.67 (m, 1H), 2.44-2.49 (m, 1H), 2.28 (s, 3H), 2.15-2.19 (m, 1H), 2.06-2.08 (m, 1H), 1.73 (ddd, *J*= 12.3, 2.3, 1.8 Hz, 1H), 1.54-1.57 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 203.5, 196.1, 65.6, 49.2, 46.3, 44.1, 42.0, 39.3, 37.6, 36.4, 28.5.

IR (ν, cm^{-1}, CCl_4): 3054, 2973, 2876, 1713, 1626, 1469, 1449, 1319, 1285, 1238, 1213, 1150, 1073.

HRMS (EI): Calcd. for $C_{12}H_{15}NO_3S$: 253.0773 Found: 253.0769

S-3-(Cyclopent-3-enyl)-3-hydroxy-2-oxobutyl *O*-ethyl carbonodithioate 57b



$C_{12}H_{18}O_3S_2$
M= 274.4 g.mol^{-1}

Following general procedure **A**, the reaction was carried out using 1-(cyclopent-3-enyl)ethanone (770 mg, 7.0 mmol). The adduct obtained was transformed following general procedure **B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford the xanthate **57b** (1.02 g, 53% over 3 steps) as a colorless oil.

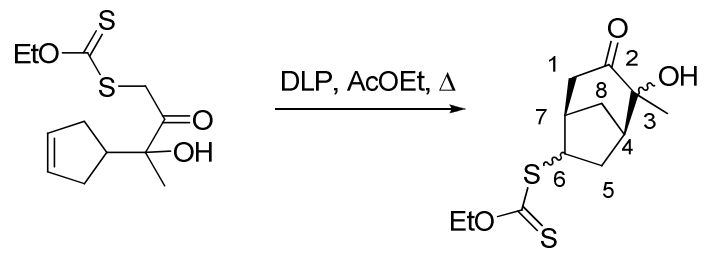
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.63-5.69 (m, 2H), 4.64 (q, *J*= 7.1 Hz, 2H), 4.30-4.41 (m, 2H), 2.73-2.82 (m, 1H), 2.47-2.51 (m, 1H), 2.25-2.37 (m, 2H), 2.04-2.29 ((m, 2H), 1.46 (s, 3H), 1.42 (t, *J*= 7.1 Hz, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.3, 206.9, 129.6, 129.5, 80.4, 71.0, 45.0, 42.0, 33.4, 33.3, 24.6, 13.8.

IR (ν, cm^{-1}, CCl_4) 3616, 3505, 3059, 2984, 2934, 2853, 1717, 1444, 1358, 1228, 1149, 1114, 1053, 1027.

HRMS (EI) Calcd. for $C_{12}H_{18}O_3S_2$: 274.0697 Found: 274.0705

2-Hydroxy-2-methylbicyclo[3.2.1]octan-3-one 58a,b



$C_{12}H_{18}O_3S_2$
M= 274.4 g.mol^{-1}

Following general procedure **C**, the reaction was carried out using the xanthate **57b** (870 mg, 2.75 mmol) and needed 10 mol % of DLP to go to completion. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford the xanthate **58a,b** (551 mg, 73%) as a mixture of diastereomers in a 10:1 ratio of the 2 epimers at C-3 as two yellow oils. The diastereomers **58a** and **58b** were separated at this step and mixed together after characterization for the next step.

Major diastereomer **58a**;

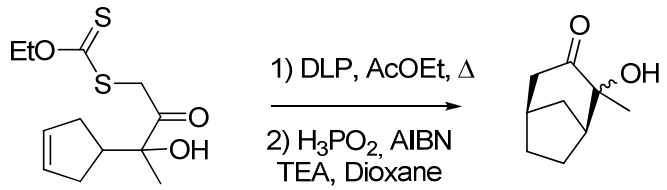
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	4.58-4.64 (m, 2H), 3.77 (s, 1H), 3.60 (ddd, *J*= 9.1, 5.2, 1.6 Hz, 1H), 2.74 (dd, *J*= 15.7, 4.4 Hz, 1H), 2.64-2.69 (m, 2H), 2.47 (t, *J*= 5.1 Hz, 1H), 2.38 (ddd, *J*= 15.3, 9.1, 2.0 Hz, 1H), 2.06-2.10 (m, 1H), 1.92-1.97 (m, 1H), 1.49 (ddd, *J*= 15.3, 6.8, 5.2 Hz, 1H), 1.41 (t, *J*= 7.1 Hz, 3H), 1.39 (s, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	214.2, 213.7, 79.1, 69.7, 49.2, 47.7, 45.5, 44.6, 33.1, 29.9, 25.5, 13.8.
IR (ν, cm^{-1}, CCl_4)	3601, 3510, 2984, 2958, 2935, 2872, 1720, 1452, 1413, 1377, 1294, 1218, 1146, 1113, 1054.
HRMS (EI)	Calcd. for $C_{12}H_{18}O_3S_2$: 274.0697 Found: 274.0696

Minor diastereomer **58b**:

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	4.58-4.67 (m, 2H), 3.67 (ddd, *J*= 8.8, 5.1, 1.5 Hz, 1H), 2.94 (dd, *J*= 15.5, 4.4 Hz, 1H), 2.41-2.60 (m, 4H), 1.99 (ddd, *J*= 15.4, 8.9, 1.9, 1H), 1.65-1.76 (m, 2H), 1.41 (t, *J*= 7.1 Hz, 3H), 1.31 (s, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	214.0, 209.8, 77.6, 69.7, 49.8, 47.1, 46.1, 43.4, 30.8, 30.4, 21.9, 13.8.

IR (ν, cm^{-1}, CCl_4)	3512, 2985, 2937, 2877, 1717, 1452, 1419, 1372, 1361, 1340, 1295, 1219, 1145, 1112, 1053.
HRMS (EI)	Calcd. for $C_{12}H_{18}O_3S_2$: 274.0697 Found: 274.0695

2-Hydroxy-2-methylbicyclo[3.2.1]octan-3-one 59



$C_9H_{14}O_2$
M= 154.2 g.mol^{-1}

Following general procedure **C**, the reaction was carried out using the xanthate **57b** (274 mg, 1.0 mmol), and needed 10 mol % of DLP to go to completion. Crude xanthate was then transformed following general procedure **D**. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford the α-hydroxyketone **59** (106 mg, 69%) as a colorless oil.

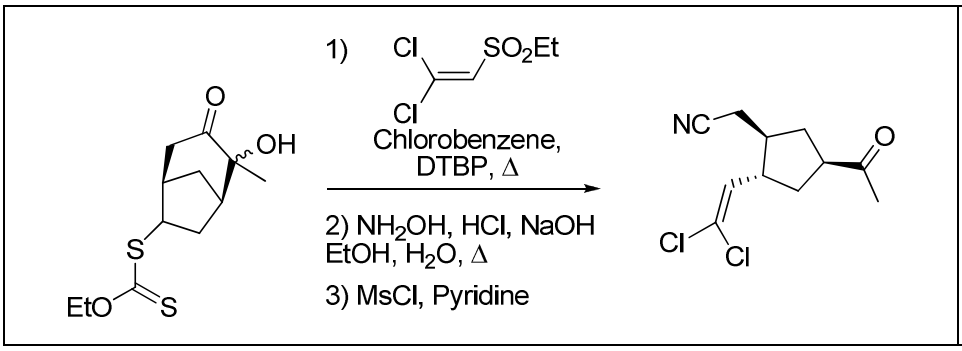
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 3.80 (s, 1H), 2.61 (ddd, *J*= 14.9, 3.5, 2.1 Hz, 1H), 2.52-2.56 (m, 1H), 2.38 (t, *J*= 5.6 Hz, 1H), 2.31 (dt, *J*= 14.9, 3.0 Hz, 1H), 2.07-2.11 (m, 1H), 1.54-1.81 (m, 4H), 1.38 (s, 3H), 1.30-1.38 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 215.2, 79.4, 48.1, 46.1, 36.9, 36.1, 28.0, 25.7, 23.7.

IR (ν, cm^{-1}, CCl_4): 3604, 3501, 2960, 2928, 2855, 1731, 1466, 1377, 1261, 1097.

HRMS (EI): Calcd. for $C_9H_{14}O_2$: 154.0994 Found: 154.0997

2-(4-Acetyl-2-(2,2-dichlorovinyl)cyclopentyl)acetonitrile 61



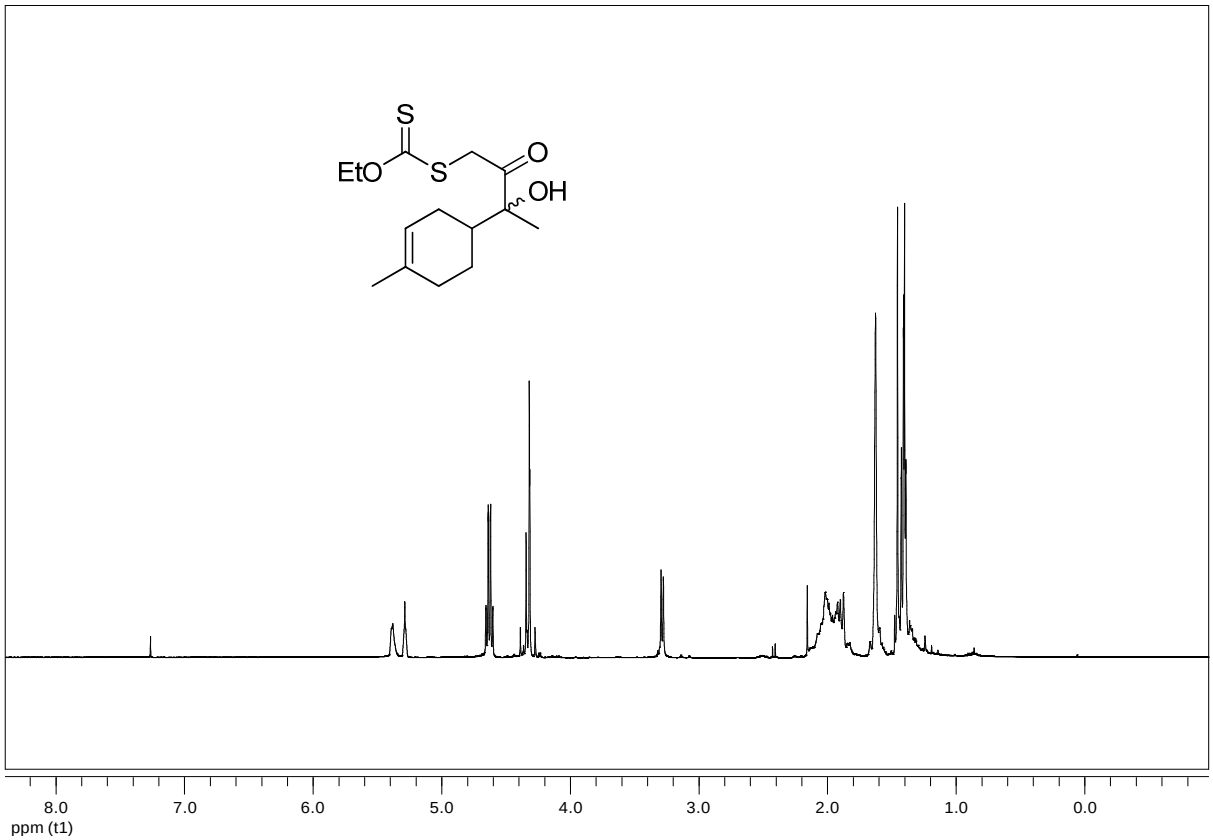
$C_{11}H_{13}ClNO$
M= 246.1 g.mol^{-1}

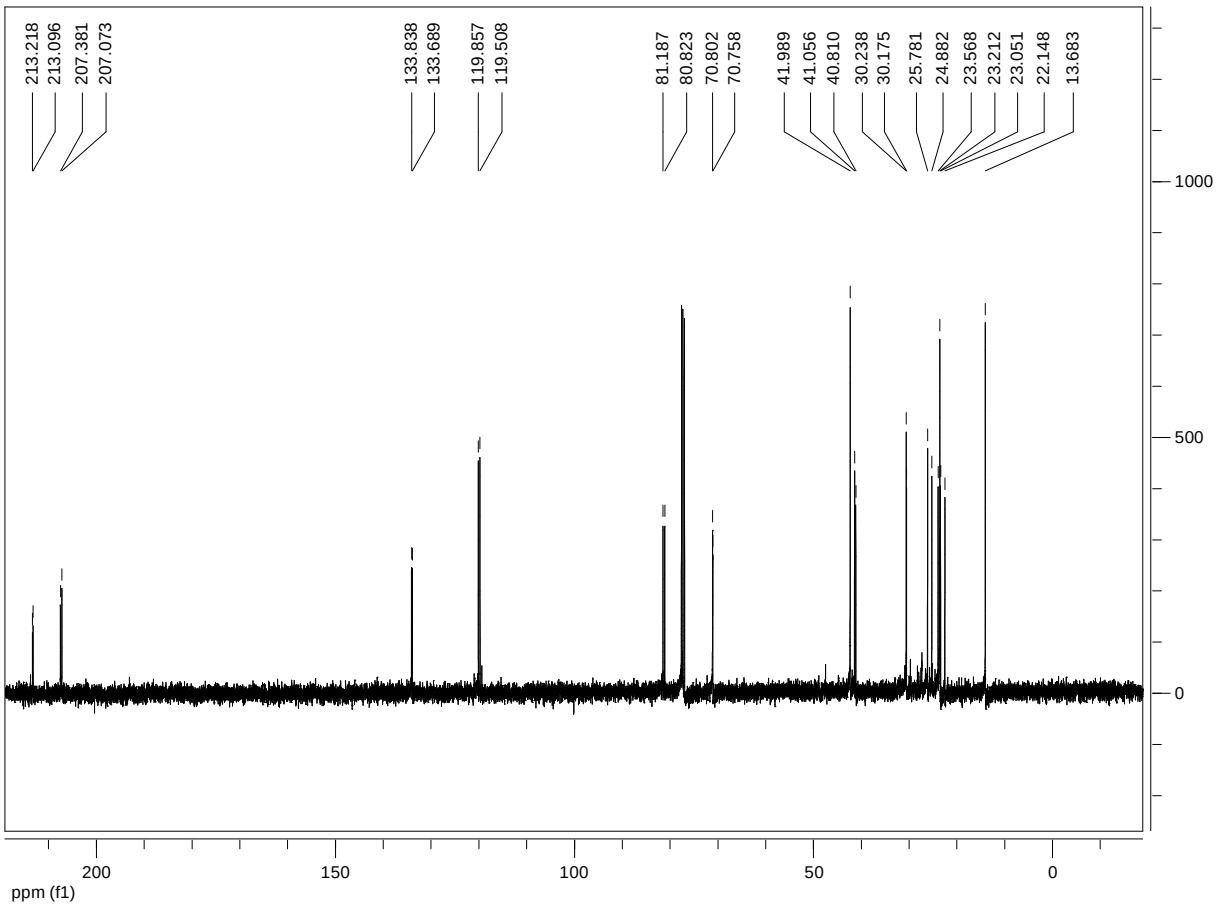
A solution of xanthate **58a,b** (162 mg, 0.67 mmol) and dichlorovinyl ethyl sulfone (253 mg, 1.34 mmol, 2.0 equiv.) in chlorobenzene (670 µL) was heated to reflux under N_2 atmosphere for 10 min. To the solution 3 drops of DTBP was added at intervals of 4 hours. After refluxing for 12 hours, the reaction mixture was allowed to cool to 20°C. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ether 8:2) to afford the dichlorovinyl adduct **60a,b** (100 mg, 60%) as a mixture of diastereomers in a 10:1 ratio of the 2 epimers at C-3.
Following general procedure **E**, the reaction was carried out using the hydroxyketone **60a,b** (86 mg, 0.34 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 8:2) to afford the nitrile **61** (58 mg, 69% over 2 steps) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	5.69 (d, *J*= 9.5 Hz, 1H), 3.09 (dtd, *J*= 10.3, 8.4, 4.5 Hz, 1H), 2.57-2.66 (m, 1H), 2.53 (dd, *J*= 16.9, 4.8 Hz, 1H), 2.34 (dd, *J*= 16.9, 8.4 Hz, 1H), 2.25-2.37 (m, 2H), 2.19 (s, 3H), 1.97-2.07 (m, 1H), 1.63-1.76 (m, 2H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	208.5, 130.3, 122.7, 118.1, 49.2, 45.1, 43.1, 38.9, 33.4, 28.8, 20.6.
IR (ν, cm^{-1}, CCl_4)	2934, 2873, 2251, 1716, 1621, 1455, 1424, 1361, 1327, 1154, 1063.
HRMS (EI)	Calcd. for $C_{12}H_{18}O_2S_2$: 245.0374 Found: 245.0383

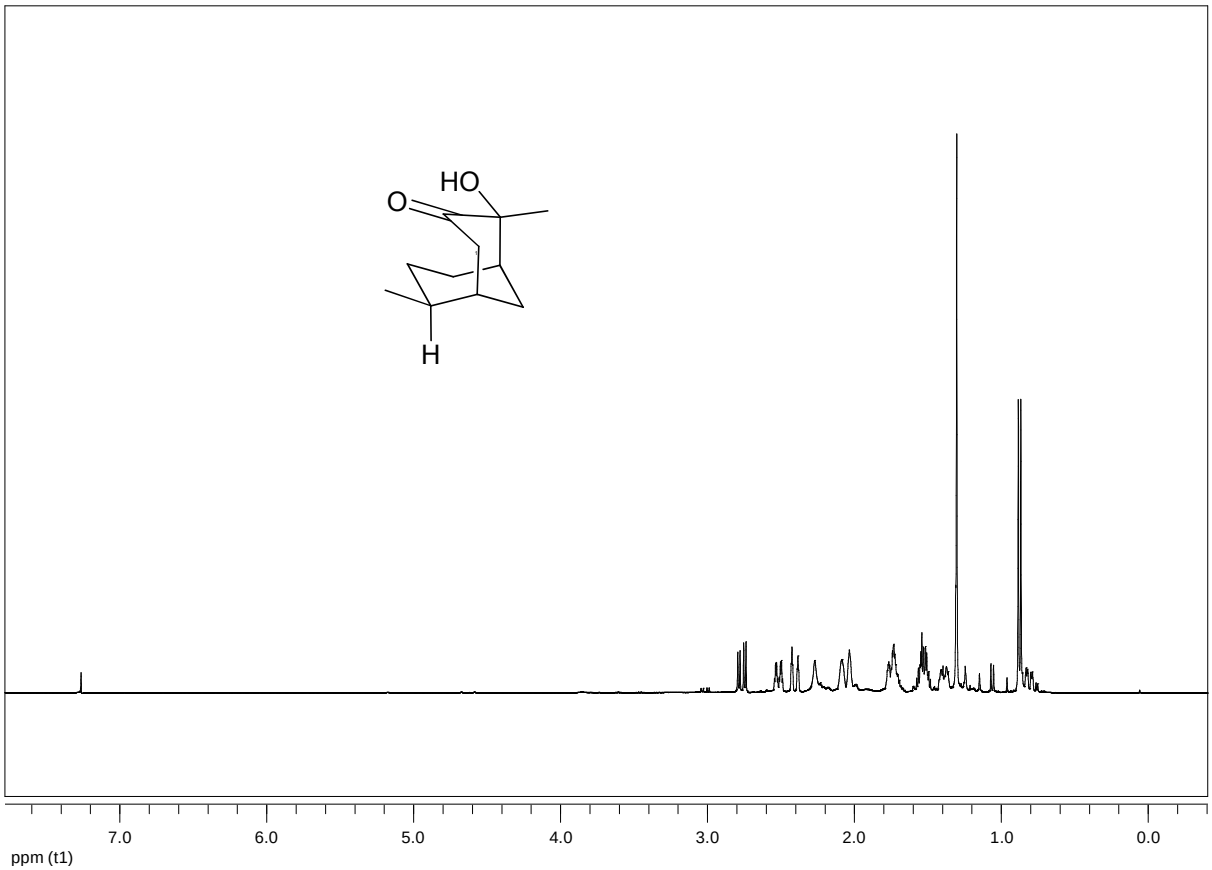
Copies of ^{1}H and ^{13}C NMR Spectra

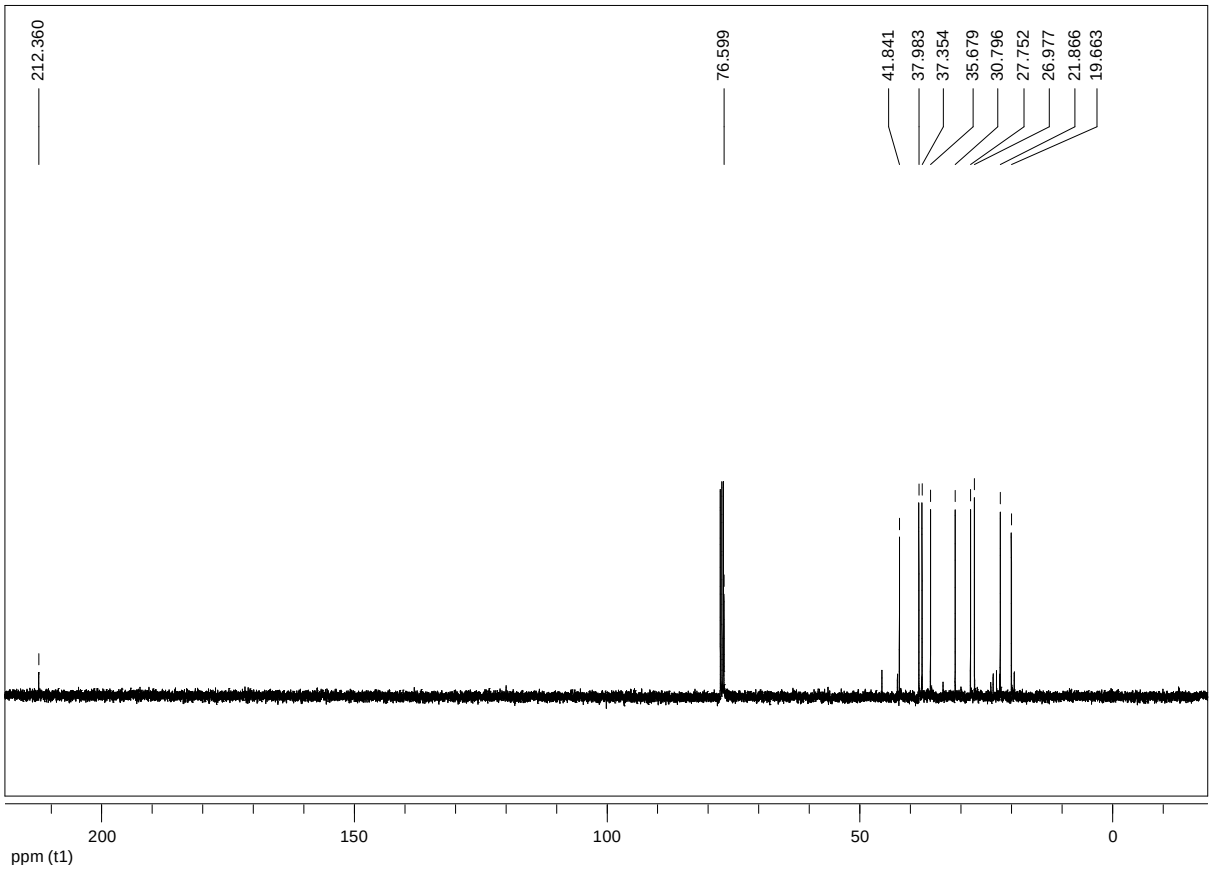
Compound **6b**



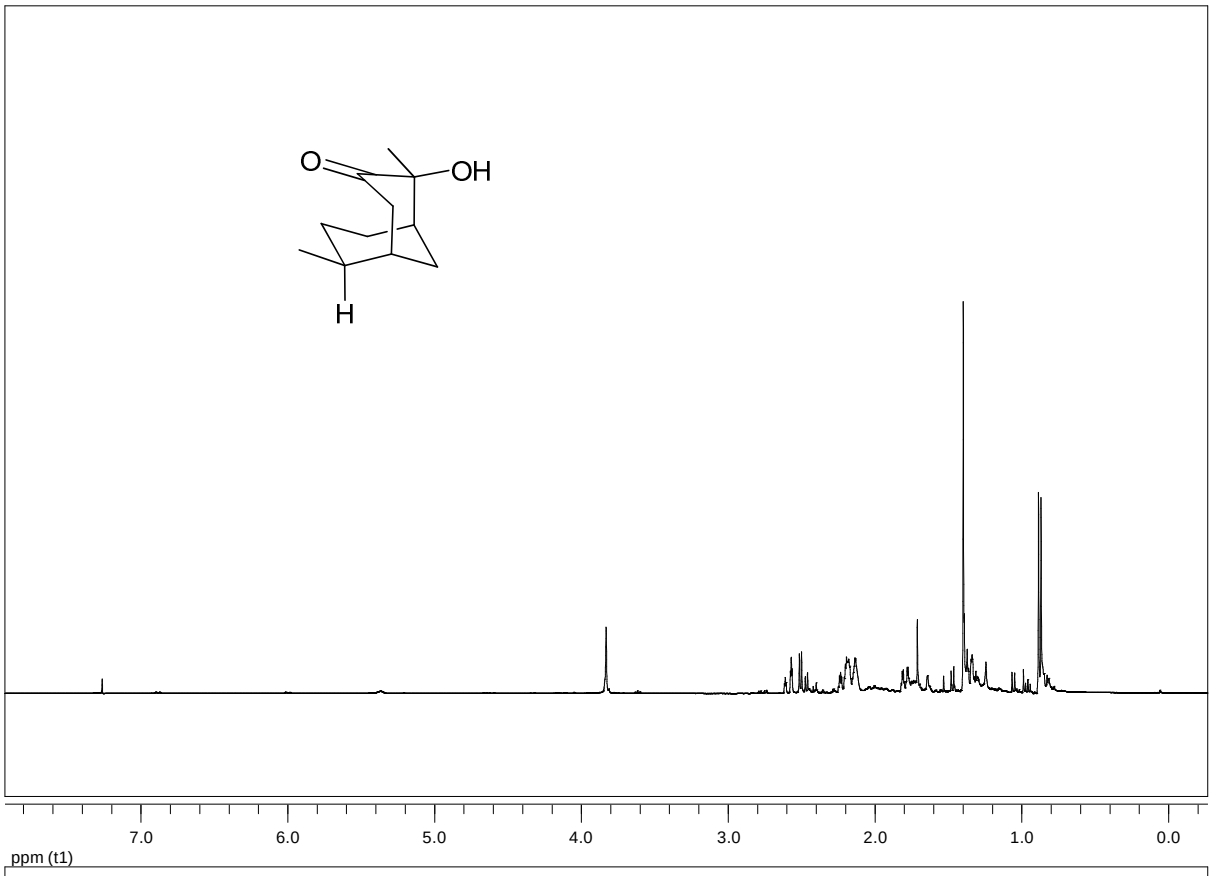


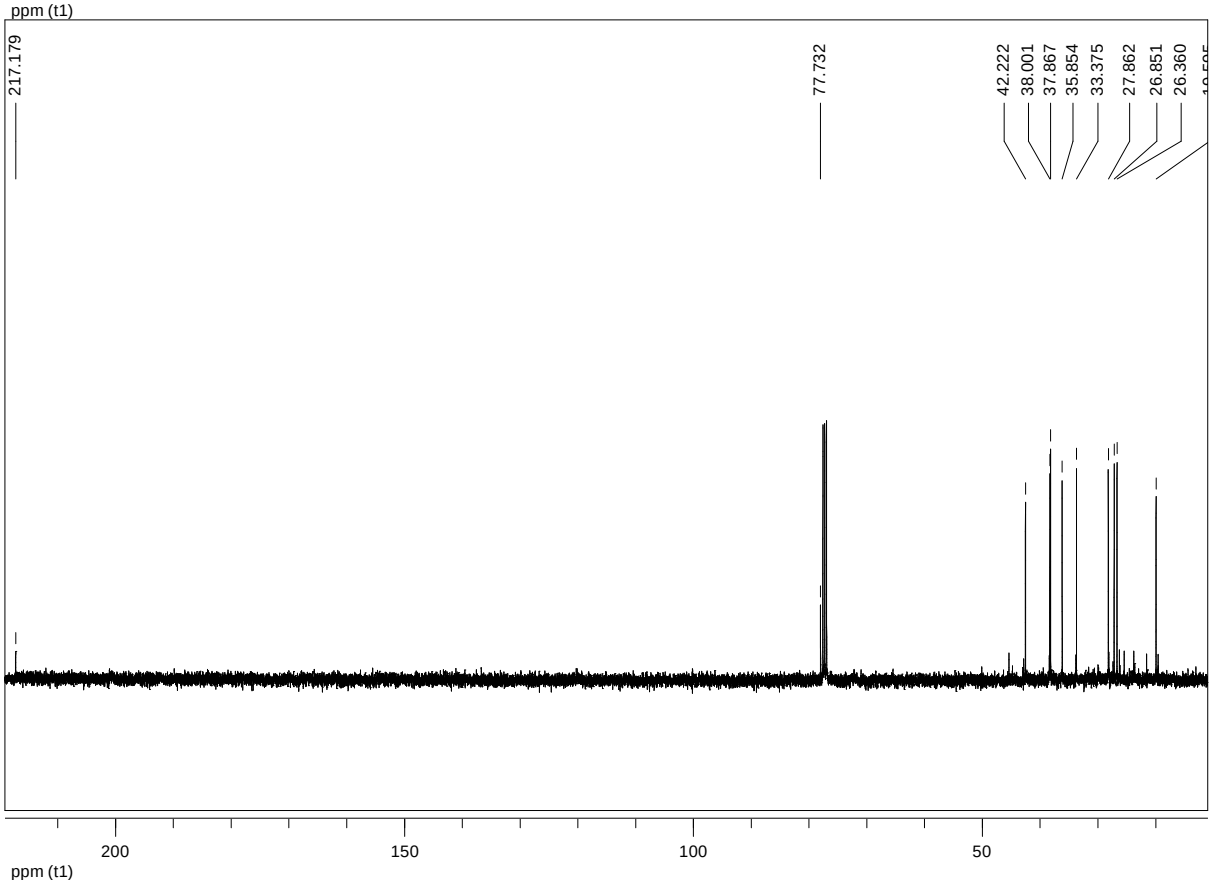
Compound **24a**



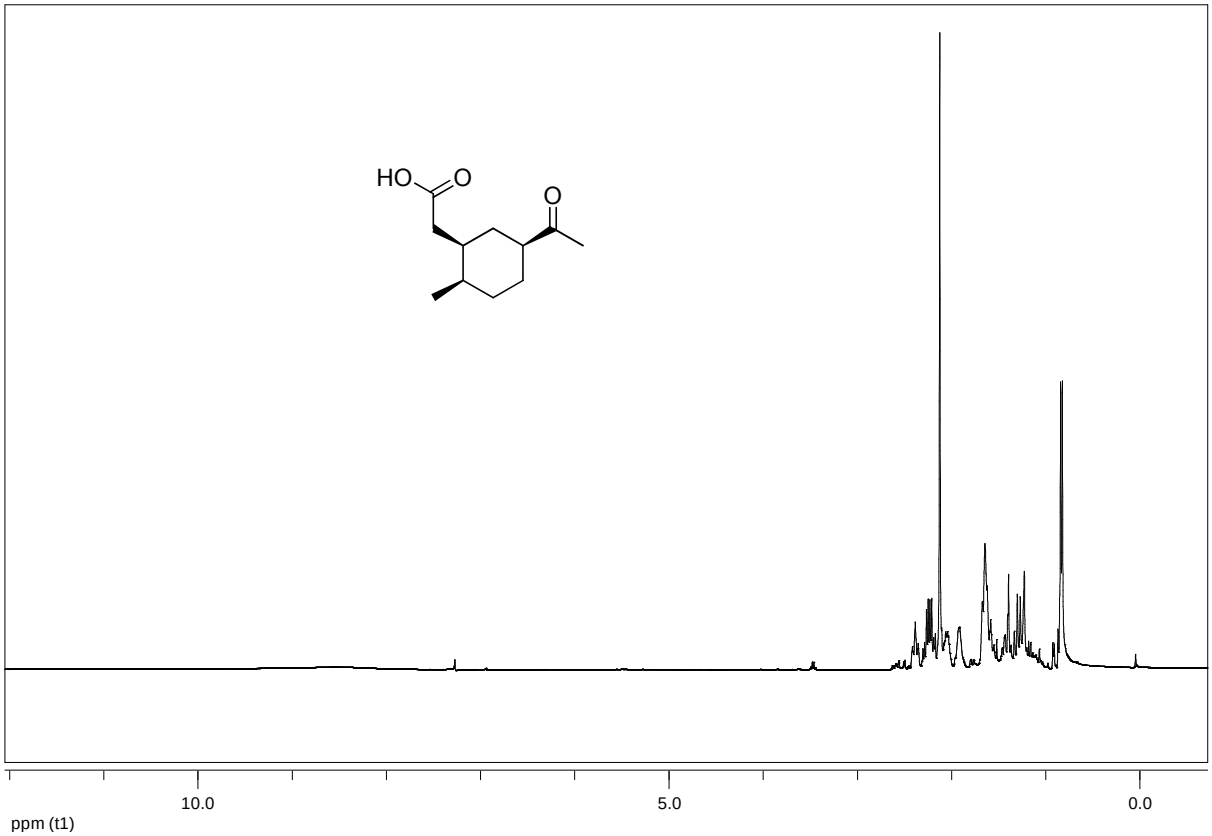


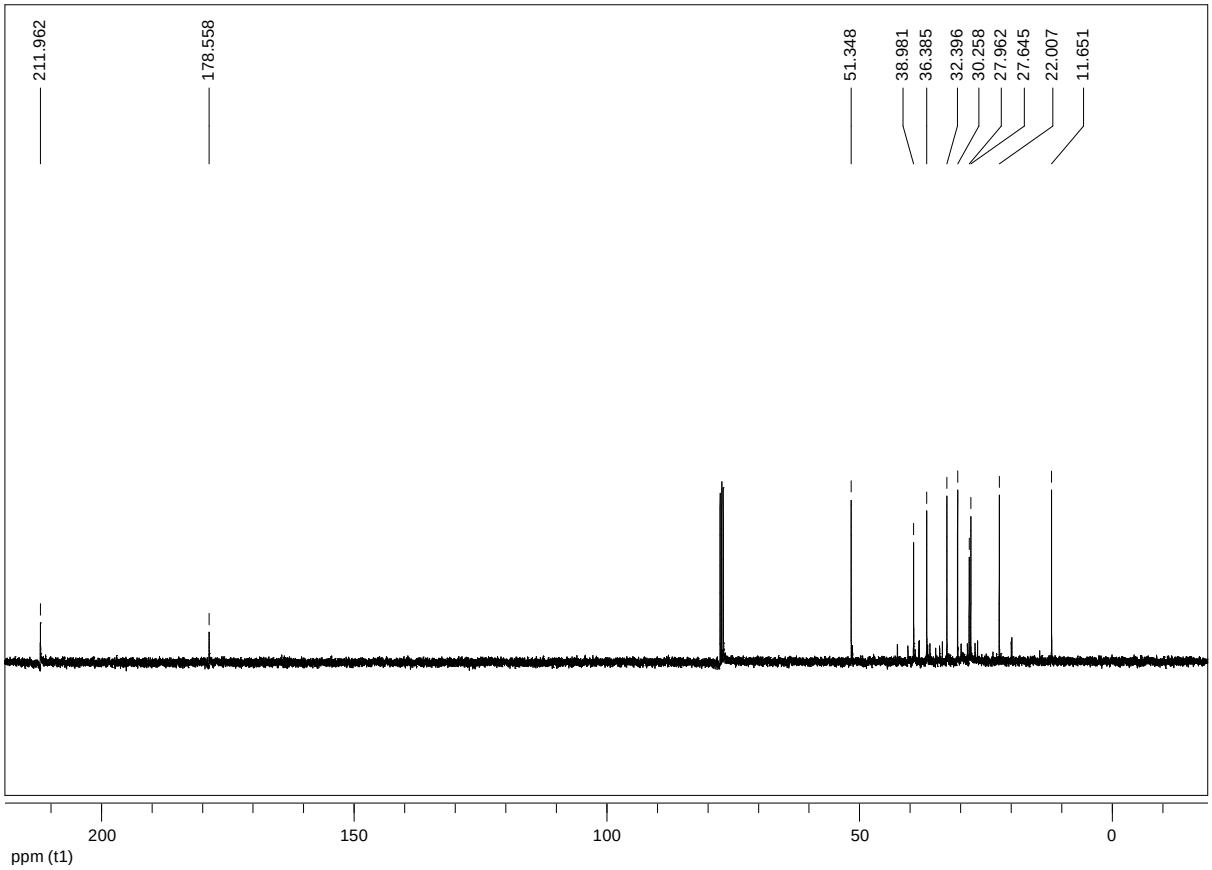
Compound **24b**



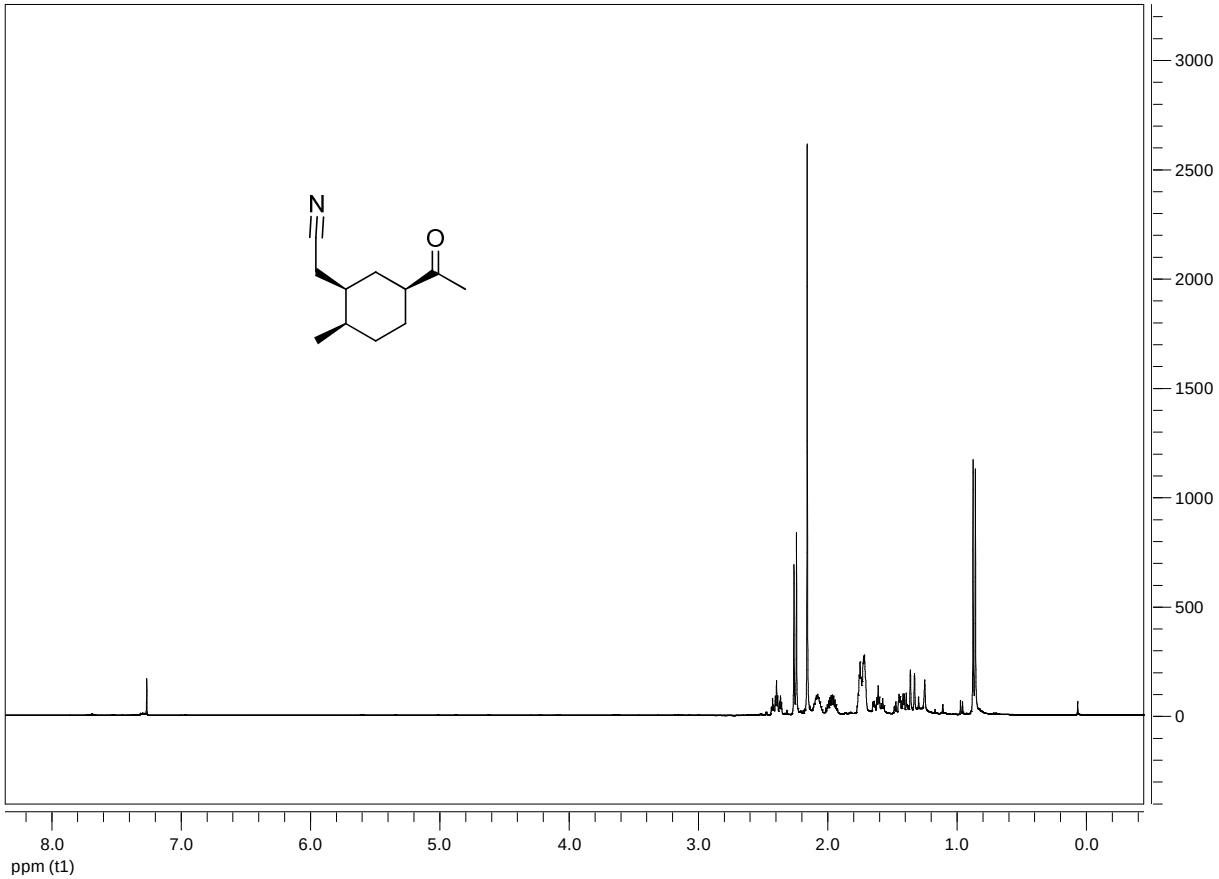


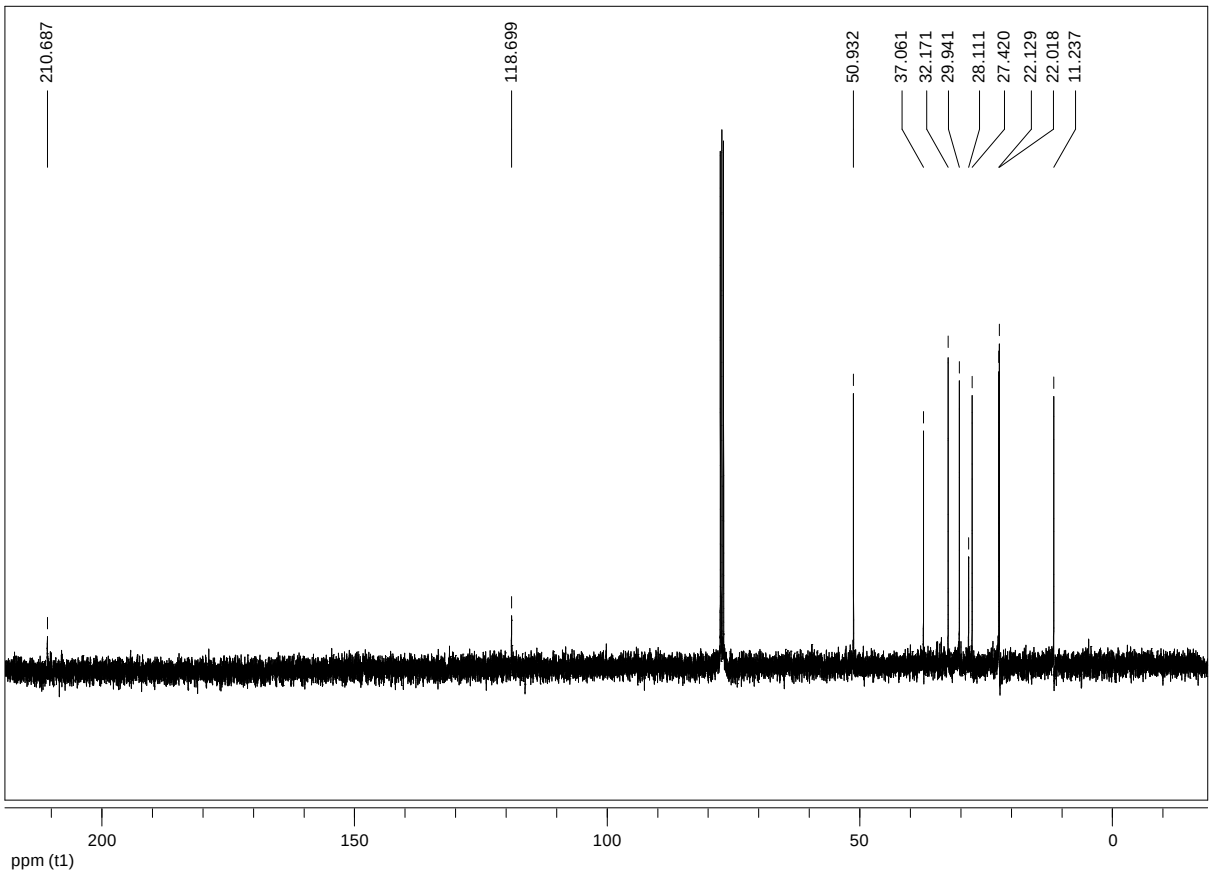
Compound **25**


HO
O
O
10.0
5.0
0.0
ppm (t1)

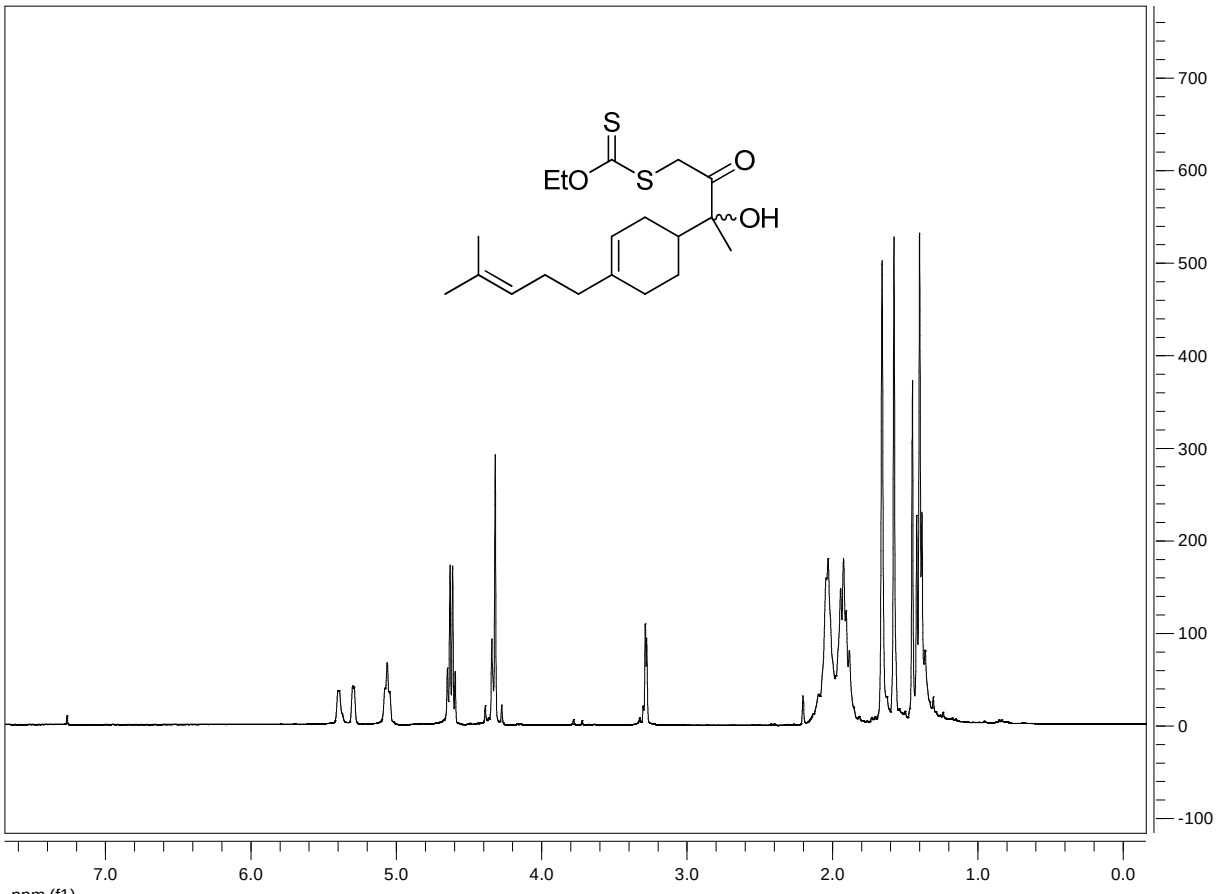

211.962
178.558
51.348
38.981
36.385
32.396
30.258
27.962
27.645
22.007
11.651
200
150
100
50
0
ppm (t1)

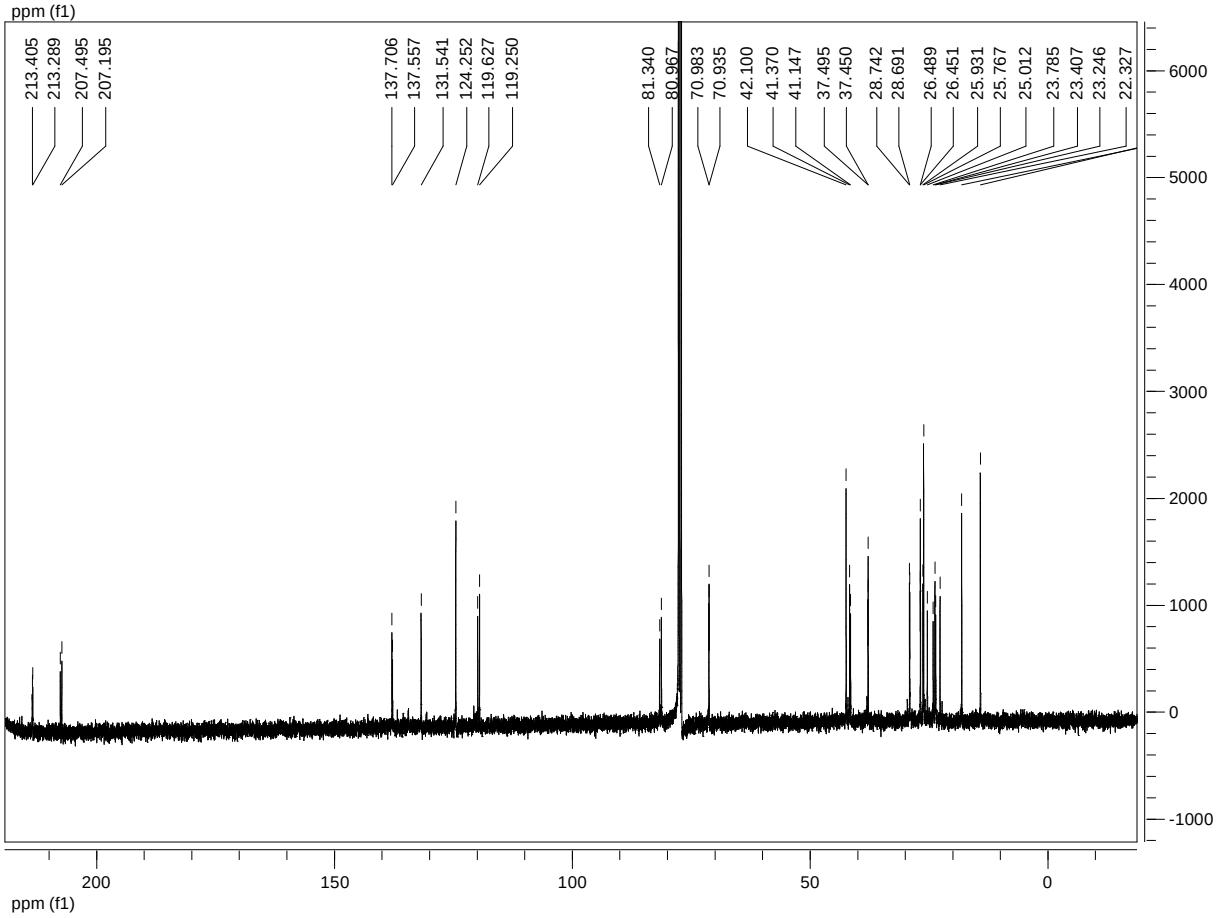
Compound **27**


N
O
3000
2500
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

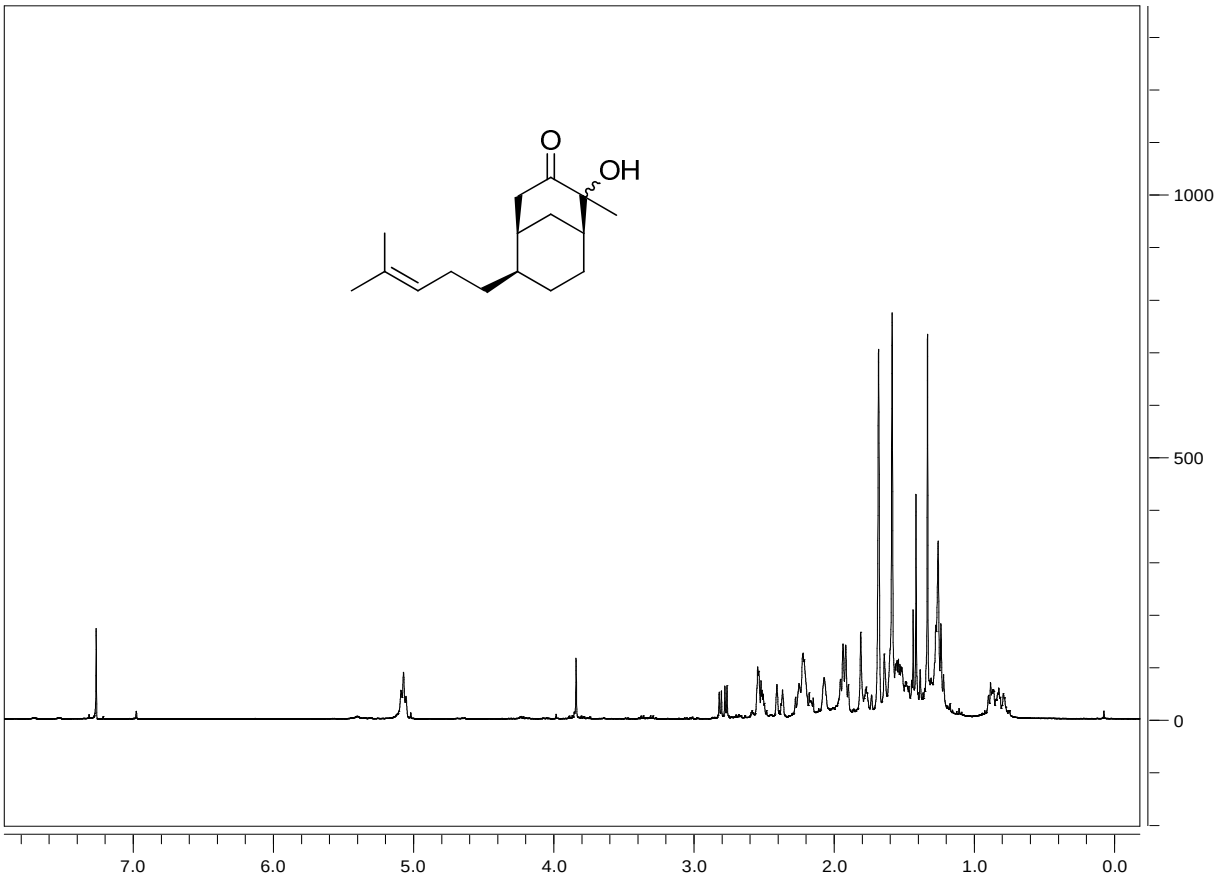

210.687
118.699
50.932
37.061
32.171
29.941
28.111
27.420
22.129
22.018
11.237
200
150
100
50
0
ppm (t1)

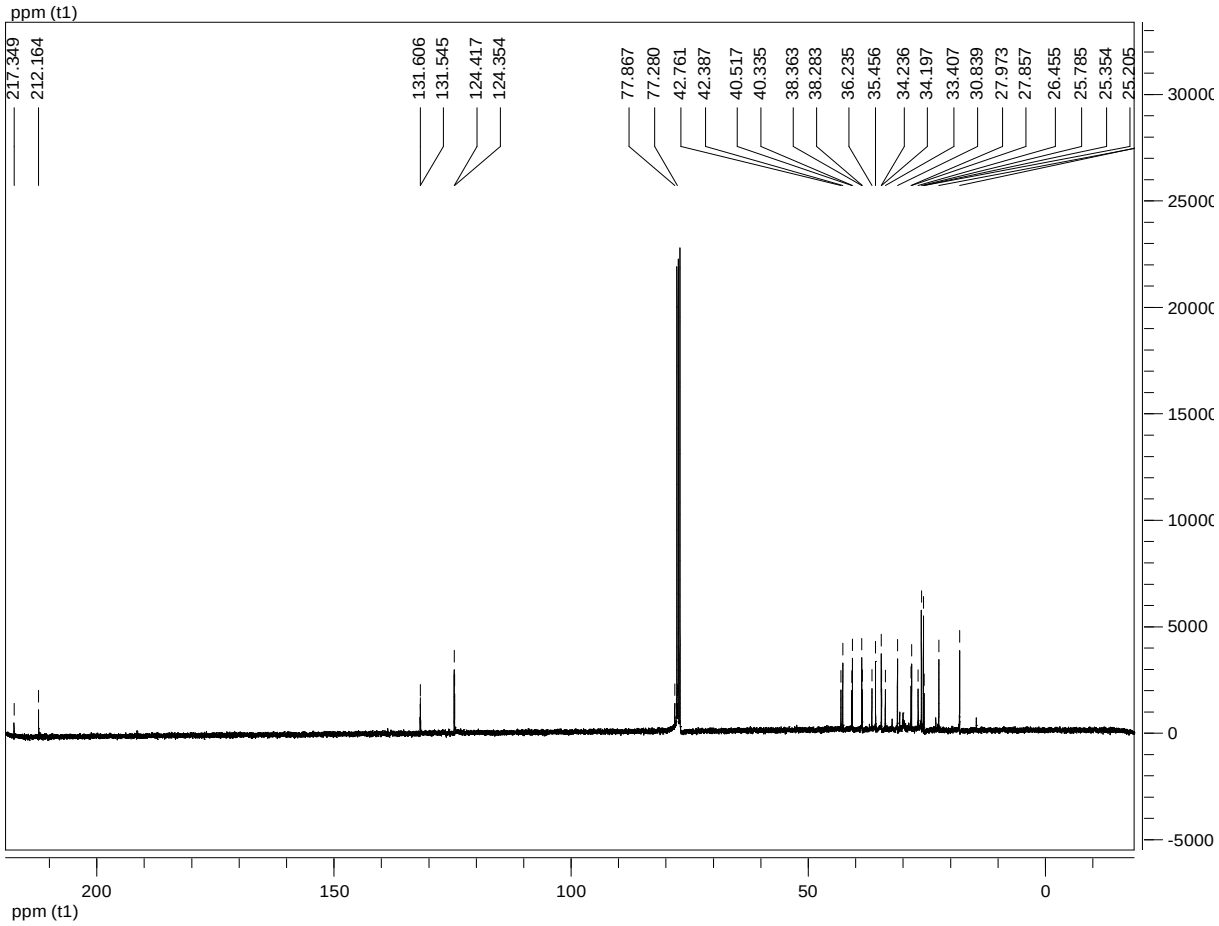
Compound **30b**



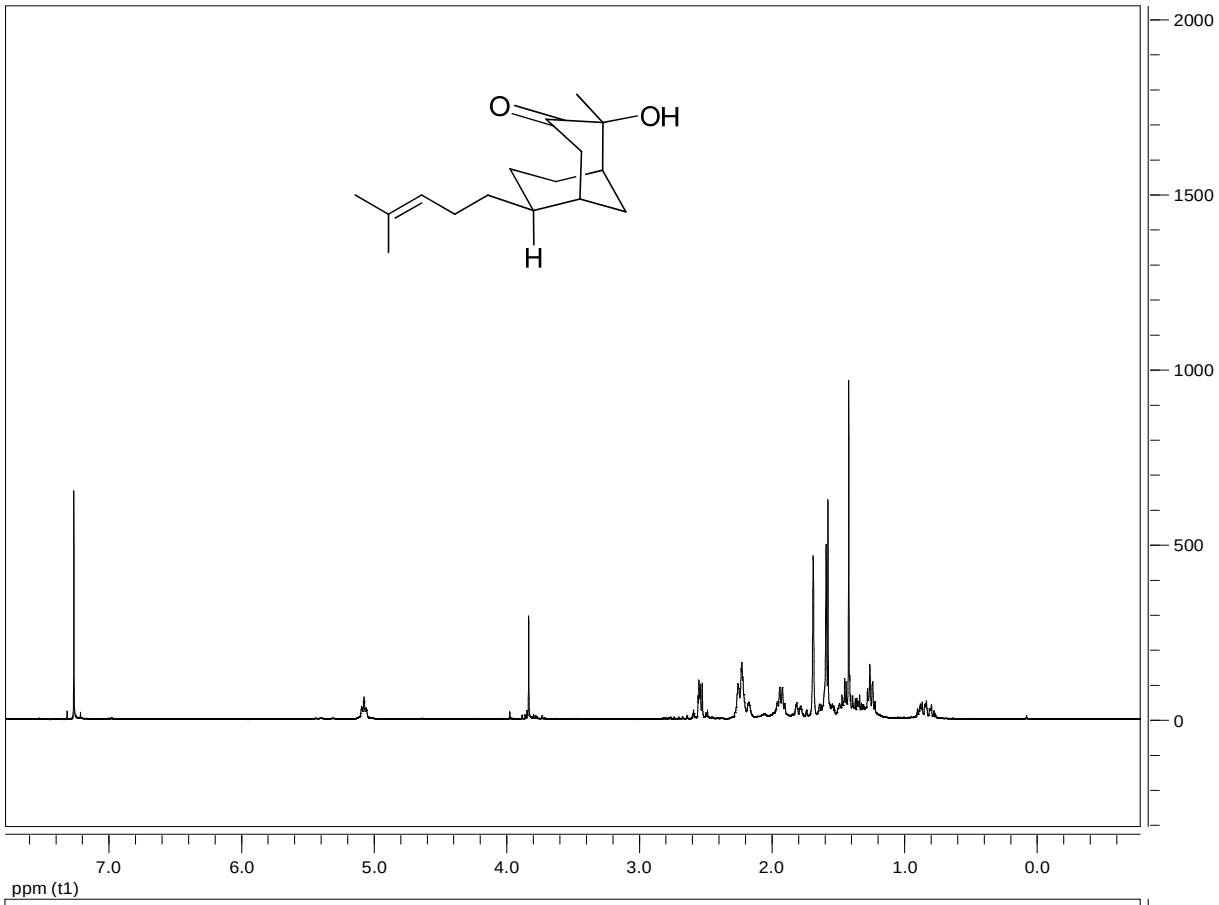


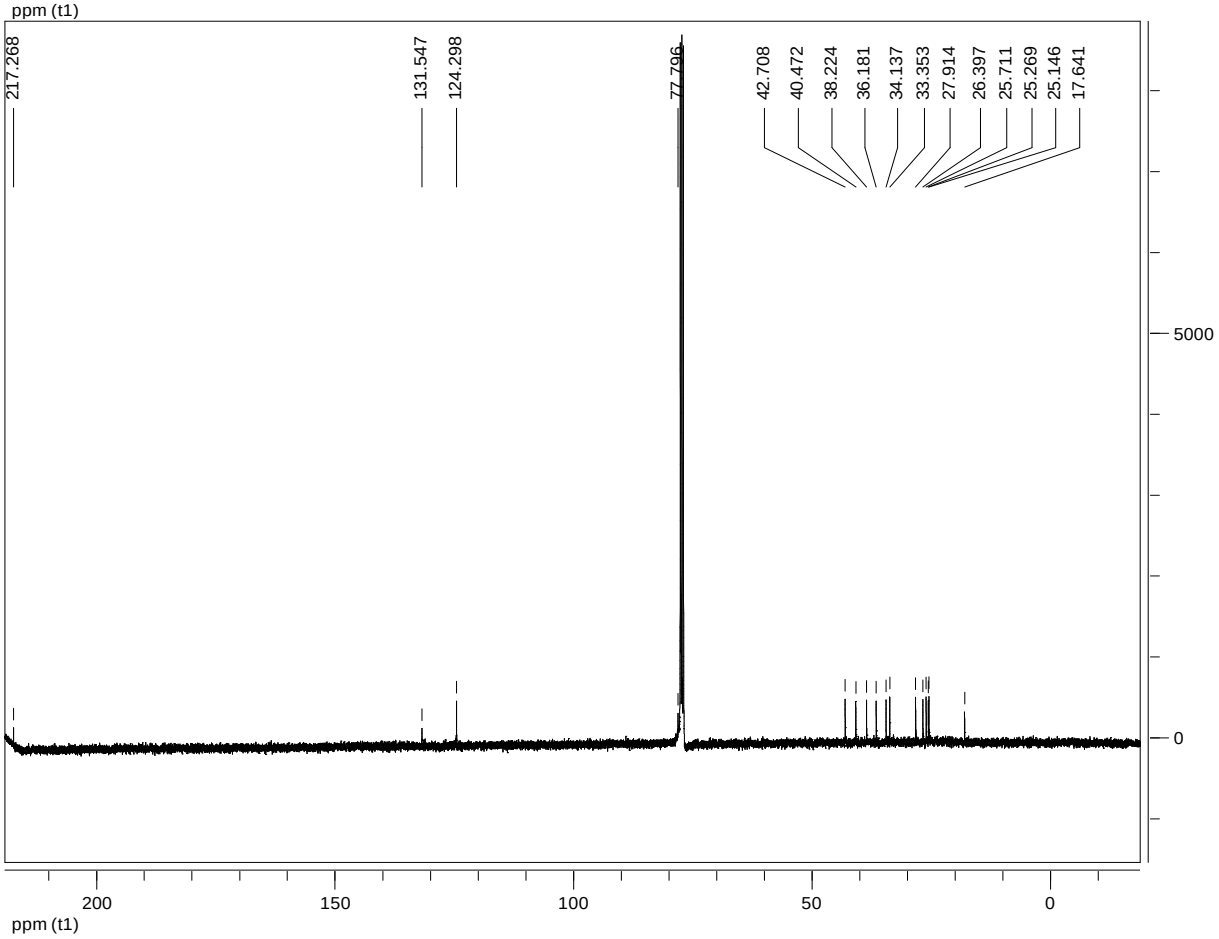
Compound **31a,b**



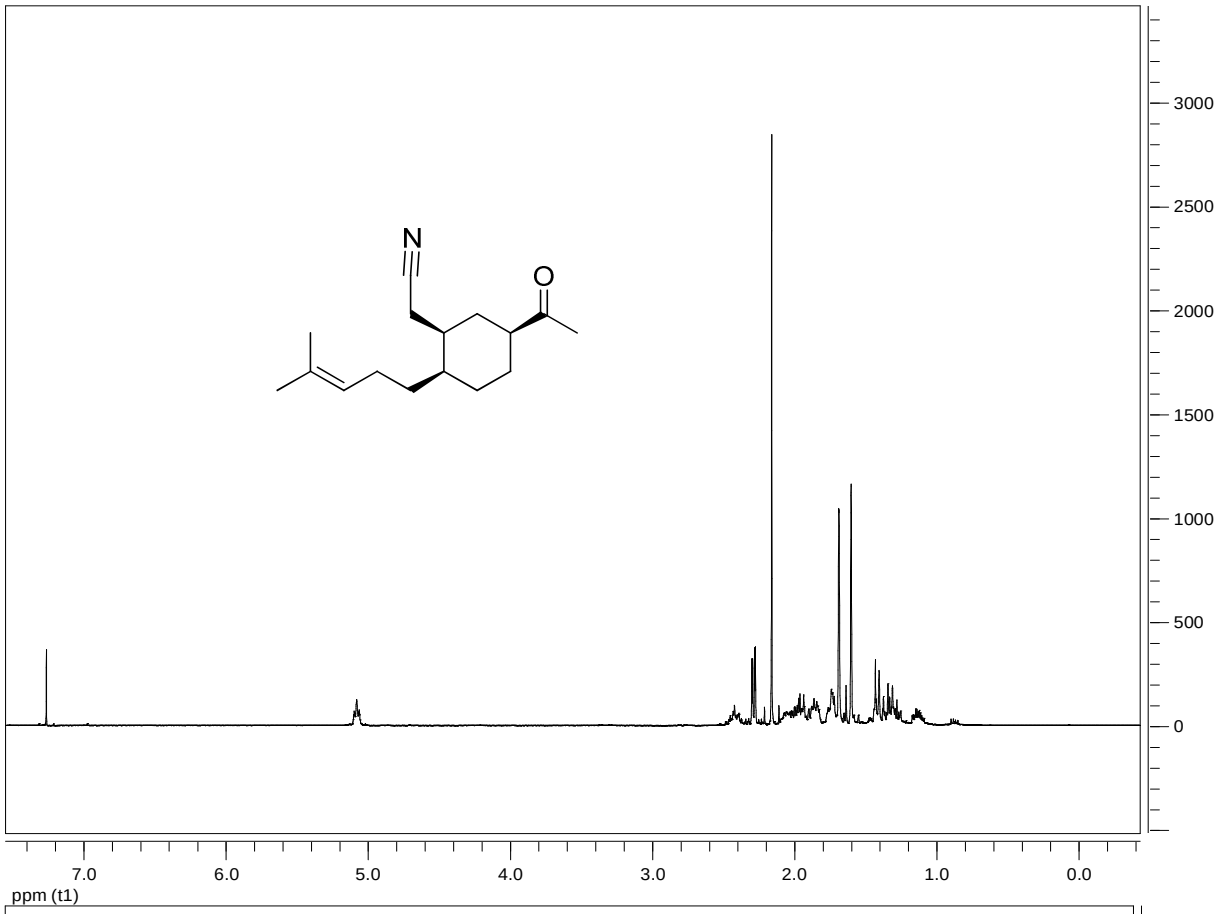


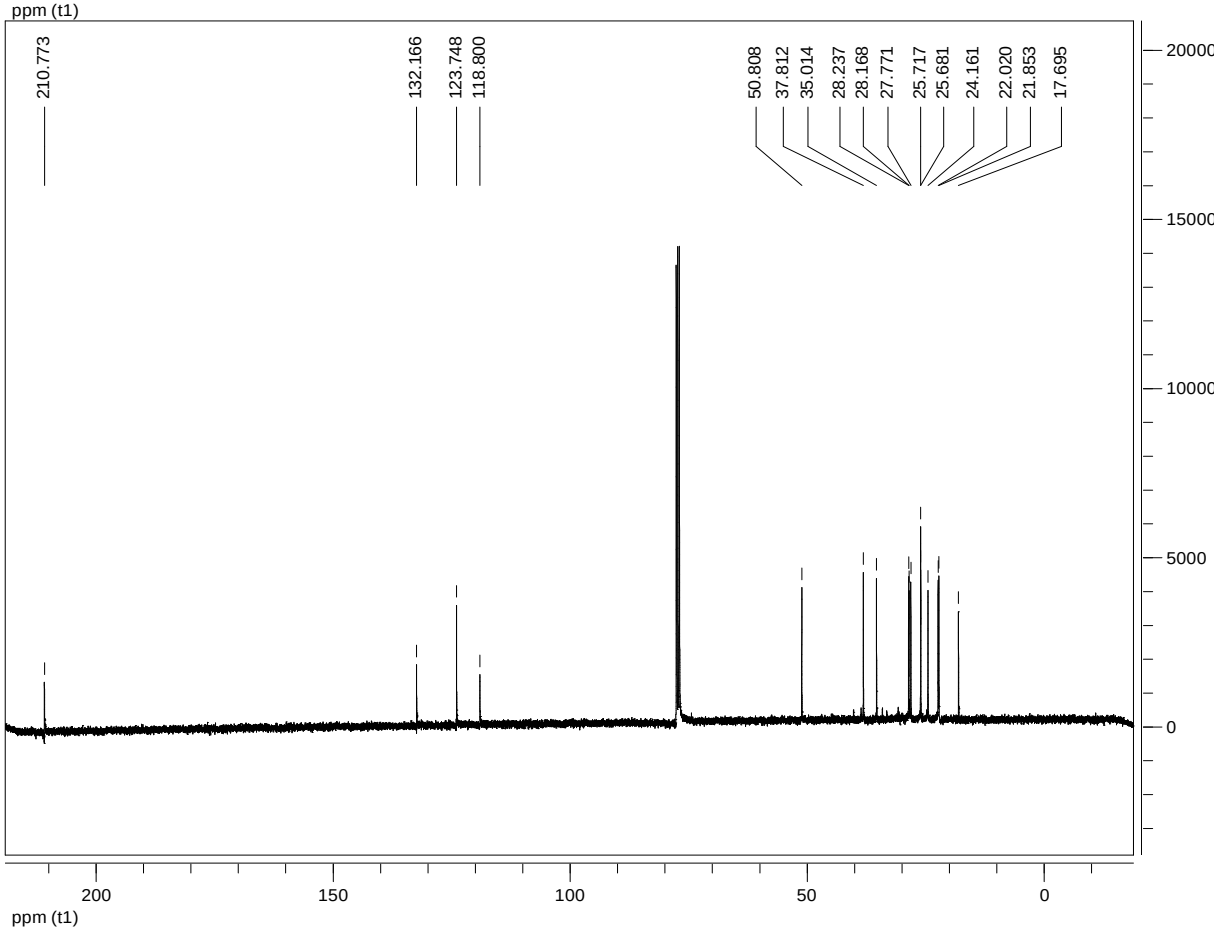
Compound **31b**



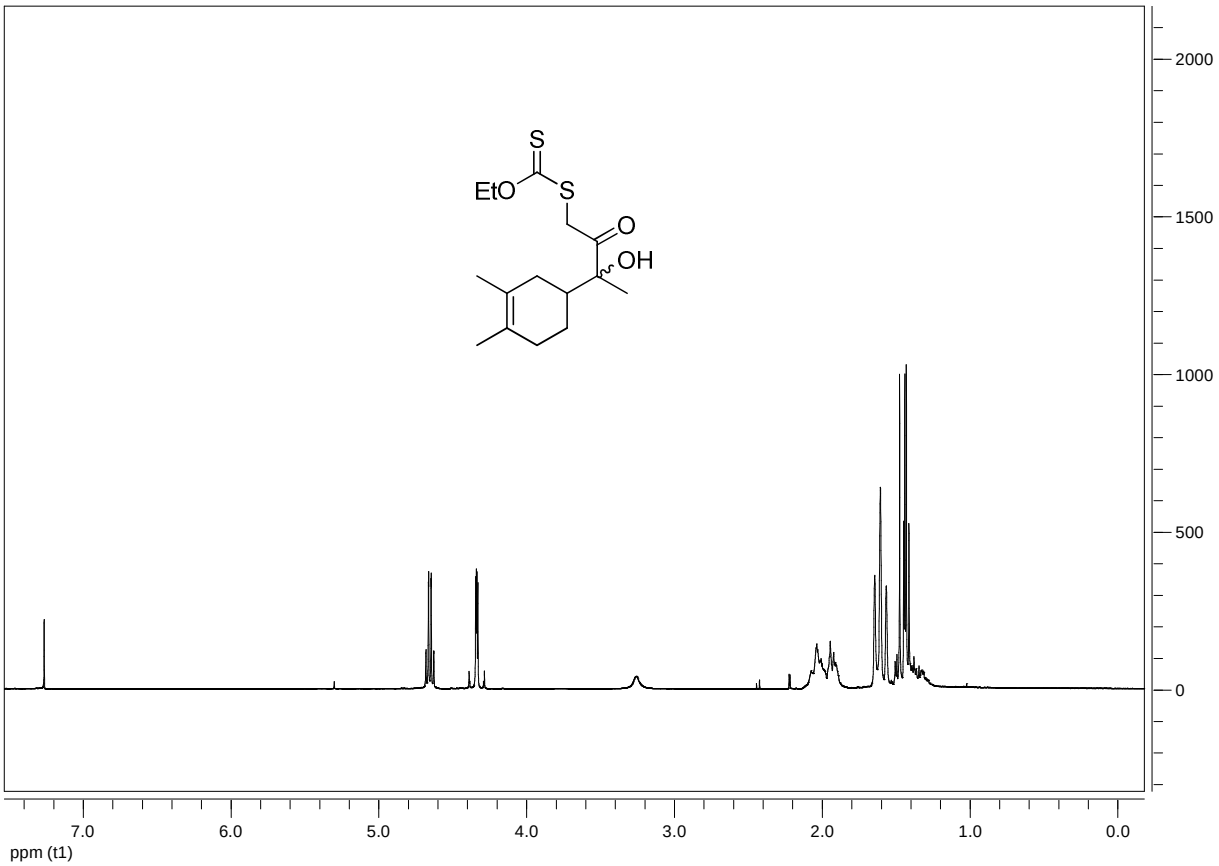


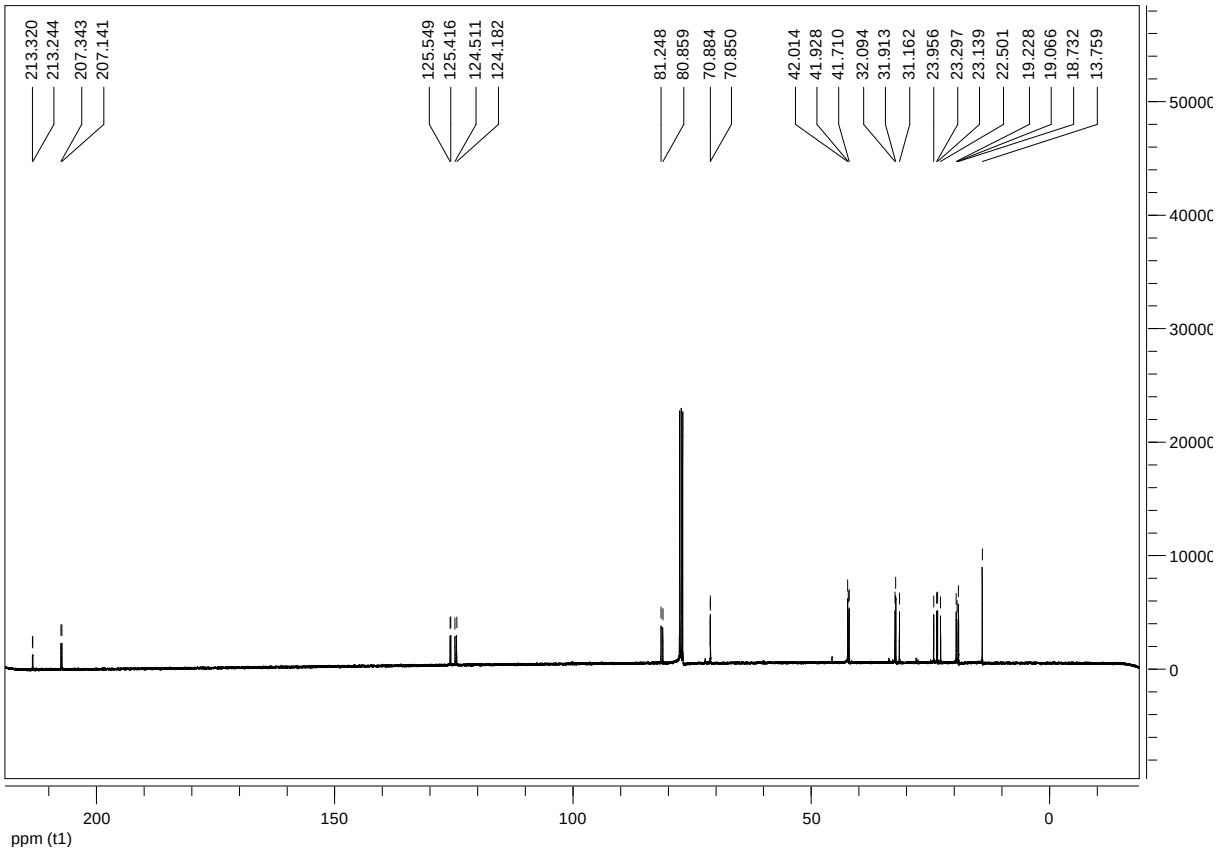
Compound **32**


N
O
3000
2500
2000
1500
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

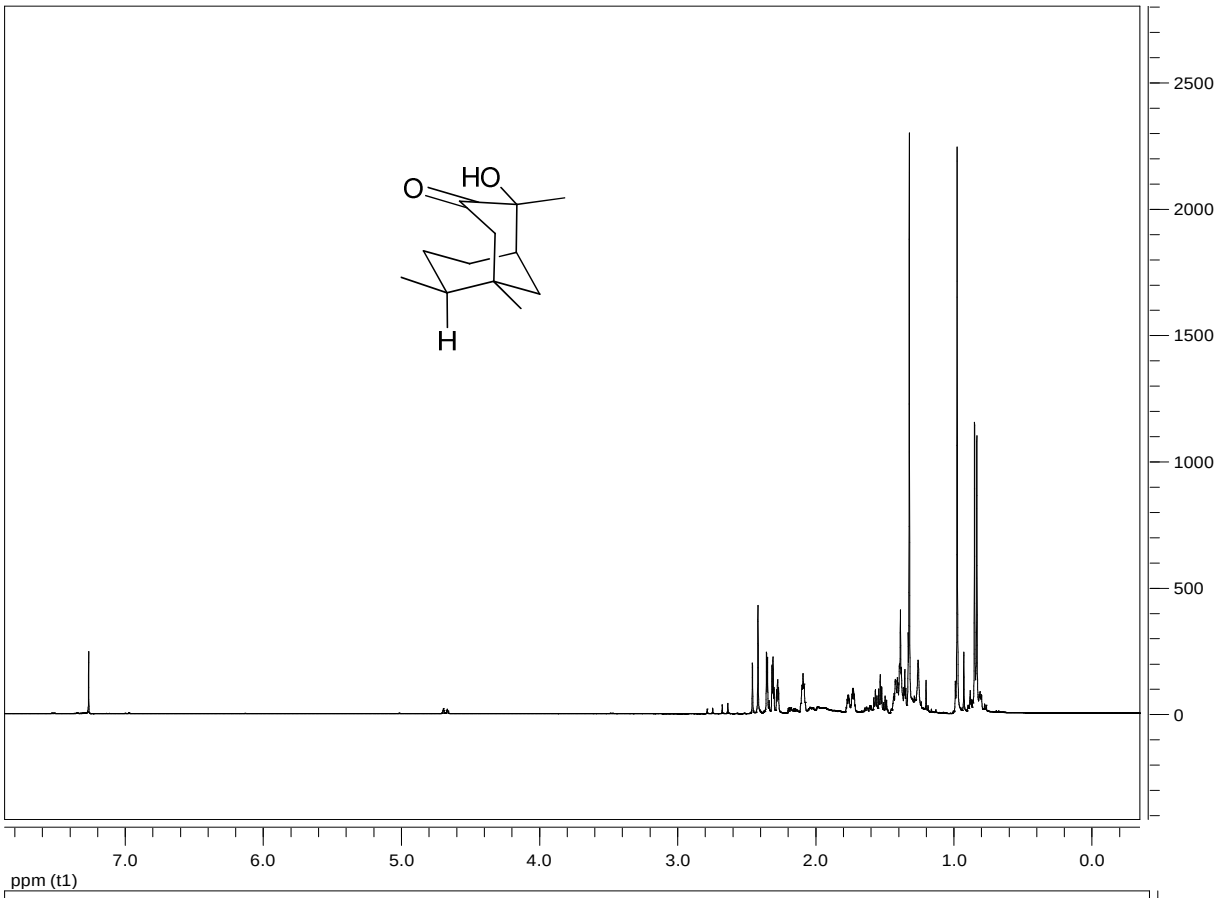

210.773
132.166
123.748
118.800
50.808
37.812
35.014
28.237
28.168
27.771
25.717
25.681
24.161
22.020
21.853
17.695
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

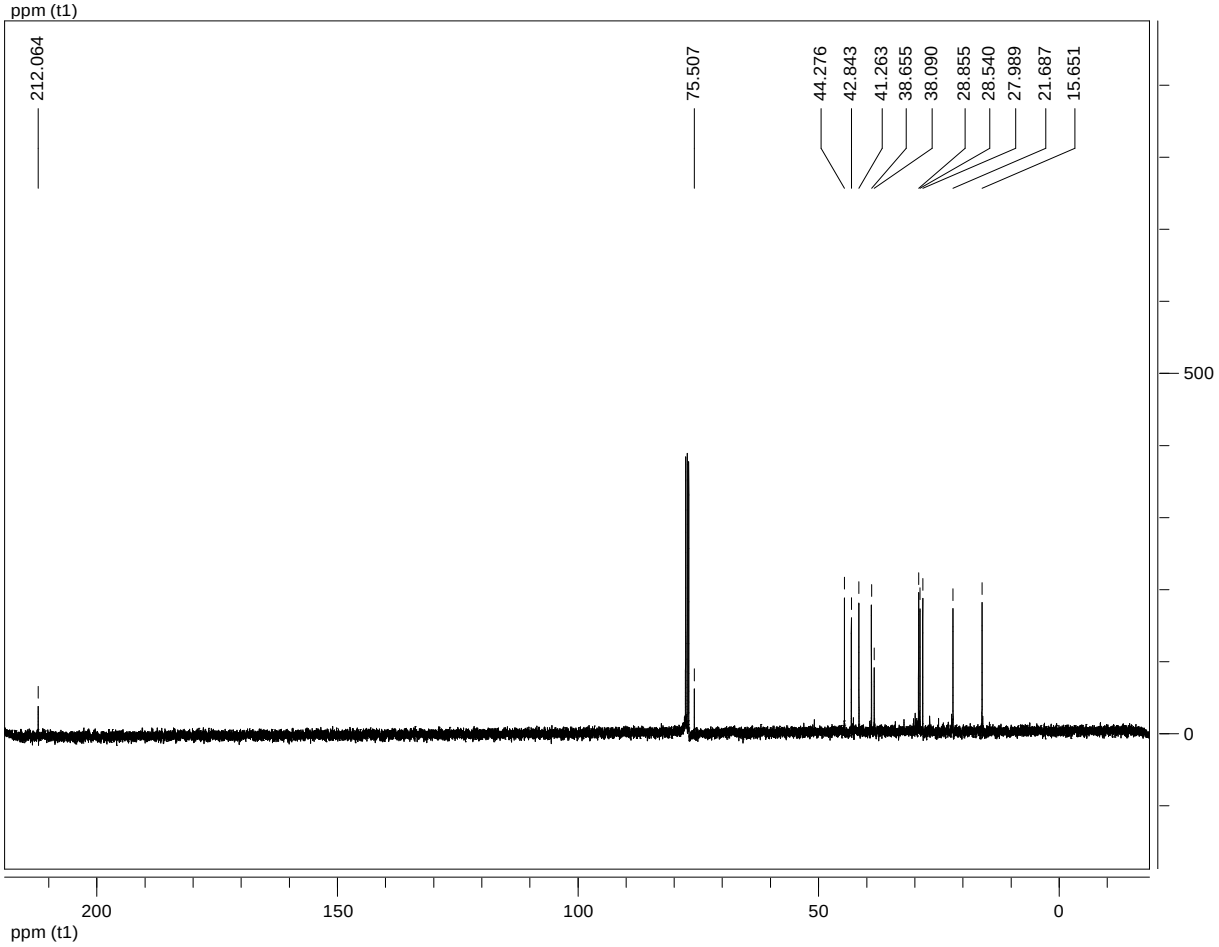
Compound **35b**



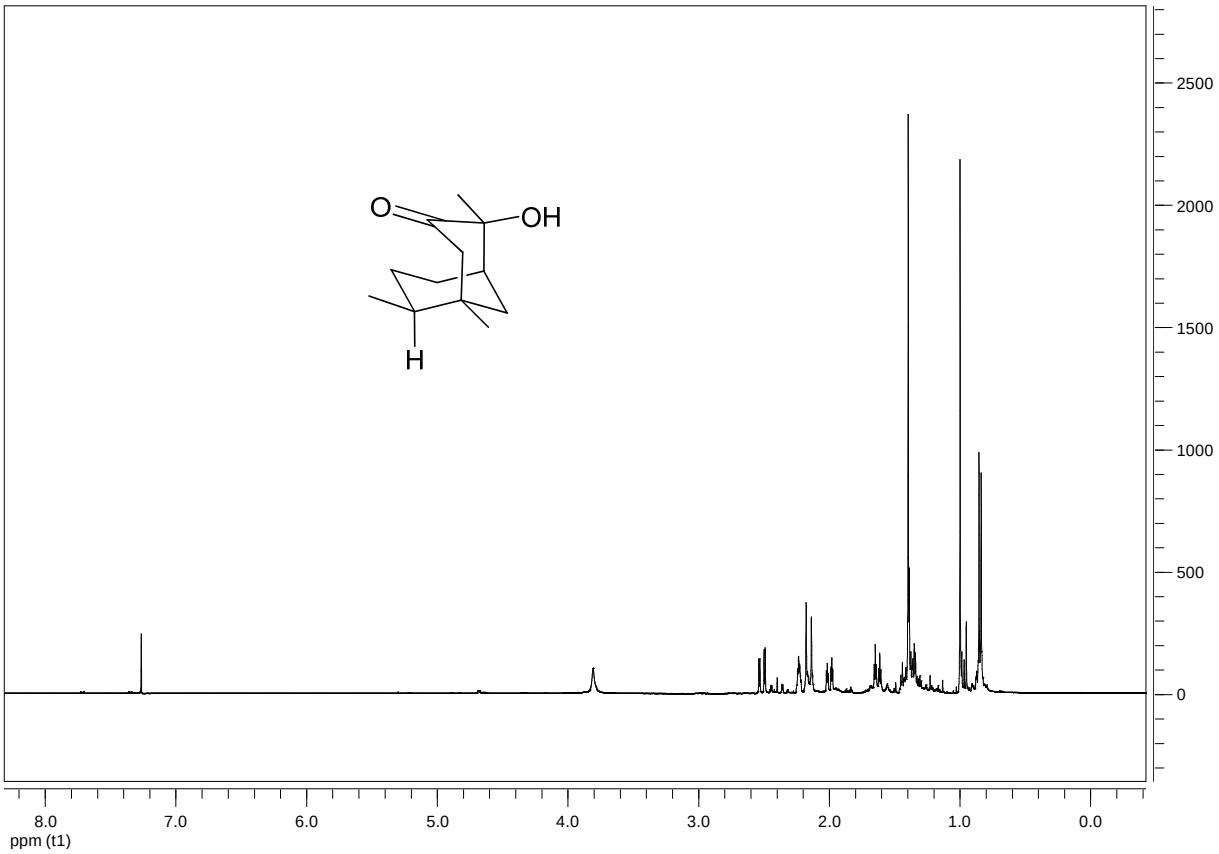


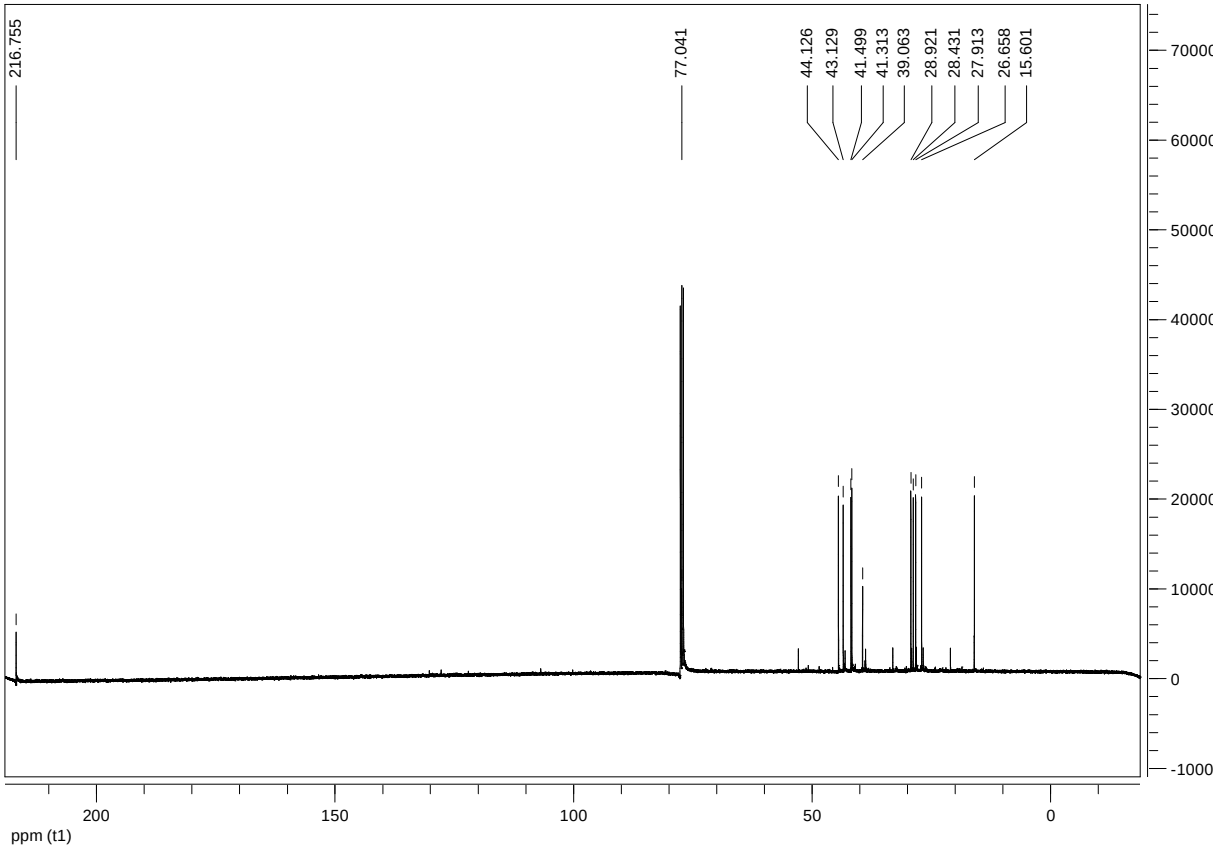
Compound **36a**



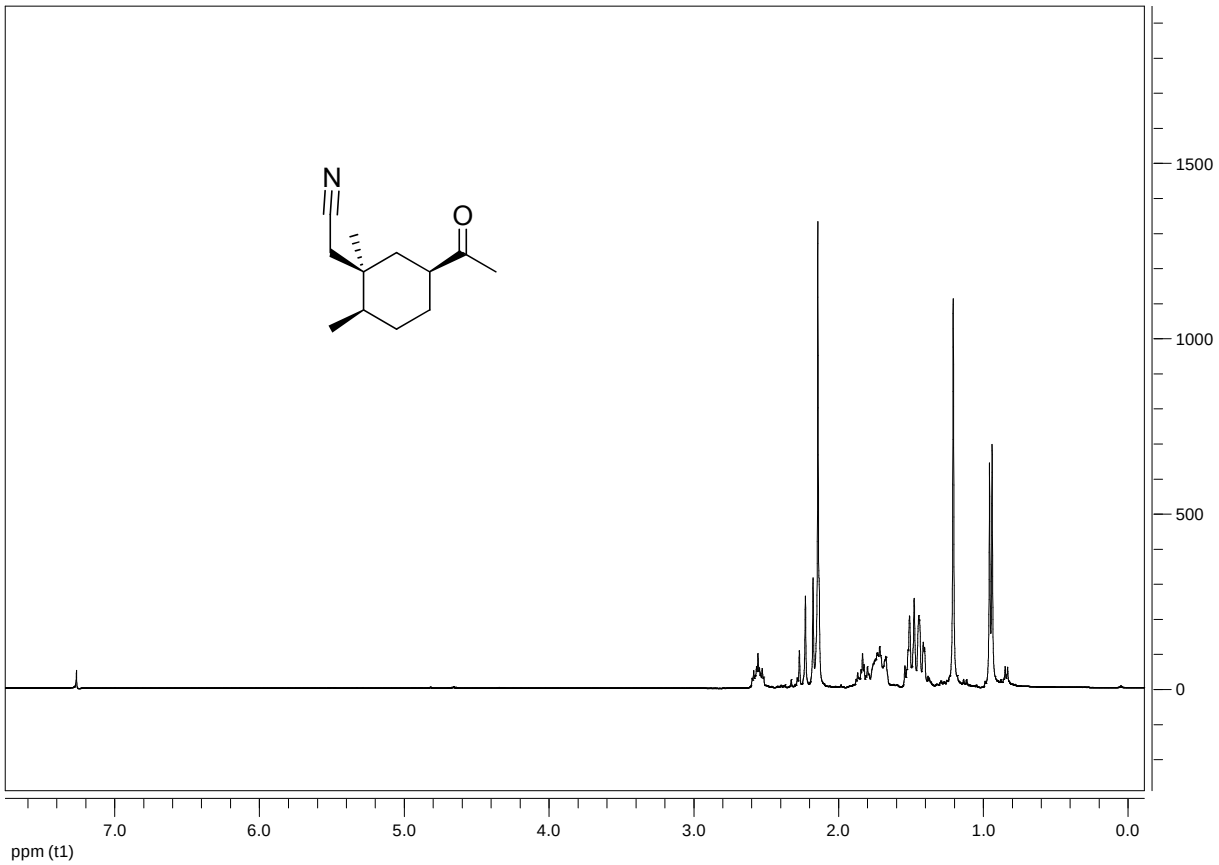


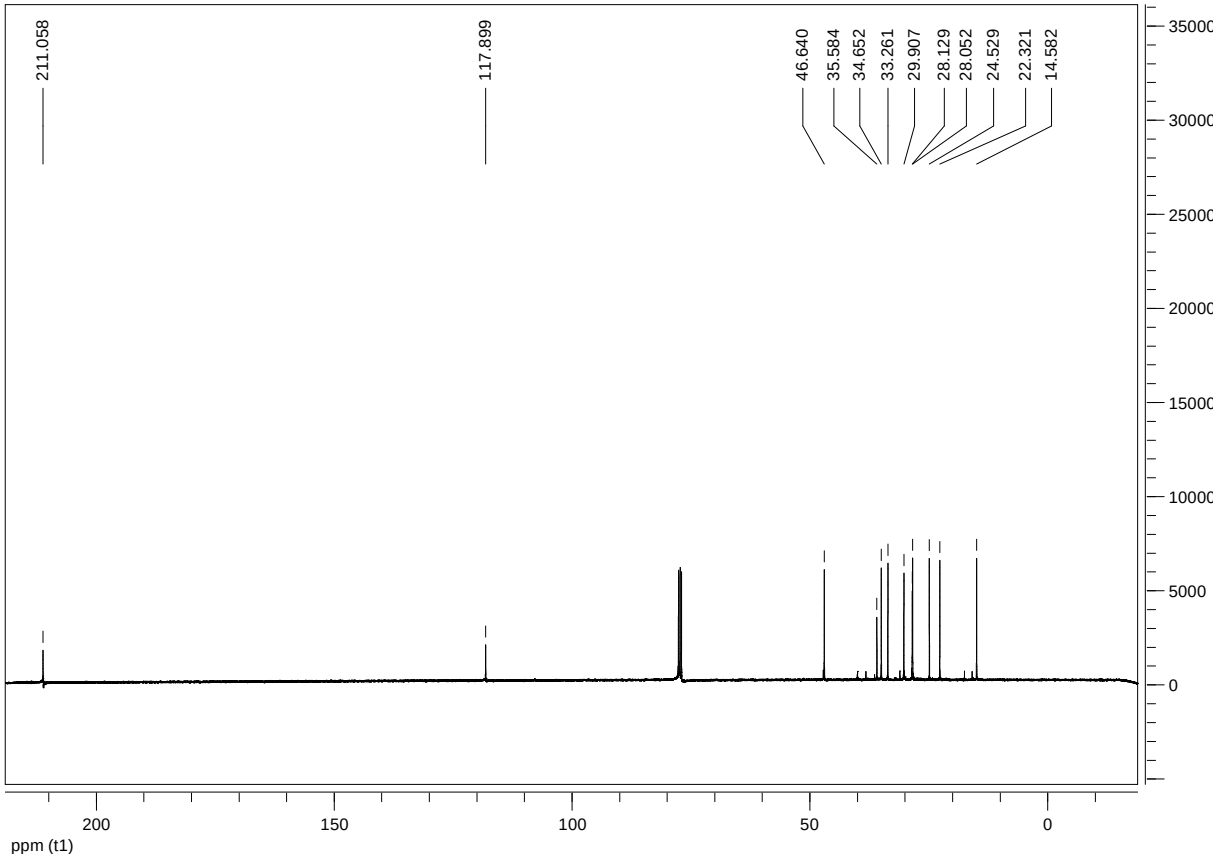
Compound **36b**



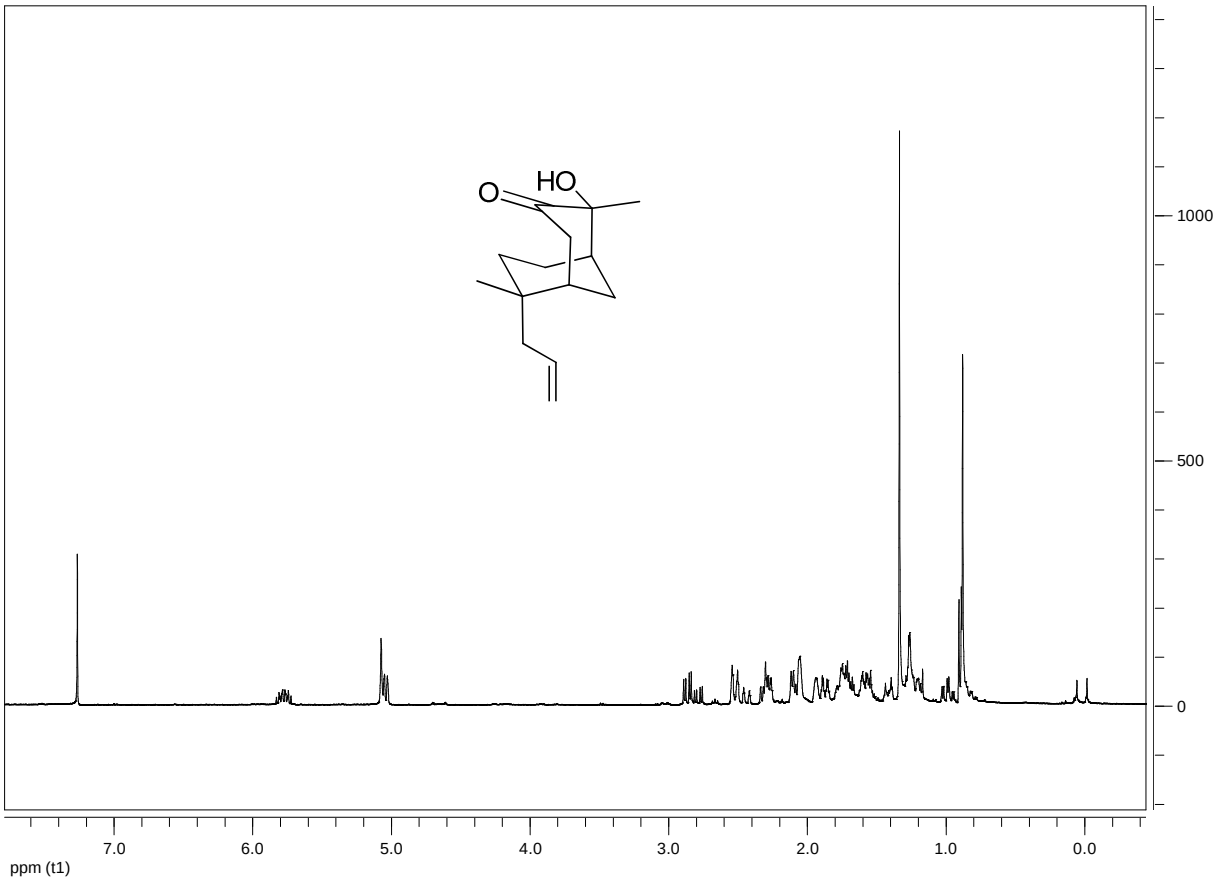


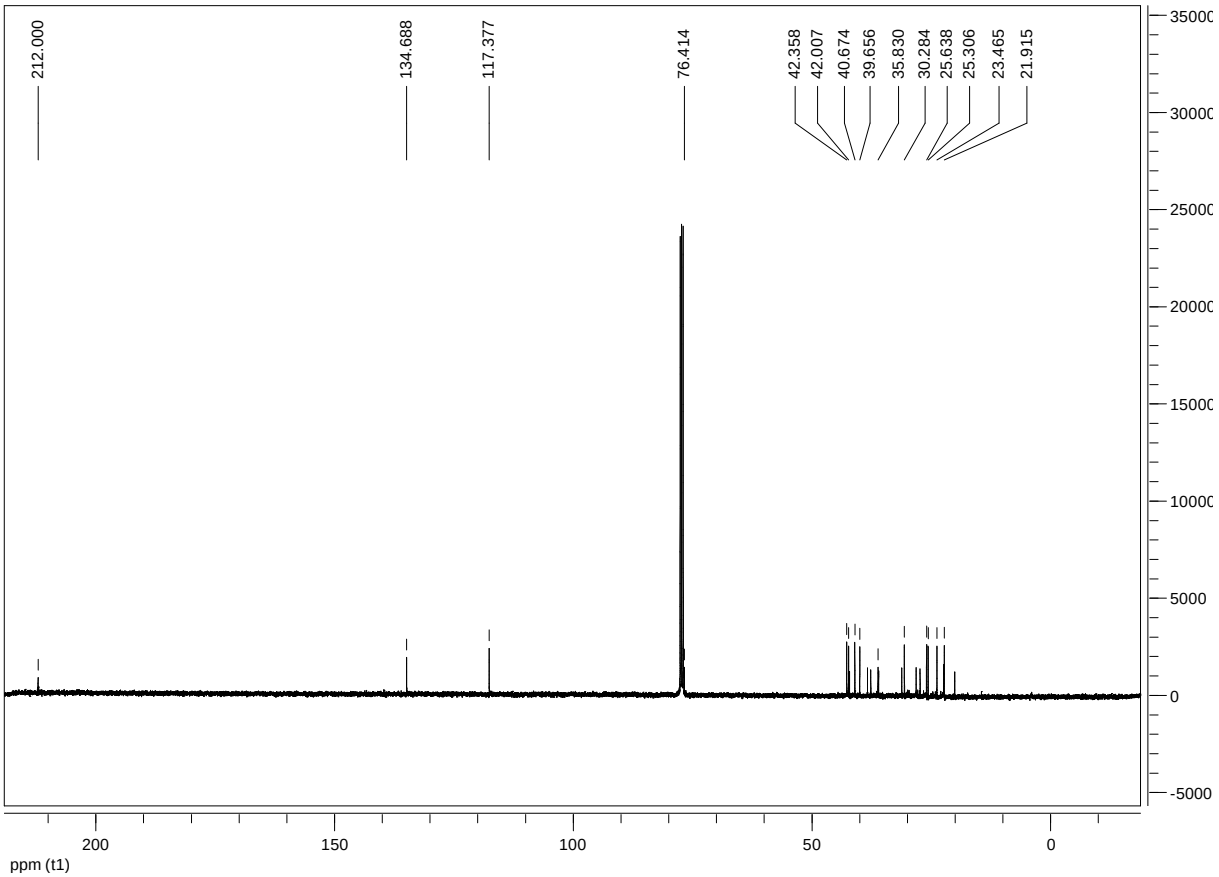
Compound **37**


N
O
1500
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

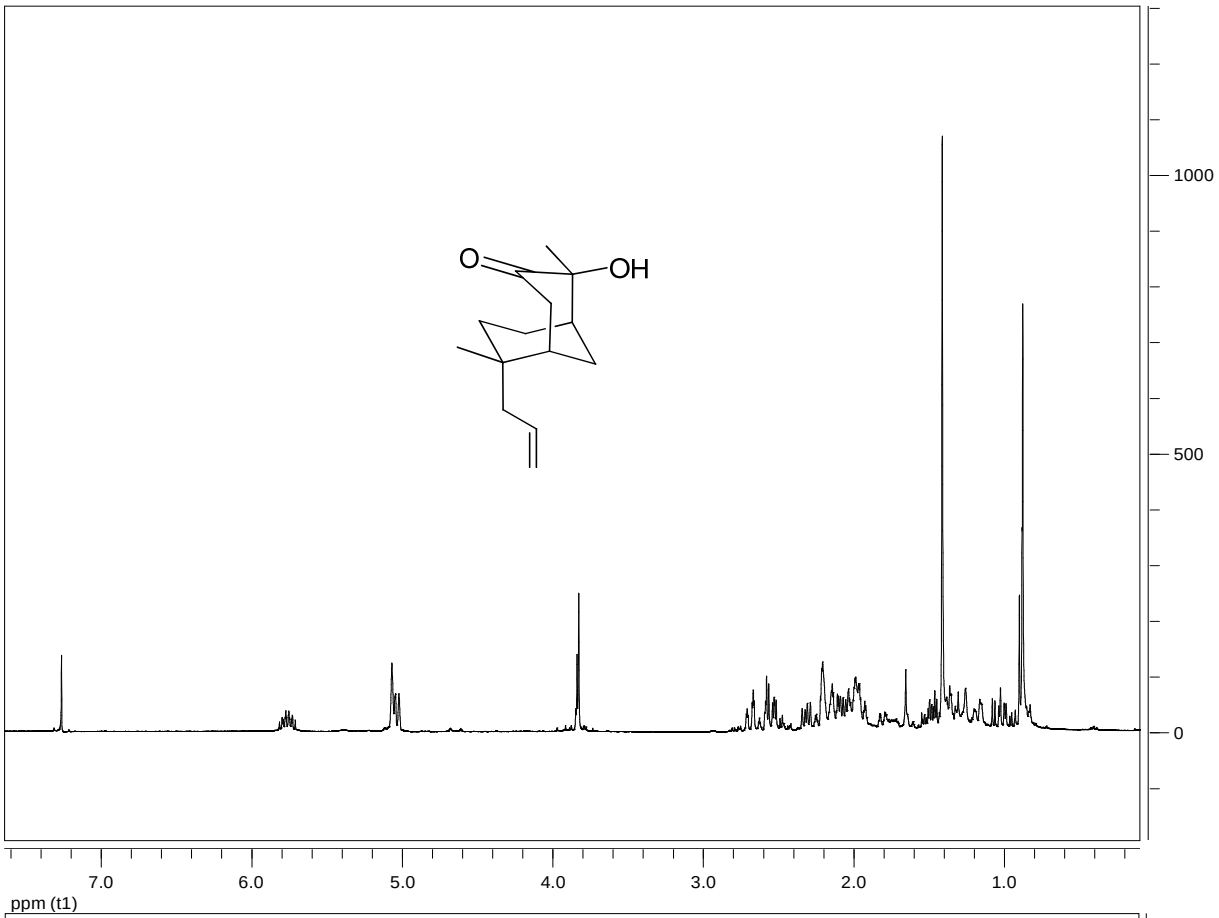

211.058
117.899
46.640
35.584
34.652
33.261
29.907
28.129
28.052
24.529
22.321
14.582
35000
30000
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

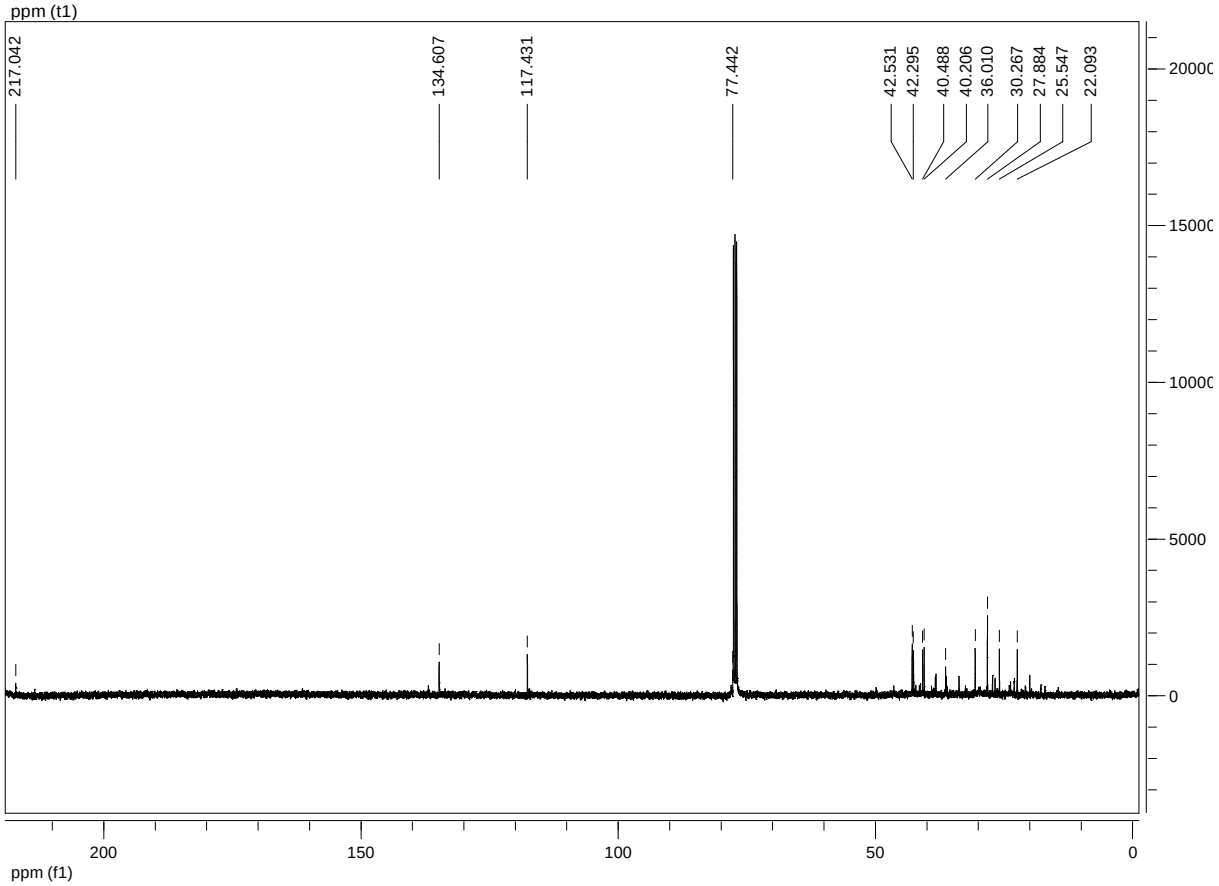
Compound **39a**



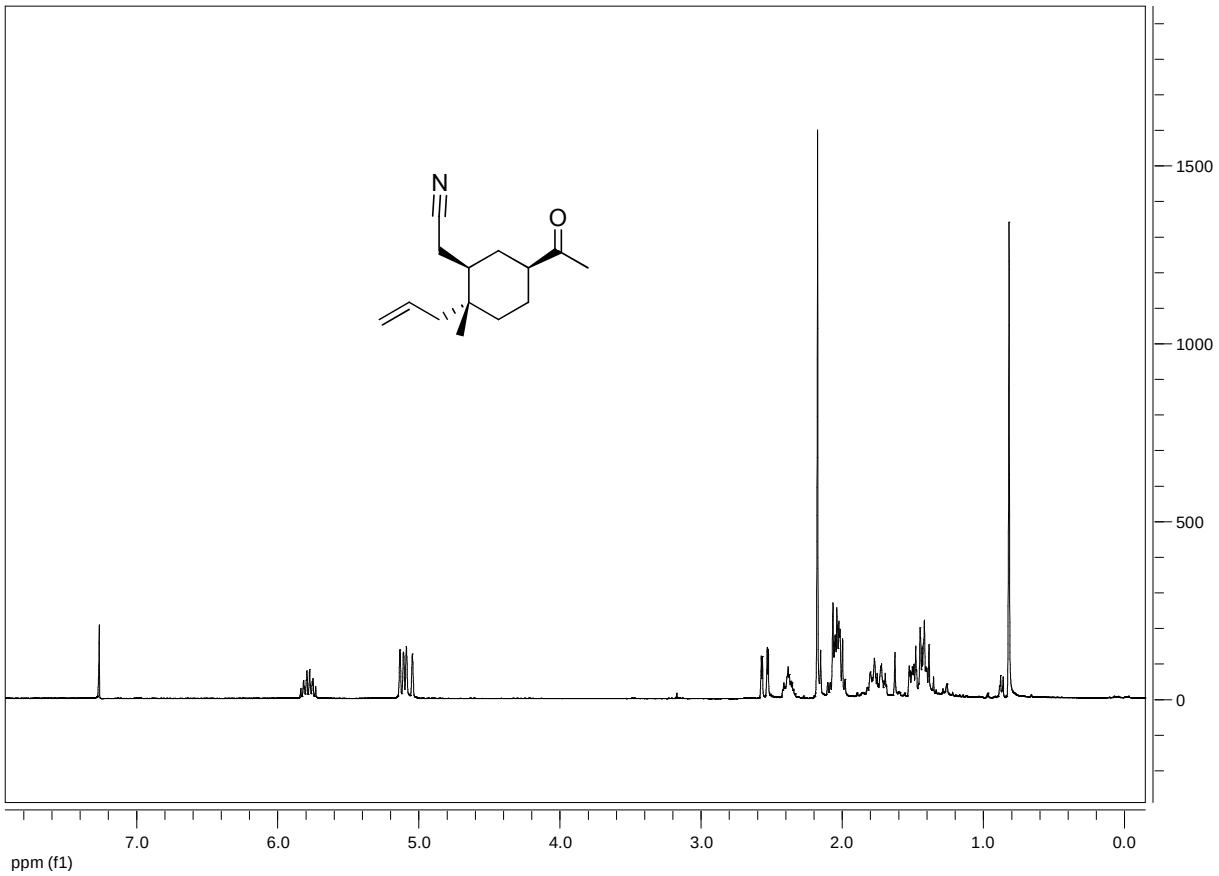


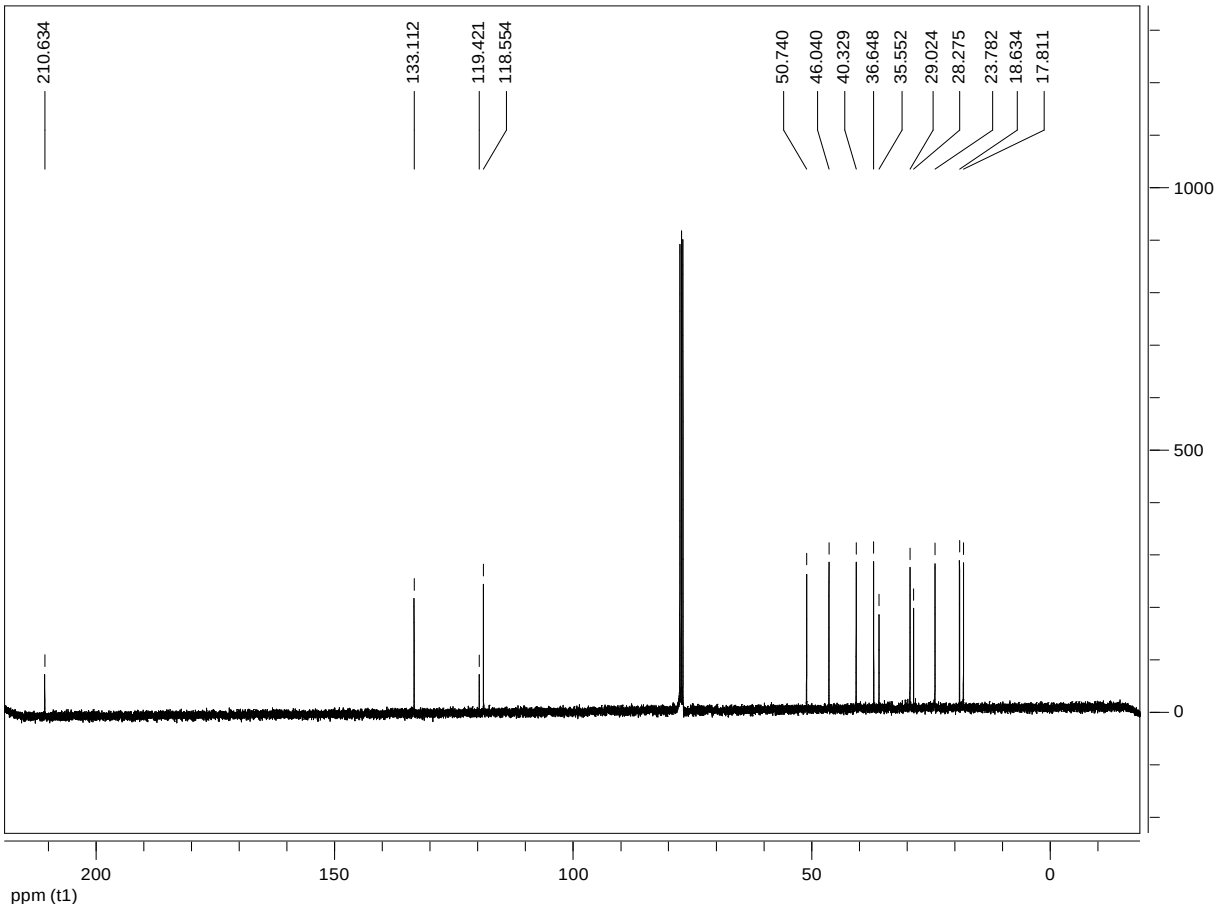
Compound **39b**



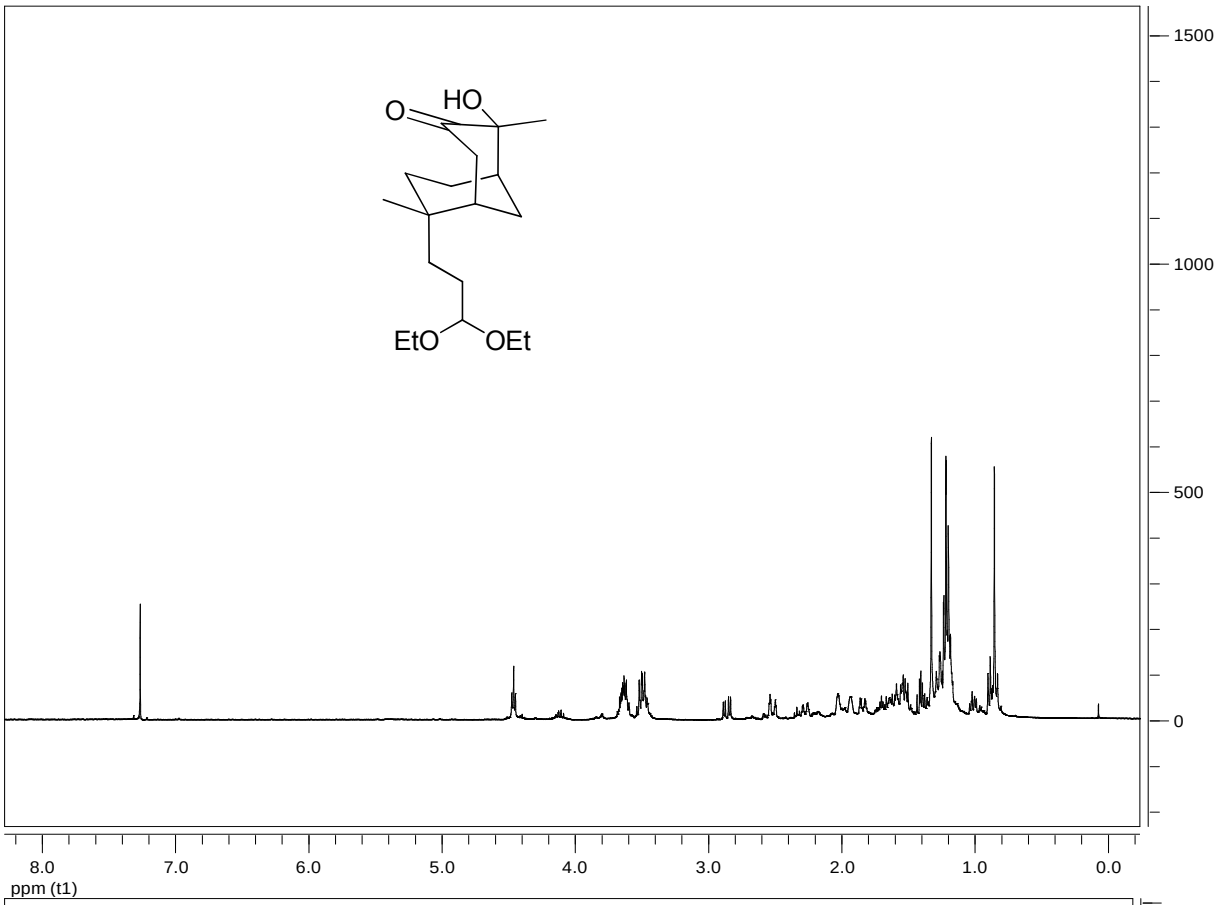


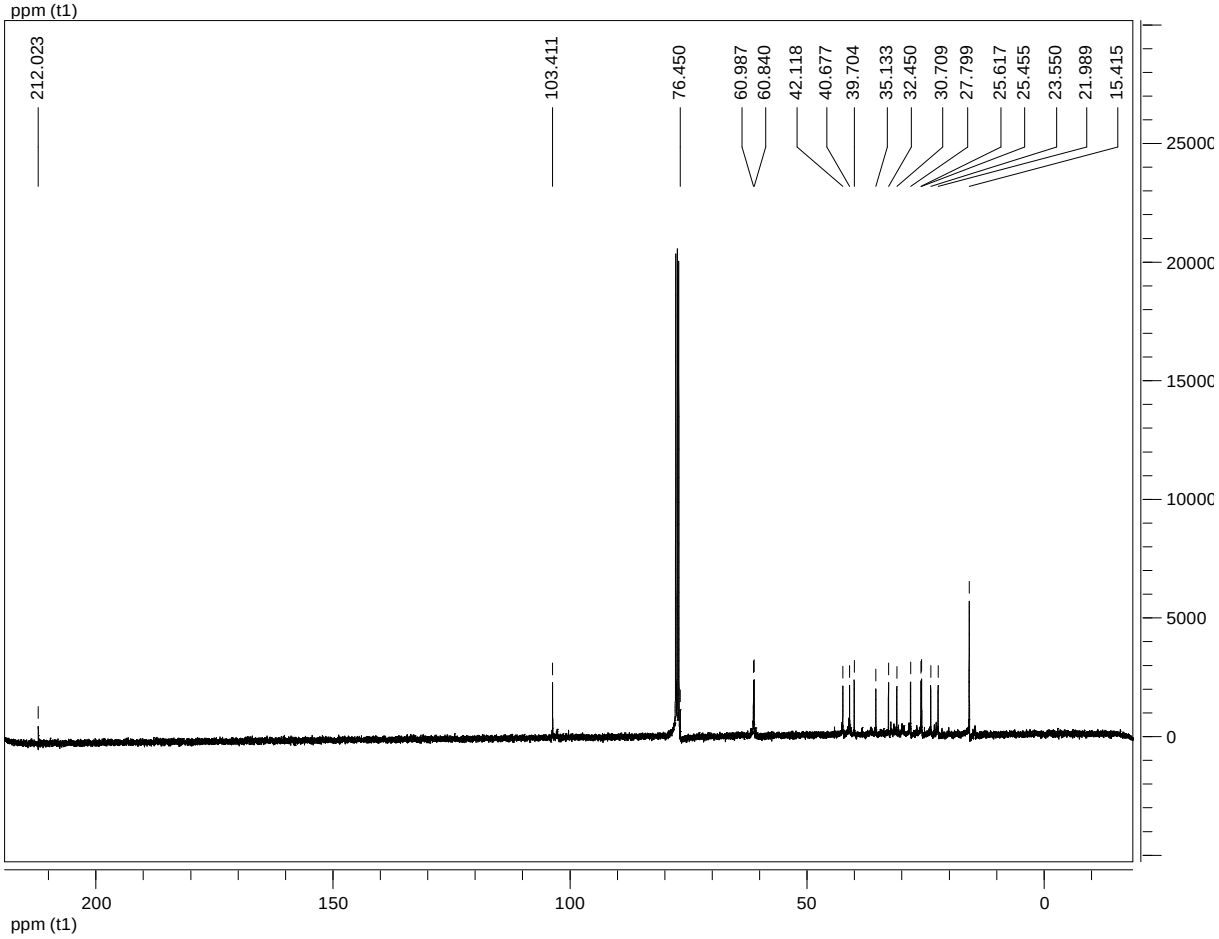
Compound **40**


N
O
1500
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

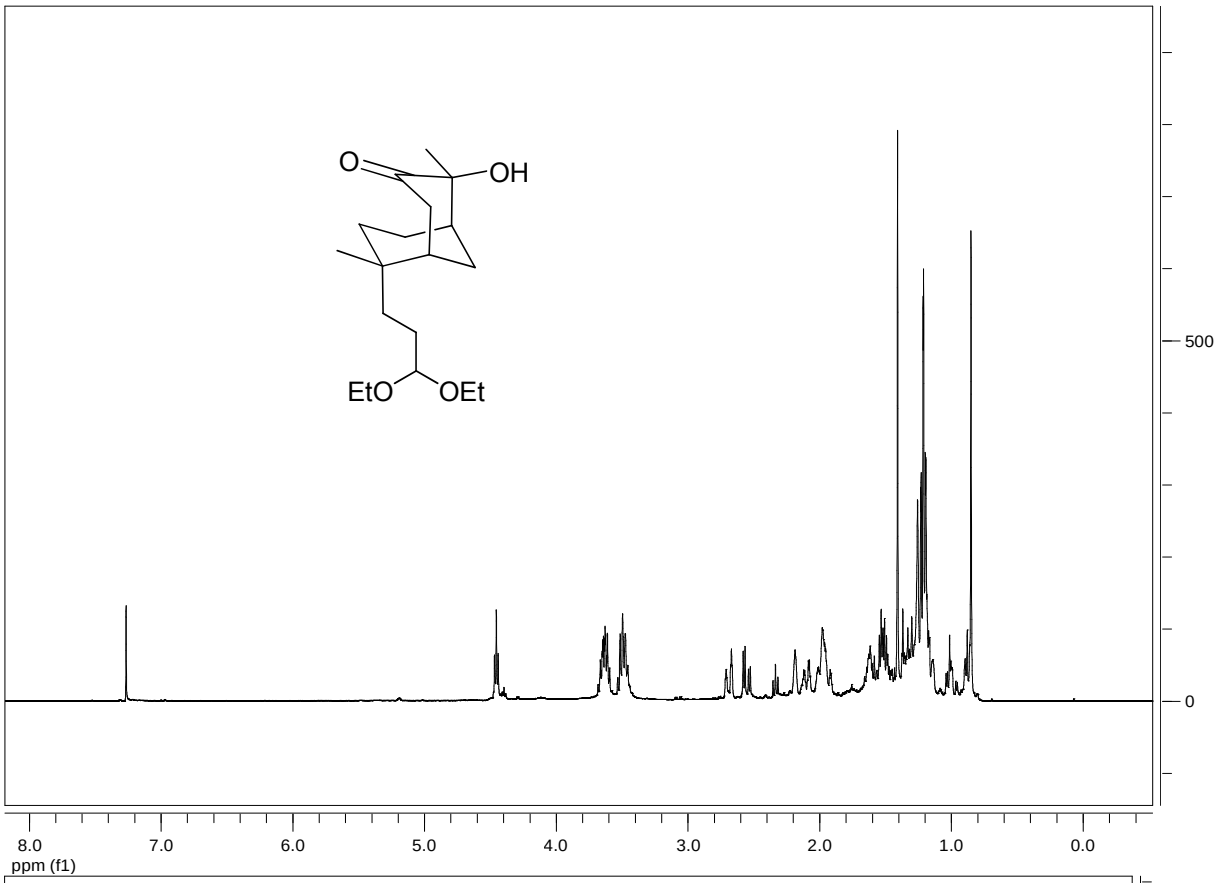

210.634
133.112
119.421
118.554
50.740
46.040
40.329
36.648
35.552
29.024
28.275
23.782
18.634
17.811
1000
500
0
200
150
100
50
0
ppm (t1)

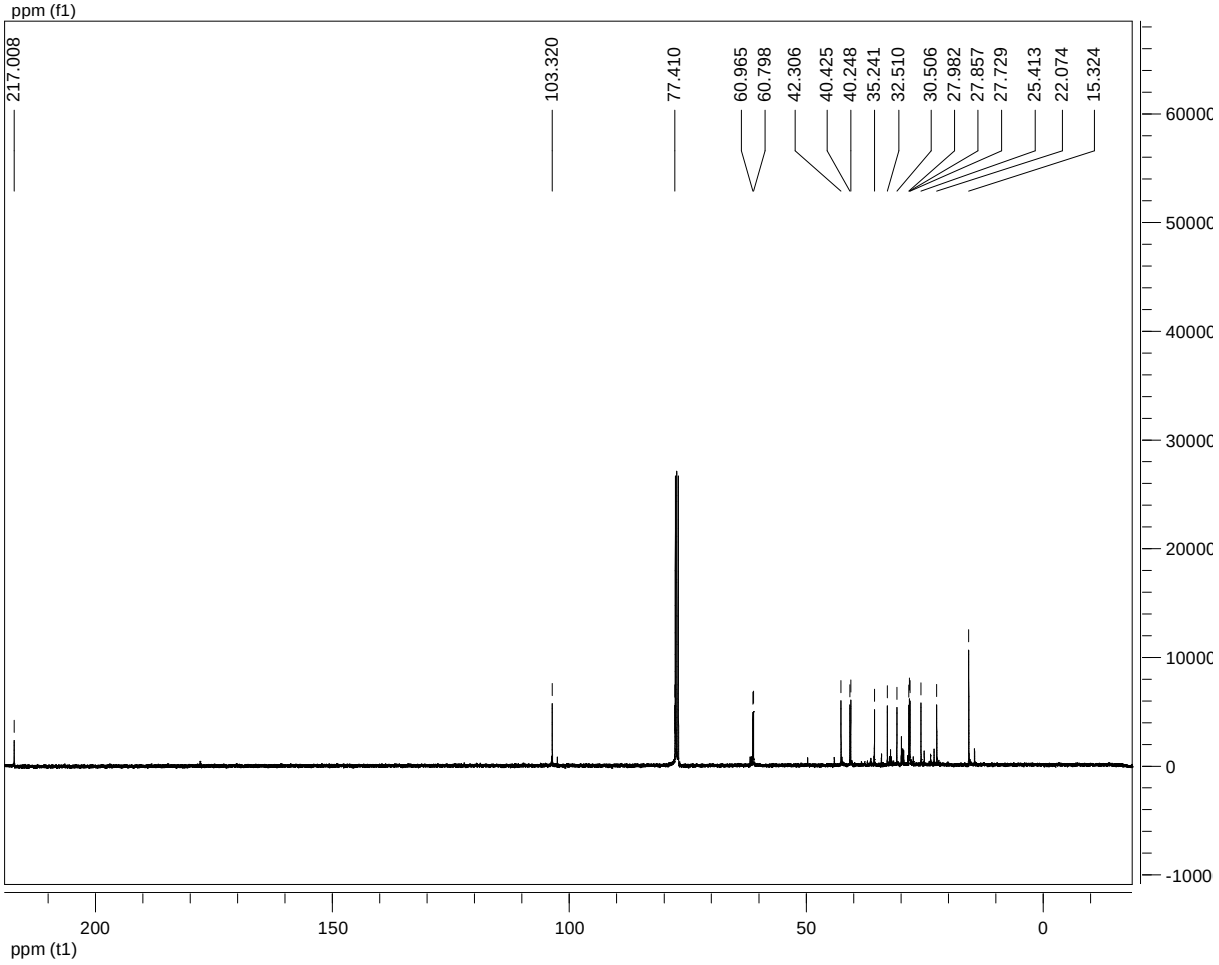
Compound **41a**



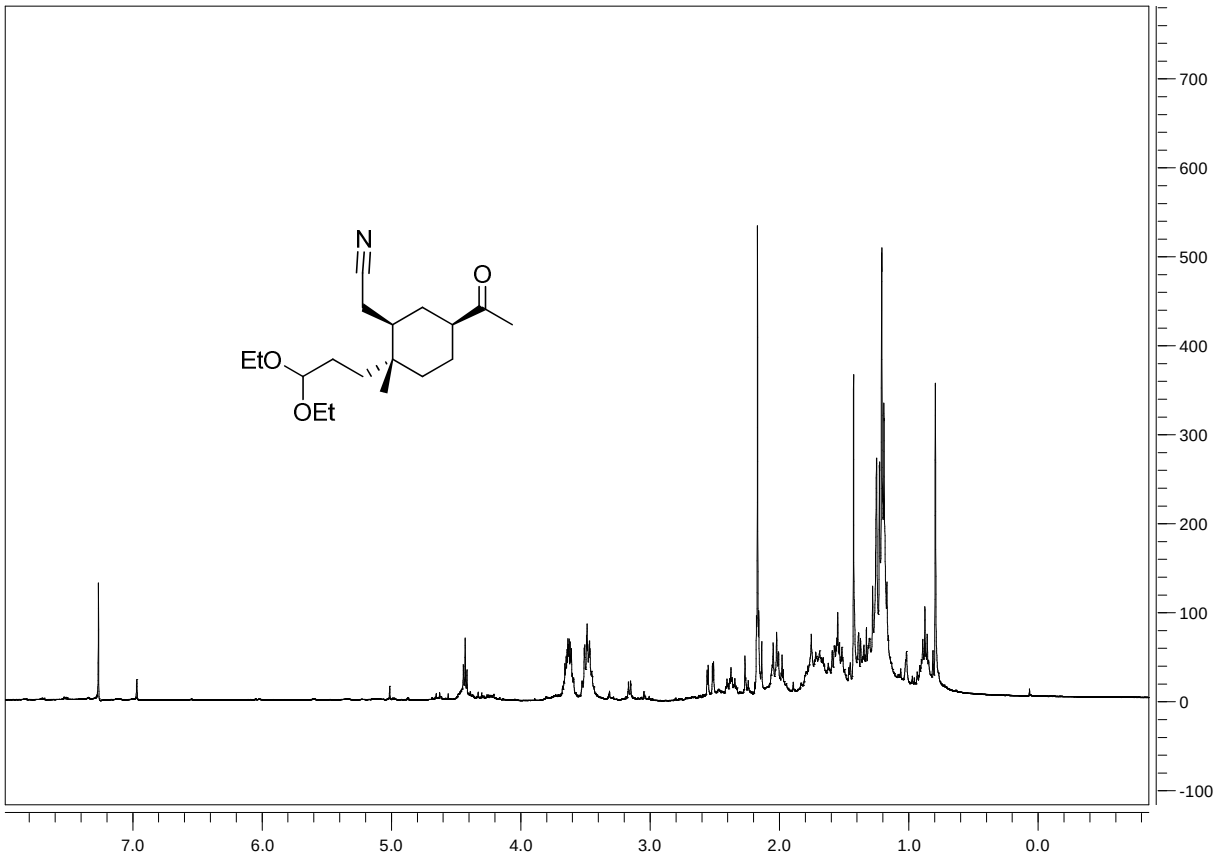


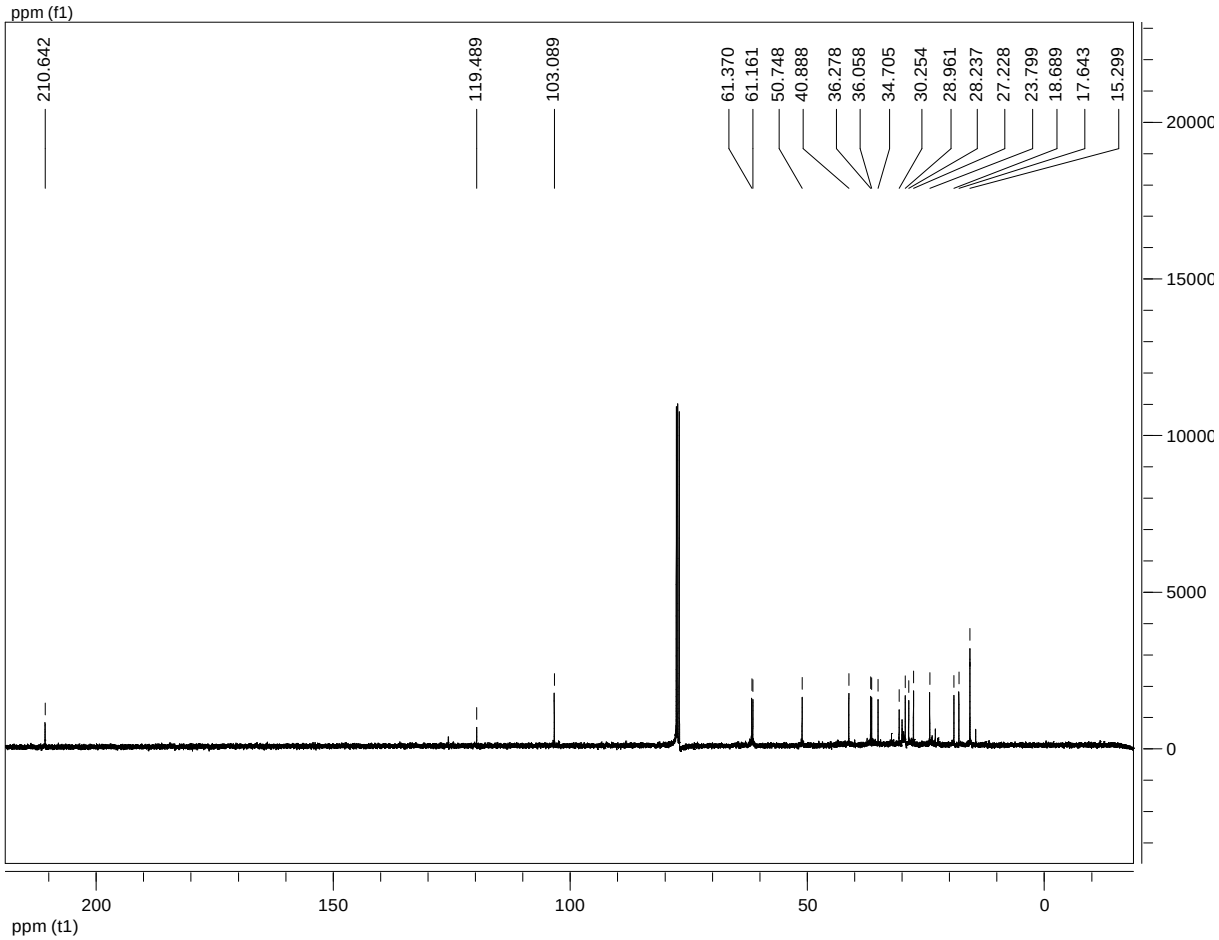
Compound **41b**



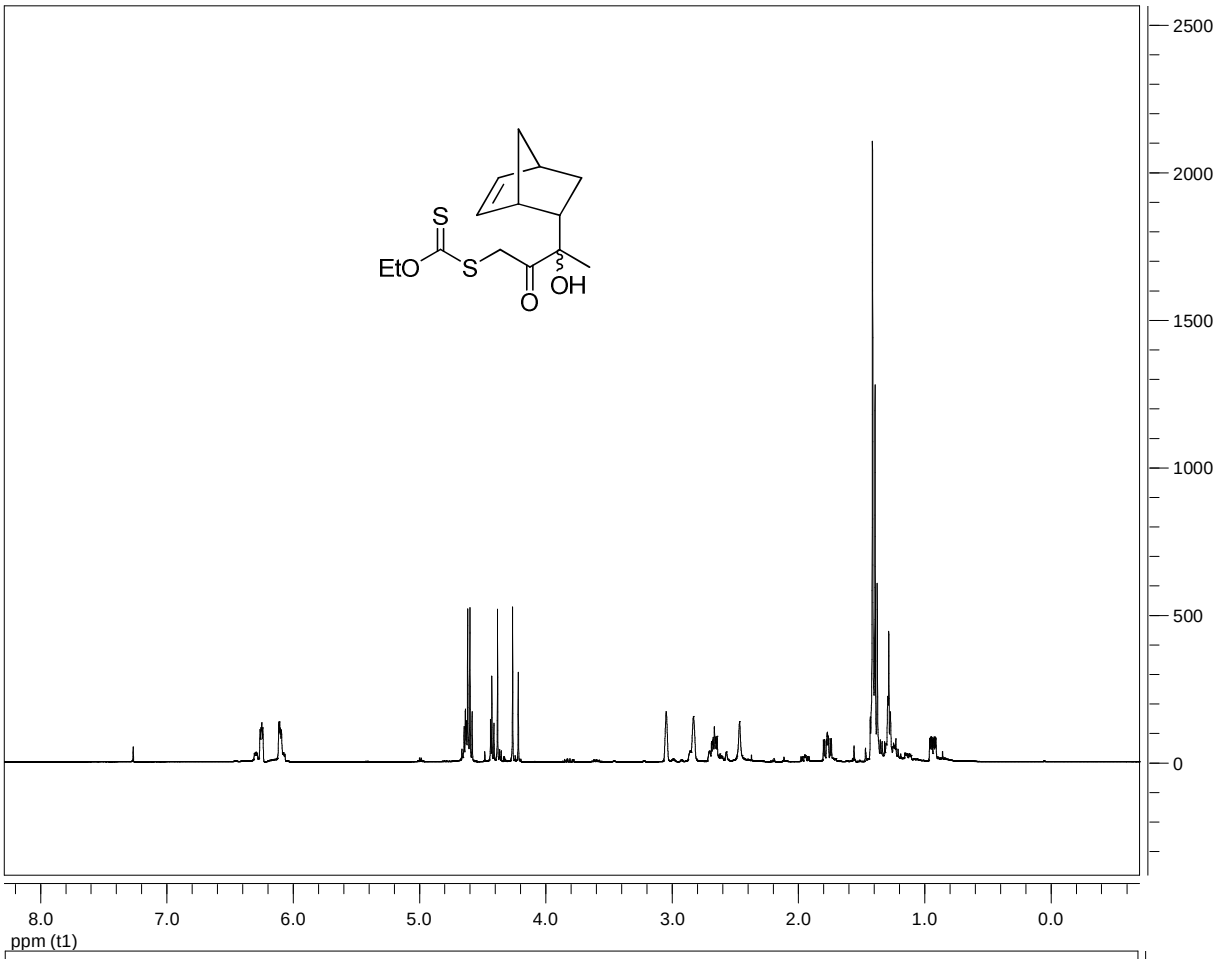


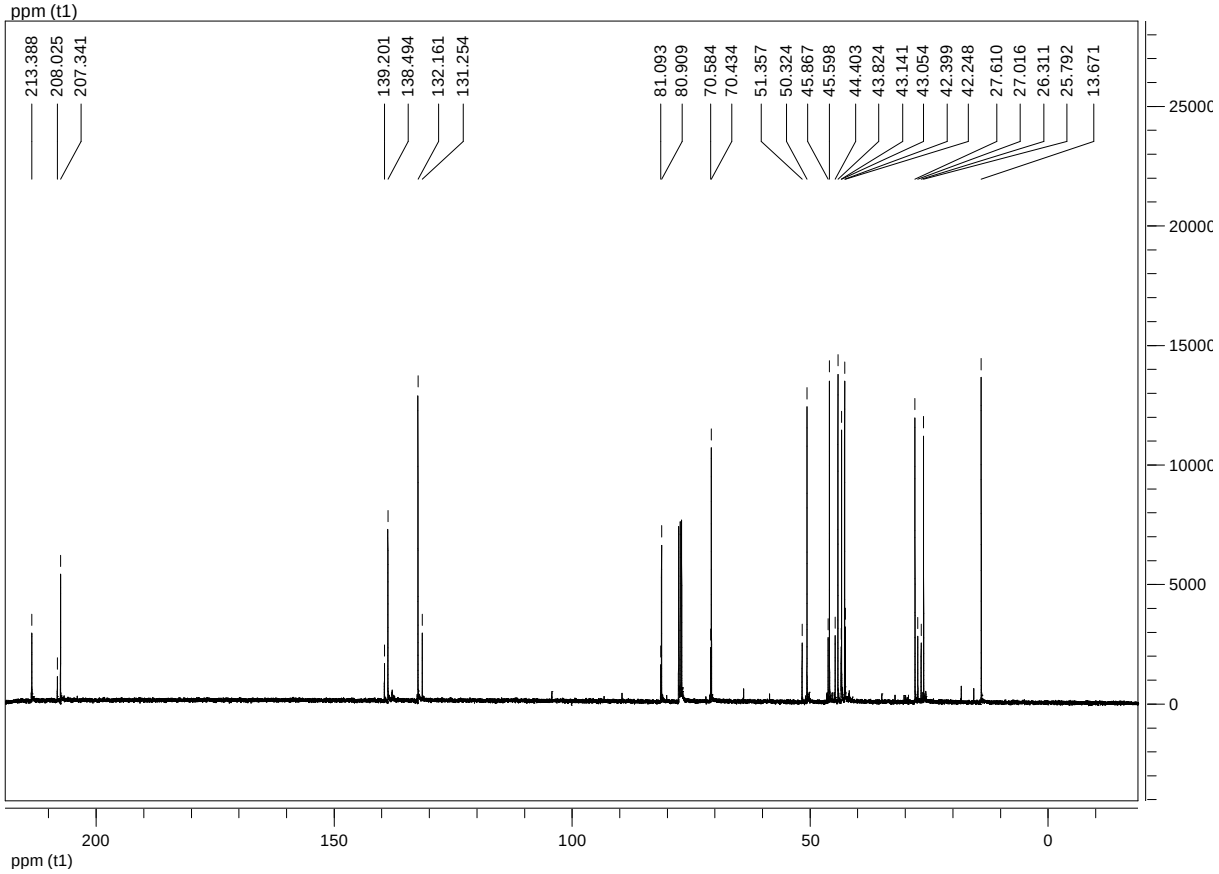
Compound **42**


N
O
EtO
OEt
700
600
500
400
300
200
100
0
-100
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

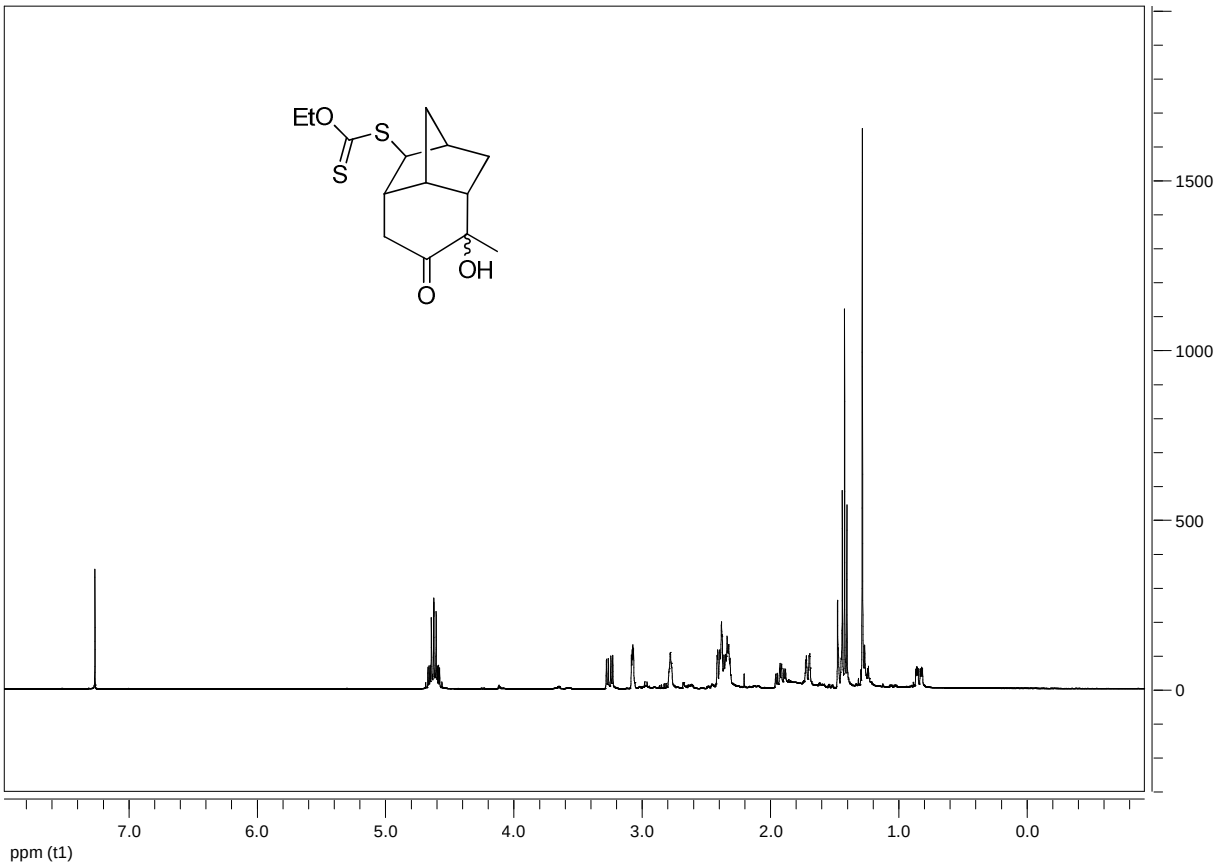

210.642
119.489
103.089
61.370
61.161
50.748
40.888
36.278
36.058
34.705
30.254
28.961
28.237
27.228
23.799
18.689
17.643
15.299
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

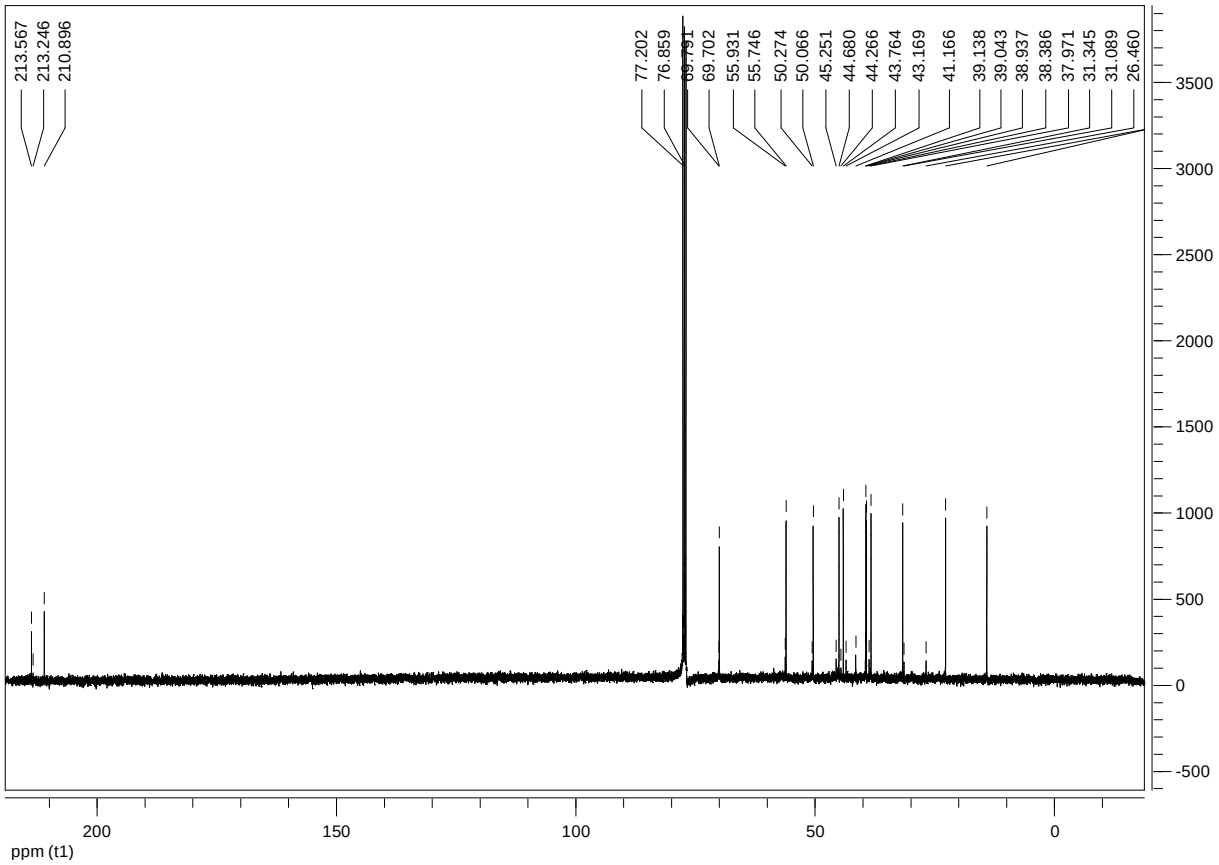
Compound **46b**



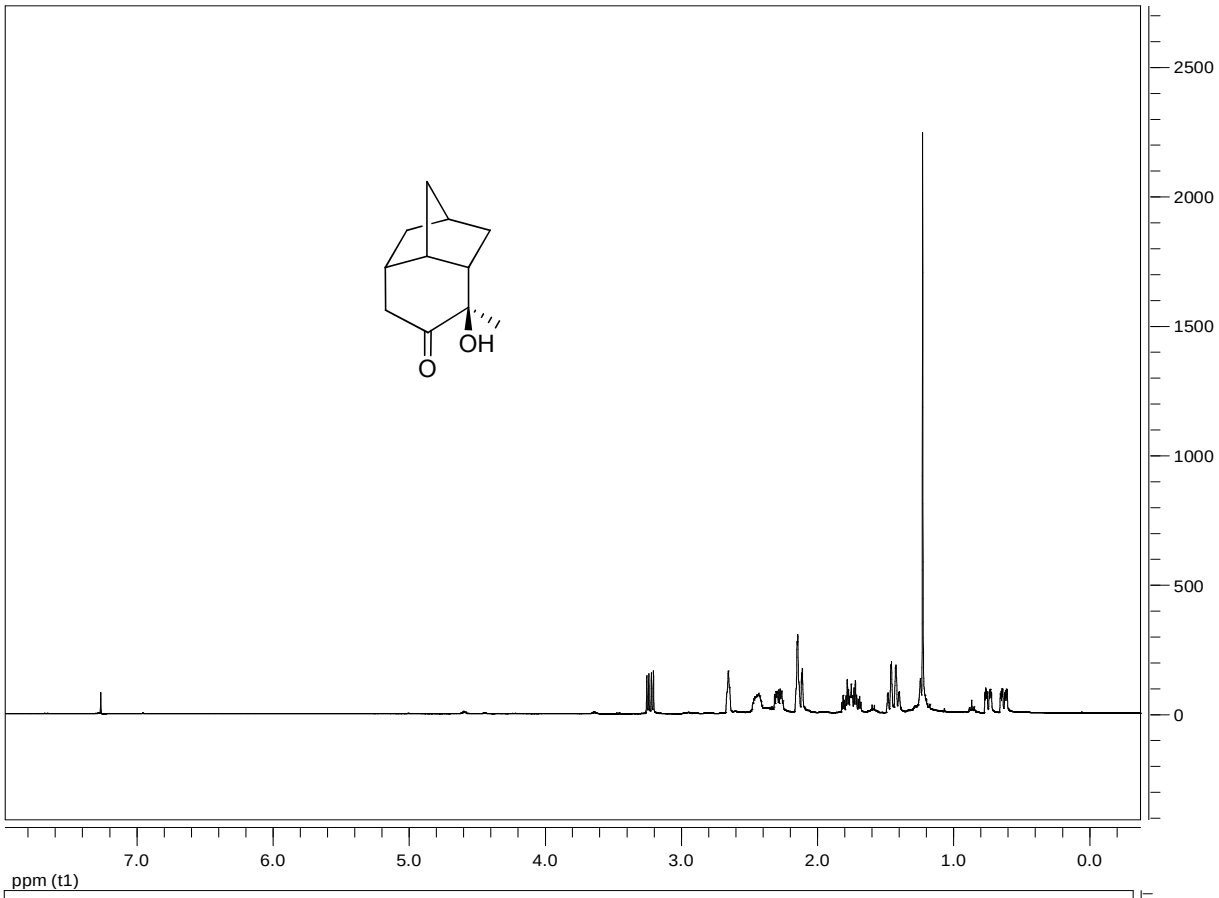


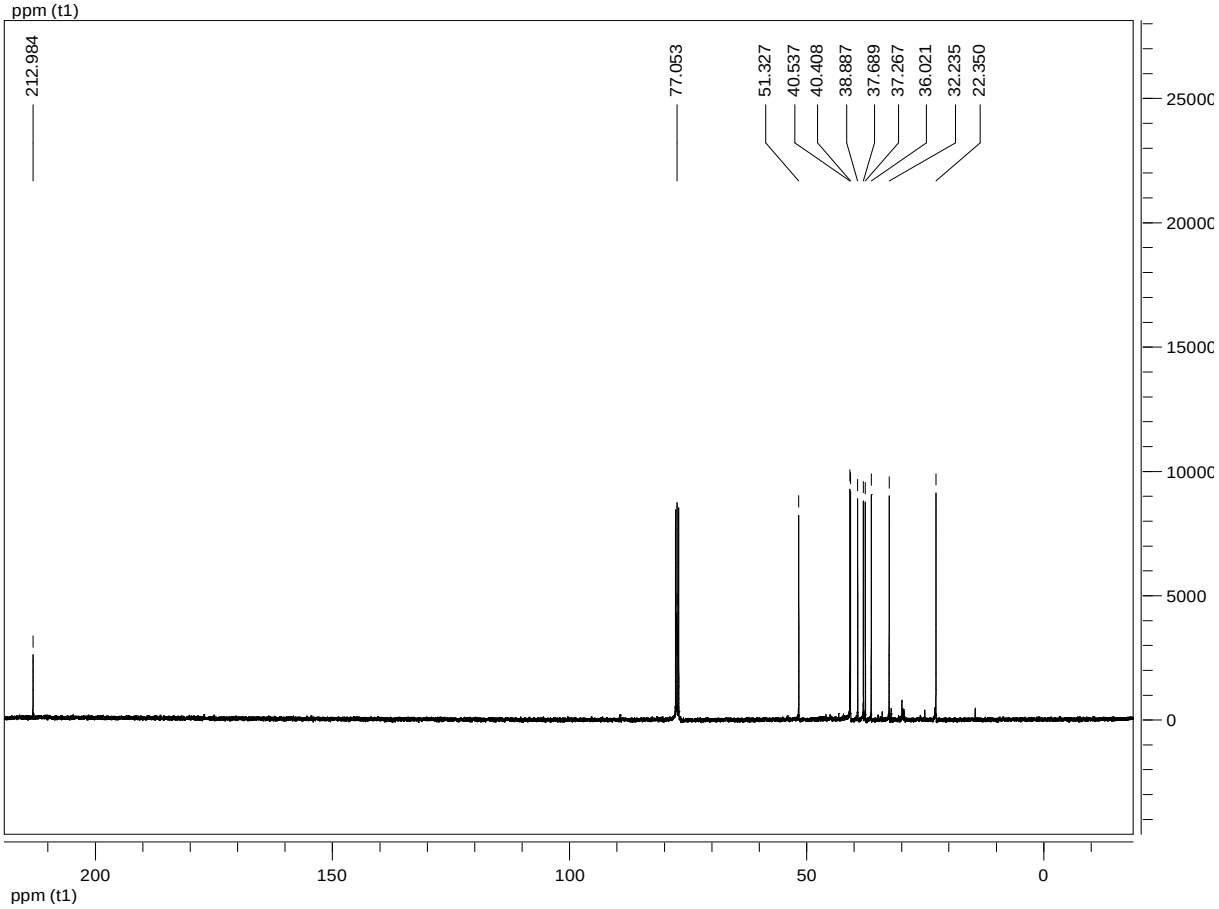
Compound **47a,b**



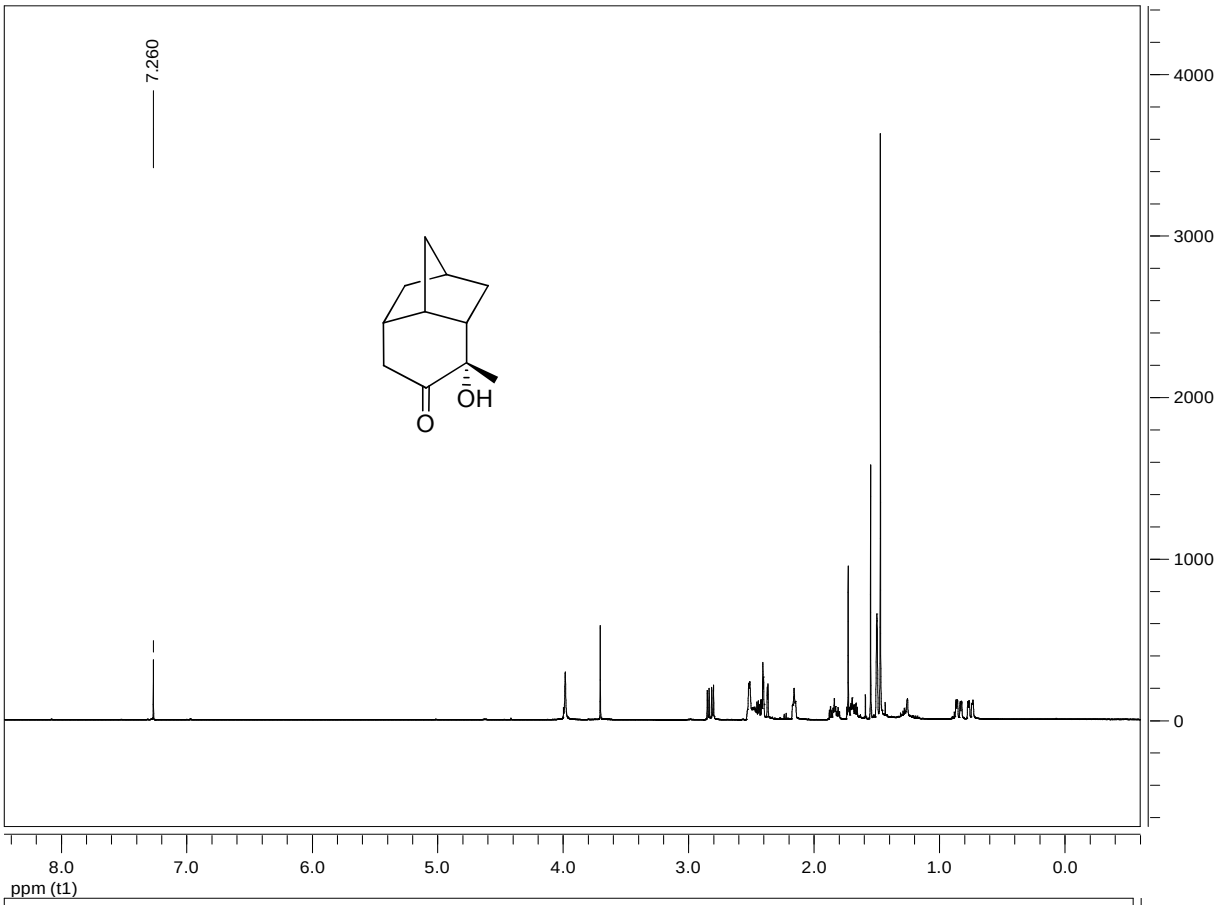


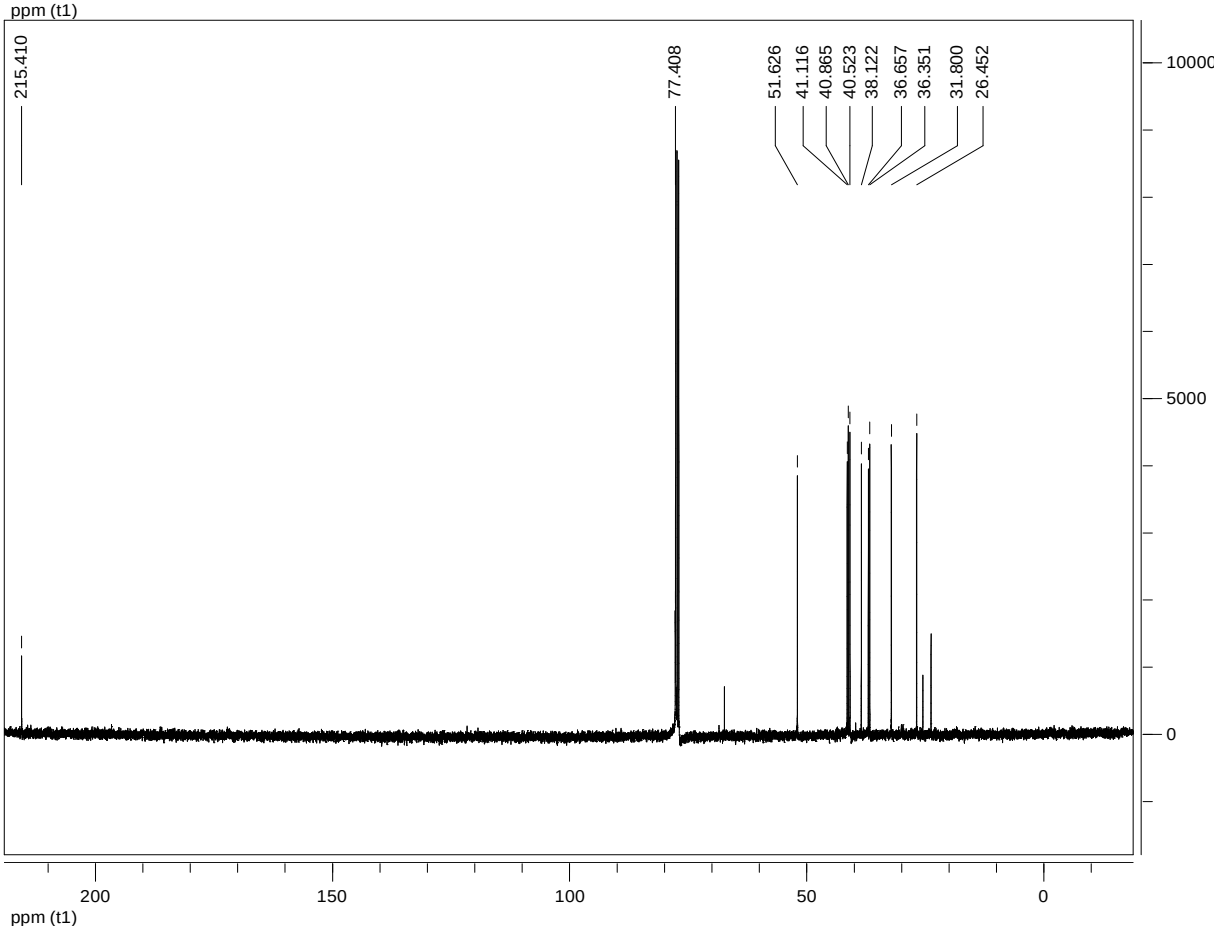
Compound **48a**



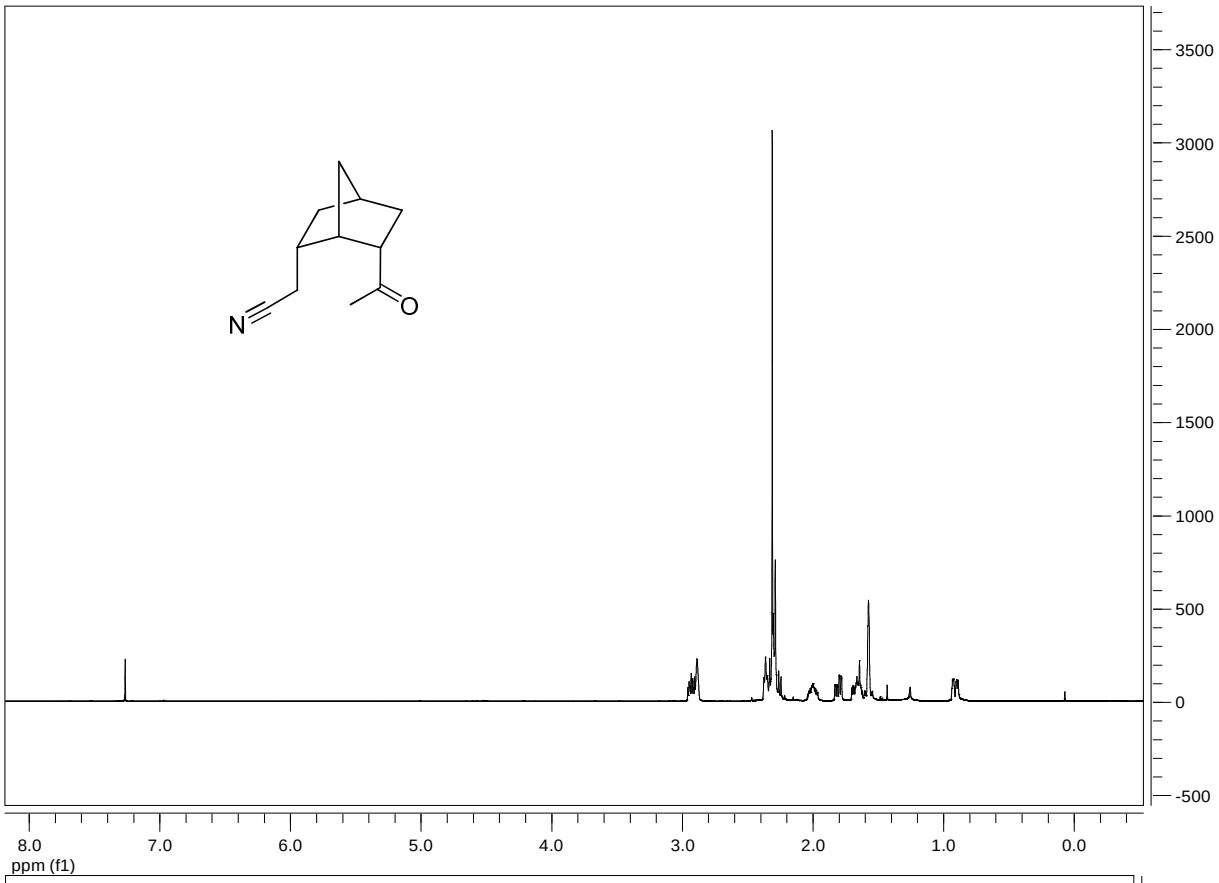


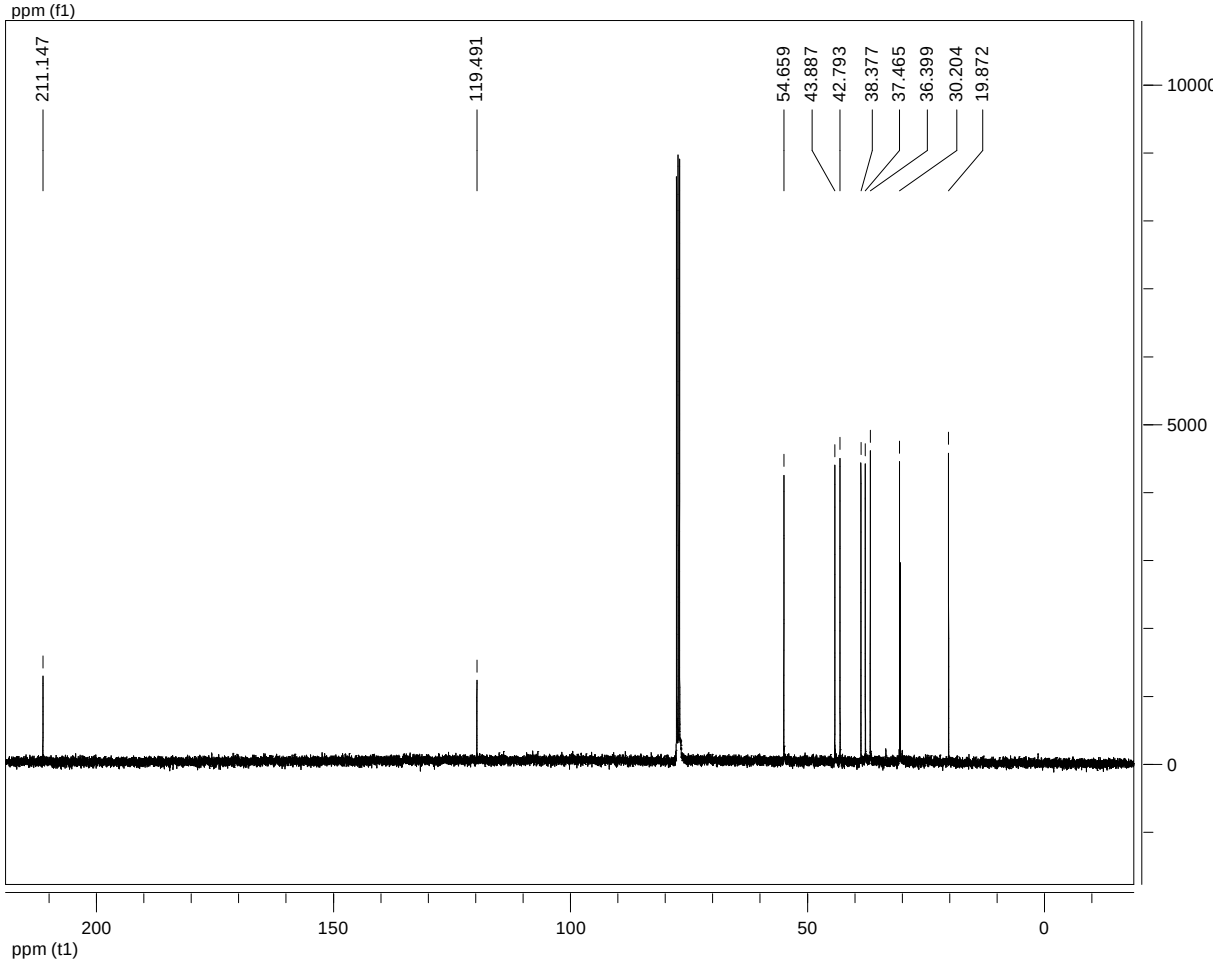
Compound **48b**



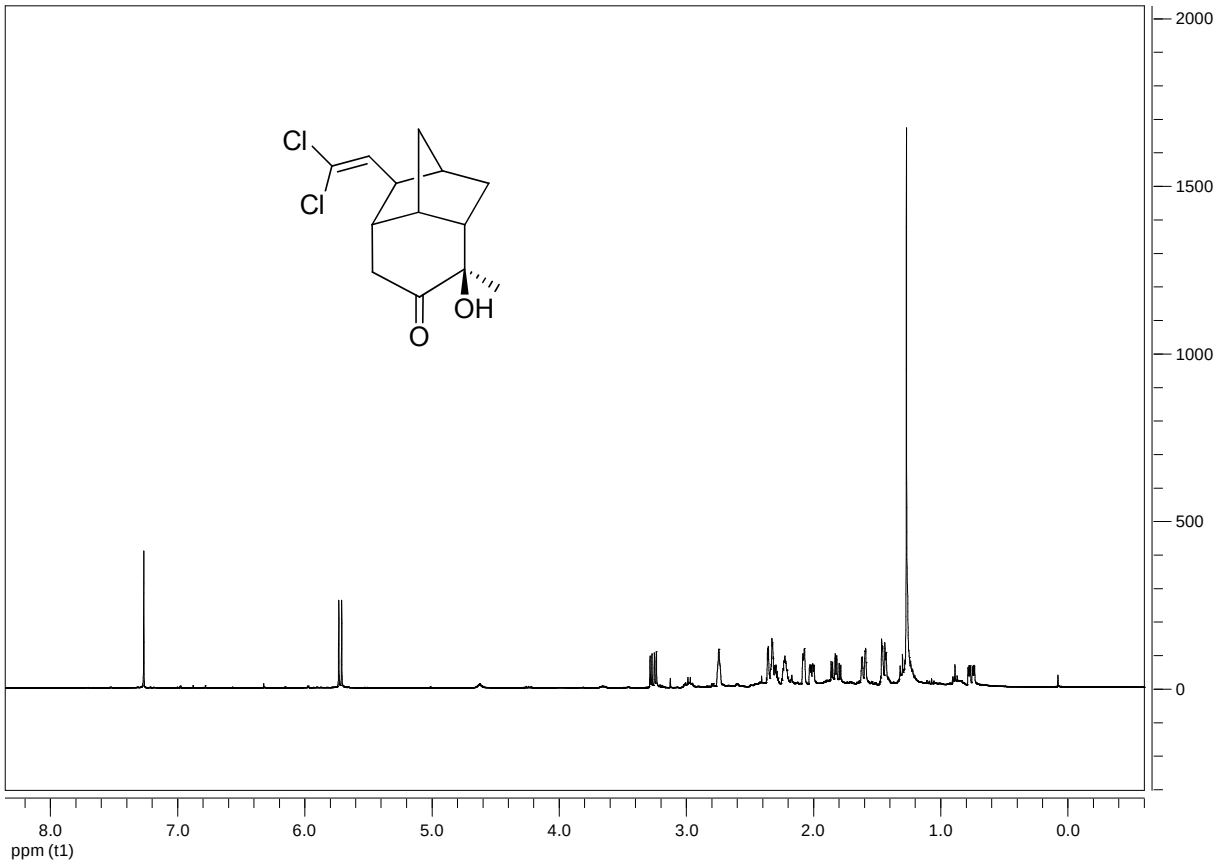


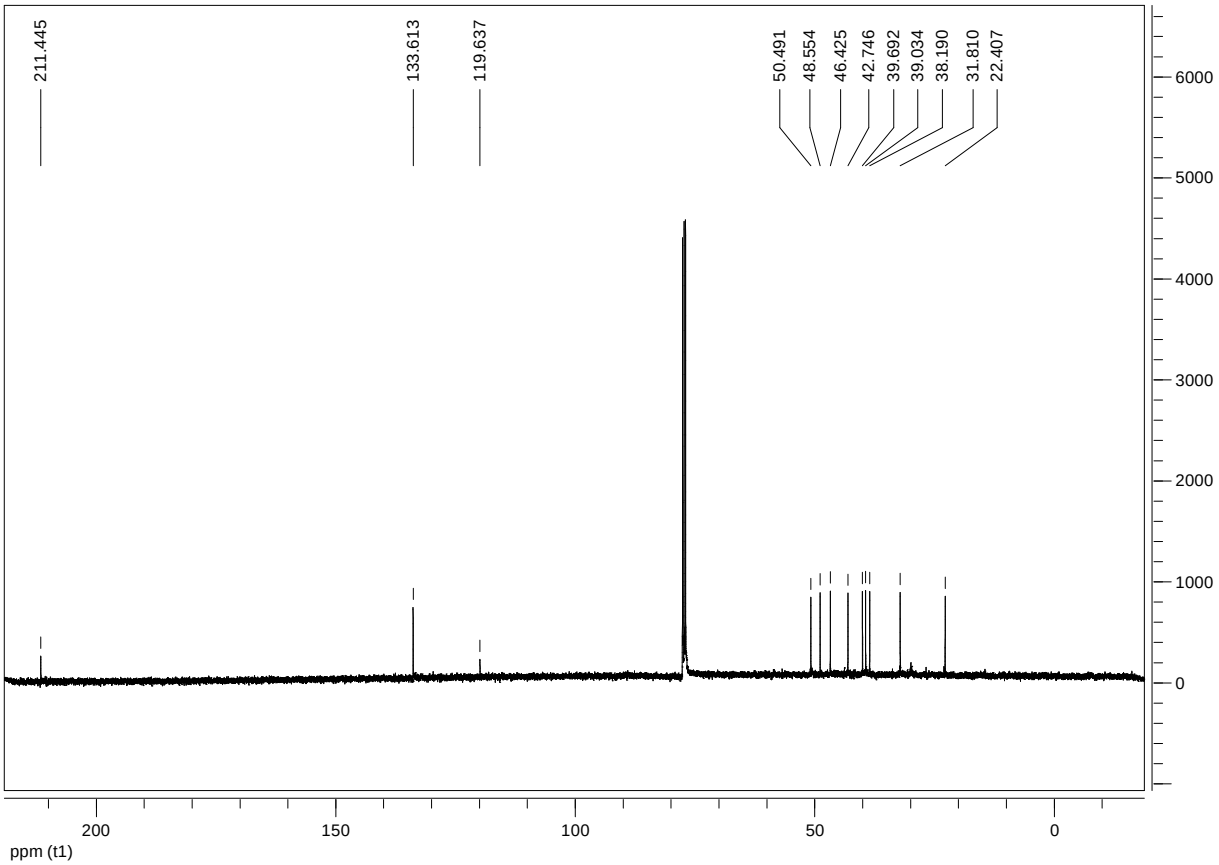
Compound **49**


N
O
3500
3000
2500
2000
1500
1000
500
0
-500
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

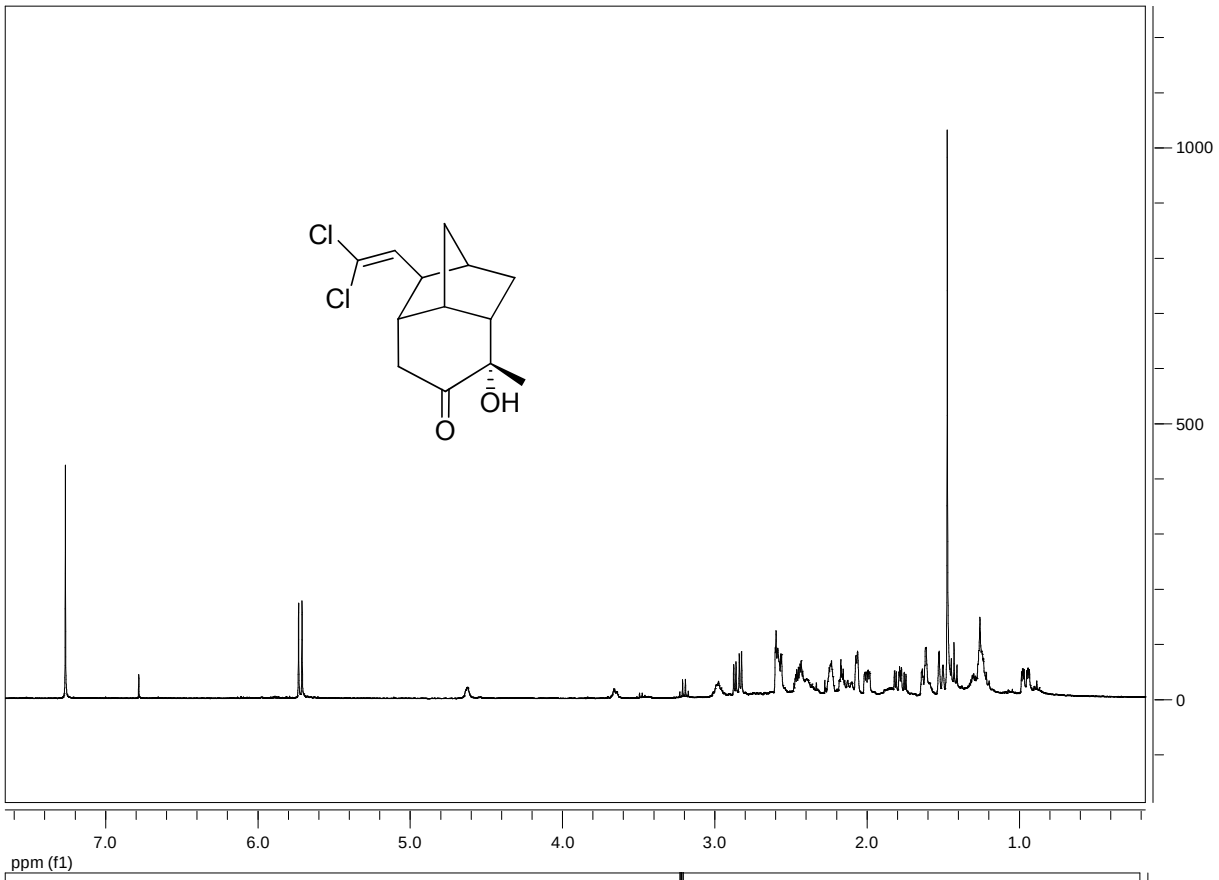

211.147
119.491
54.659
43.887
42.793
38.377
37.465
36.399
30.204
19.872
10000
5000
0
200
150
100
50
0
ppm (t1)

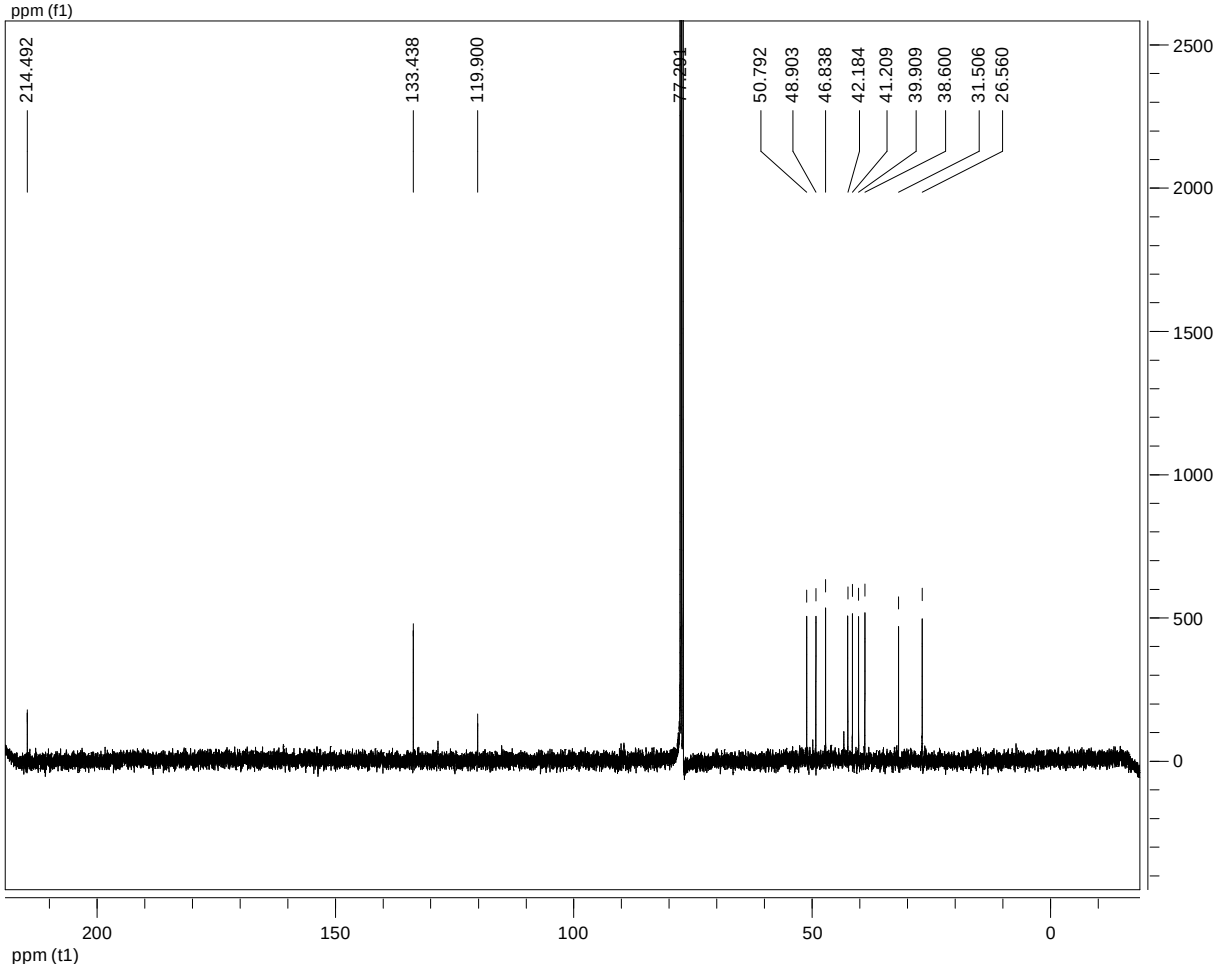
Compound **50a**



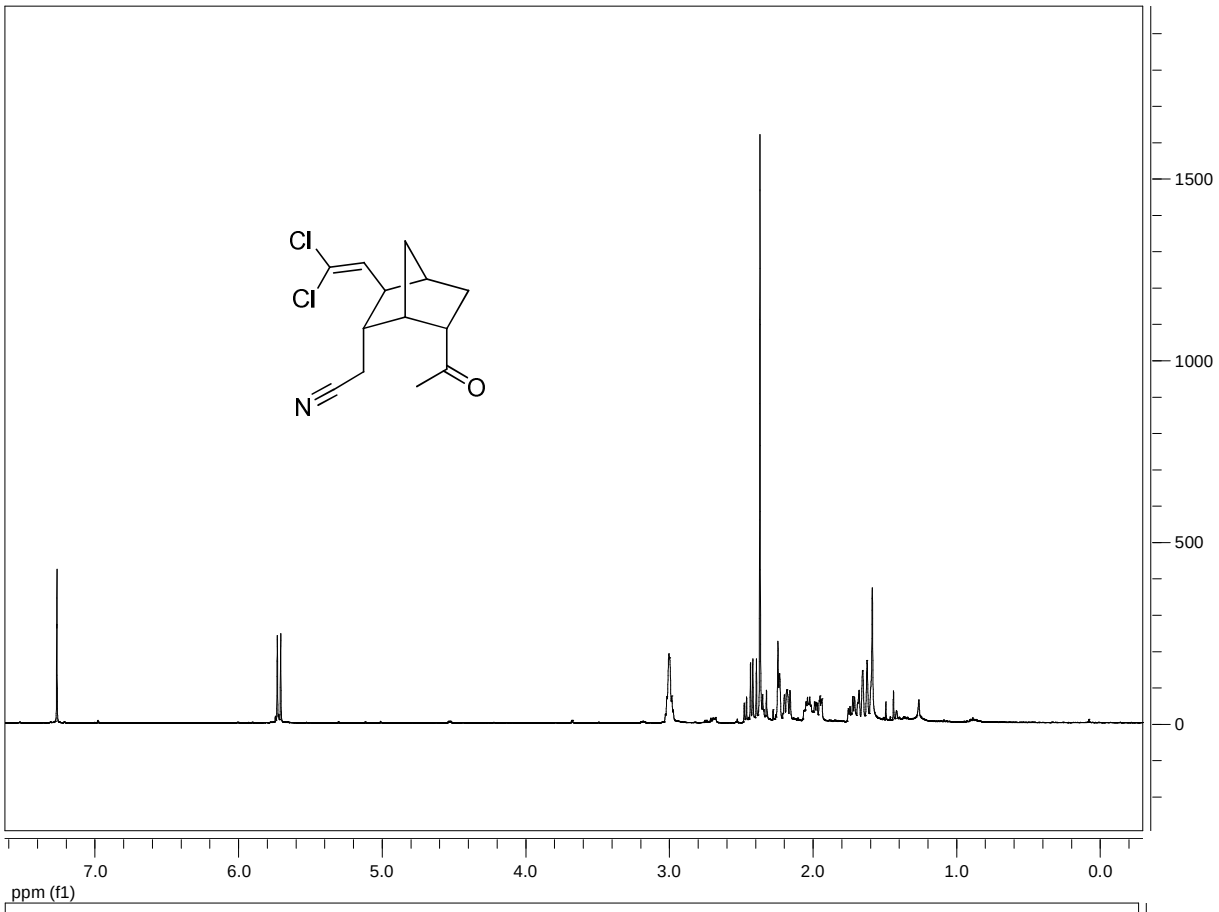


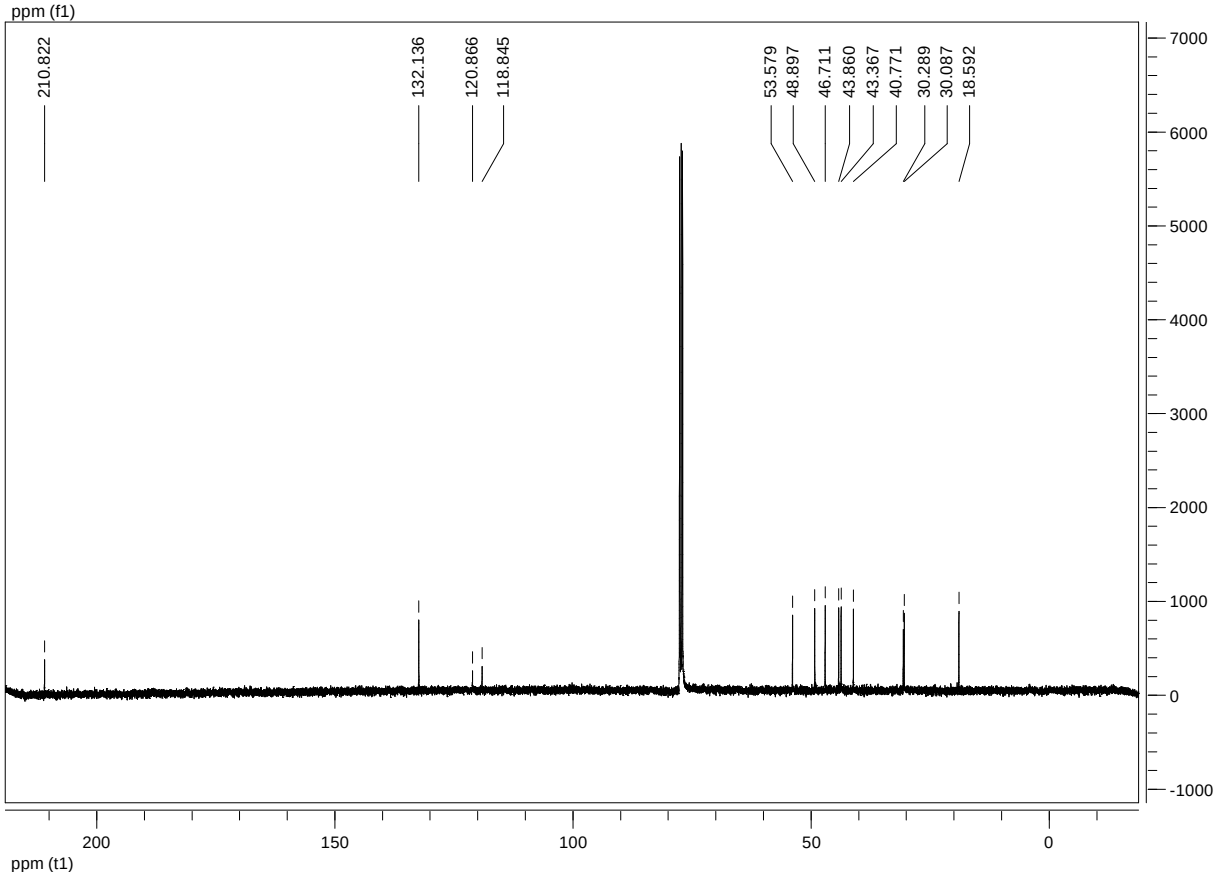
Compound **50b**



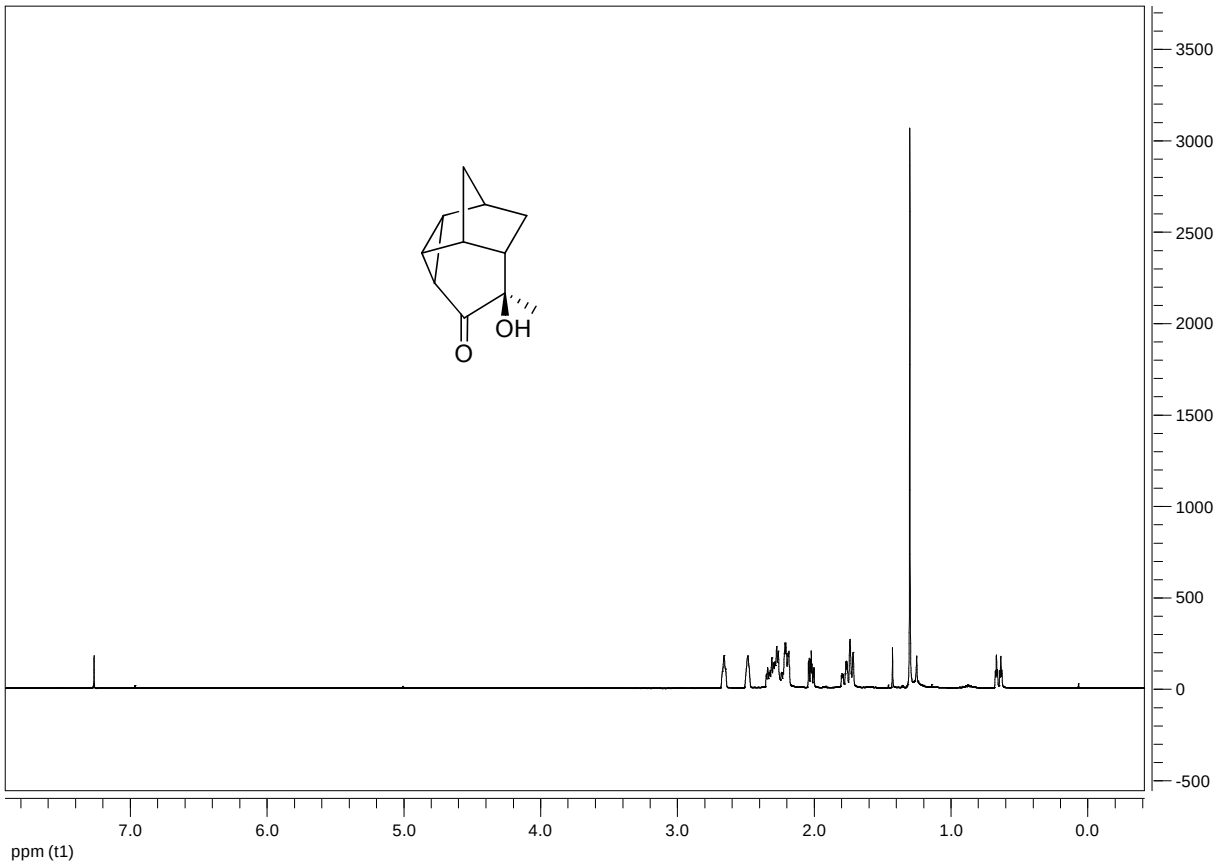


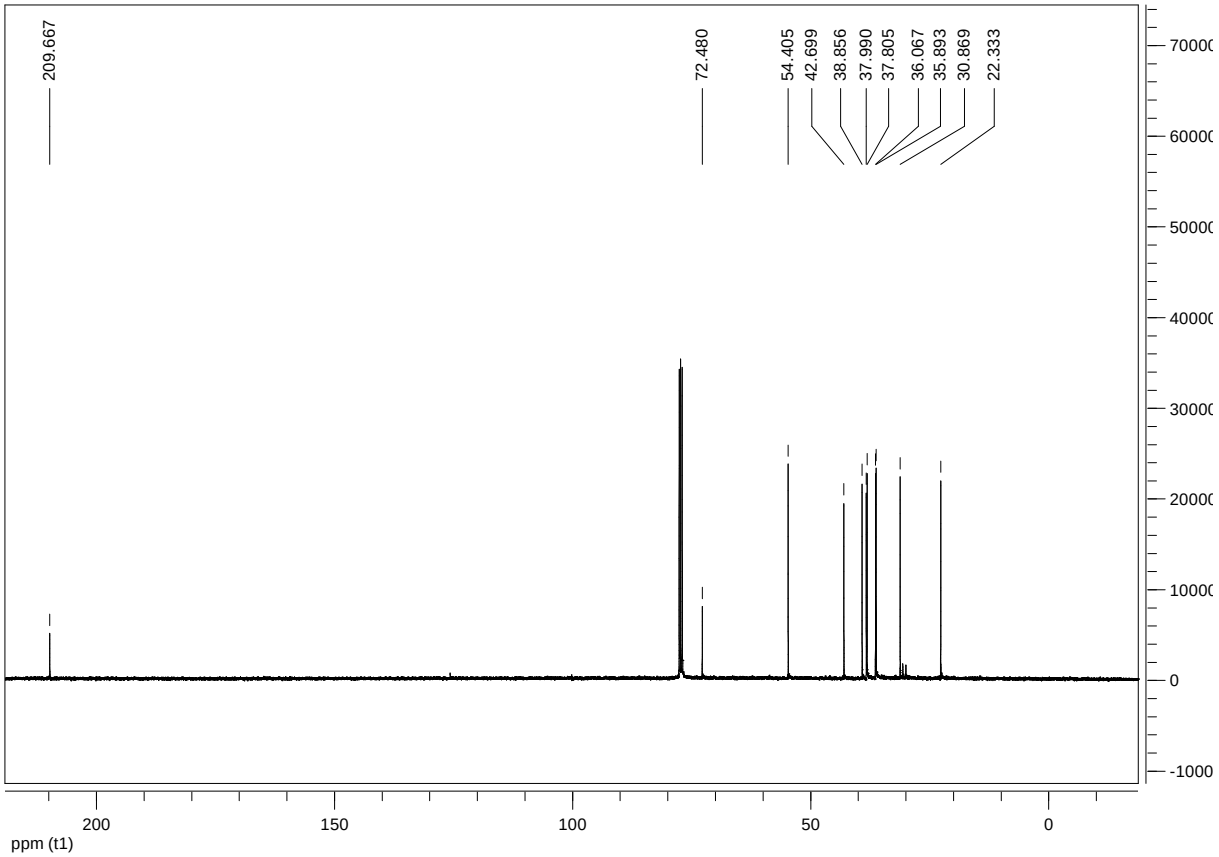
Compound **51**


Cl
Cl
N
O
1500
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

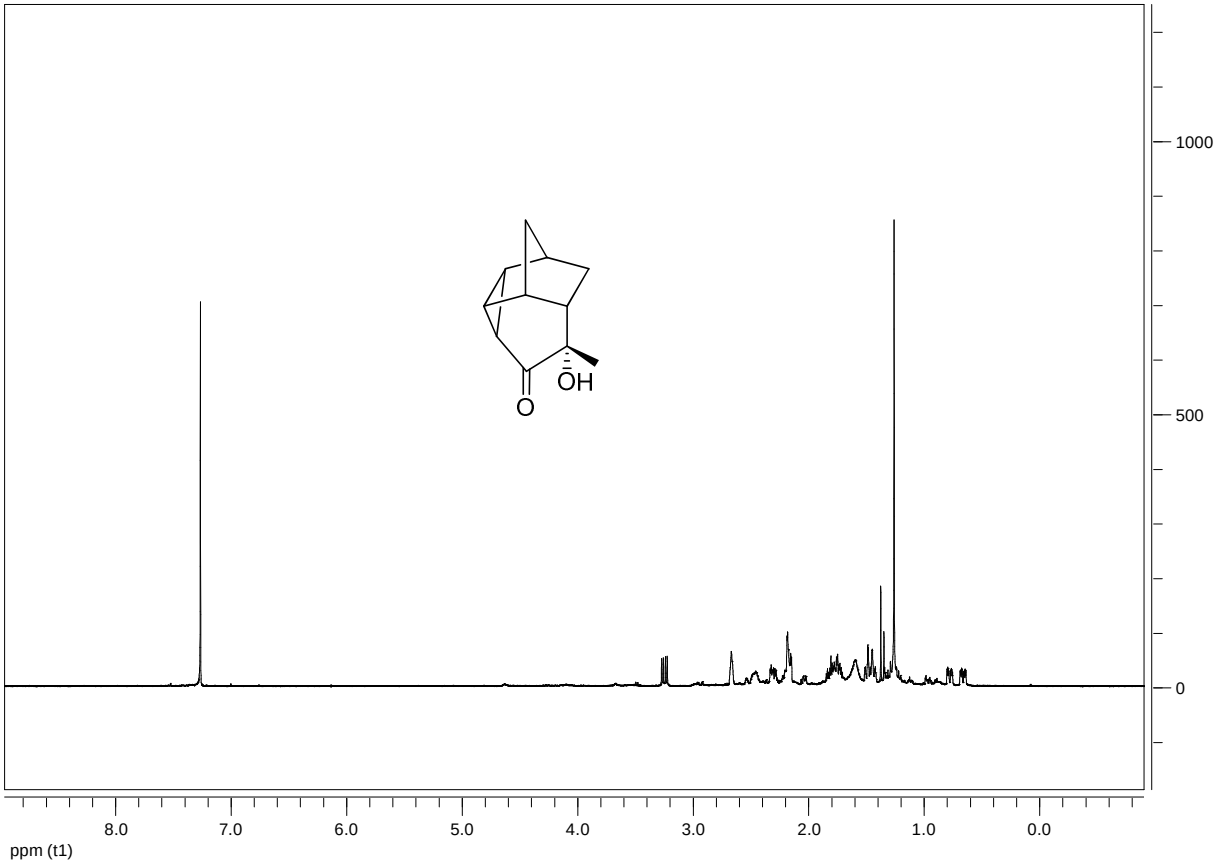

210.822
132.136
120.866
118.845
53.579
48.897
46.711
43.860
43.367
40.771
30.289
30.087
18.592
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
150
100
50
0
ppm (t1)

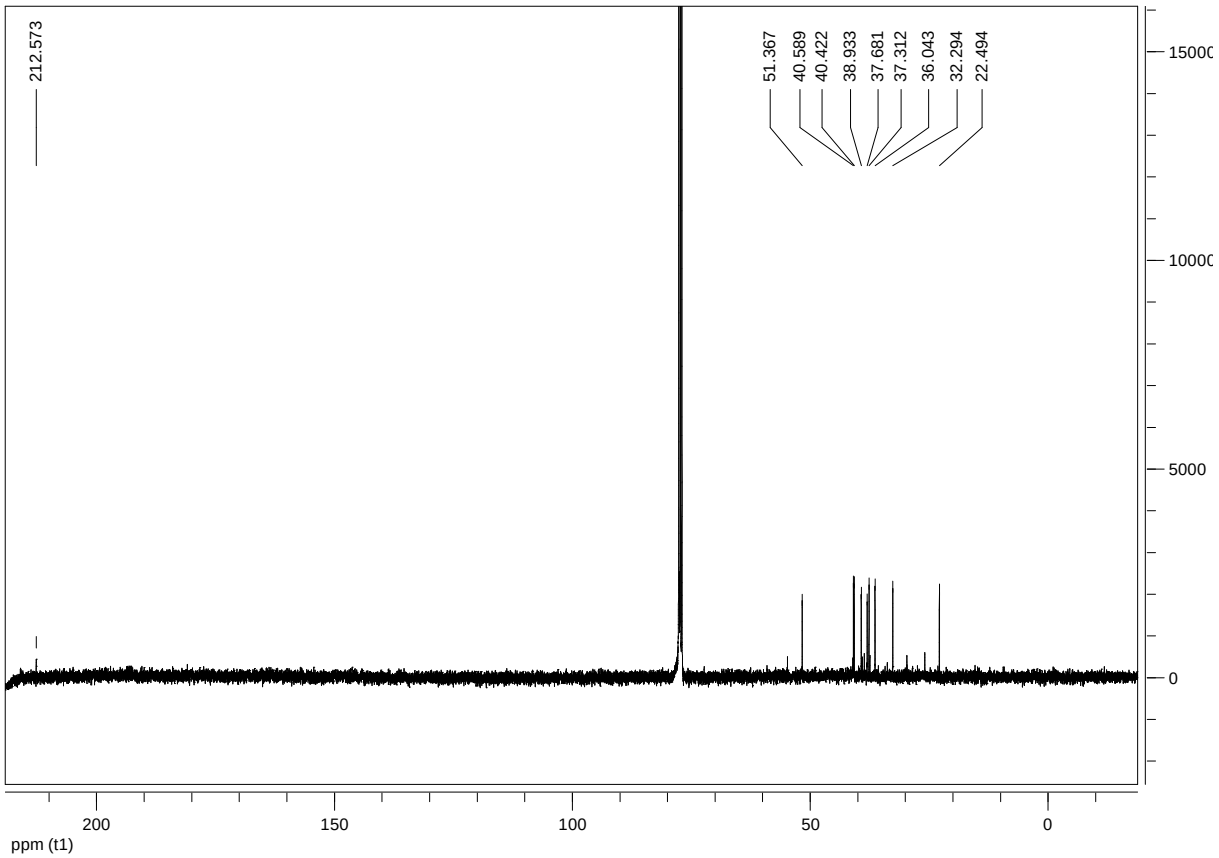
Compound **53a**



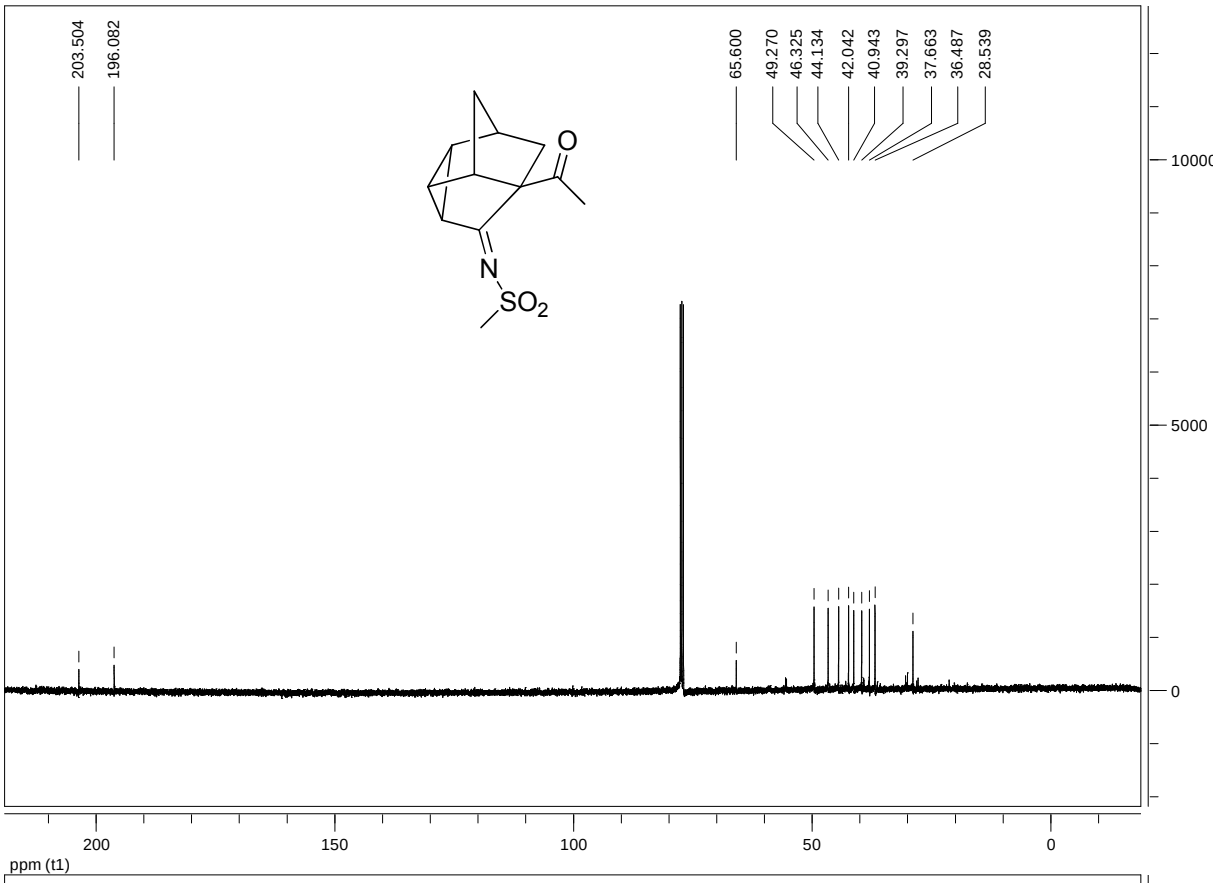


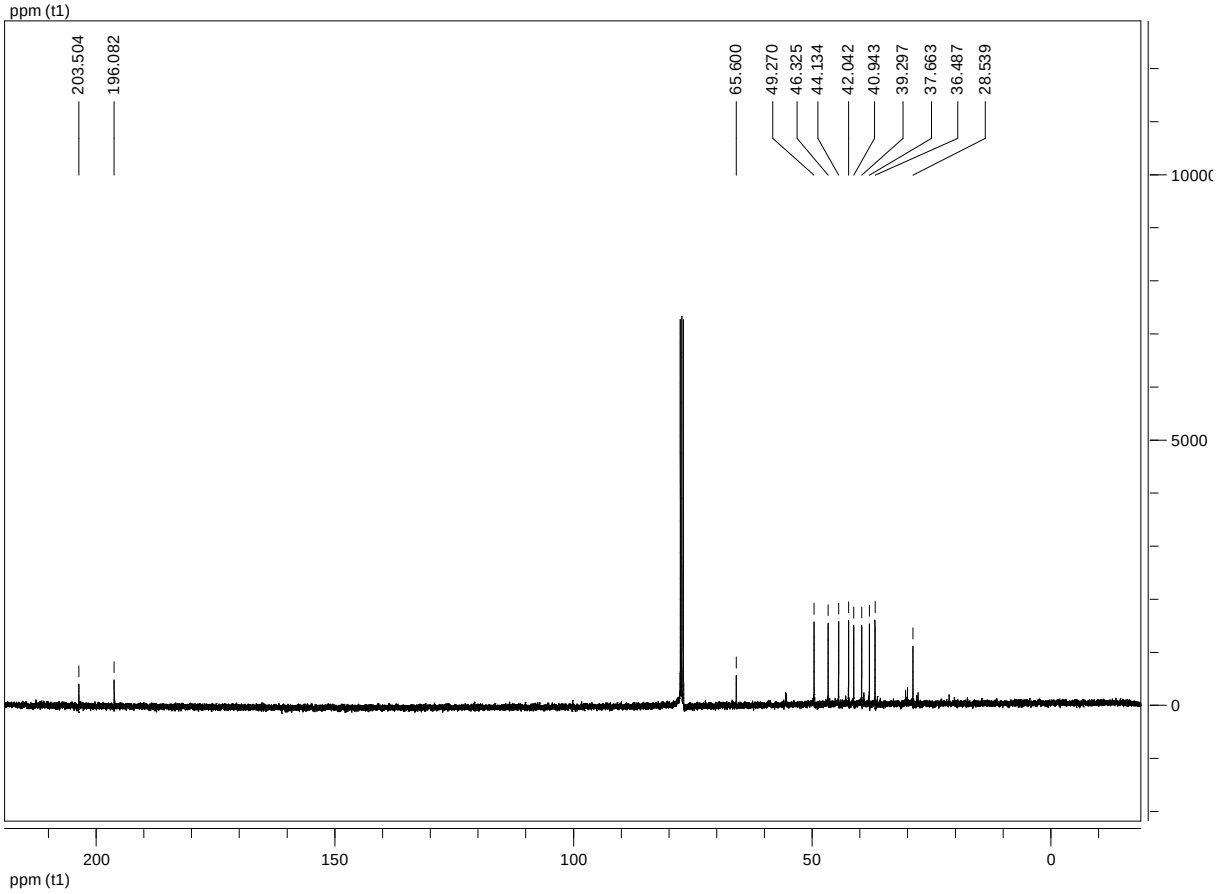
Compound **53b**



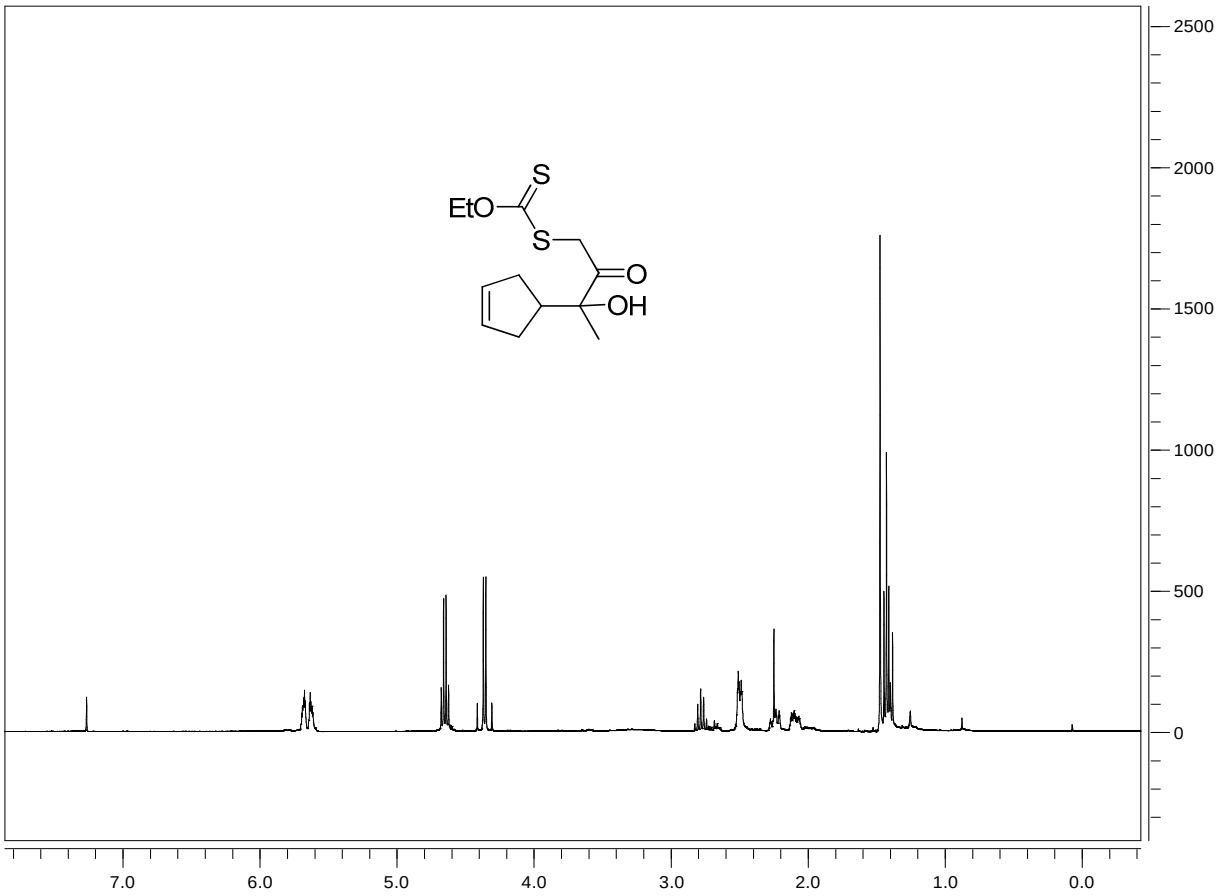


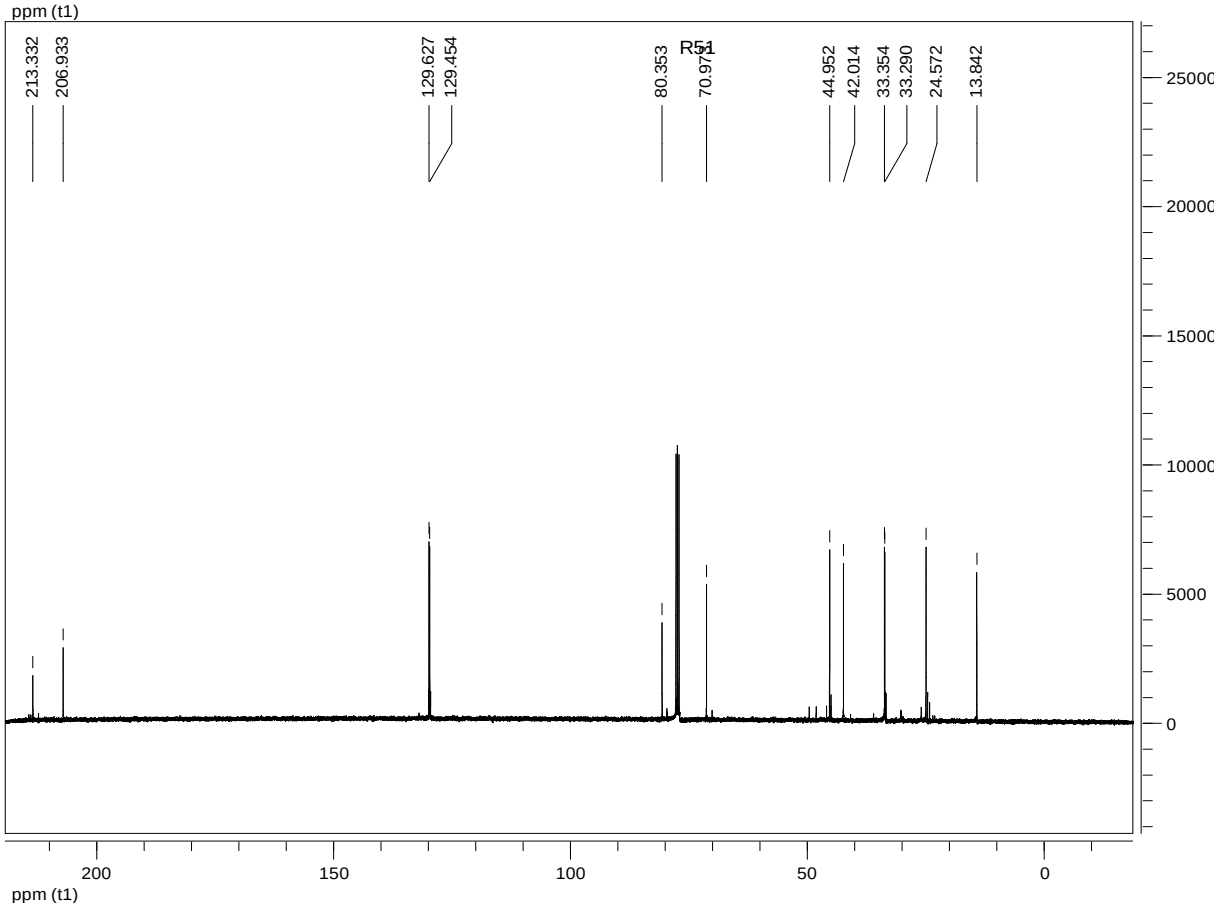
Compound **54**


203.504
196.082
65.600
49.270
46.325
44.134
42.042
40.943
39.297
37.663
36.487
28.539
O
N
SO2
10000
5000
0
200
150
100
50
0
ppm (t1)

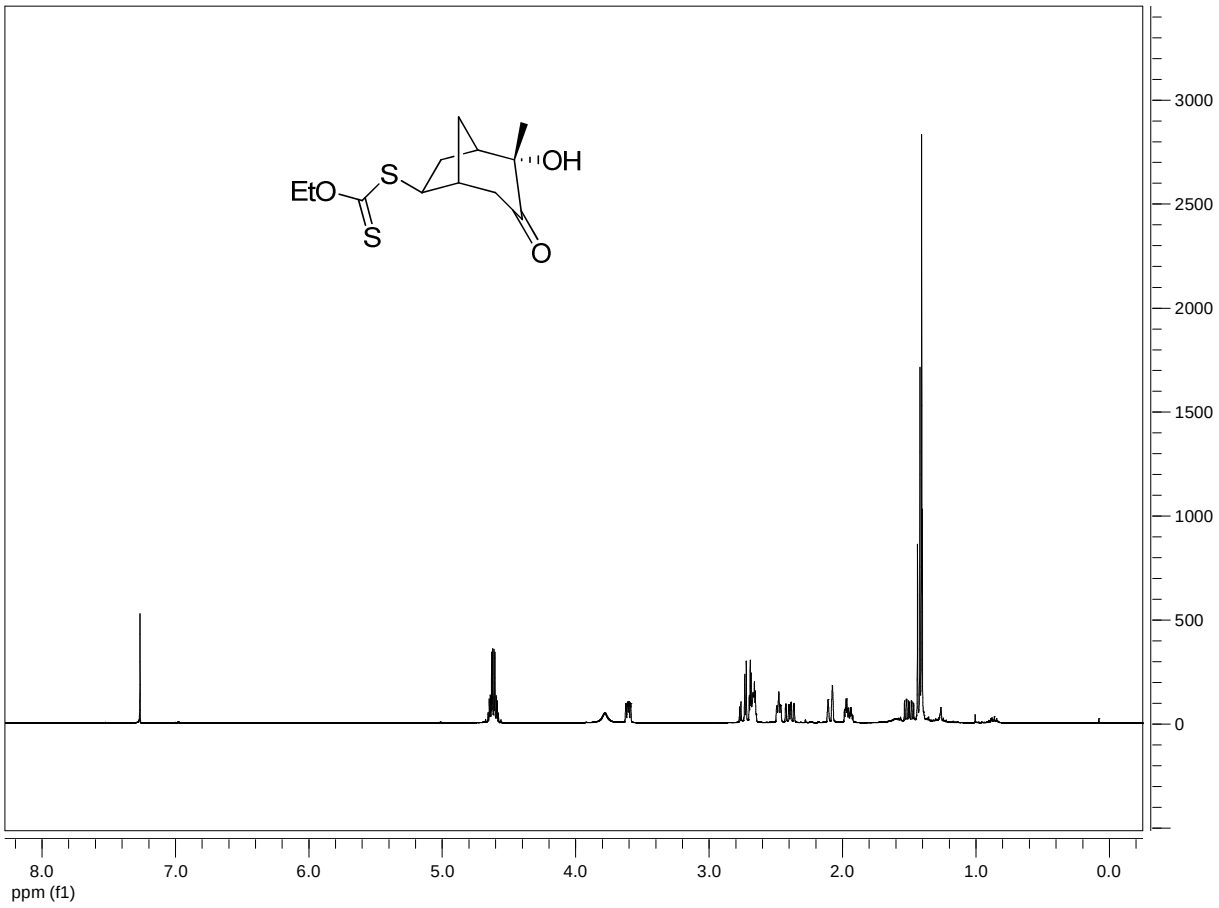

203.504
196.082
65.600
49.270
46.325
44.134
42.042
40.943
39.297
37.663
36.487
28.539
10000
5000
0
200
150
100
50
0
ppm (t1)

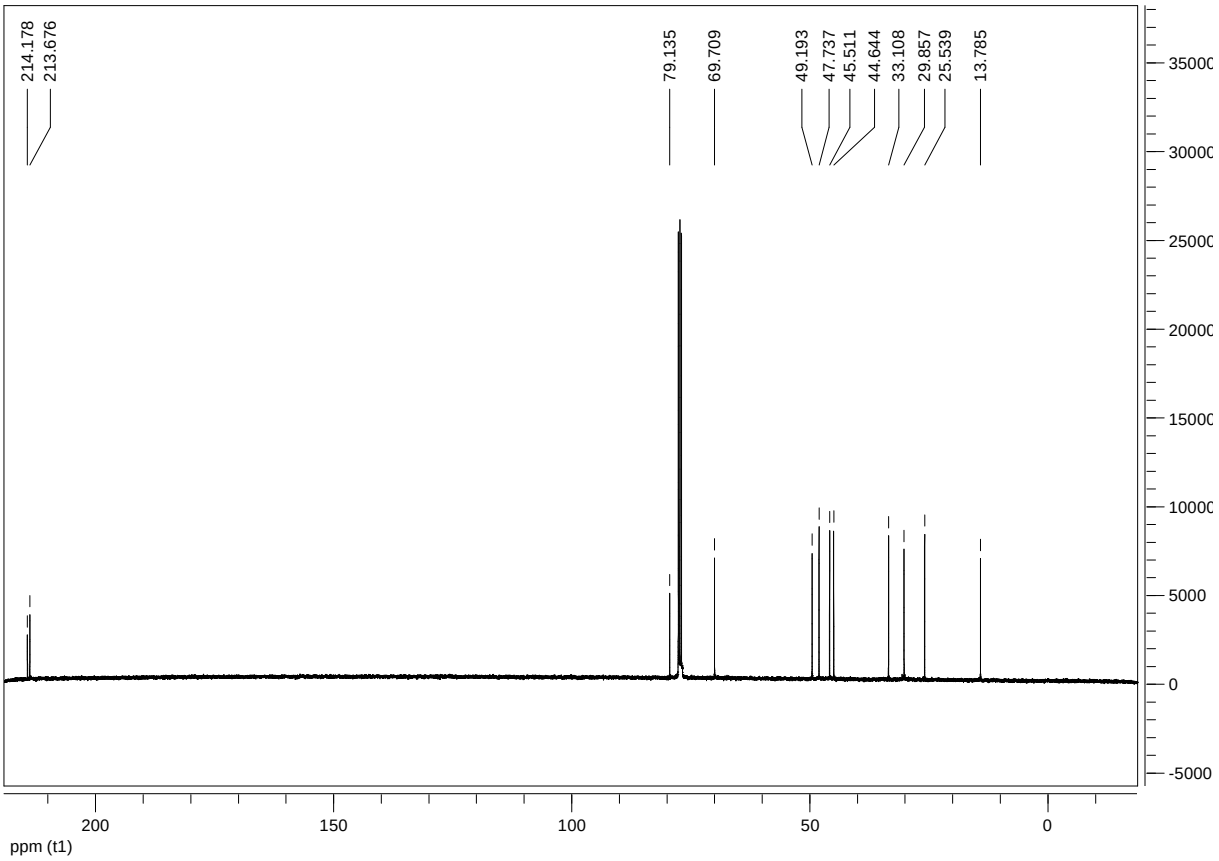
Compound **57b**



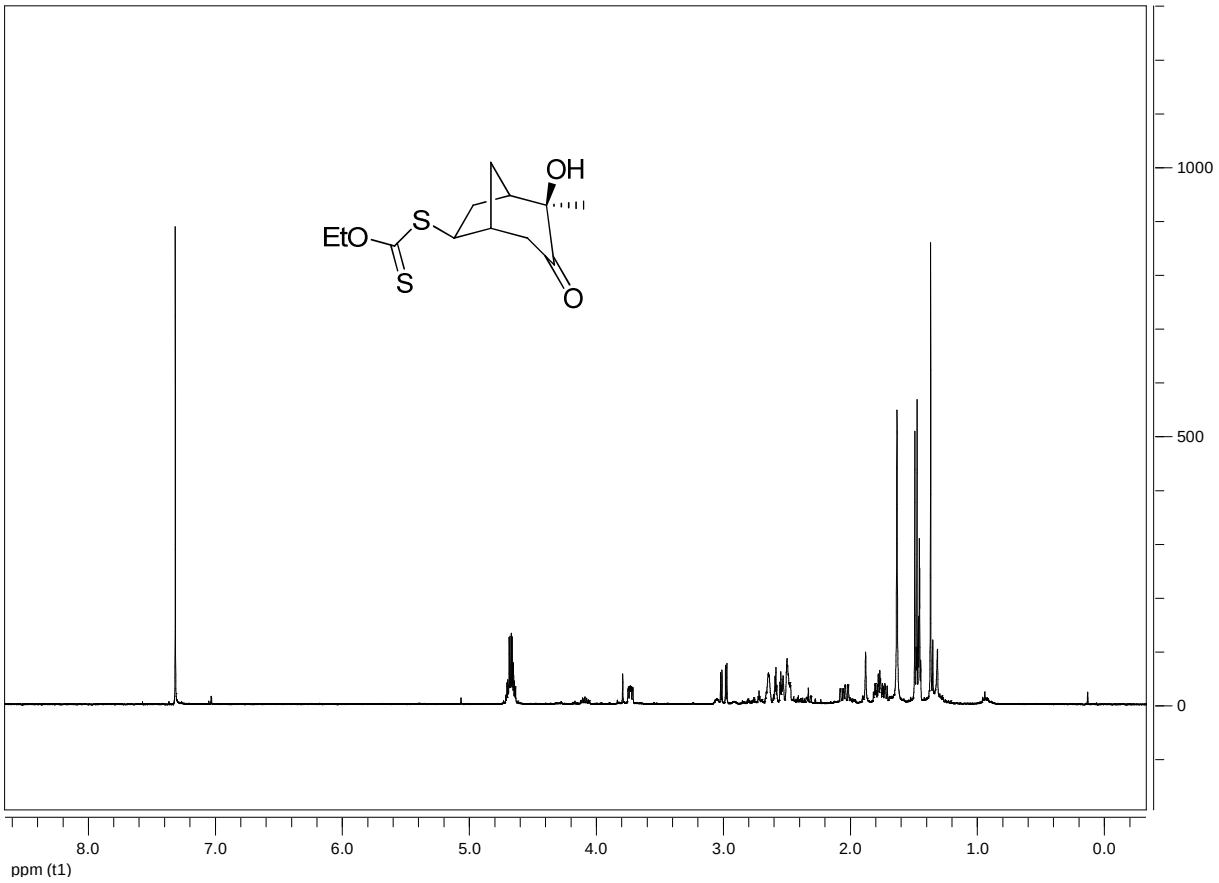


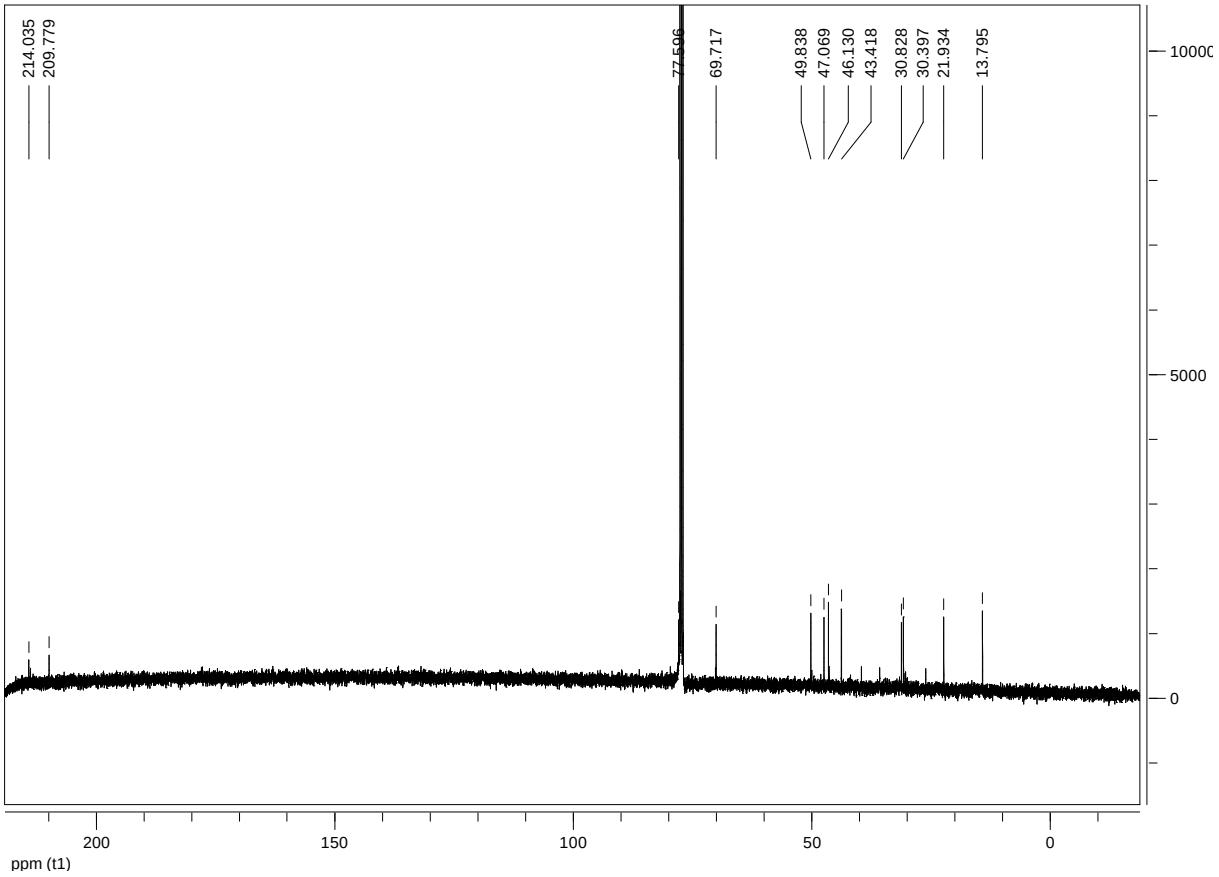
Compound **58a**



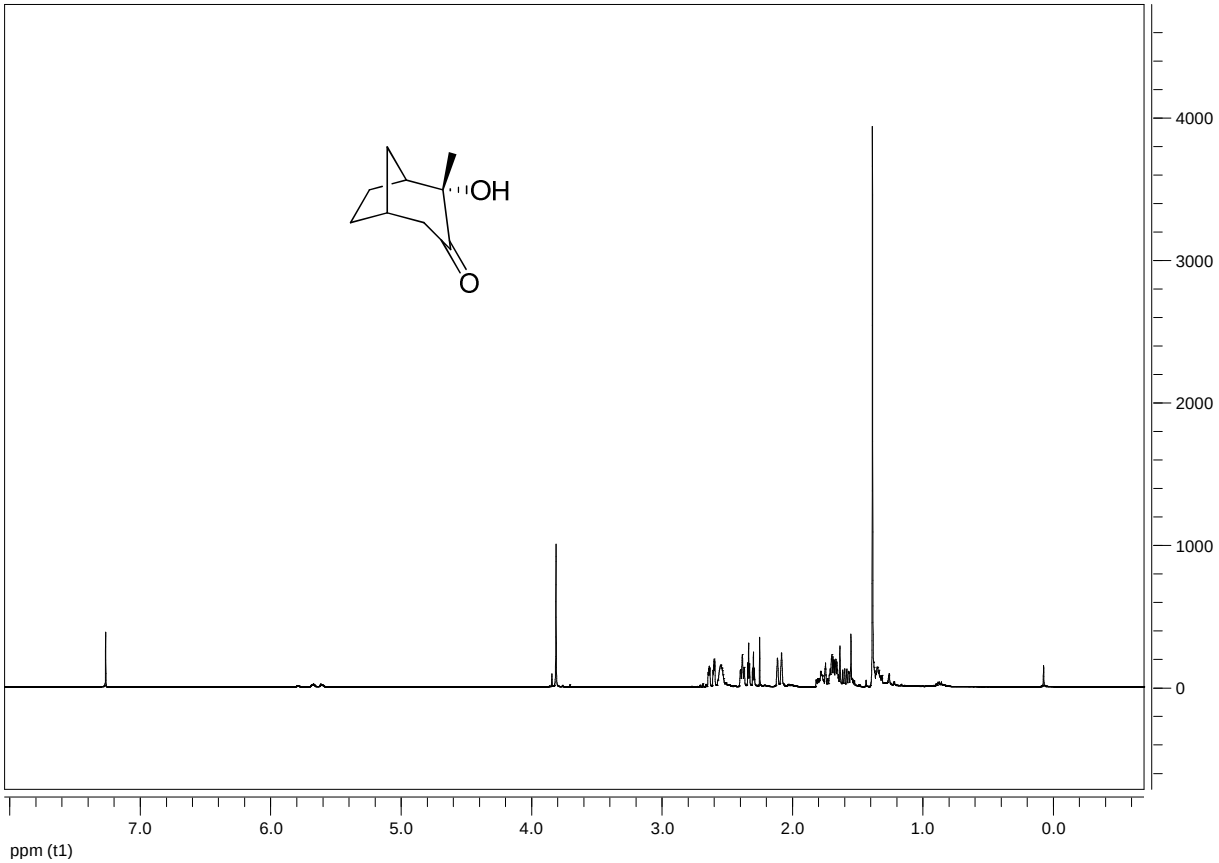


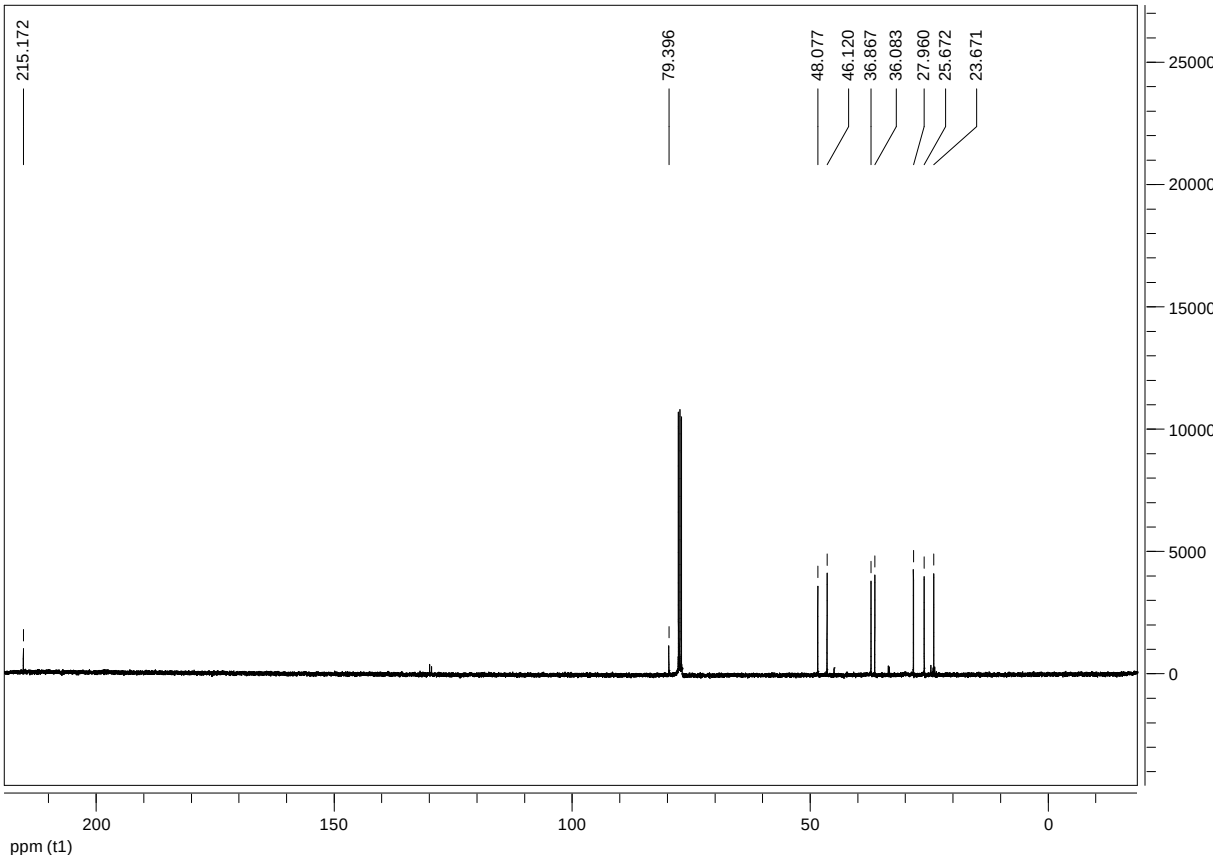
Compound **58b**



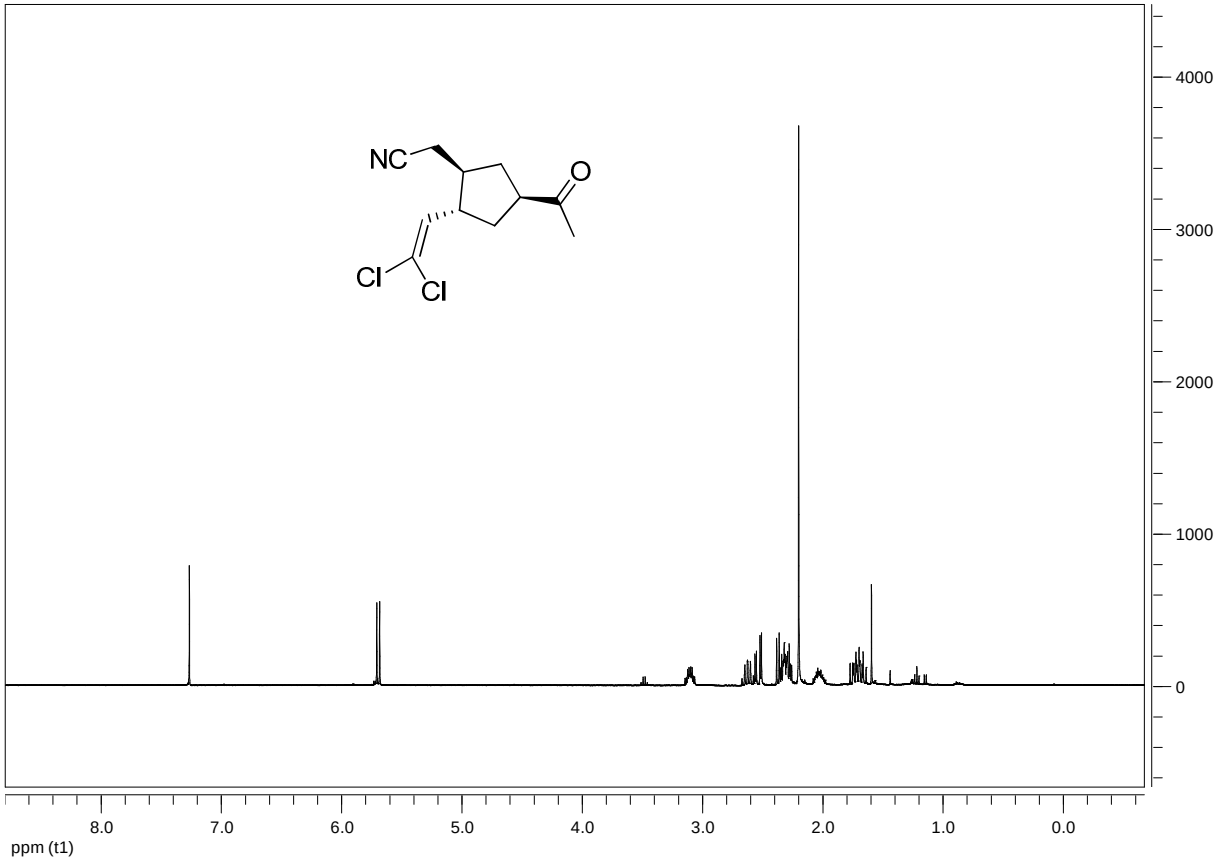


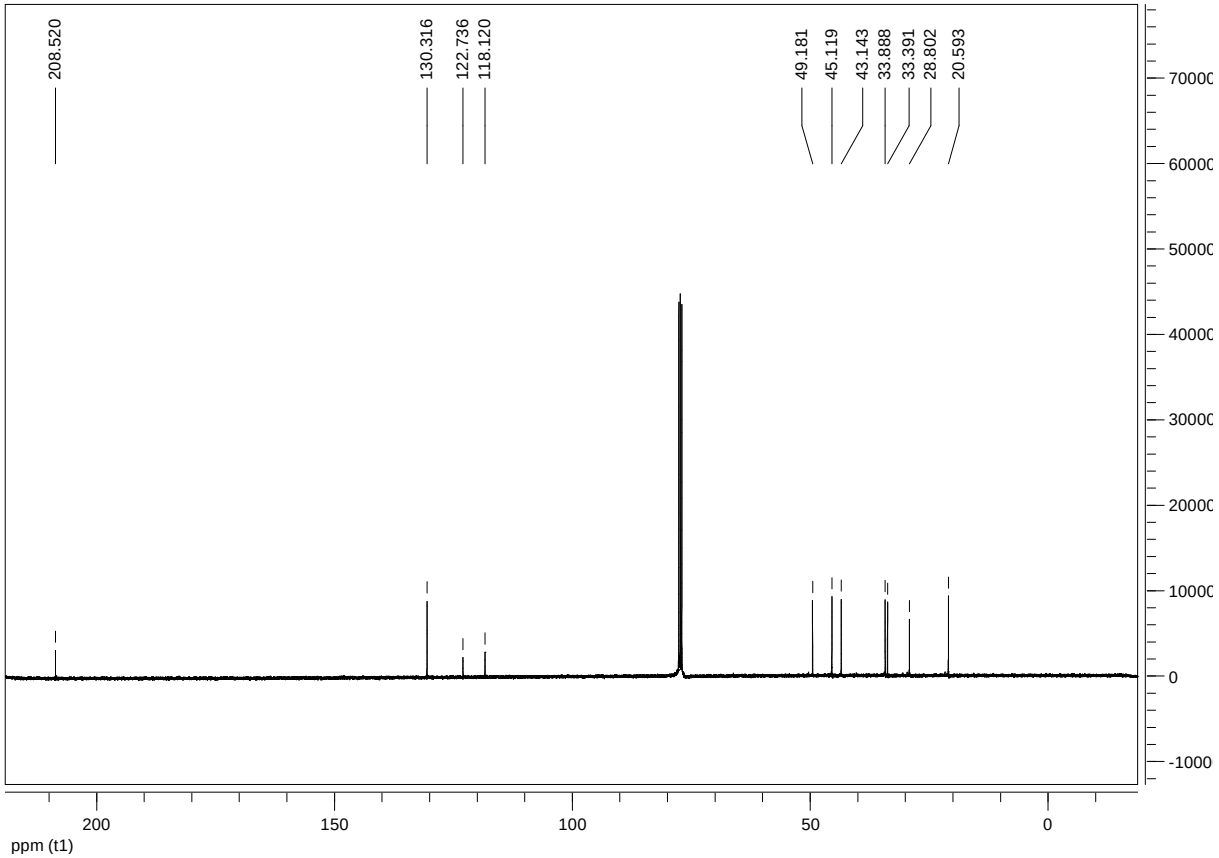
Compound **59**


OH
O
4000
3000
2000
1000
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


215.172
79.396
48.077
46.120
36.867
36.083
27.960
25.672
23.671
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

Compound **61**


NC
O
Cl
Cl
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


208.520
130.316
122.736
118.120
49.181
45.119
43.143
33.888
33.391
28.802
20.593
70000
60000
50000
40000
30000
20000
10000
0
-1000
200
150
100
50
0
ppm (t1)