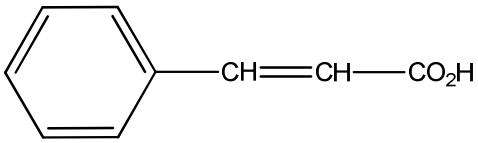
Universitetet i Oslo

Det matematisk-naturvitenskaplige fakultet

Exam in: **KJM3000 and KJM4000**
Day of exam: **2010-06-03**
Exam hours: **14.30 – 17.30 (3hours)**
This examination paper consists of 2 page(s).
Appendices: **3 (1, 2 and 2 pages respectively)**
Permitted materials: Ruler, calculator and molecular modelling kit

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

Question 1 (20%)



1

The structure of cinnamic acid is shown in figure **1**. There are 6 possible isomers of hydroxy-cinnamic acid. Draw the structures of all six isomers.

a) Explain briefly how you can use ^{1}H NMR to determine if the double bond in **1** is *cis* or *trans*.

b) Which of the isomers have the following ^{1}H-NMR data: δ= 7.53 (d, 1H, *J* = 16 Hz), 7.23 (t, 1H, *J* = 8 Hz), 7.12 (d, 1H, *J* = 8 Hz), 7.04 (d, 1H, *J* = 3.6 Hz), 6.85 (dd, 1H, *J* = 8 and 3.6 Hz), 6.44 (d, 1H, *J* = 16 Hz). The signals for the acid proton and the OH-proton are not included. Explain briefly the reason for your proposed structure and comment on symmetry, chemical shift and coupling constants.

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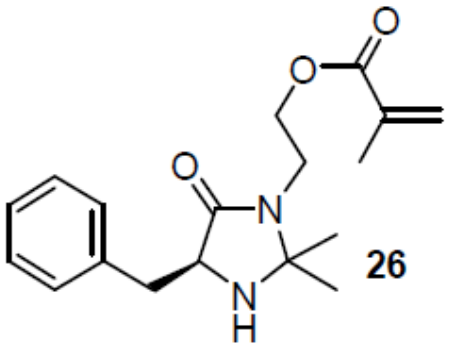
Question 2 (30%)



26

Spectroscopic data for compound **26** are found in attachment 2.

a) Assign as many of the signals as possible in the ^{13}C-NMR spectrum of **26** and give a very brief explanation for your assignment.
b) Assign as many of the signals as possible in the ^{1}H-NMR spectrum of **26** and give a very brief explanation for your assignment.

Question 3 (50%).

a) An “unknown” compound has been studied spectroscopically. Propose a molecular structure for the “unknown” compound based on the spectroscopic data found in attachment 3. Assign as many of the signals in the ^{13}C- and ^{1}H-NMR spectra as possible and give a brief explanation for your assignments. Elemental analysis: C 75.0 %, H 6.25%. HR-MS gave *m/z* = 256.1099 for the molecular ion. IR: 3100 (m), 2930 (s), 1740 (s), 1715 (s). UV: ε = 13000 (222 nm) og 6000 (275 nm). Draw structural equations with arrows to account for the fragmentation reactions which produce the following fragments: 157, 156, 169, 168, 142, 141, 115.
b) Approximately 10% of the ”unknown” compound exists in an isomeric form. This give rise to several additional (small) peaks both in the ^{13}C- and the ^{1}H-NMR spectrum. Draw the structure of the isomeric compound and assign the peaks at 12.3 (s, 0.1H), 4.77 (s, 0.1H) og 3.98 (s, 0.2H) in the ^{1}H-NMR spectrum.

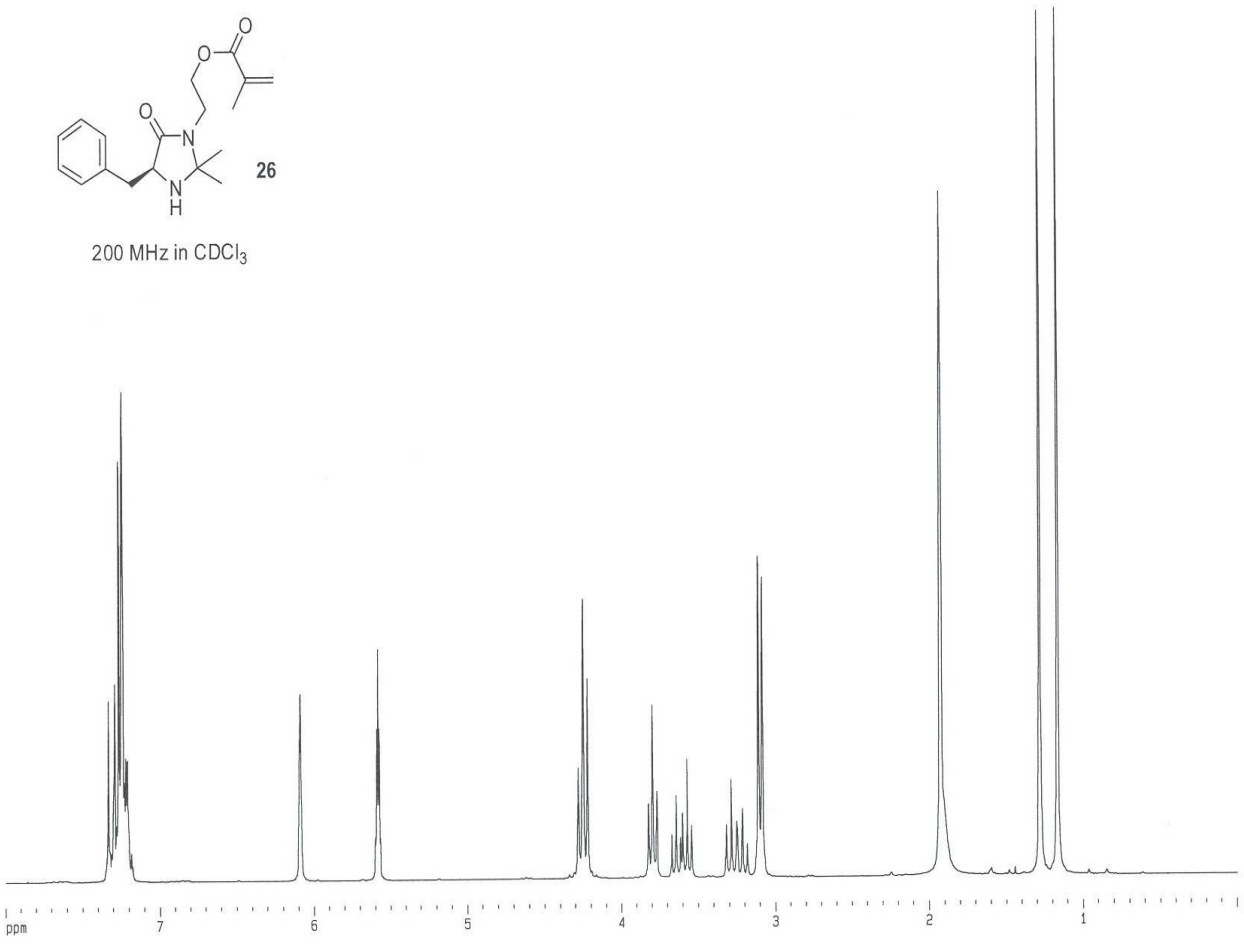
Vedlegg 1 / Attachment 1

Table 4.3 Atomic weights and approximate natural abundance of some isotopes

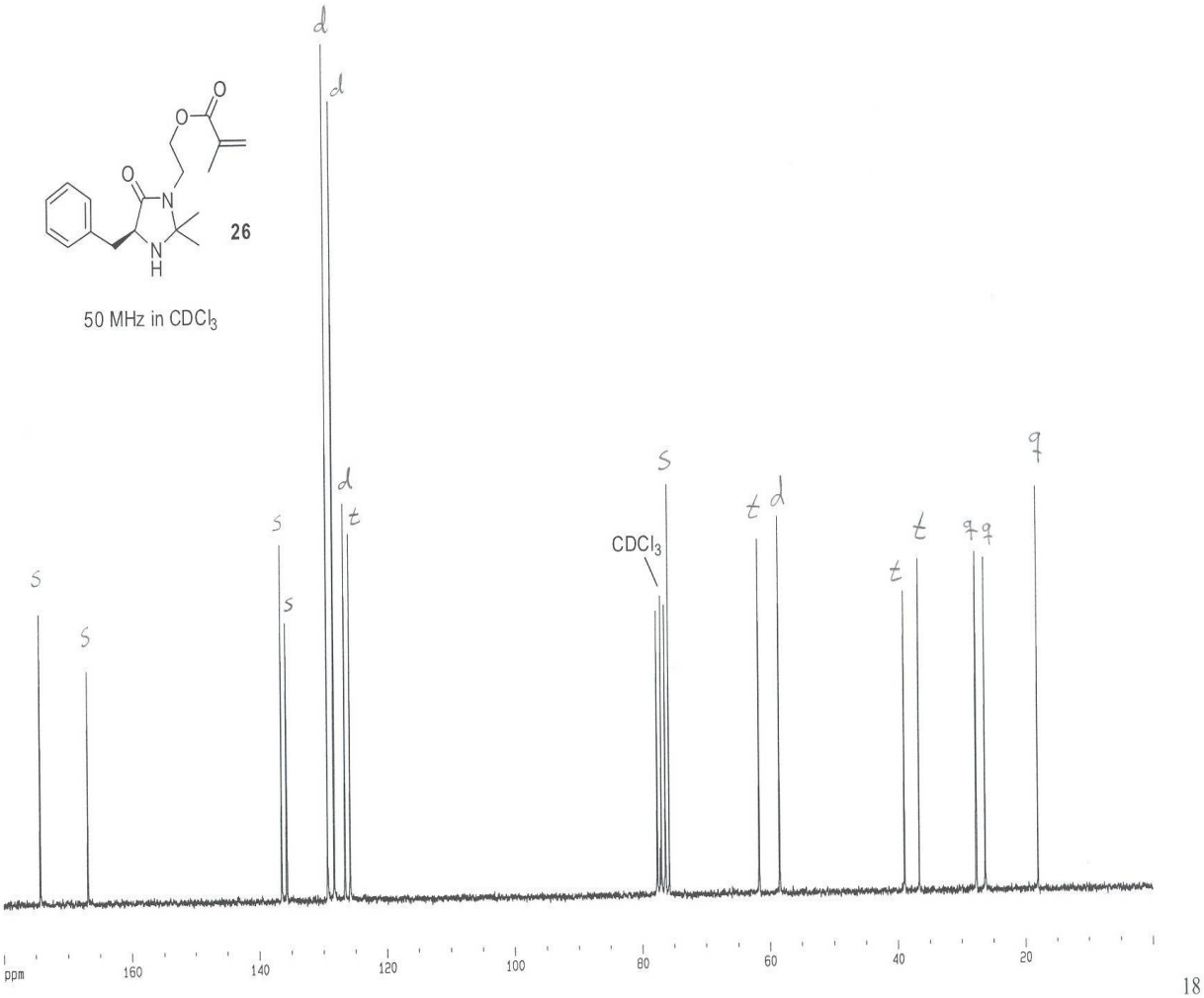
Isotope	*Atomic weight* ($^{12}C = 12.000\,000$)	*Natural abundance* (%)
^{1}H	1.007 825	99.985
^{2}H	2.014 102	0.015
^{12}C	12.000 000	98.9
^{13}C	13.003 354	1.1
^{14}N	14.003 074	99.64
^{15}N	15.000 108	0.36
^{16}O	15.994 915	99.8
^{17}O	16.999 133	0.04
^{18}O	17.999 160	0.2
^{19}F	18.998 405	100
^{28}Si	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

Vedlegg 2 / Attachment 2

The ^{13}C-NMR and ^{1}H-NMR spectra are recorded on a 200 MHz instrument with $CDCl_3$ as solvent.
The intergral for the signal at 1.9 ppm in the ^{1}H-NMR spectrum is reduced from 4 to 3 when the sample is shaken with D_2O.
^{1}H NMR (200MHz, $CDCl_3$): δ = 1.17 (s, 3H), 1.28 (s, 3H), 1.86-1.95 (m, 4H), 3.10 (d, 2H, *J* = 5.4 Hz), 3.25 (dt, 1H, *J* = 14.3 Hz and 6.6 Hz), 3.61 (dt, 1H, *J* = 14.3 Hz and 5.7 Hz), 3.80 (t, 1H, *J* = 5.4 Hz), 4.19-4.32 (m, 2H), 5.58 (quint, 1H, *J* = 1.2 Hz), 6.09 (m, 1H), 7.17-7.35 (m, 5H) ppm.

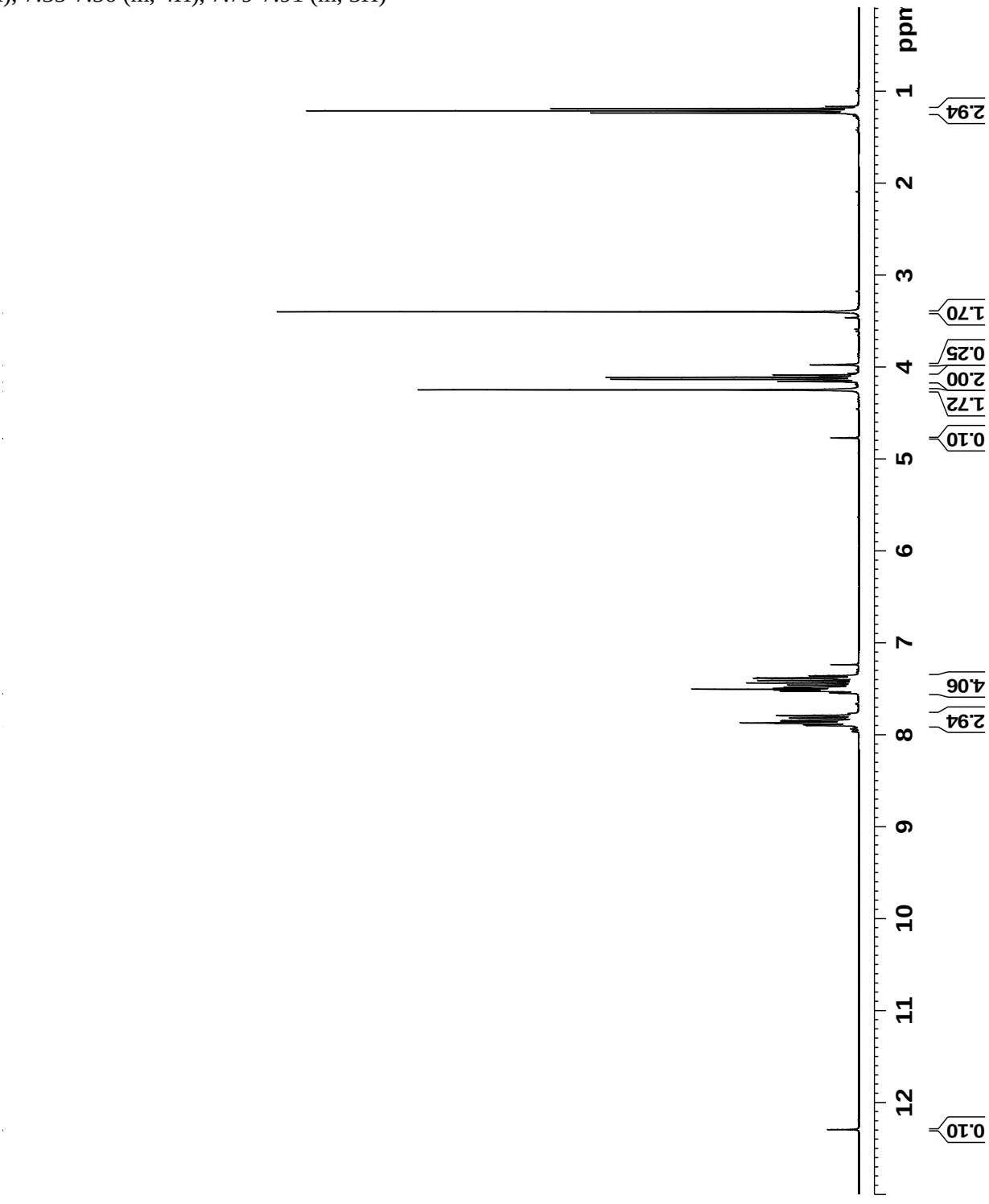


^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.1, 26.3, 27.7, 36.7, 39.0, 58.5, 61.7, 75.8, 125.8, 126.7, 128.3, 129.3, 135.7, 136.5, 166.9, 174.3 ppm.

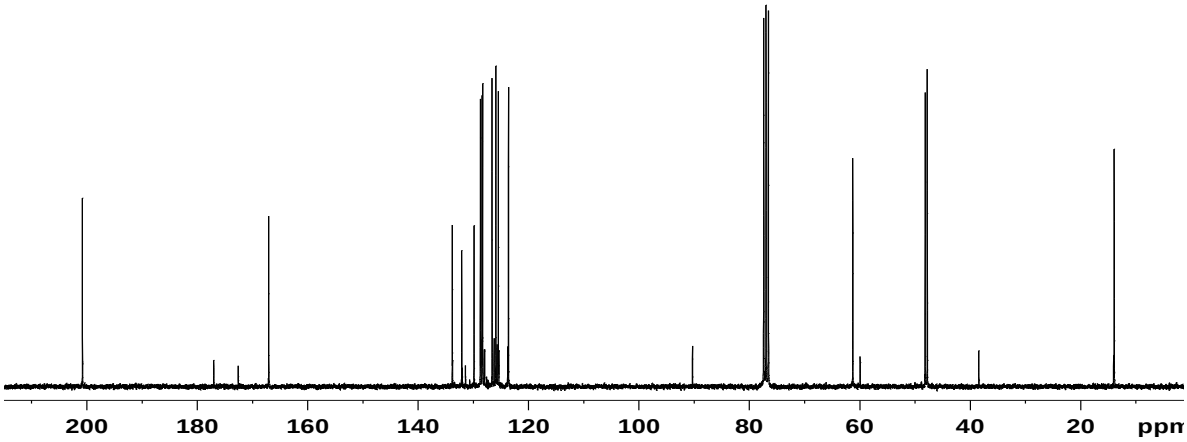


Vedlegg 3 / Attachment 3

300 MHz; $CDCl_3$): δ 1.22 (t, 3H, *J*=7.1 Hz), 3.40 (s, 2H), 4.12 (q, 2H, *J*=7.1 Hz), 4.25 (s, 2H), 7.35-7.56 (m, 4H), 7.79-7.91 (m, 3H)



^{13}C-NMR: (75 MHz; $CDCl_3$): δ 13.9 (q), 47.8 (t), 48.2 (t), 61.3 (t), 123.6 (d), 125.5 (d), 125.9 (d), 126.6 (d), 128.3 (d), 128.4 (d), 128.7 (d), 129.9 (s), 132.1 (s), 133.8 (s), 173.0 (s), 201.2 (s).



MS: EI, 70eV.