

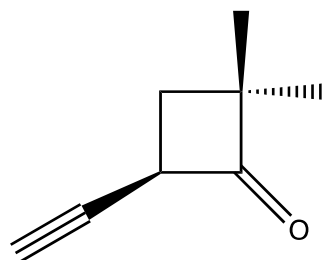
# Universitetet i Oslo

Det matematisk-naturvitenskaplige fakultet

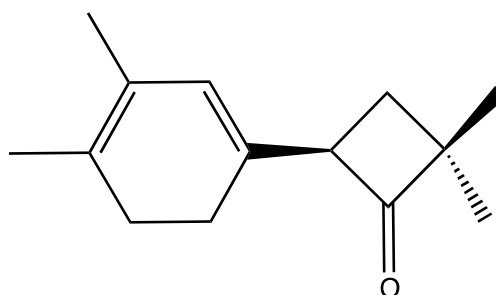
**Exam in:** KJM3000 and KJM4000  
**Day of exam:** 2012-06-07  
**Exam hours:** 14.30 – 18.30 (4 hours)  
**This examination paper consists of 2 page(s).**  
**Appendices:** 3 (3, 5 and 1 pages respectively)  
**Permitted materials:** Ruler, calculator and molecular modelling kit

*Make sure that your copy of this examination paper is complete before answering*

## Task 1 (30%)



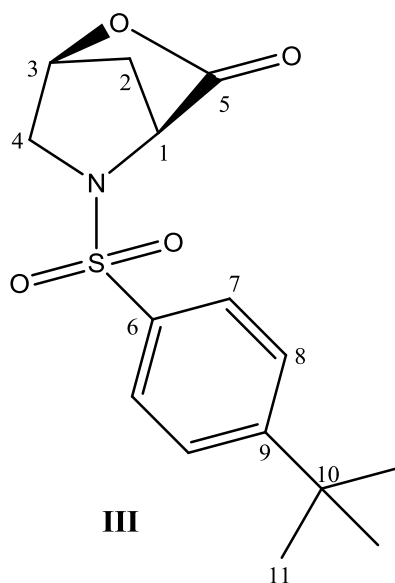
I



II

- a. The following data are given for compound I:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  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). Assign the signals and explain briefly the coupling pattern.
- b. Calculate  $\lambda_{\text{max}}$  og estimate  $\epsilon_{\text{max}}$  for compound II. Give a very brief explanation.
- c. Identify the compound whose mass spectrum are found in attachment 1, page 2. Draw structural equations with arrows and explain briefly your reasoning.

Task 2 (30%)



Spectroscopic data for compound **III** are found in attachment 2.

- a) Assign the signals in the attached  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra by setting up a table with values for: Chemical shift, multiplicity (coupling), coupling constants, and number of atoms (integrals)
- b) Write structural equations with arrows to account for the following values in the attached mass spectrum: (EI, 70 eV): 267, 266, 265, 252, 197, 133.

Task 3 (40%).

Identify the compound whose spectroscopic data are found in attachment 3. Assign as many of the signals in the  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectra as possible and give a brief explanation. Comment briefly on the given EA/MS-, IR- og UV-data.

## Vedlegg 1 / Attachment 1


**Table 4.3** Atomic weights and approximate natural abundance of some isotopes

Isotope	Atomic weight ( <sup>12</sup> C = 12.000 000)	Natural abundance (%)
<sup>1</sup> H	1.007 825	99.985
<sup>2</sup> H	2.014 102	0.015
<sup>12</sup> C	12.000 000	98.9
<sup>13</sup> C	13.003 354	1.1
<sup>14</sup> N	14.003 074	99.64
<sup>15</sup> N	15.000 108	0.36
<sup>16</sup> O	15.994 915	99.8
<sup>17</sup> O	16.999 133	0.04
<sup>18</sup> O	17.999 160	0.2
<sup>19</sup> F	18.998 405	100
<sup>28</sup> Si	27.976 927	92.2
<sup>29</sup> Si	28.976 491	4.7
<sup>30</sup> Si	29.973 761	3.1
<sup>31</sup> P	30.973 763	100
<sup>32</sup> S	31.972 074	95.0
<sup>33</sup> S	32.971 461	0.76
<sup>34</sup> S	33.967 865	4.2
<sup>35</sup> Cl	34.968 855	75.8
<sup>37</sup> Cl	36.965 896	24.2
<sup>79</sup> Br	78.918 348	50.5
<sup>81</sup> Br	80.916 344	49.5
<sup>127</sup> 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 <sub>2</sub>	60 nm
$\lambda_{\text{calc}}$	Total

**TABLE 4.1**  
APPROXIMATE <sup>13</sup>C CHEMICAL SHIFT RANGES (ppm) FOR SELECTED TYPES OF CARBON

R-CH <sub>3</sub>	8-30	C≡C	65-90
R <sub>2</sub> CH <sub>2</sub>	15-55	C=C	100-150
R <sub>3</sub> CH	20-60	C≡N	110-140
C-I	0-40		110-175
C-Br	25-65		
C-N	30-65	R-C(=O)-OR, R-C(=O)-OH	155-185
C-Cl	35-80	R-C(=O)-NH <sub>2</sub>	155-185
C-O	40-80	R-C(=O)-R, R-C(=O)-H	185-220

## 2.10 Absorption frequencies of triple bonds and cumulated double bonds

Table 2.8 Triple bonds

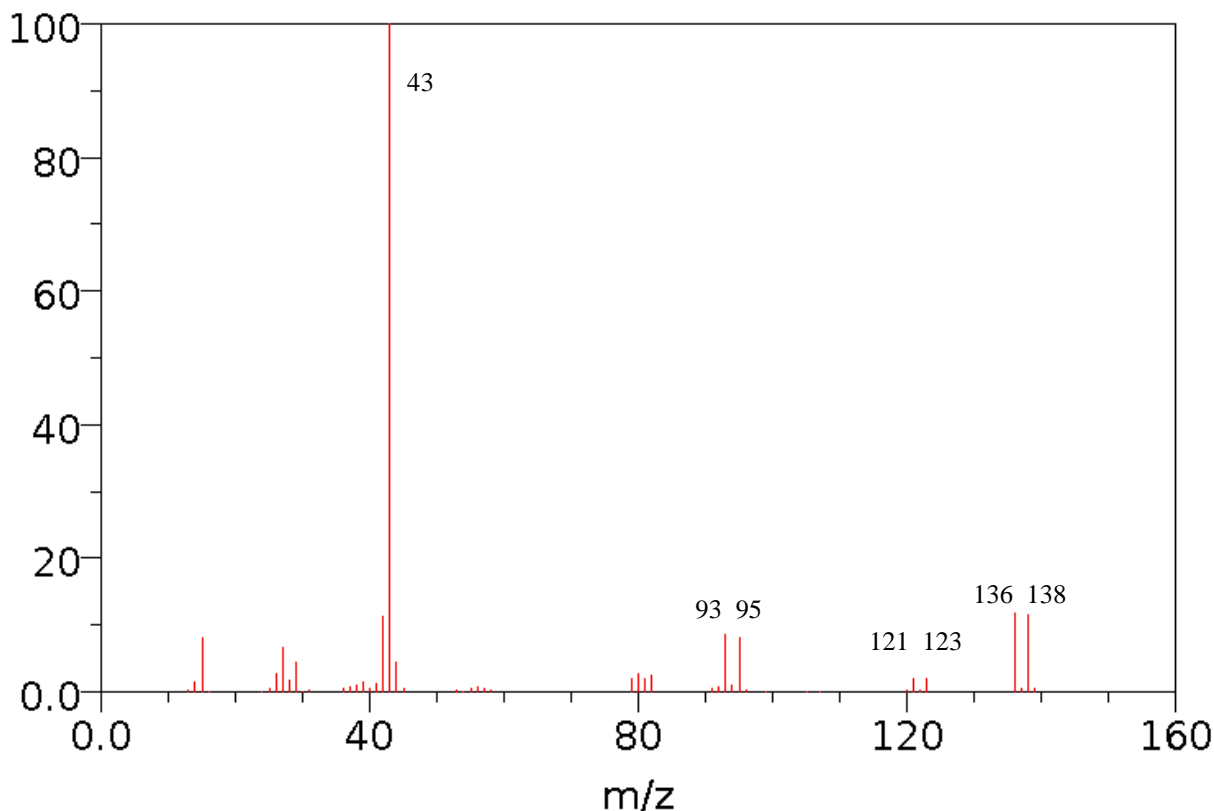
Group	Band	Remarks
$-\text{C}\equiv\text{C}-\text{H}$	3300(m) 2140–2100(w)	C–H stretching C $\equiv$ C stretching
$-\text{C}\equiv\text{C}-$	2260–2150(v)	† (See Fig. 2.9)
$-\text{C}\equiv\text{N}$	2260–2200(v)	C $\equiv$ N stretching; stronger and to the lower end of the range when conjugated; occasionally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

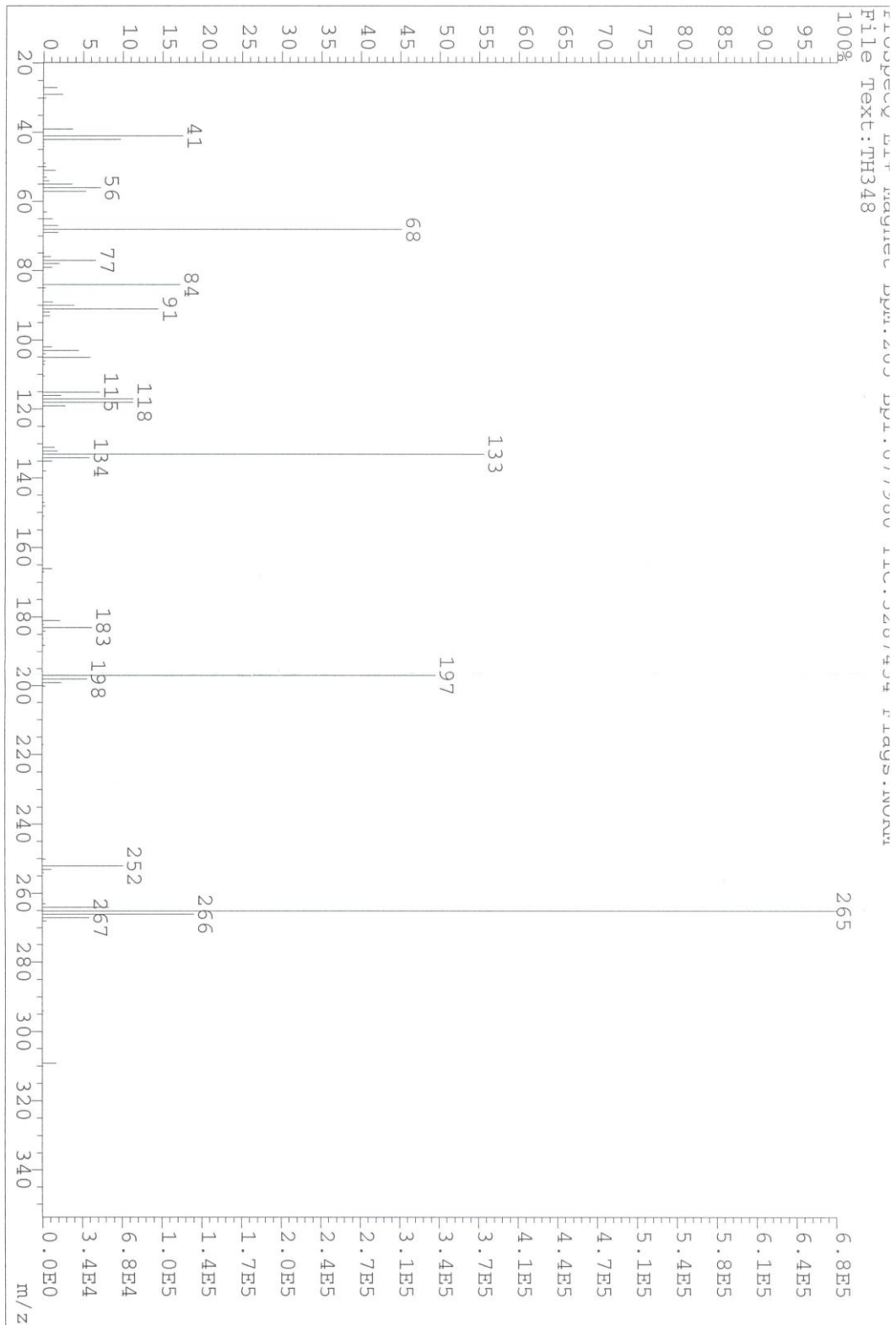
## Task 1c: MS (EI, 70 eV):

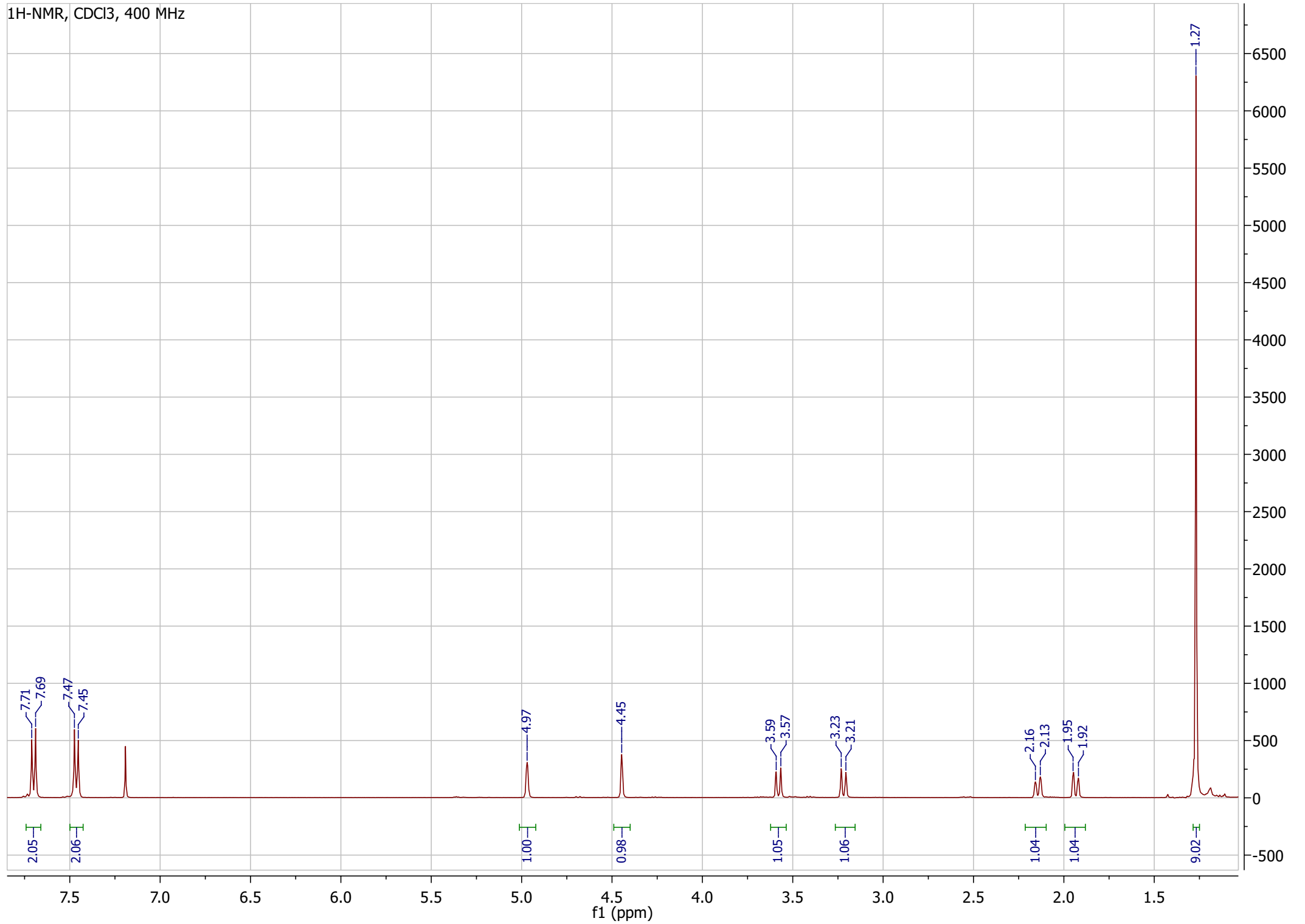


Vedlegg 2 / Attachment 2

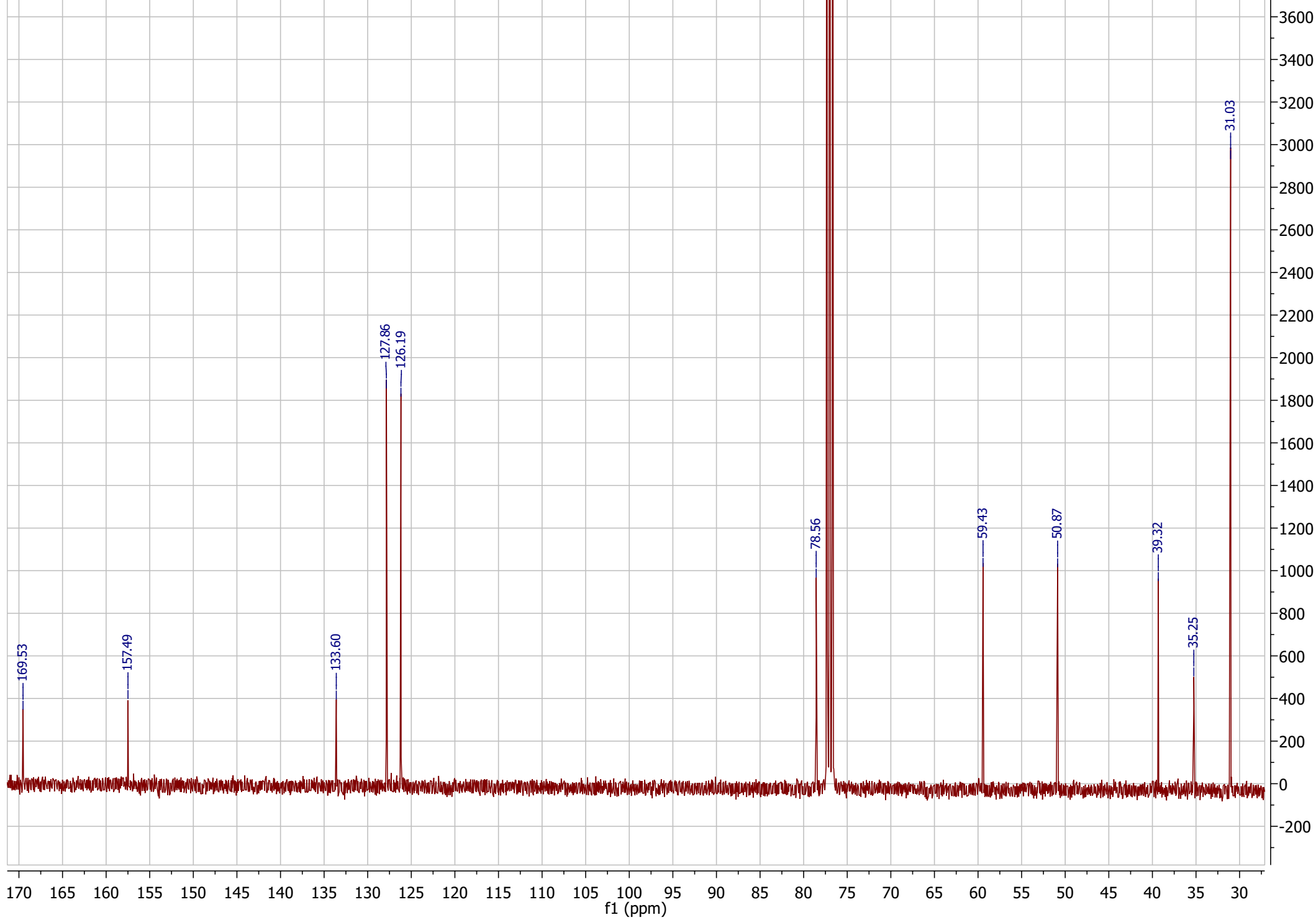
MS-data og NMR-data for forbindelse **III** / MS-data and NMR-data for compound **III**.

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

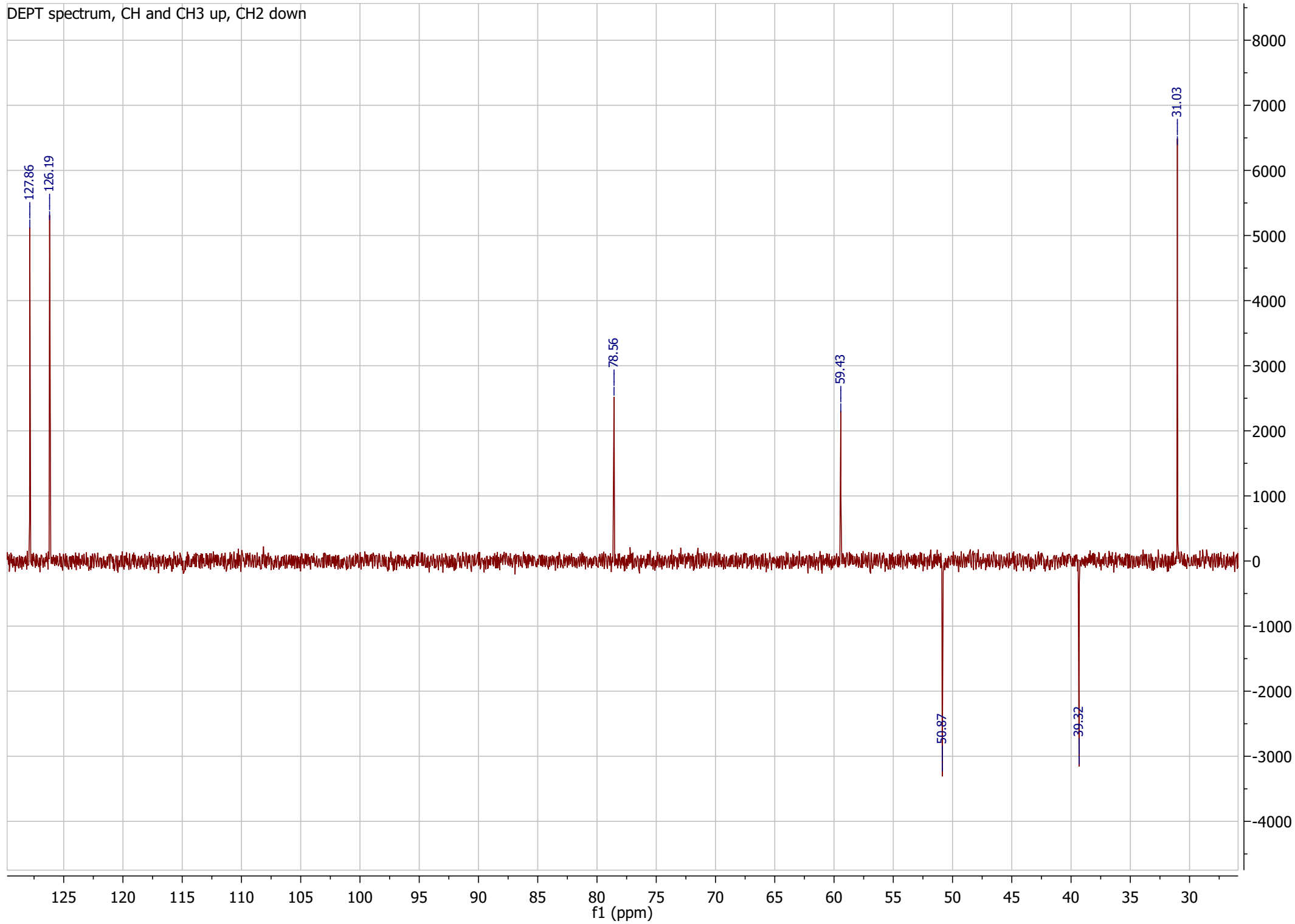




<sup>13</sup>C-NMR, CDCl<sub>3</sub>, 100 MHz

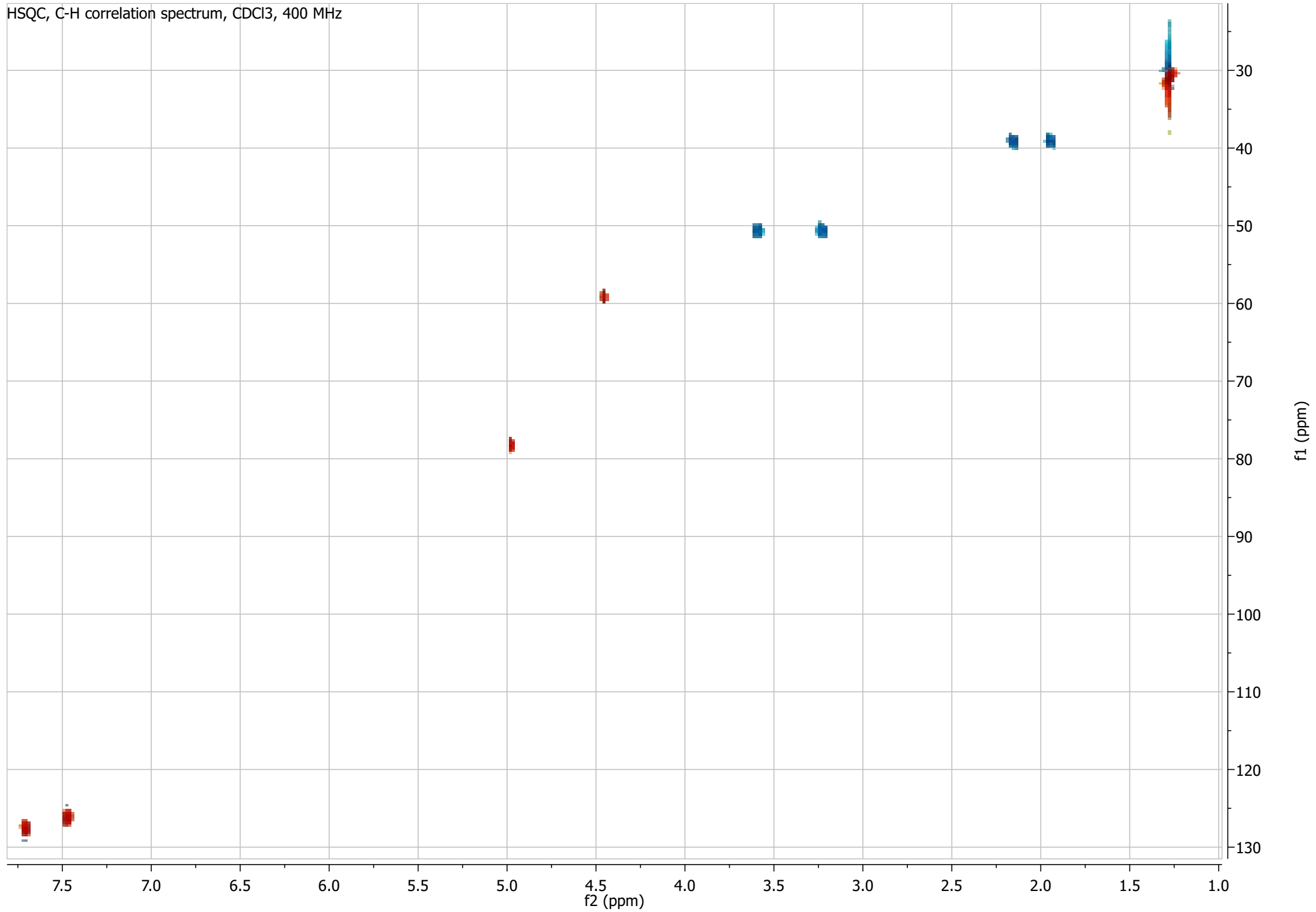


DEPT spectrum, CH and CH3 up, CH2 down





HSQC, C-H correlation spectrum, CDCl<sub>3</sub>, 400 MHz



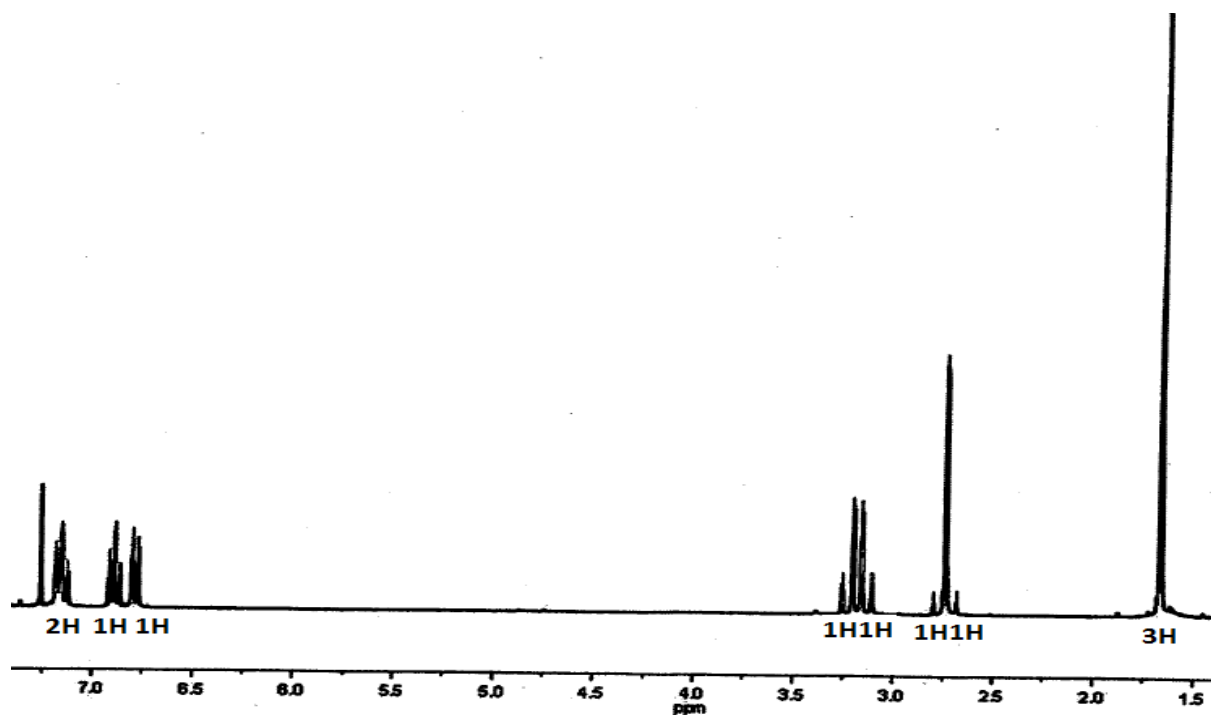
Attachment 3 / Vedlegg 3

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

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

UV:  $\lambda_{\text{max}} = 210 \text{ nm}$ ,  $\epsilon_{\text{max}} = 7000$ .

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.67 (s, 3H), 2.71 (d,  $J = 16.5 \text{ Hz}$ , 1H), 2.77 (d,  $J = 16.5 \text{ Hz}$ , 1H), 3.14 (d,  $J = 16.4 \text{ Hz}$ , 1H), 3.23 (d,  $J = 16.4 \text{ Hz}$ , 1H), 6.79 (d,  $J = 7.8 \text{ Hz}$ , 1H), 6.89 (m, 1H), 7.13-7.18 (m, 2H).



$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).

