Universitetet i Oslo

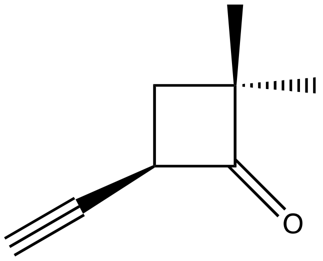
Det matematisk-naturvitenskaplige fakultet

Eksamen i :	KJM3000 og KJM4000.
Eksamensdag:	Torsdag 7. juni 2012.
Tid for eksamen:	kl. 14.30 – 18.30 (4 timer).
Oppgavesettet er på 2 sider.	
Vedlegg:	3 vedlegg på hhv. 2, 5 og 1 sider.
Tillatte hjelpemidler:	Lommekalkulator, linjal og molekylbyggesett

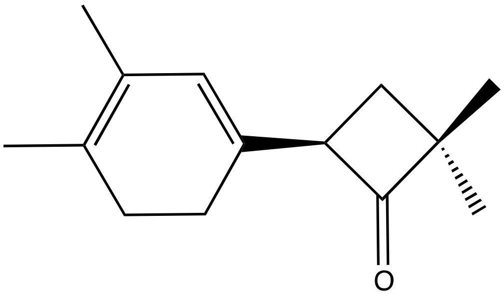
Kontroller at oppgavesettet er komplett før du begynner å svare på spørsmålene.

Ved bedømmelse vektlegges oppgavene som angitt.

Oppgave 1 (30%)



I



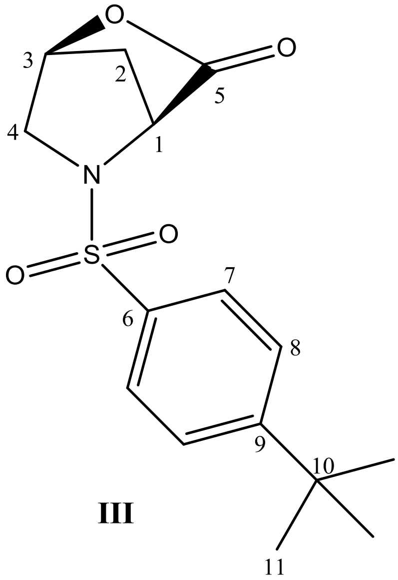
II

a. Følgende data er gitt for forbindelse **I**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.22 (s, 3H), 1.27 (s, 3H), 1.89 (dd, *J* 7.5 og 9.0 Hz, 1H), 2.13 (dd, *J* 3.5 og 9.0 Hz, 1H), 2.83 (d, *J* 2.5 Hz, 1H), 4.03 (m, 1H). Gi en tilordning av disse signalene og forklar kort hvordan koblingsmønsteret oppstår.

b. Beregn λ_{max} og anslå ε_{max} for forbindelse **II**. Begrunn svaret kort.

c. Identifiser forbindelsen som gir opphav til massespekteret (EI, 70 eV) gjengitt på vedlegg I, side 2. Gjør rede for din tankegang slik at vi kan se hvordan du har kommet fram til strukturen.

Oppgave 2 (30%)



III

Spektroskopiske data for forbindelse **III** er gitt i vedlegg 2.

a) Gi en så fullstendig tilordning av ^{1}H- og ^{13}C-NMR spektrene som mulig ved å sette opp en tabell med verdier for kjemiske skift, multiplisitet, koblingskonstanter og antall atomer (integral).
b) Skriv reaksjonligninger med piler som gjør rede for følgende verdier i det vedlagte massespekteret (EI, 70 eV): 267, 266, 265, 252, 197, 133.

Oppgave 3 (40%).

Identifiser forbindelsen som gir opphav til spektrene i vedlegg 3. Gi en så fullstendig tilordning av signalene i ^{13}C- og ^{1}H-NMR spektrene som mulig og gi en kortfattet forklaring. Kommenter kort på EA/MS-, IR- og UV-data som er gitt.

Vedlegg 1 / Attachment 1

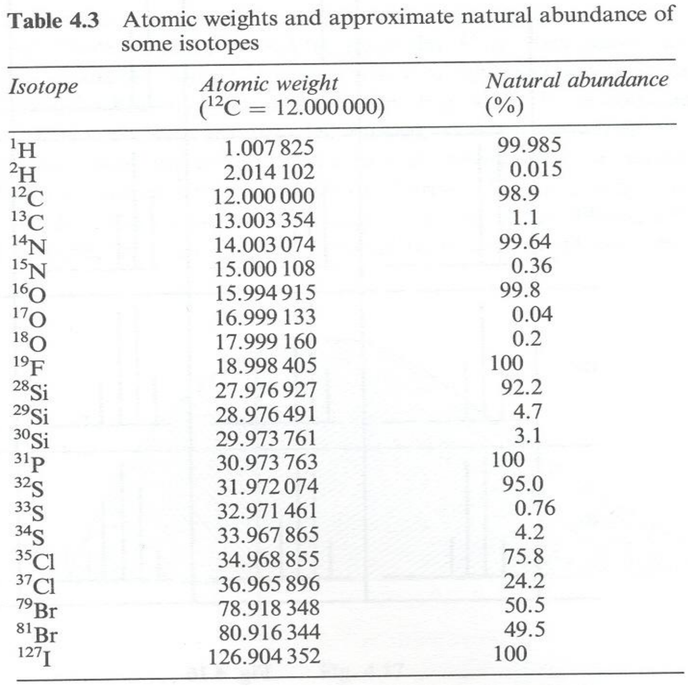


Table 4.3 Atomic weights and approximate natural abundance of some isotopes

Isotope	*Atomic weight* (^{12}C = 12.000 000)	*Natural abundance* (%)
^{1}H	1.007 825	99.985
^{2}H	2.014 102	0.015
^{12}C	12.000 000	98.9
^{13}C	13.003 354	1.1
^{14}N	14.003 074	99.64
^{15}N	15.000 108	0.36
^{16}O	15.994 915	99.8
^{17}O	16.999 133	0.04
^{18}O	17.999 160	0.2
^{19}F	18.998 405	100
^{28}Si	27.976 927	92.2
^{29}Si	28.976 491	4.7
^{30}Si	29.973 761	3.1
^{31}P	30.973 763	100
^{32}S	31.972 074	95.0
^{33}S	32.971 461	0.76
^{34}S	33.967 865	4.2
^{35}Cl	34.968 855	75.8
^{37}Cl	36.965 896	24.2
^{79}Br	78.918 348	50.5
^{81}Br	80.916 344	49.5
^{127}I	126.904 352	100

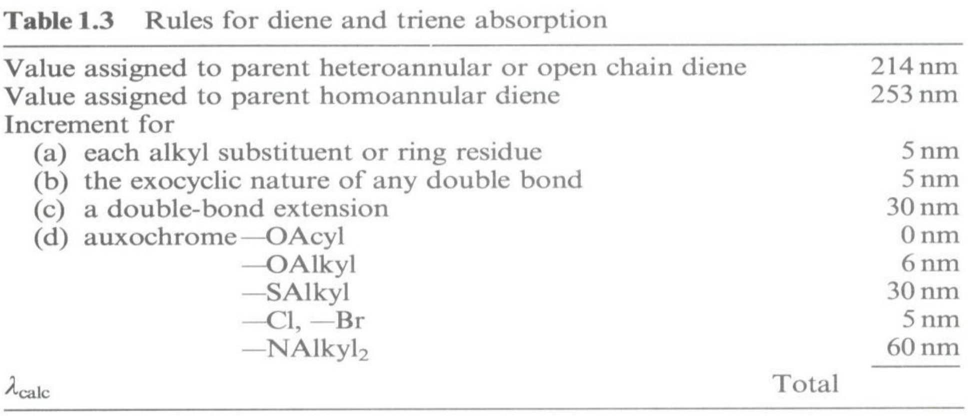


Table 1.3 Rules for diene and triene absorption

Value assigned to parent heteroannular or open chain diene	214 nm
Value assigned to parent homoannular diene	253 nm
Increment for	
(a) each alkyl substituent or ring residue	5 nm
(b) the exocyclic nature of any double bond	5 nm
(c) a double-bond extension	30 nm
(d) auxochrome —OAcyl	0 nm
—OAlkyl	6 nm
—SAlkyl	30 nm
—Cl, —Br	5 nm
—NAlkyl$_2$	60 nm
λ_{calc} Total	

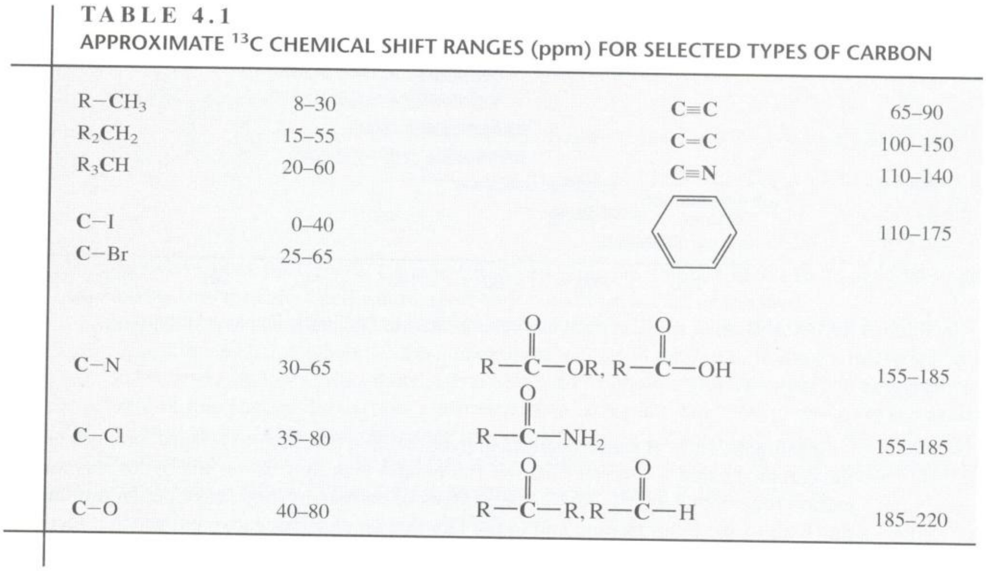
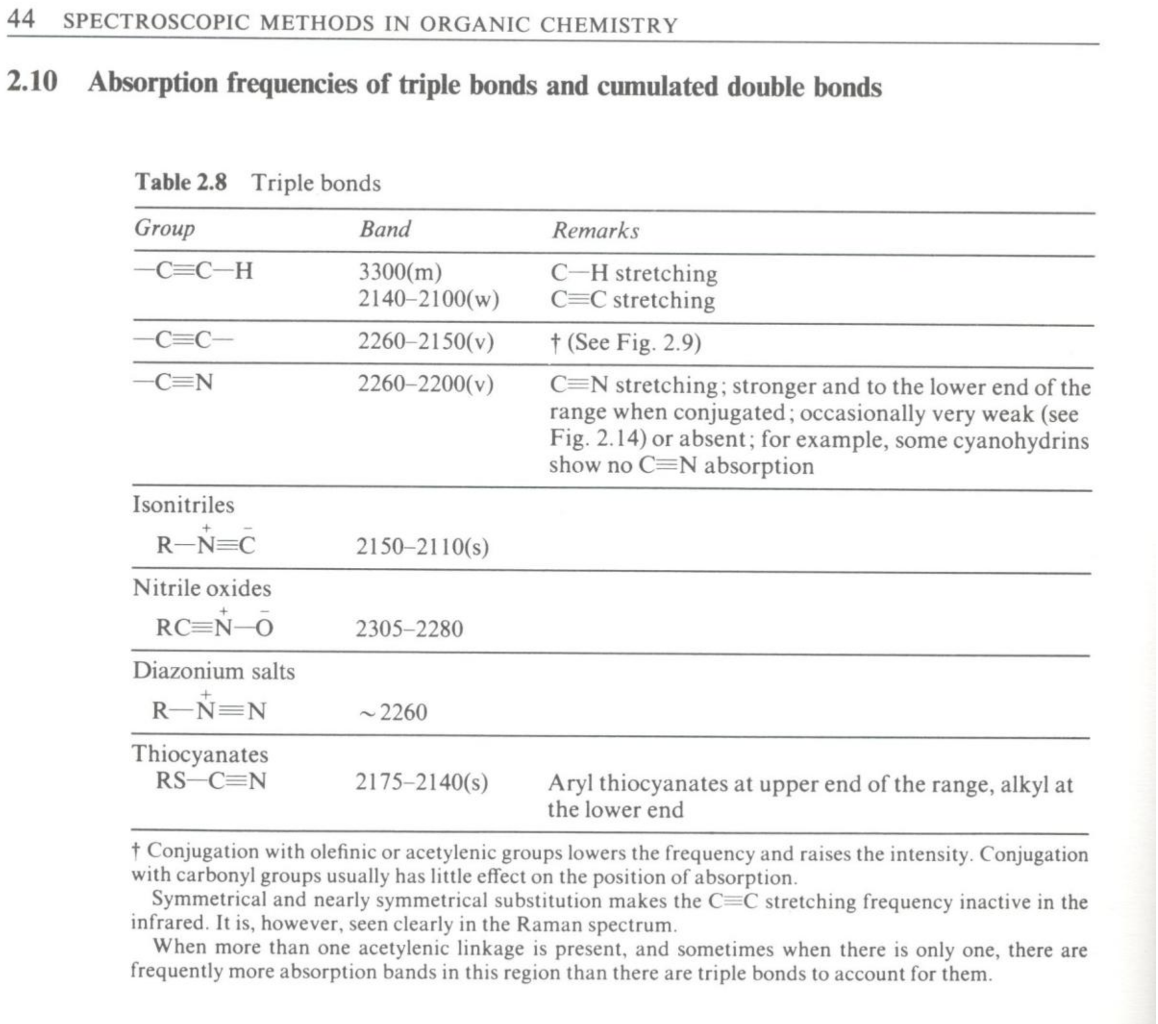


TABLE 4.1

APPROXIMATE ^{13}C CHEMICAL SHIFT RANGES (ppm) FOR SELECTED TYPES OF CARBON

$R-CH_3$	8–30	$C\equiv C$	65–90
R_2CH_2	15–55	$C=C$	100–150
R_3CH	20–60	$C\equiv N$	110–140
C–I	0–40		110–175
C–Br	25–65		
C–N	30–65	$R-\overset{O}{\overset{\|}{C}}-OR,\ R-\overset{O}{\overset{\|}{C}}-OH$	155–185
C–Cl	35–80	$R-\overset{O}{\overset{\|}{C}}-NH_2$	155–185
C–O	40–80	$R-\overset{O}{\overset{\|}{C}}-R,\ R-\overset{O}{\overset{\|}{C}}-H$	185–220



2.10 Absorption frequencies of triple bonds and cumulated double bonds

Table 2.8 Triple bonds

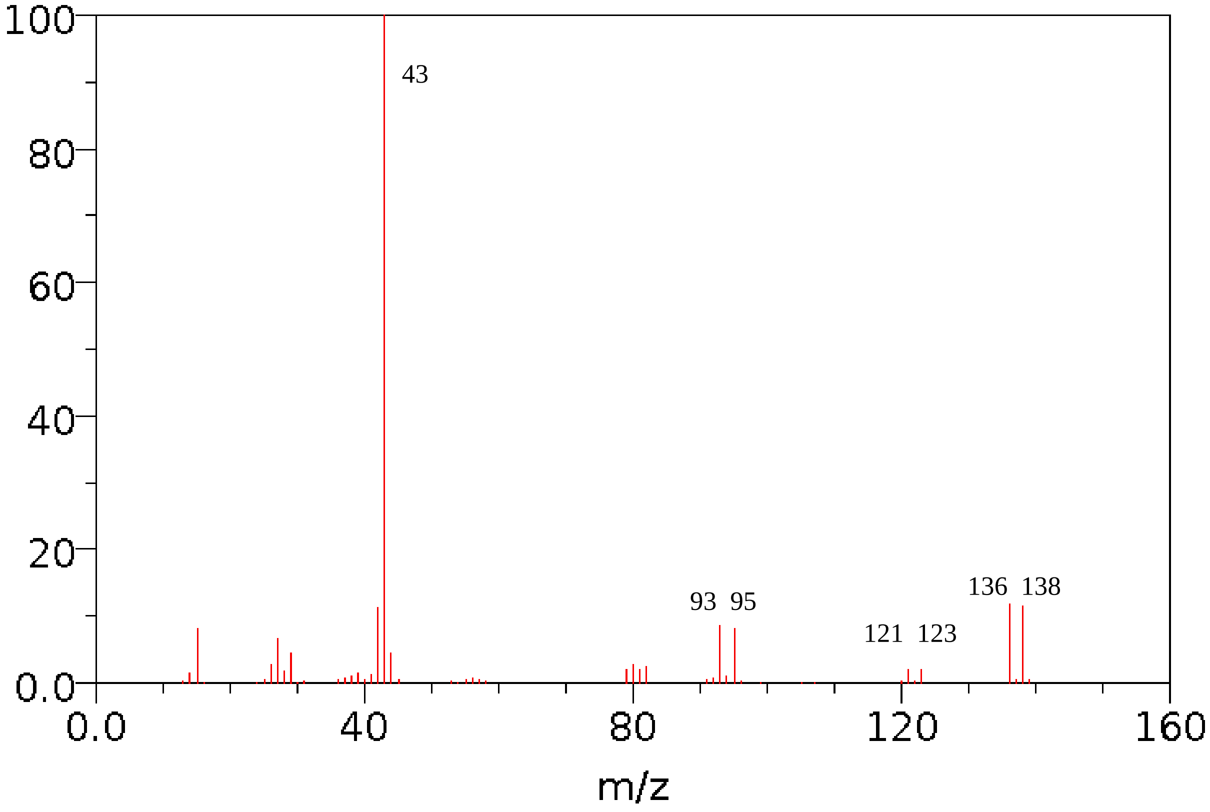
Group	*Band*	*Remarks*
$-C{\equiv}C-H$	3300(m) 2140–2100(w)	C—H stretching C≡C stretching
$-C{\equiv}C-$	2260–2150(v)	† (See Fig. 2.9)
$-C{\equiv}N$	2260–2200(v)	C≡N stretching; stronger and to the lower end of the range when conjugated; occasionally very weak (see Fig. 2.14) or absent; for example, some cyanohydrins show no C≡N absorption
Isonitriles $R{-}\overset{+}{N}{\equiv}\overset{-}{C}$	2150–2110(s)	
Nitrile oxides $RC{\equiv}\overset{+}{N}{-}\overset{-}{O}$	2305–2280	
Diazonium salts $R{-}\overset{+}{N}{\equiv}N$	~2260	
Thiocyanates $RS{-}C{\equiv}N$	2175–2140(s)	Aryl thiocyanates at upper end of the range, alkyl at the lower end

† Conjugation with olefinic or acetylenic groups lowers the frequency and raises the intensity. Conjugation with carbonyl groups usually has little effect on the position of absorption.

Symmetrical and nearly symmetrical substitution makes the C≡C stretching frequency inactive in the infrared. It is, however, seen clearly in the Raman spectrum.

When more than one acetylenic linkage is present, and sometimes when there is only one, there are frequently more absorption bands in this region than there are triple bonds to account for them.

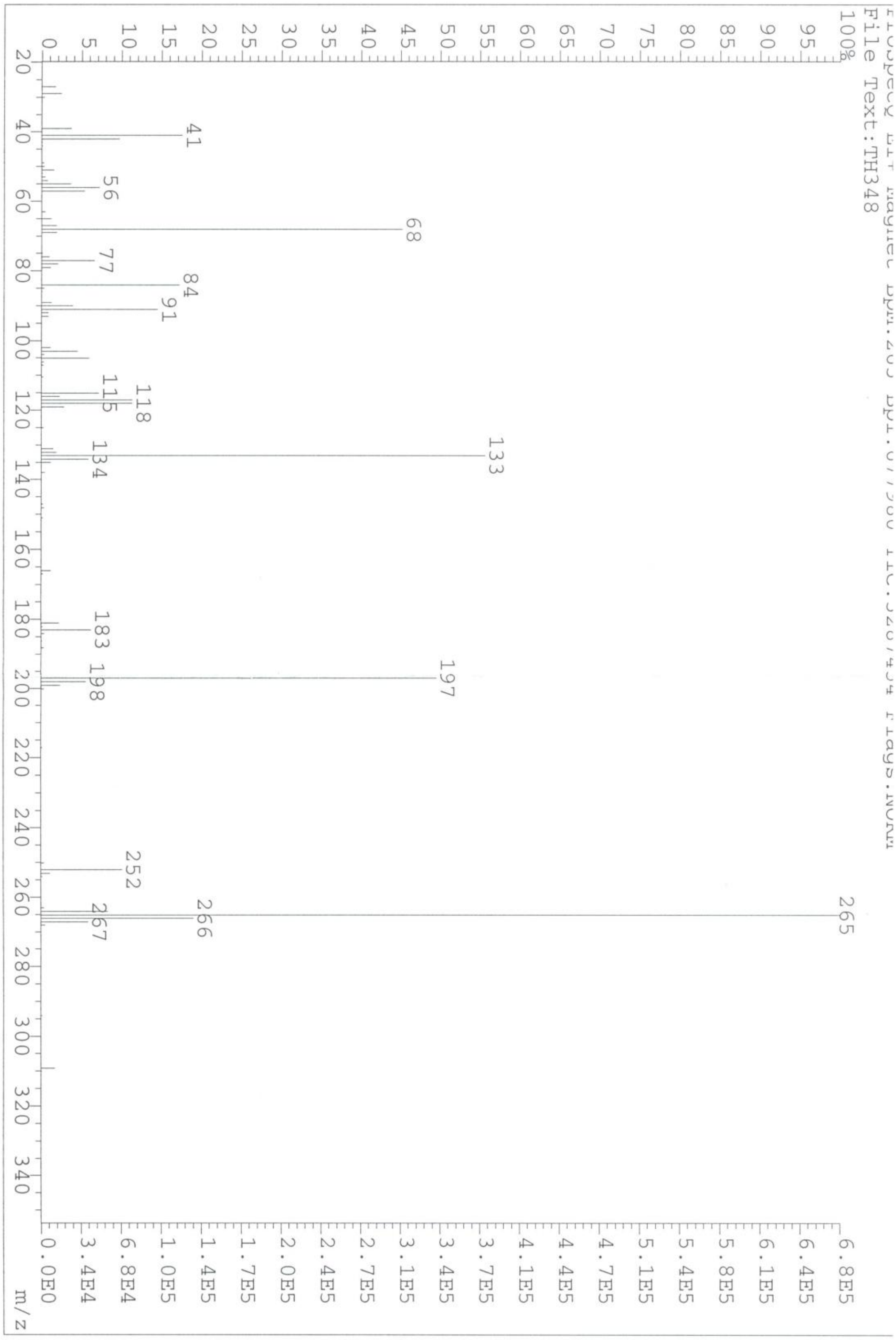
Oppgave 1c: MS (EI, 70 eV):

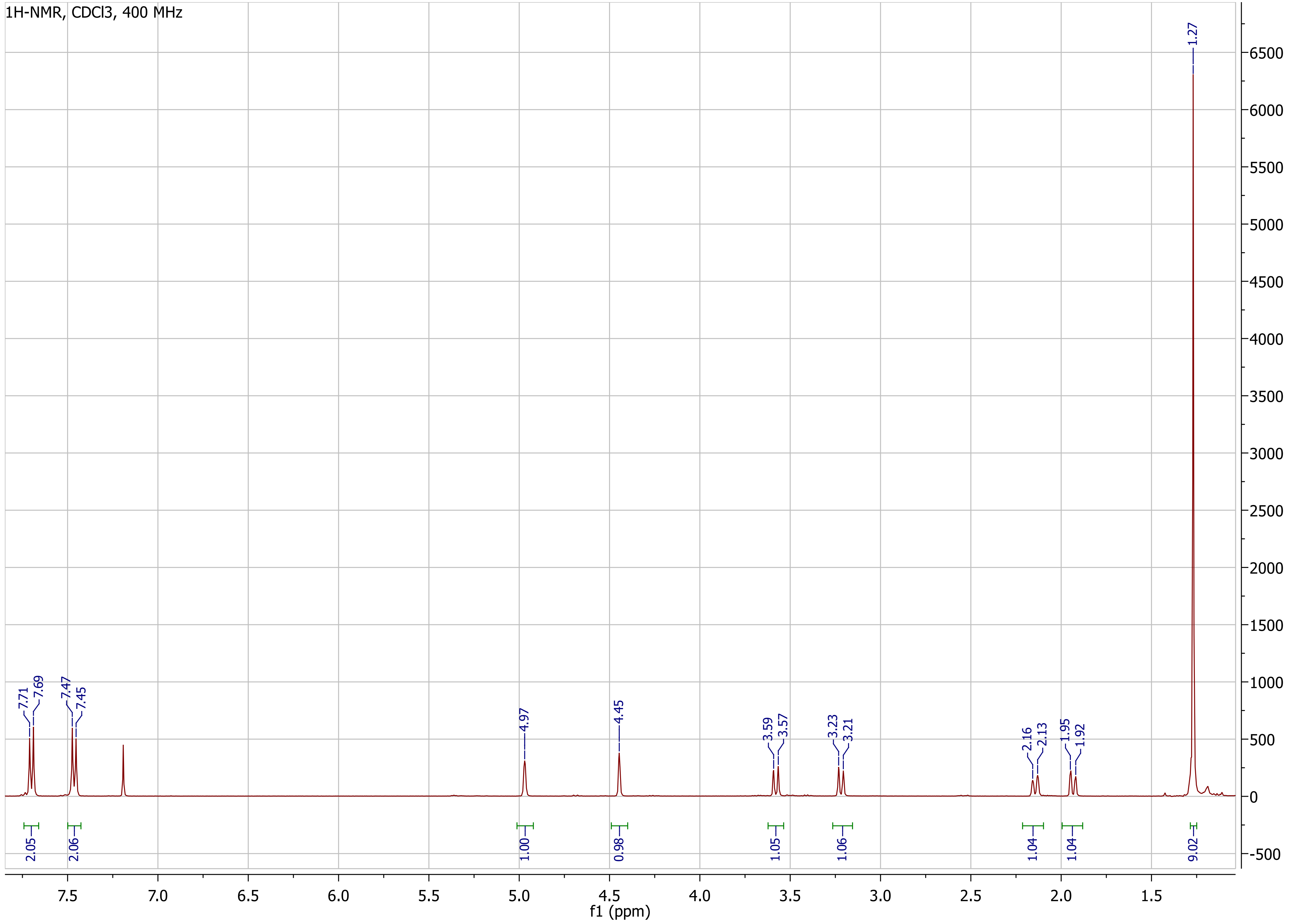


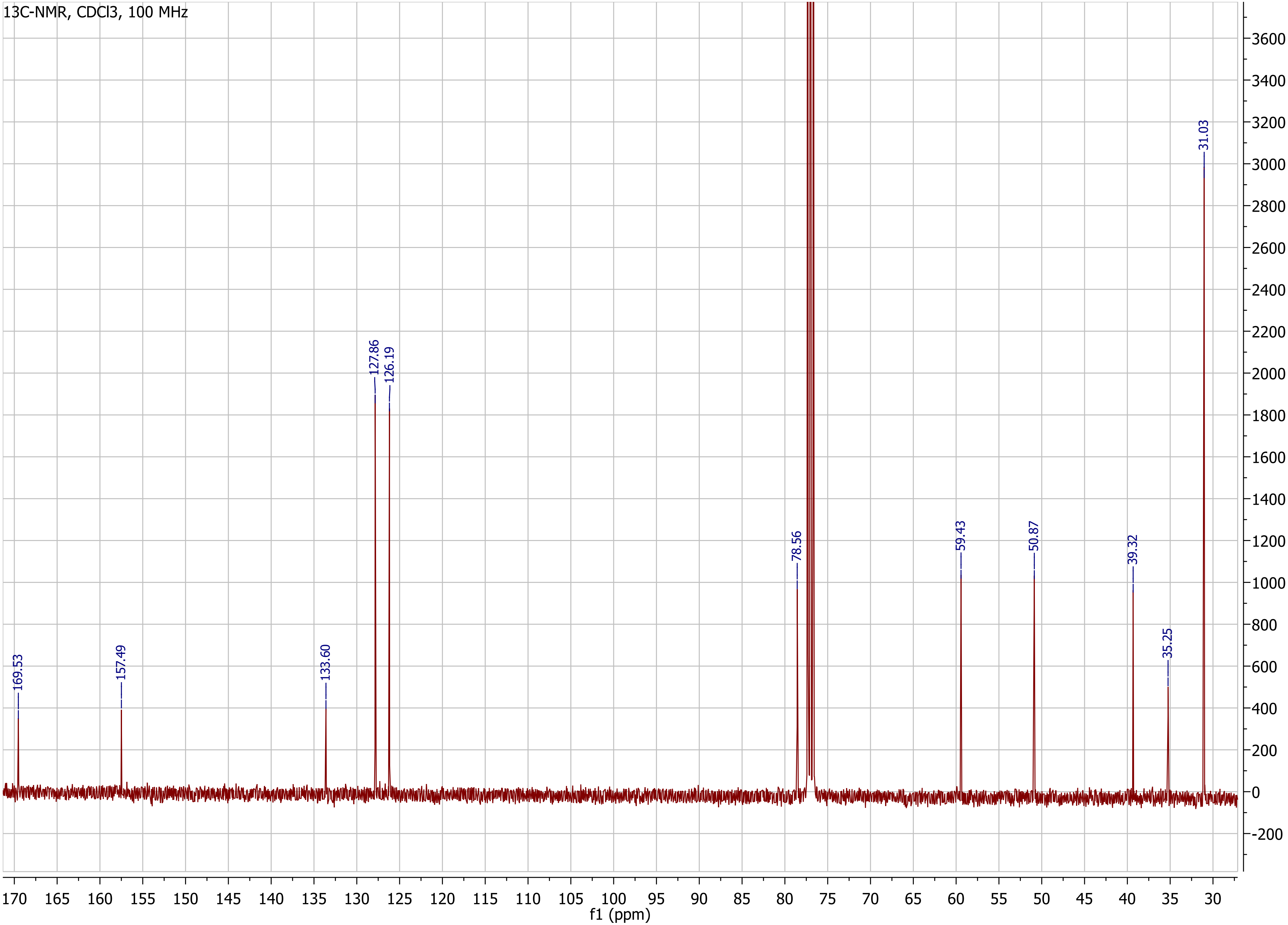
Vedlegg 2 / Attachment 2

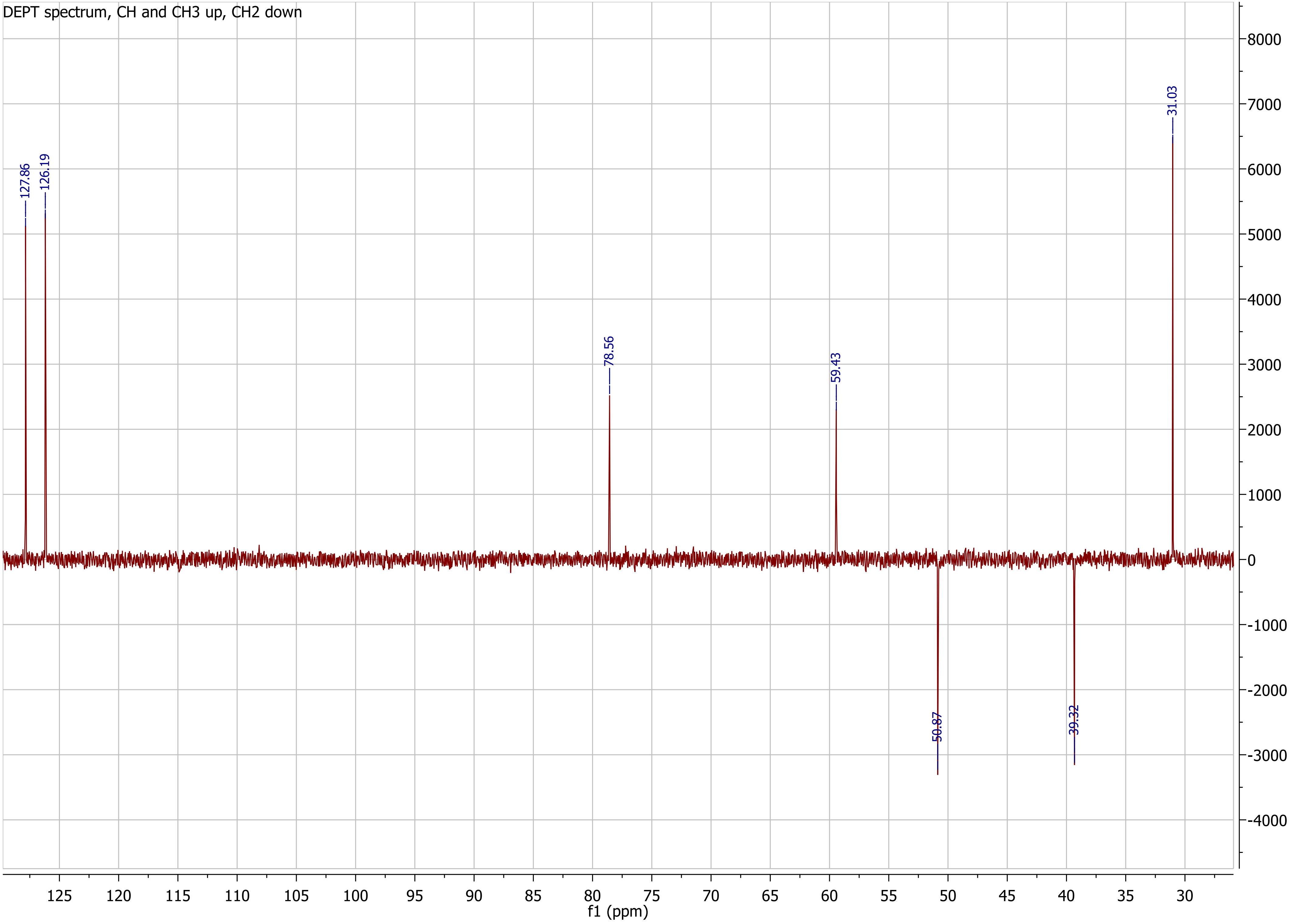
MS-data og NMR-data for forbindelse **III** / MS-data and NMR-data for compound **III**.

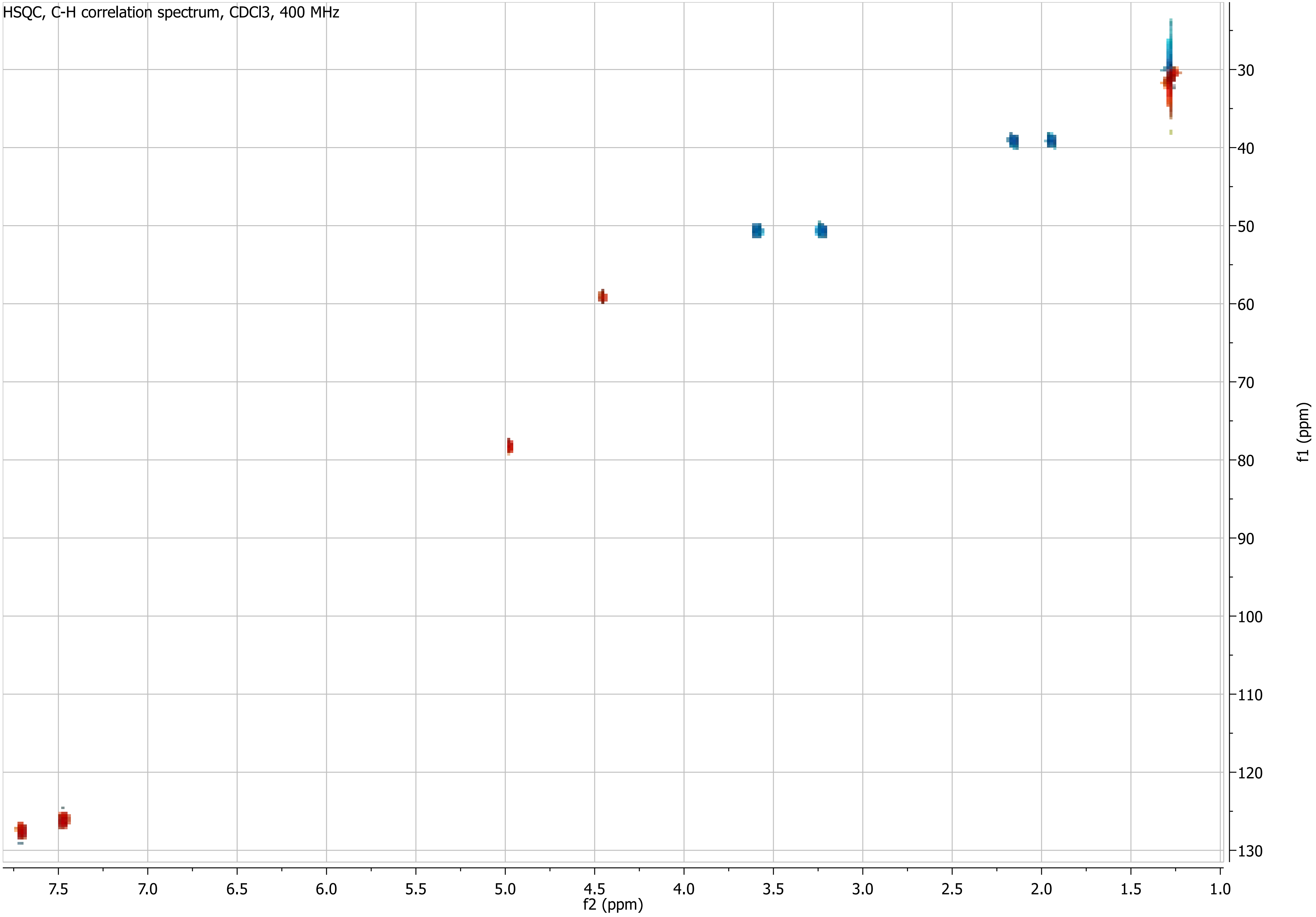
LR-MS (EI, 70 eV) **III**:




1H-NMR, CDCl3, 400 MHz
7.71
7.69
7.47
7.45
4.97
4.45
3.59
3.57
3.23
3.21
2.16
2.13
1.95
1.92
1.27
2.05
2.06
1.00
0.98
1.05
1.06
1.04
1.04
9.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


13C-NMR, CDCl3, 100 MHz
169.53
157.49
133.60
127.86
126.19
78.56
59.43
50.87
39.32
35.25
31.03
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)


DEPT spectrum, CH and CH3 up, CH2 down
127.86
126.19
78.56
59.43
50.87
39.32
31.03
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)


HSQC, C-H correlation spectrum, CDCl3, 400 MHz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)

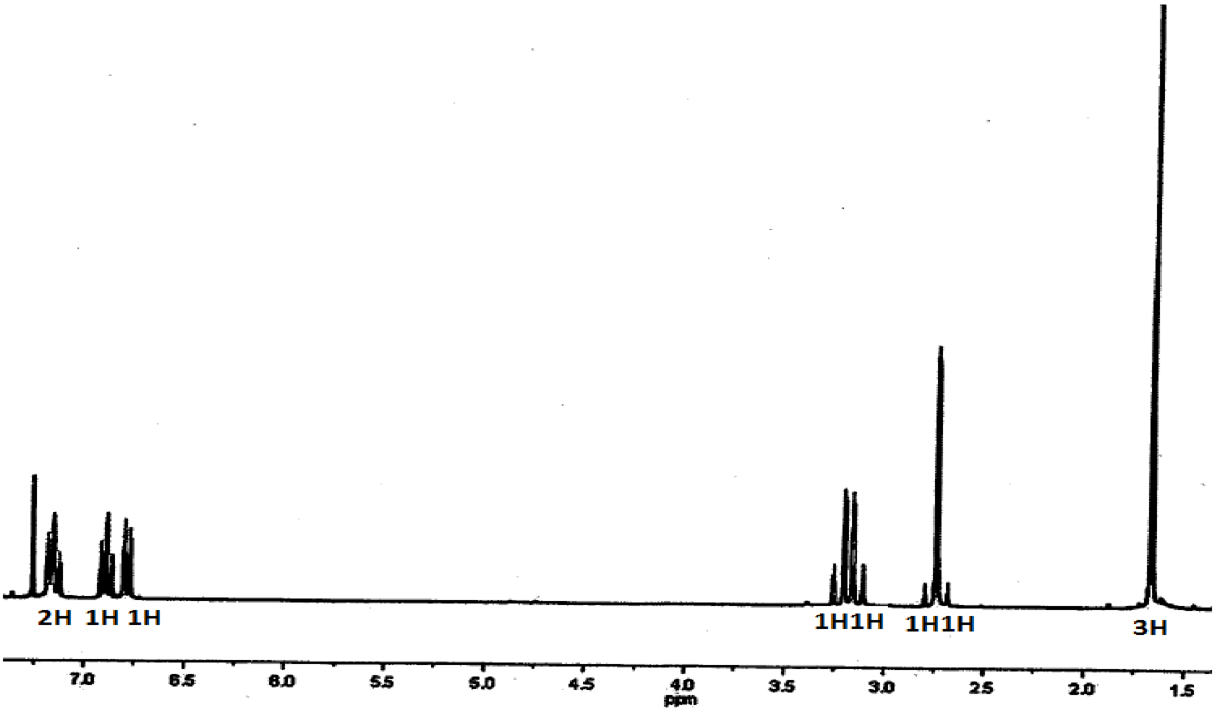
Attachment 3 / Vedlegg 3

Grunnstoff analyse / Elemental Analysis: C, 76.28; H, 6.40; N, 8.09. HRMS (CI): 174.0919.

IR (KBr disc) cm^{-1}: 3100 (s), 2959 (s), 2872 (s), 2250 (m).

UV: λ_{max} = 210 nm, ε_{max} = 7000.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.67 (s, 3H), 2.71 (d, *J* = 16.5 Hz, 1H), 2.77 (d, *J* = 16.5 Hz, 1H), 3.14 (d, *J* = 16.4 Hz, 1H), 3.23 (d, *J* = 16.4 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.89 (m, 1H), 7.13-7.18 (m, 2H).



^{13}C-NMR (75 MHz, $CDCl_3$): δ 25.9 (q), 29.7 (t), 41.2 (t), 84.6 (s), 110 (d), 116.8 (s), 121.1 (d), 125.2 (s), 125.2 (d), 128.6 (d), 157.9 (s).