Lectures 7 and 8 – Worked Problems

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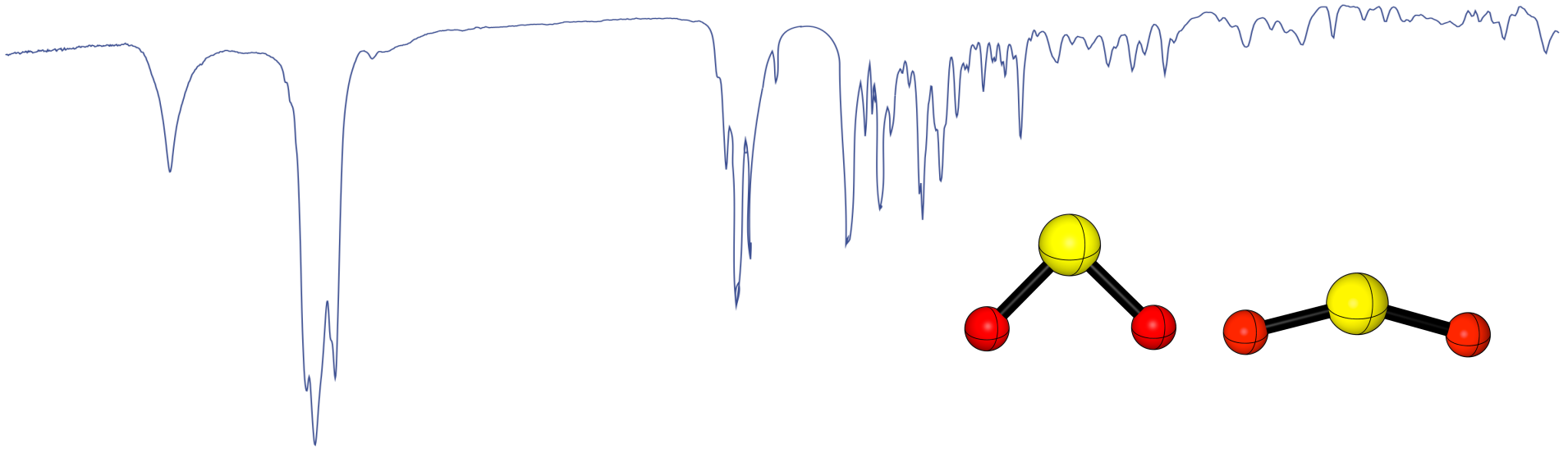


Recap of Lecture 6

IR Spectroscopy

Useful for identifying functional gropus present in organic molecules

The X-H region (> 2500cm^{-1}) contains diagnostic absorptions from N-H and O-H stretches. On occasion C-H stretches may also be a useful diagnostic tool

O-H stretches are broadened by H-bonding: intermolecular and intramolecular H-bonding are distinguished by taking spectra at different concentrations

The triple bond region (2000-2500 cm^{-1}) contains diagnostic information from e.g. nitriles and alkynes

The double bond region (1600-2000 cm^{-1}) contains absorptions from C=C (albeit weakly, around 1650) and from C=O (strongly, around 1700)

Carbonyls are strengthened by a neighbouring EWG and weakened by a neighbouring EDG

Conjugation weakens carbonyls (approx. minus 30cm^{-1})

Ring strain stiffens carbonyls (approx. 40cm^{-1} for successively smaller rings)

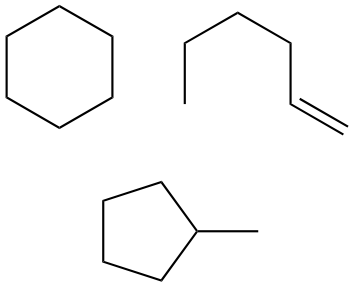
Double-bond equivalents (DBE):
If the molecular formula has been obtained from the mass spectrum, the number of *double-bond equivalents* (DBE) may be calculated. If the molecule contains only C, H, N and O atoms and is neutral, then:

$$C_aH_bN_cO_d \qquad DBE = \frac{(2a + 2) - (b - c)}{2}$$

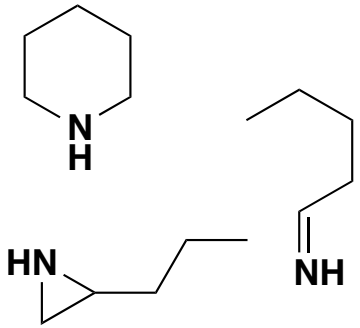
The DBE is the number of double bonds and rings in the molecule (it is useful to remember that benzene has a total of four double-bond equivalents: three C=C double-bonds and one ring).

The above formula works since $(2a + 2)$ is the number of hydrogens in a saturated hydrocarbon and so subtracting b, the actual number of hydrogens present and dividing by two gives the total number of double bonds and rings. The number of divalent atoms (e.g. O, S, etc) does not affect the DBE, but the number of mono- and trivalent atoms does. All monovalent atoms (e.g. F, Cl, Br, etc) count as hydrogens so should be added to b, whilst all trivalent atoms (e.g. N, trivalent P, etc) count towards c.

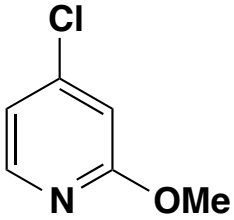
C_6H_{12}



$C_5H_{11}N$



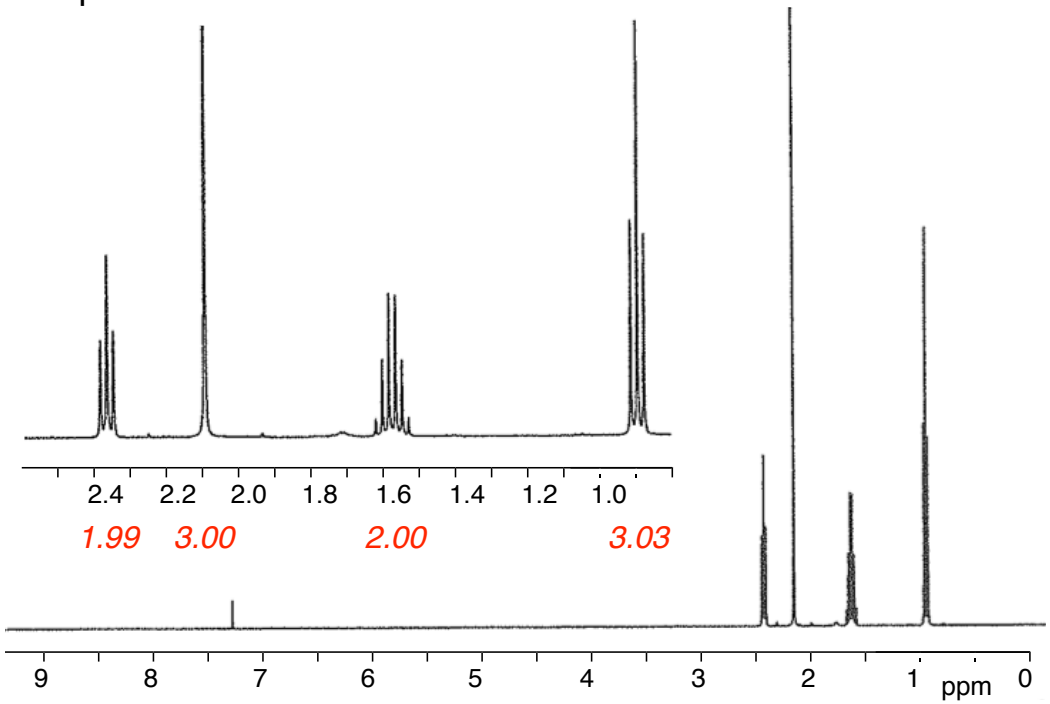
C_6H_6NOCl



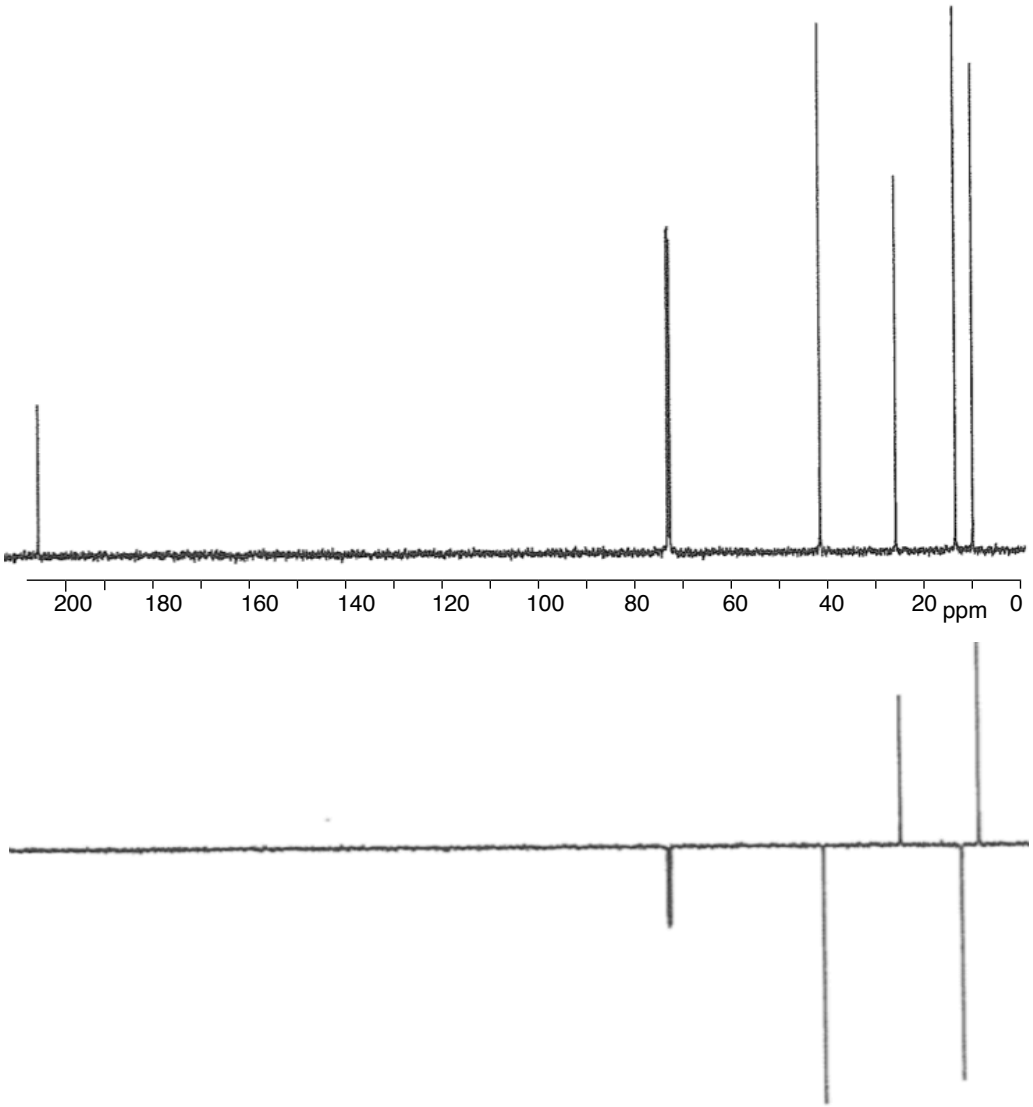
Solving Structures

Worked Problem: Determine the structures of seven isomers of $C_5H_{10}O$ using the following ^1H, ^{13}C (broadband decoupled and DEPT-edited) NMR spectra:

Compound A: ^1H NMR



^{13}C NMR



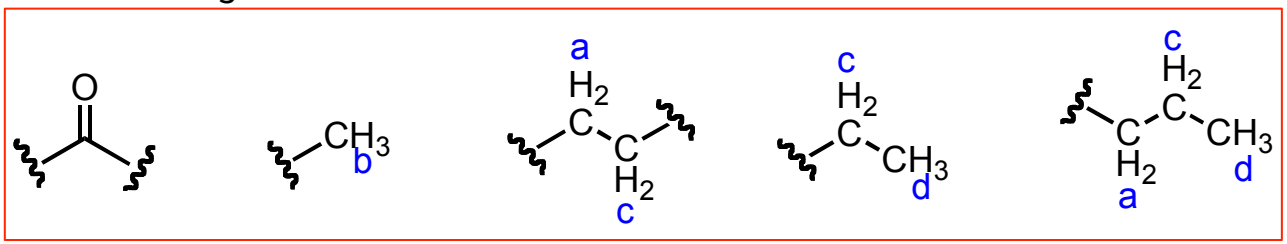
Solving Structures

Compound A: $C_5H_{10}O$

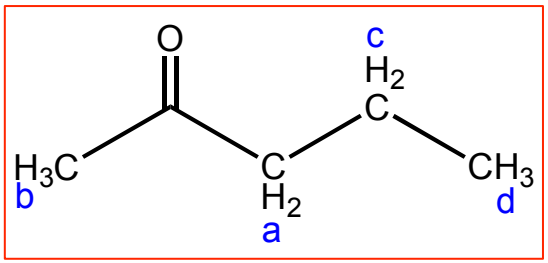
^{1}H NMR data:

H_a	2.38	2H	*t*
H_b	2.1	3H	*s*
H_c	1.58	2H	*sext*
H_d	0.9	3H	*t*

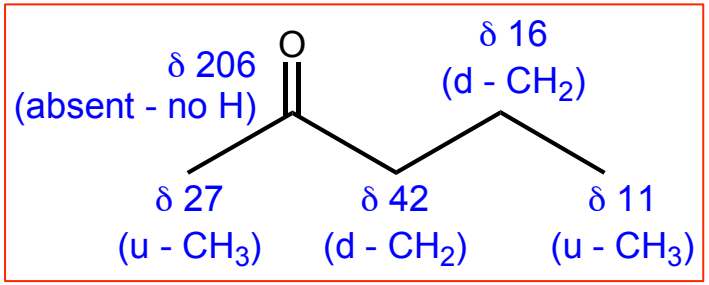
Structural Fragments:



Structure of A:

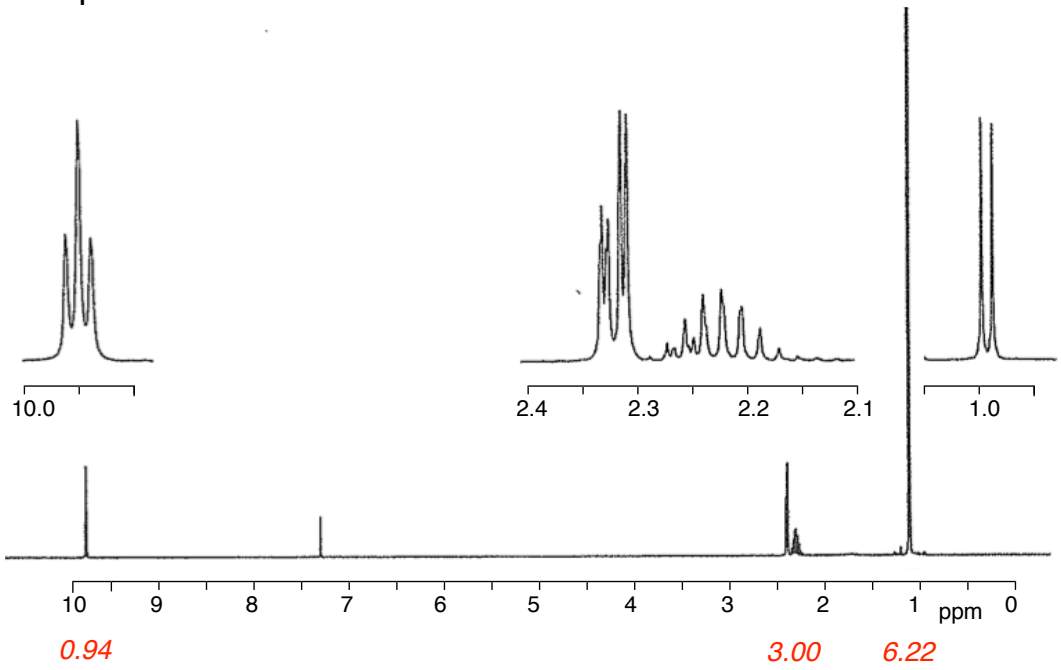


^{13}C NMR Assignment (DEPT in parentheses):

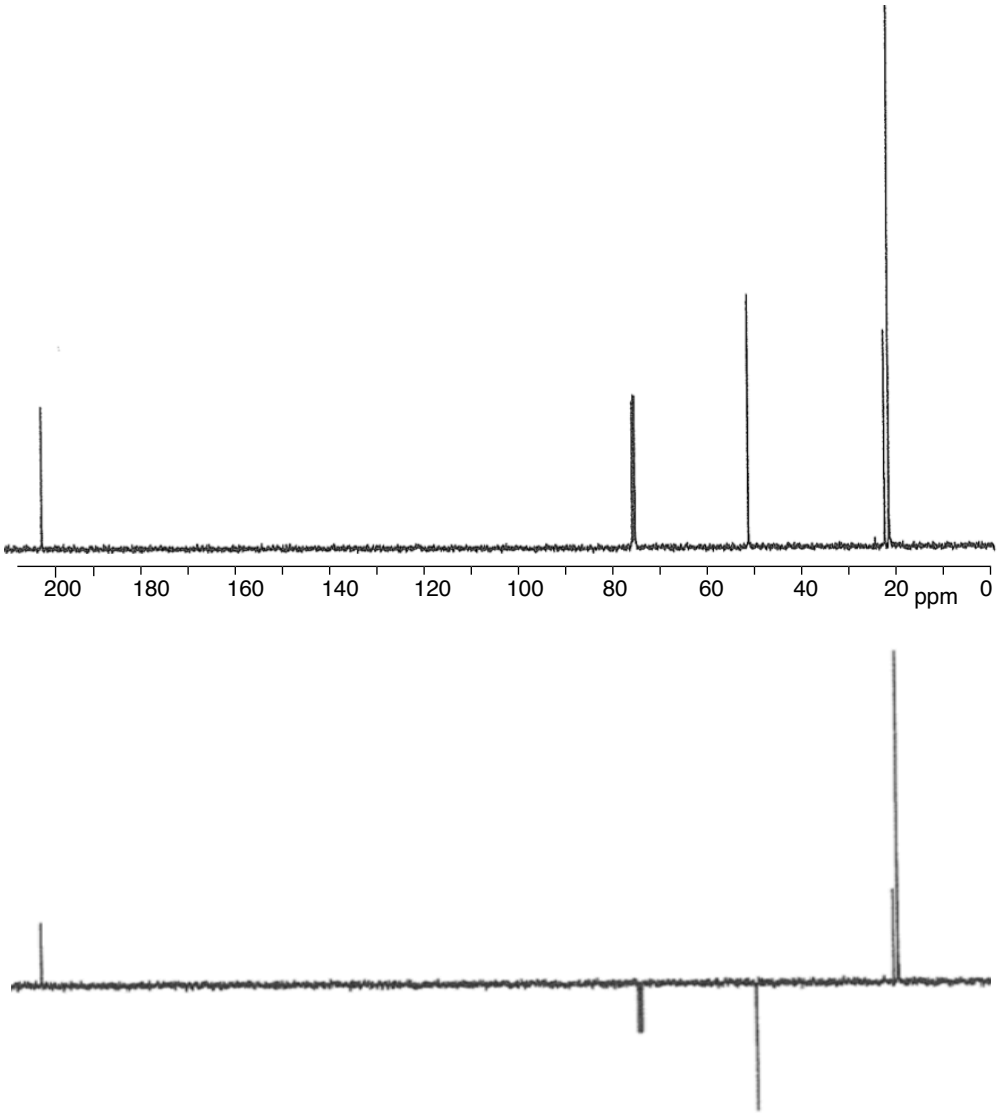


Solving Structures

Compound B: ^{1}H NMR



^{13}C NMR



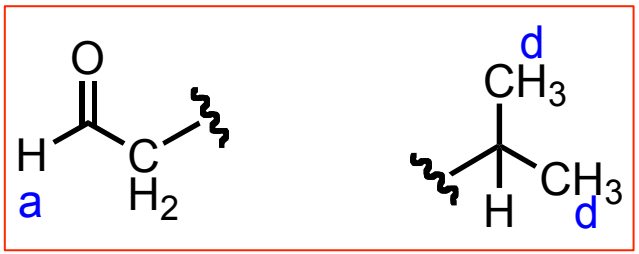
Solving Structures

Compound B: $C_5H_{10}O$

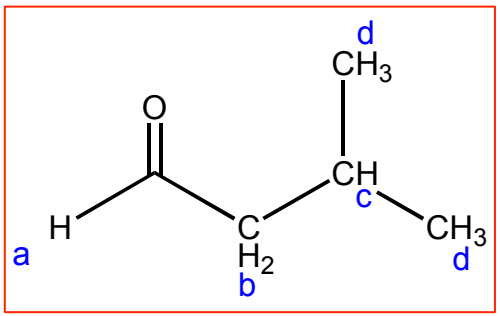
^{1}H NMR data:

H_a	9.8	1H	*t*
H_b	2.32		*dd*
H_c	2.23		*m*
H_d	1.0	6H	*d*

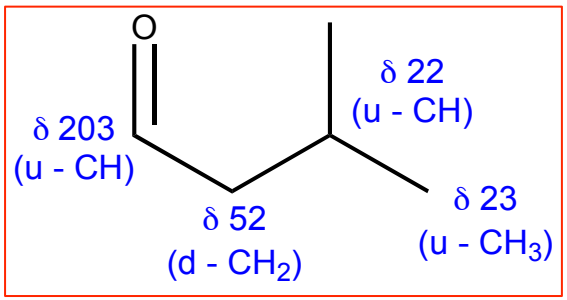
Structural Fragments:
DBEs = 1



Structure of B:

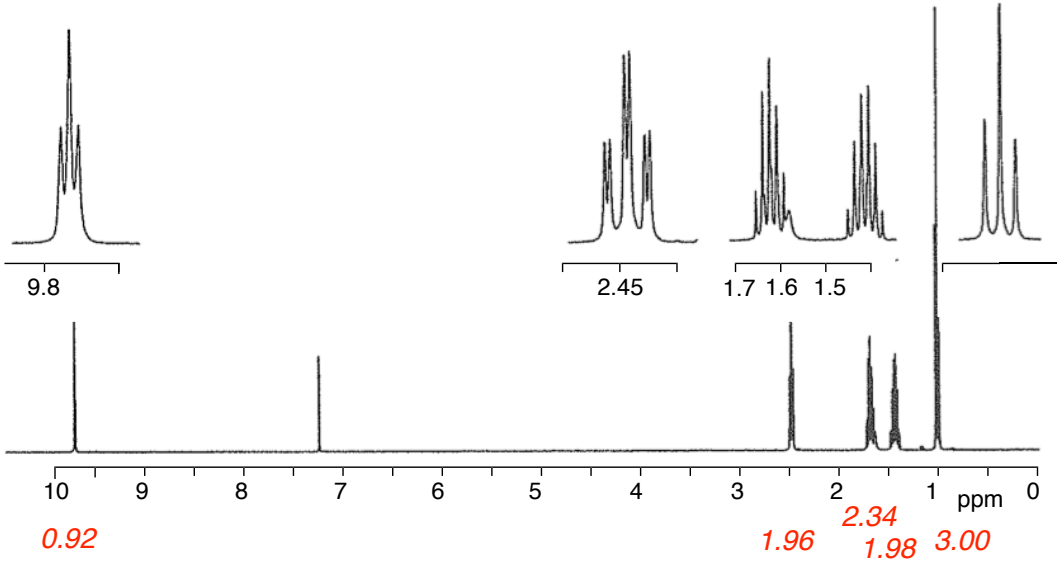


^{13}C NMR Assignment (DEPT in parentheses):

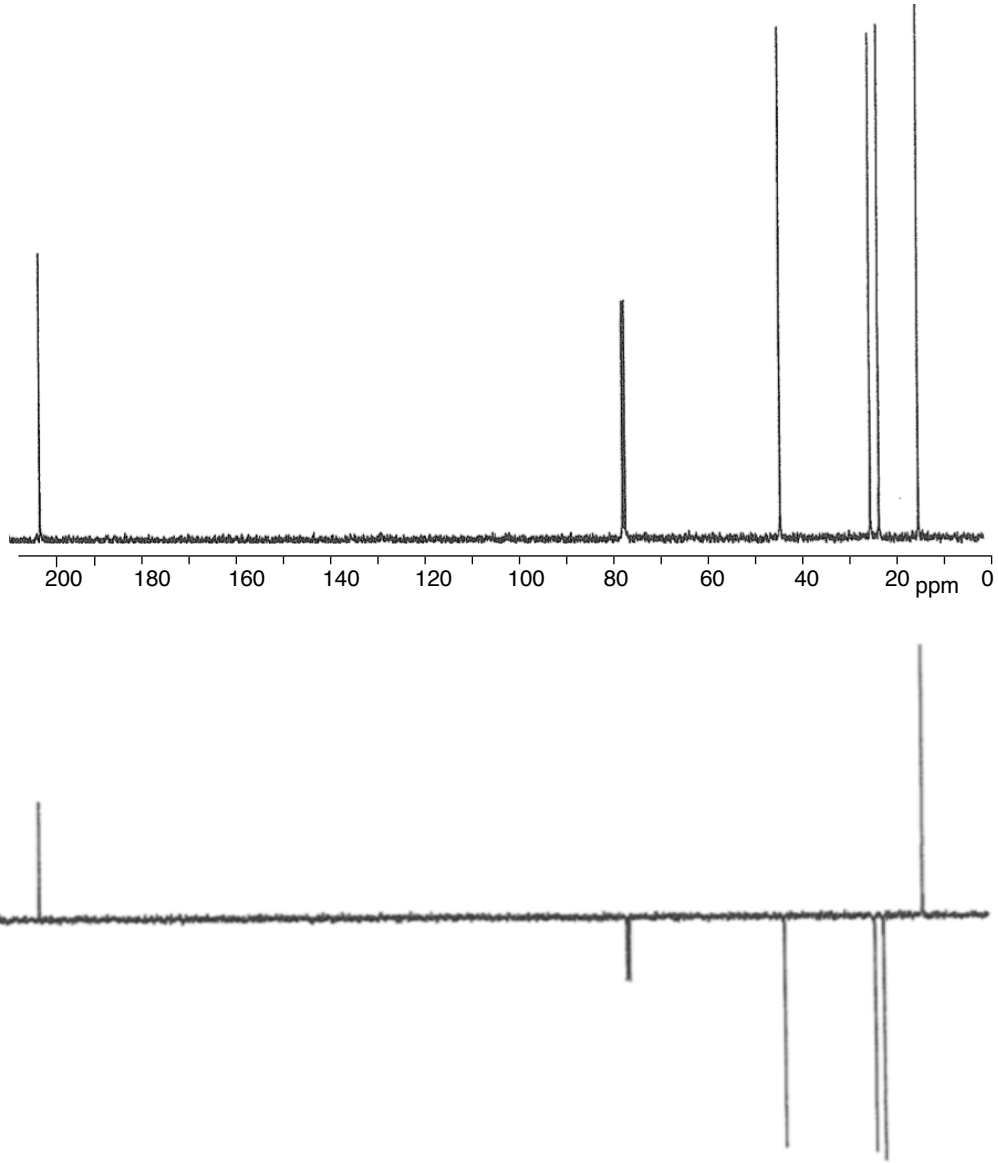


Solving Structures

Compound C: ^{1}H NMR



^{13}C NMR



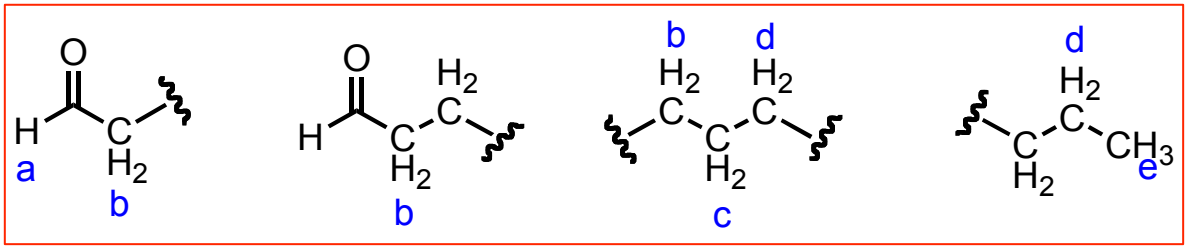
Solving Structures

Compound C: $C_5H_{10}O$

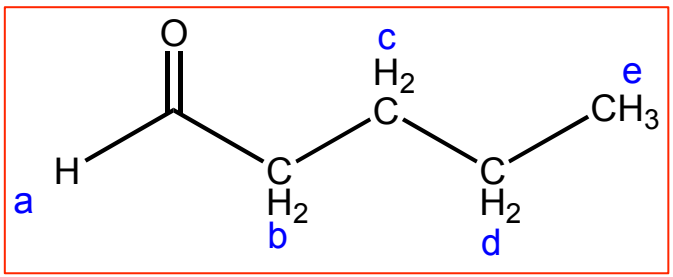
^{1}H NMR data:

H_a	9.78	1H	*t*
H_b	2.45	2H	*td*
H_c	1.64	2H	*quin*
H_d	1.38	2H	*sext*
H_e	0.95	3H	*t*

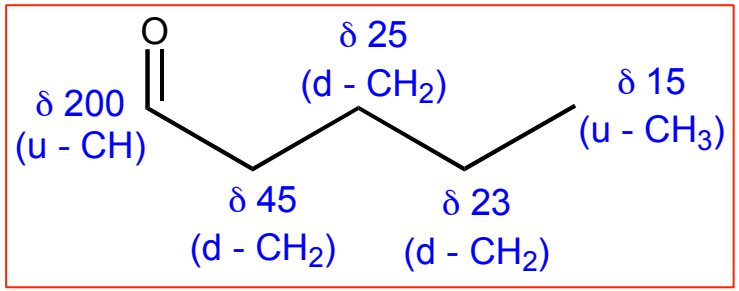
Structural Fragments:



Structure of C:

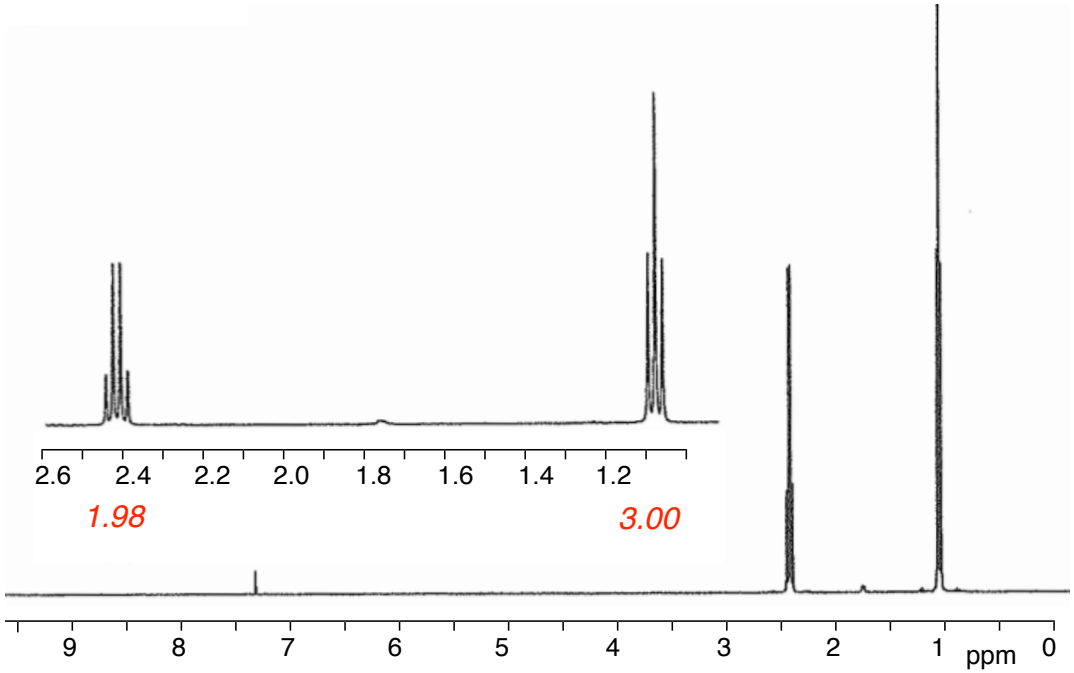


^{13}C NMR Assignment (DEPT in parentheses):

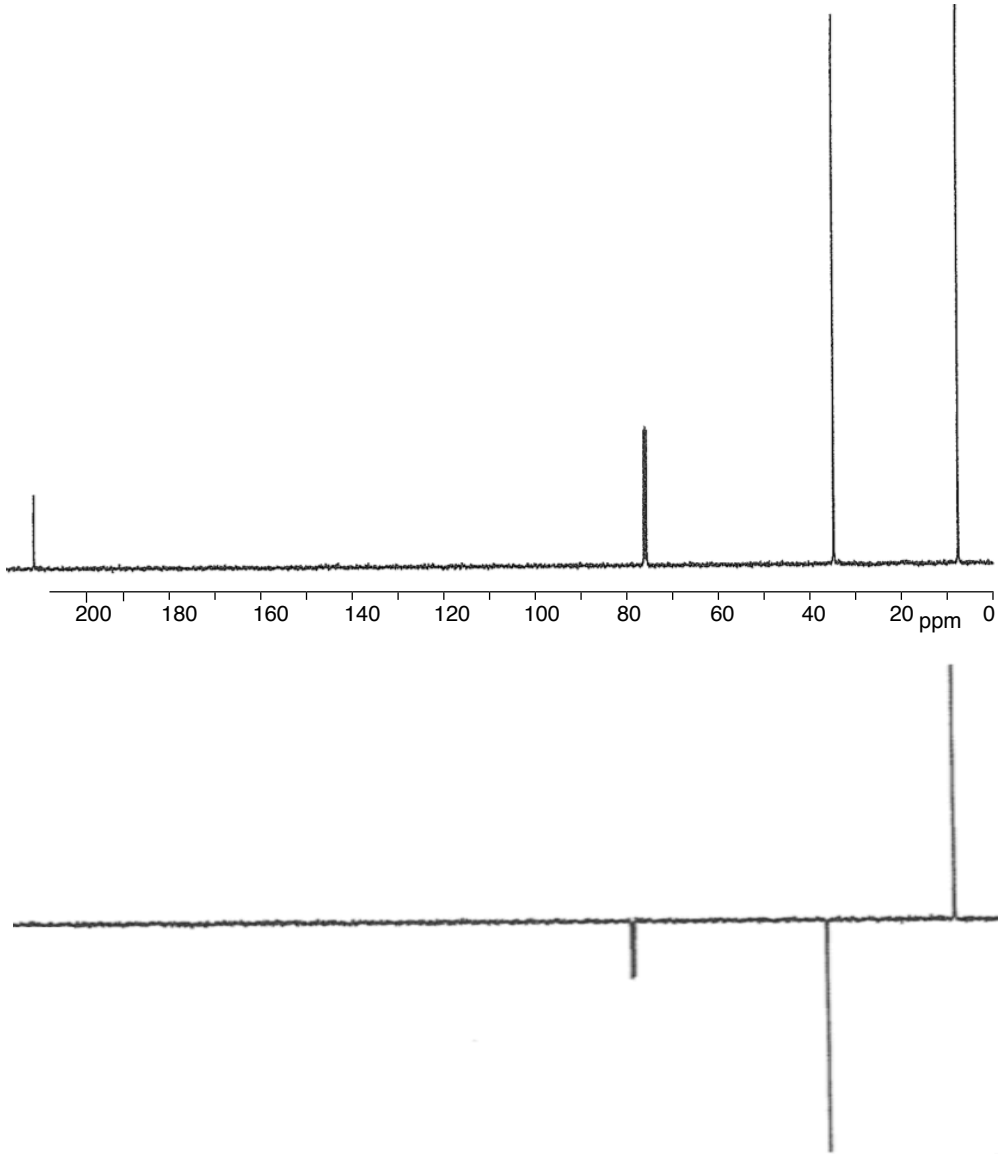


Solving Structures

Compound D: ^{1}H NMR



^{13}C NMR



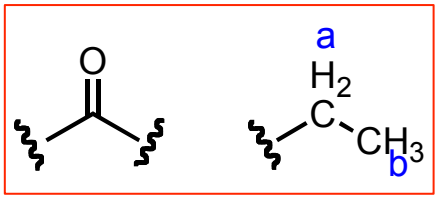
Solving Structures

Compound D: $C_5H_{10}O$

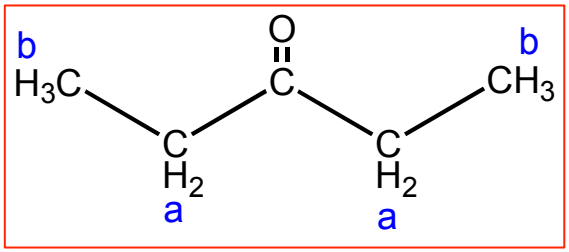
^{1}H NMR data:

H_a	2.43	4H	*q*
H_b	1.05	6H	*t*

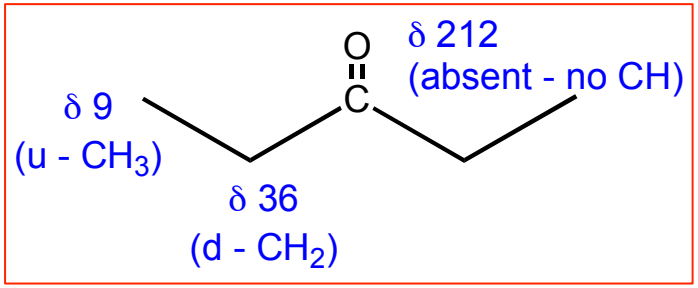
Structural Fragments:



Structure of D:

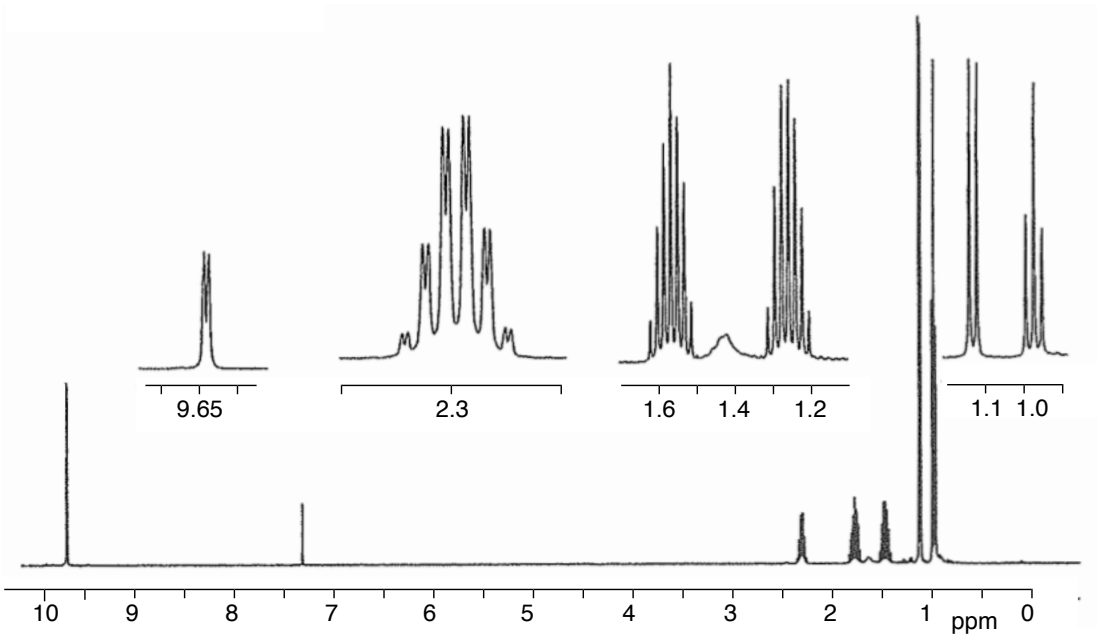


^{13}C NMR Assignment (DEPT in parentheses):



Solving Structures

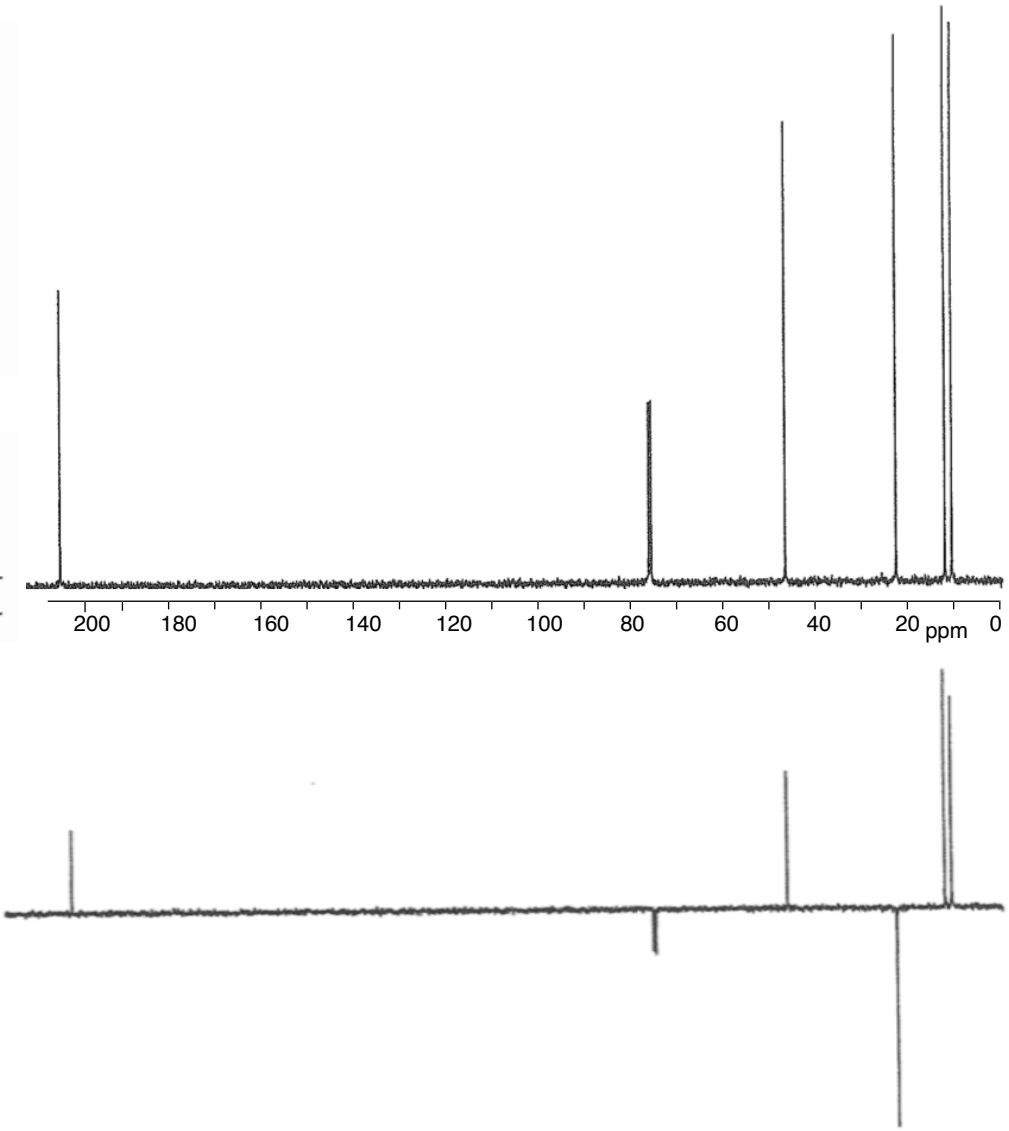
Compound E: ^{1}H NMR



0.91

1.00 1.07 3.14
1.10 3.52

^{13}C NMR



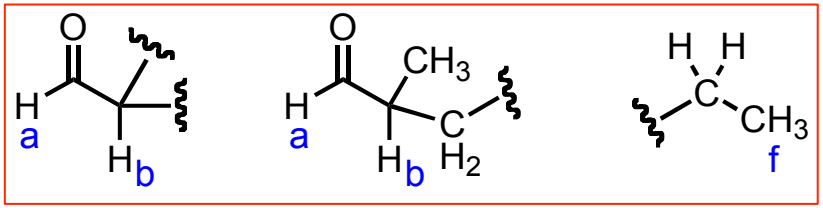
Solving Structures

Compound E: $C_5H_{10}O$

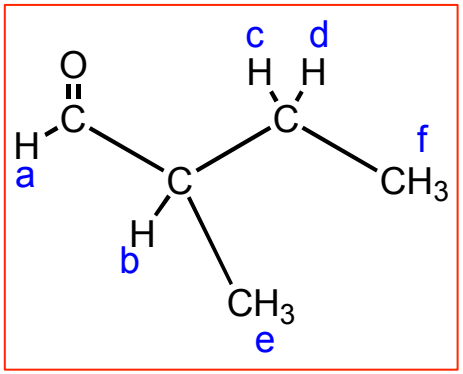
^{1}H NMR data:

H_a	9.64	1H	*d*
H_b	2.29	1H	*sext d*
H_c	1.47	1H	*complex multiplet*
H_d	1.77	1H	*complex multiplet*
H_e	1.11	3H	*d*
H_f	0.97	3H	*t*

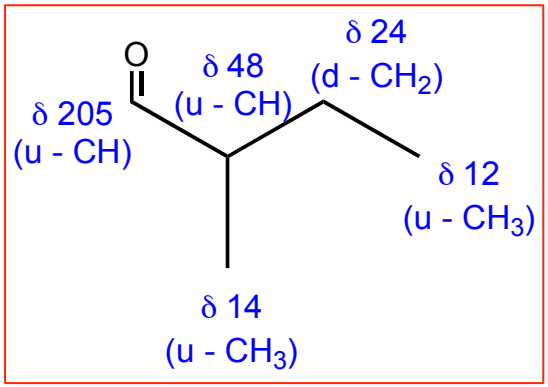
Structural Fragments:



Structure of E:

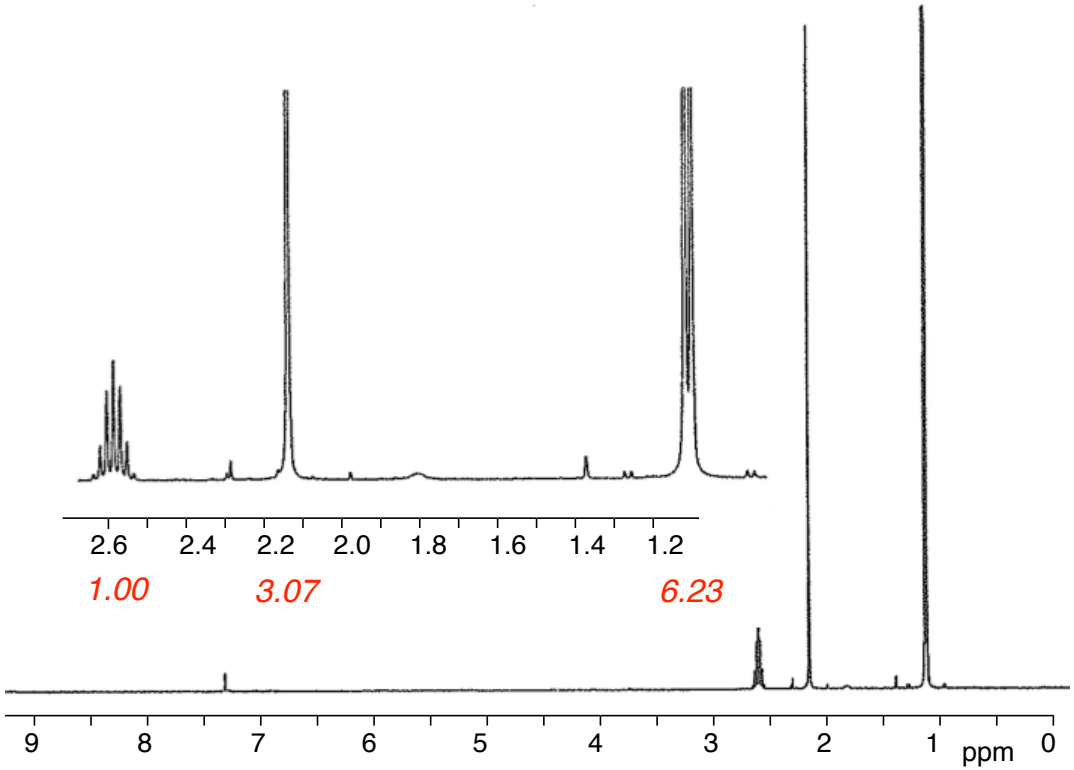


^{13}C NMR Assignment (DEPT in parentheses):

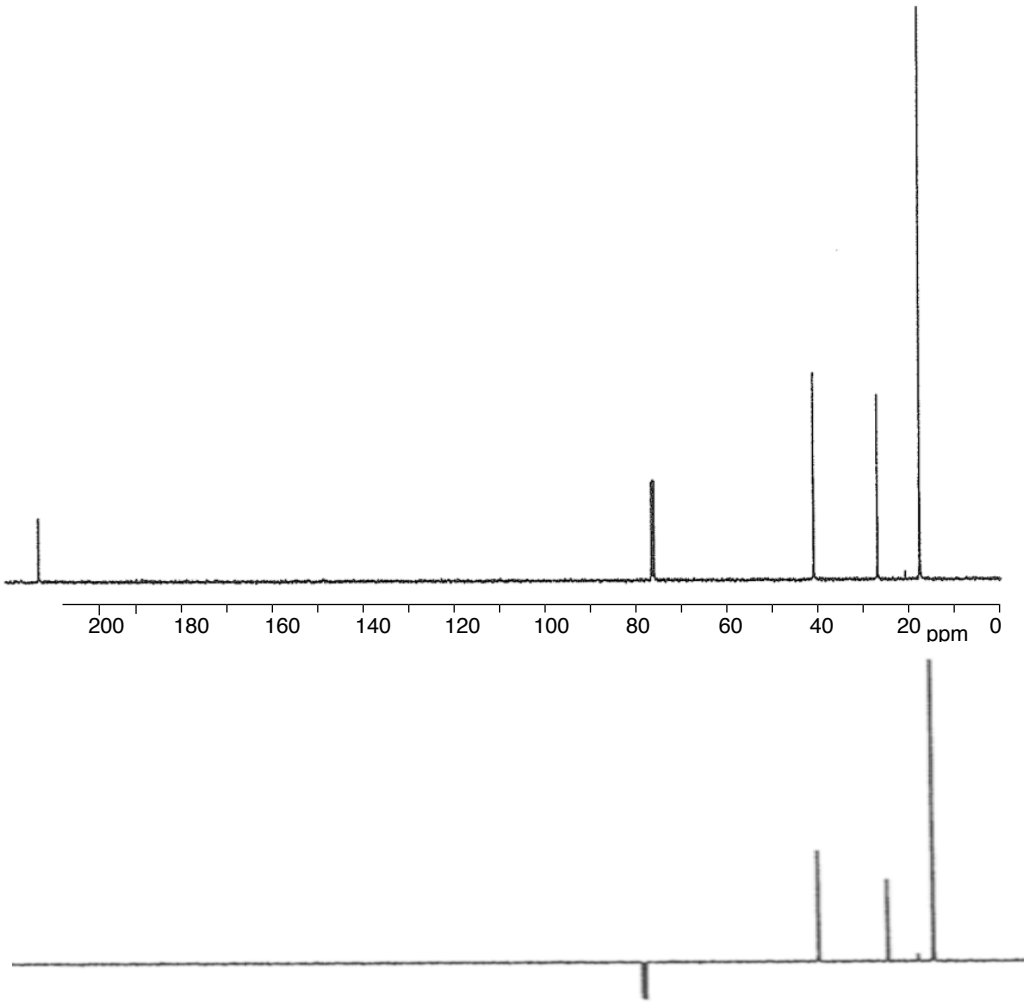


Solving Structures

Compound F: ^{1}H NMR



^{13}C NMR



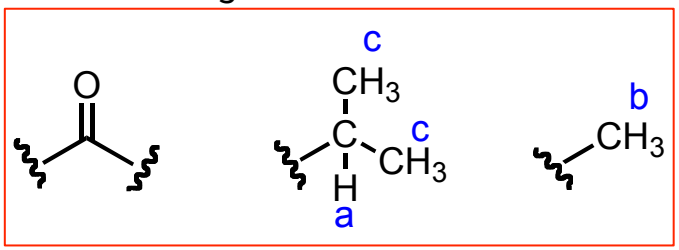
Solving Structures

Compound F: $C_5H_{10}O$

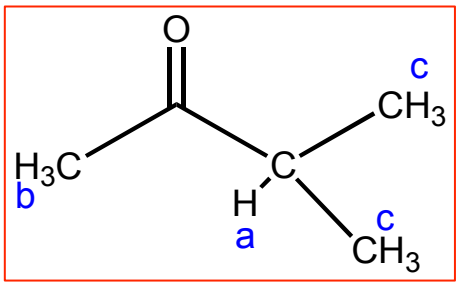
^{1}H NMR data:

H_a	2.59	1H	*sept*
H_b	2.14	3H	*s*
H_c	1.1	6H	*d*

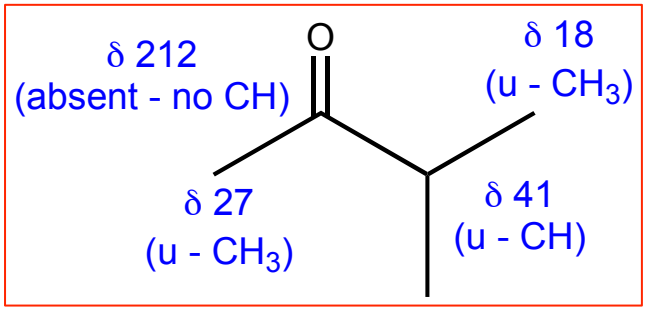
Structural Fragments:



Structure of F:

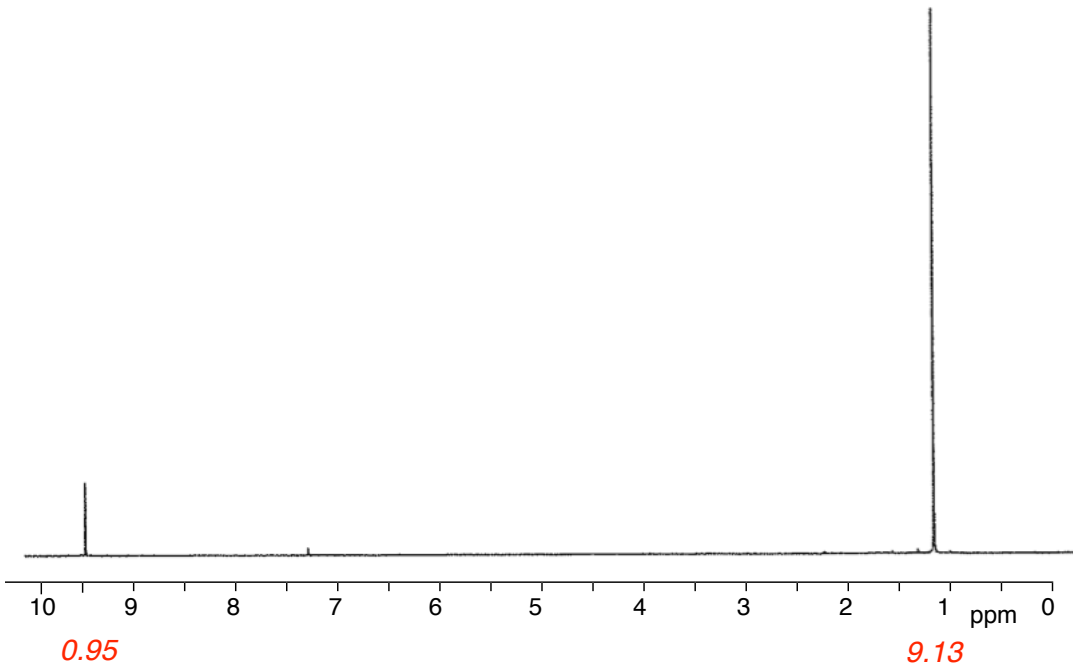


^{13}C NMR Assignment (DEPT in parentheses):

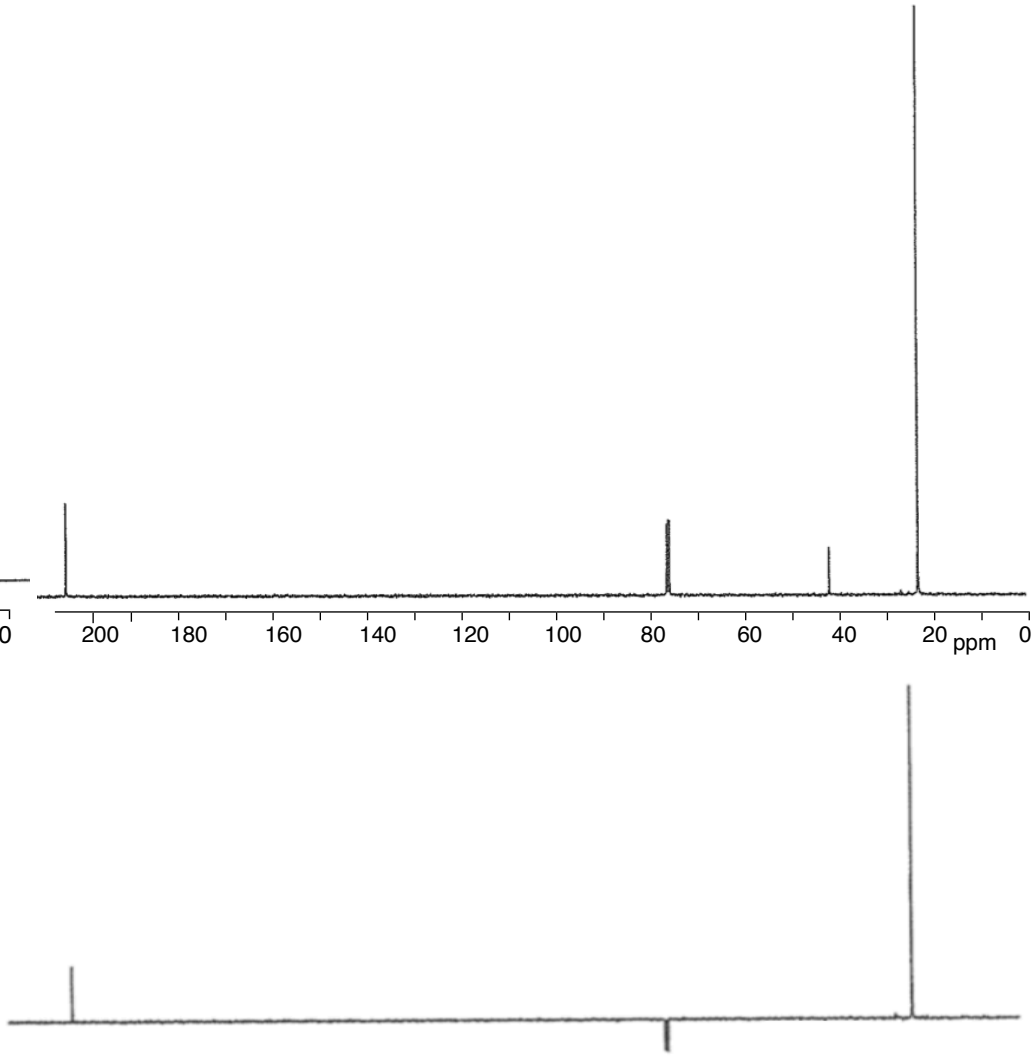


Solving Structures

Compound G: ^{1}H NMR



^{13}C NMR



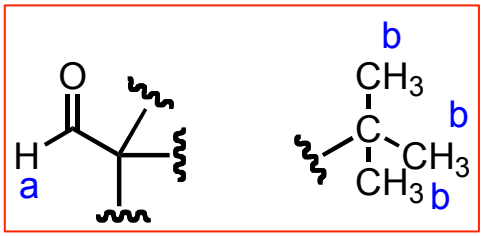
Solving Structures

Compound G: $C_5H_{10}O$

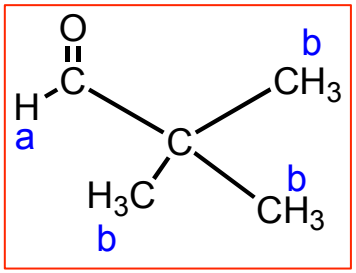
^{1}H NMR data:

H_a	9.5	1H	*s*
H_b	1.1	9H	*s*

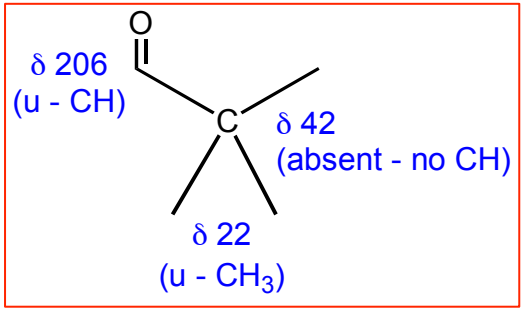
Structural Fragments:



Structure of G:



^{13}C NMR Assignment (DEPT in parentheses):



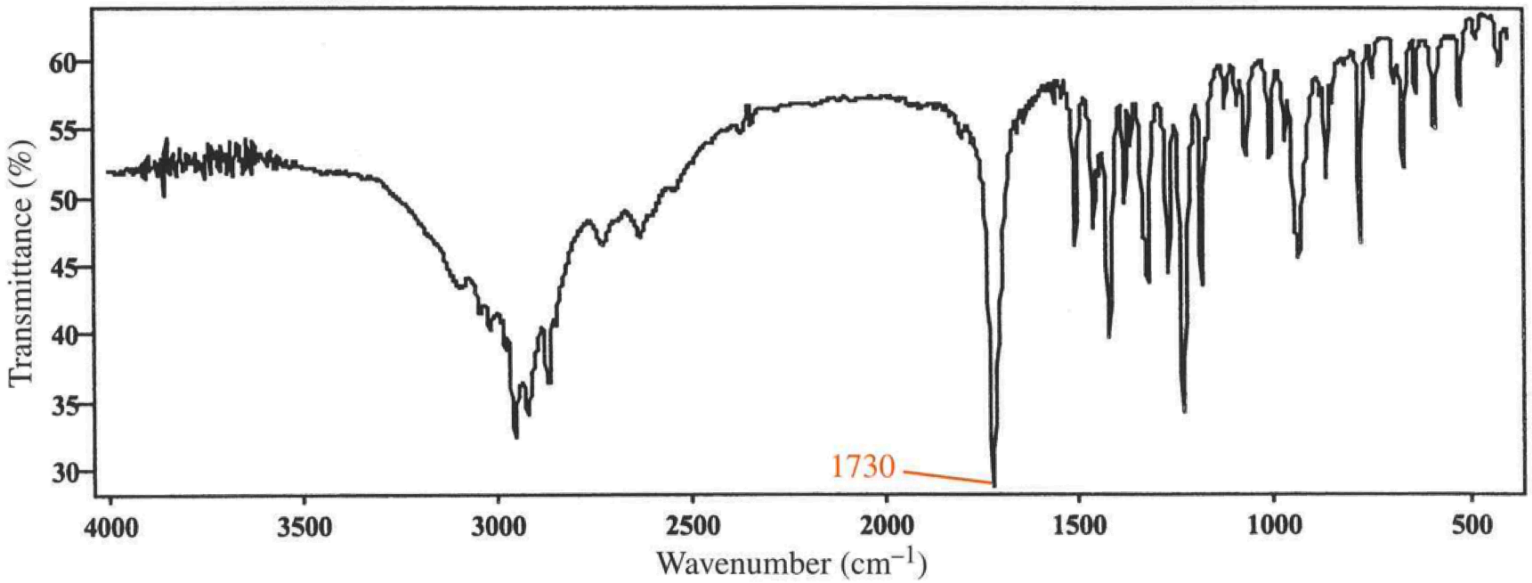
Solving Structures

Worked Problem: Determine the structure of **X**, $C_{13}H_{18}O_2$ given the following spectroscopic data:

DBEs:

(13x2 + 2) -18 / 2 = 5

IR spectrum:

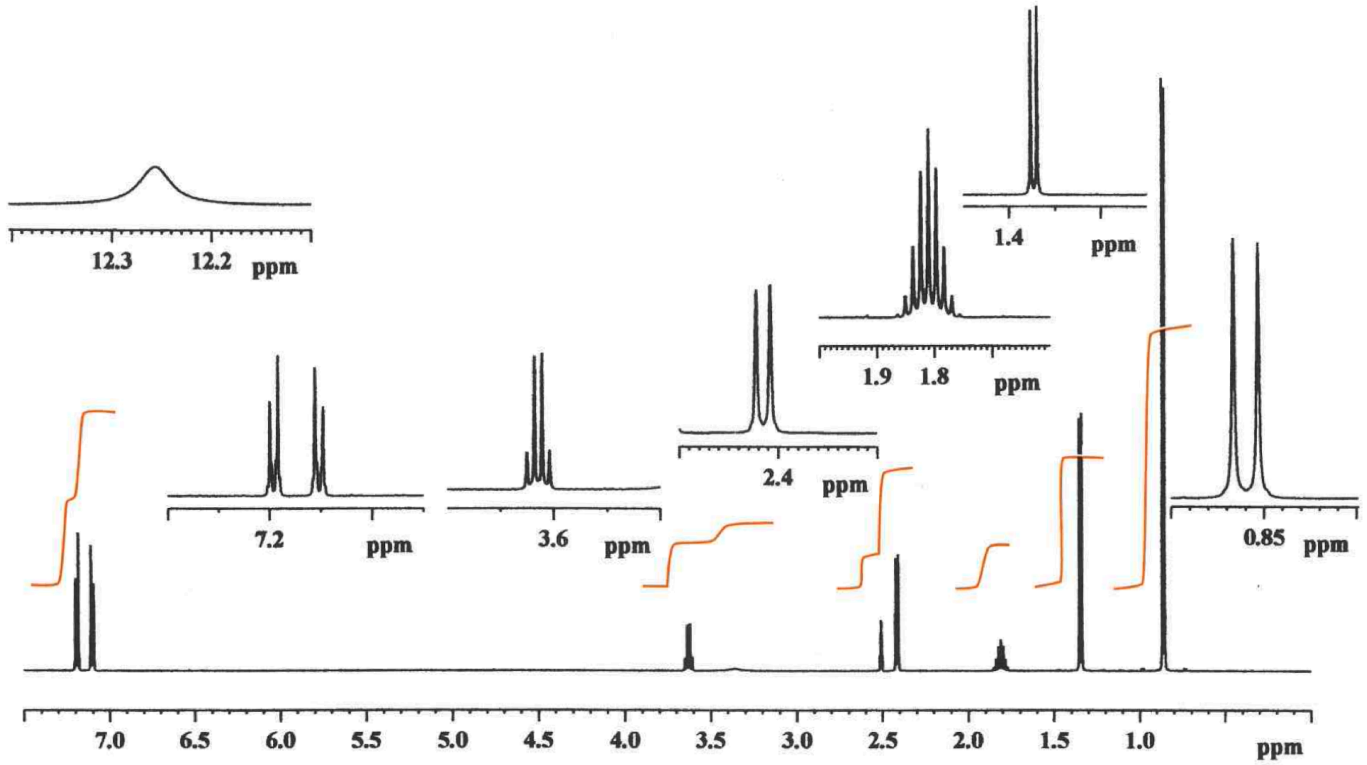


Diagnostic absorptions:

1730 (s) : aldehyde / carboxylic acid
3000-3400 (br) : OH or CO_2H
Various around 1500 : aromatic

Solving Structures

^{1}H NMR spectrum (500 MHz): d 0.86 (6H, d, J= 6.6 Hz), 1.34 (3H, d, J=7.1 Hz), 1.81 (1H, 9lines, J=6.6 Hz), 2.41 (2H, d, J=6.6 Hz), 3.63 (1H, q, J = 7.1 Hz), 7.10 (2H, d, 8.1 Hz), 7.19 (2H, d, J = 8.1 Hz) 12.25 (1H, broad s)

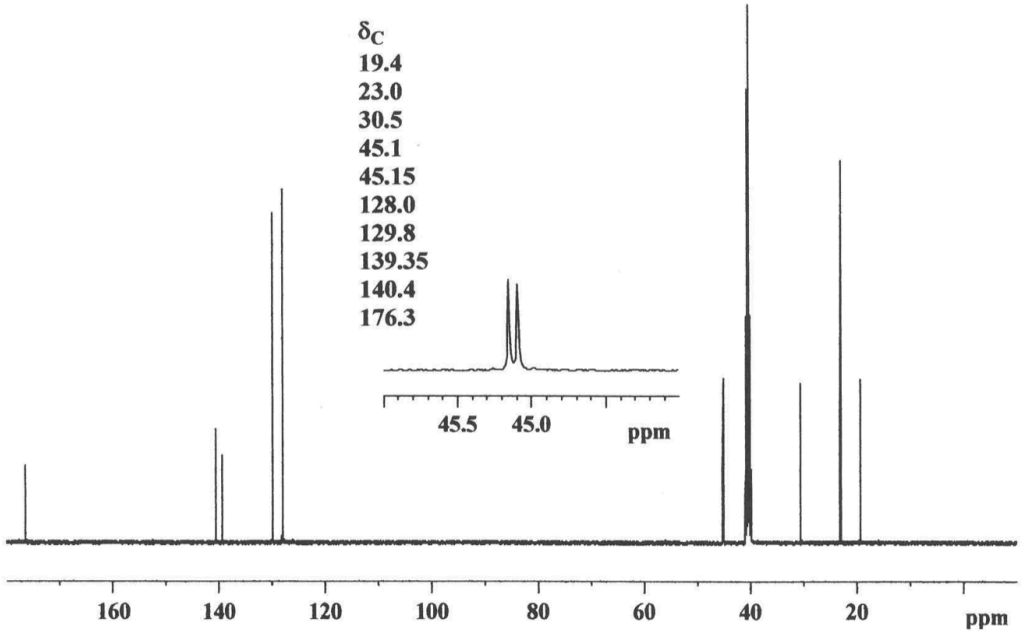


^{1}H NMR spectrum: (*8 peaks, so 8 proton environments)*

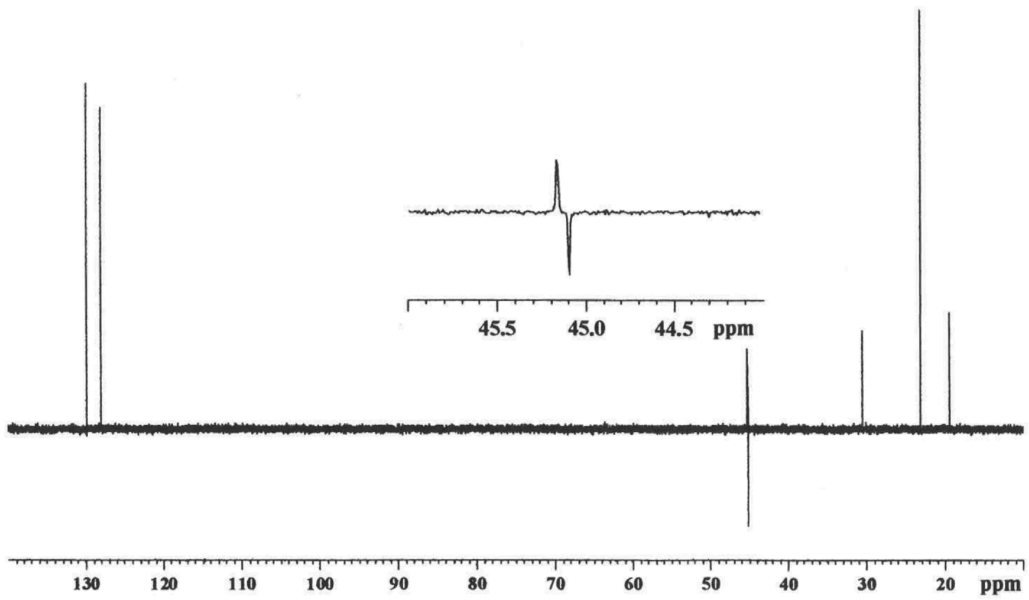
H_a	0.86	6H	d	J = 6.6 Hz
H_b	1.34	3H	d	J = 7.1 Hz
H_c	1.81	1H	9 lines	J = 6.6 Hz
H_d	2.41	2H	d	J = 6.6 Hz
H_e	3.63	1H	q	J = 7.1 Hz
H_f	7.10	2H	d	J = 8.1 Hz
H_g	7.19	2H	d	J = 8.1 Hz
H_h	12.25	1H	broad	

Solving Structures

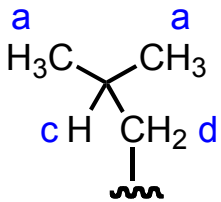
^{13}C NMR spectrum (125 MHz, proton decoupled)

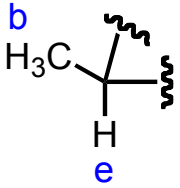


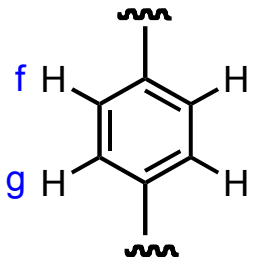
^{13}C DEPT spectrum (125 MHz, proton decoupled):

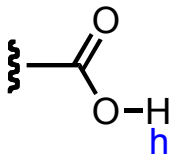


Structural fragments:

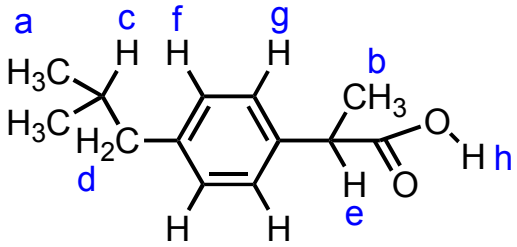


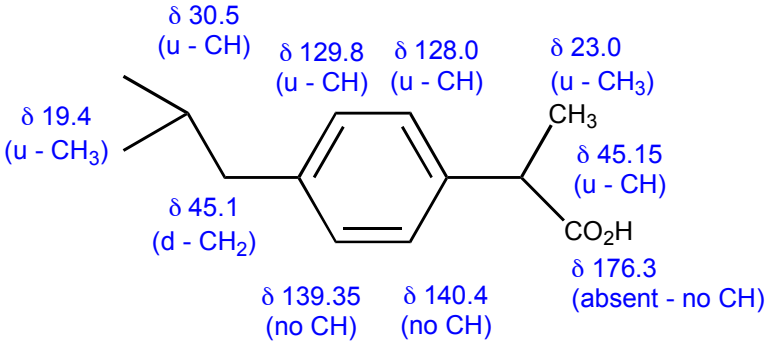






Structure of X



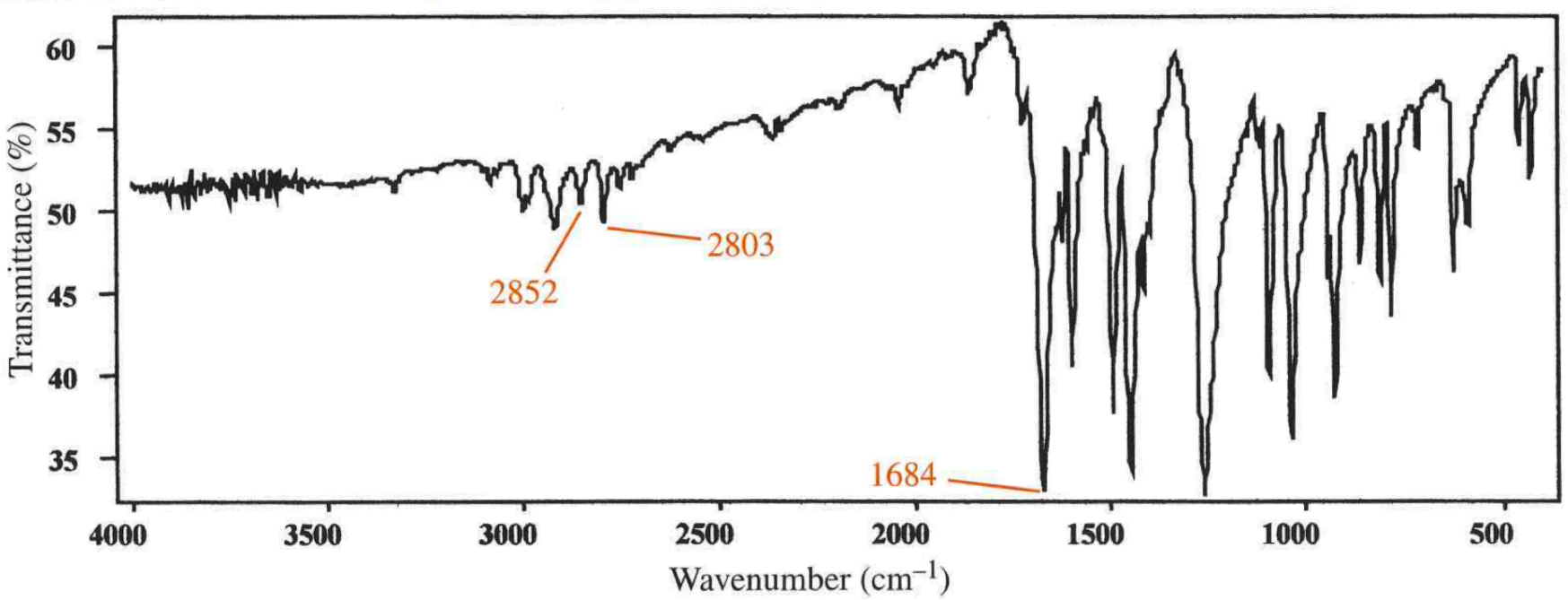


Solving Structures

Worked Problem: Determine the structure of **Y**, $C_8H_6O_3$ given the following spectroscopic data:

DBEs:
(8x2 + 2) - 6 / 2 = 6

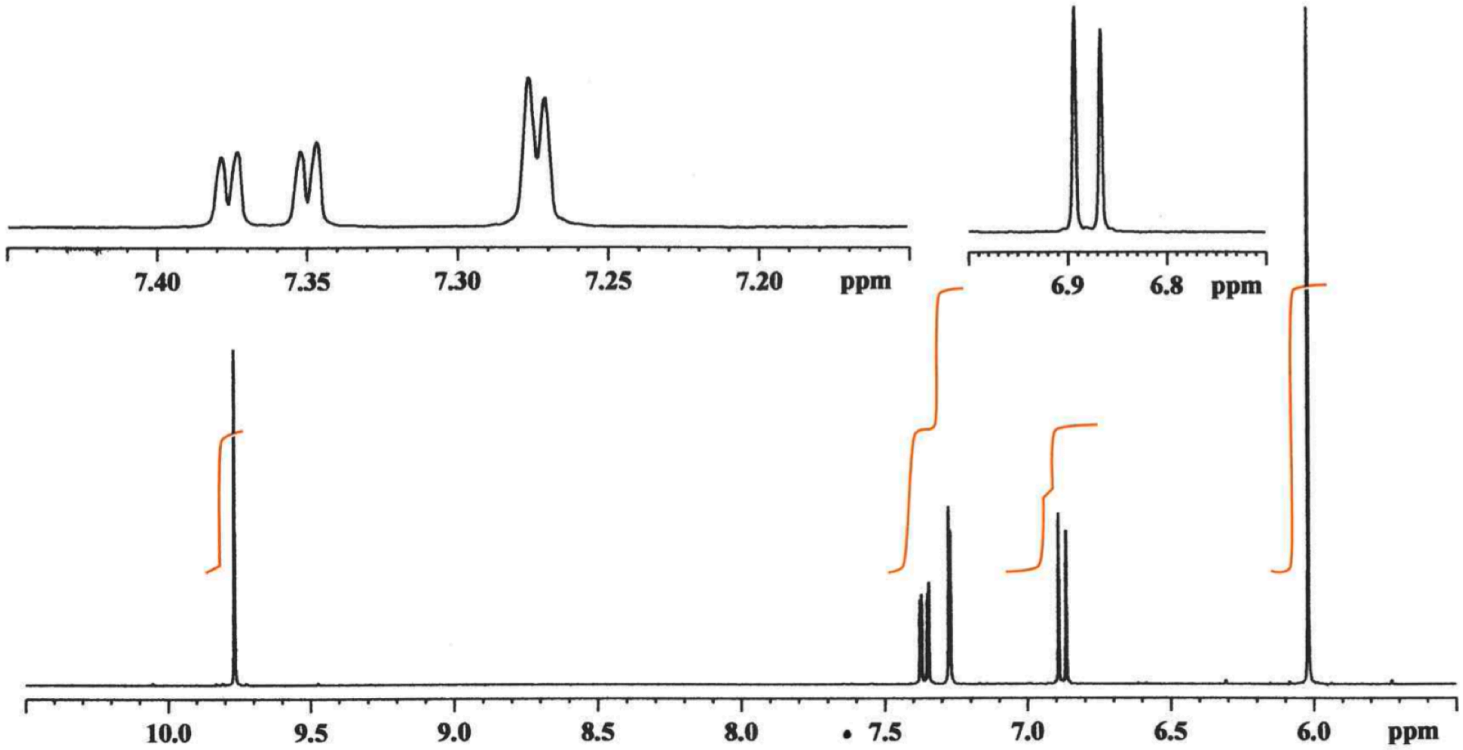
IR spectrum:



Diagnostic absorptions:
1684 (s) : conjugated carbonyl
2803 & 2852 : CH of aldehyde
Various around 1500 : aromatic

Solving Structures

^{1}H NMR spectrum (500 MHz): δ 6.04 (2H, s) 6.89 (1H, d, J=7.95 Hz), 7.28 (1H, d, J=1.6 Hz), 7.37 (1H, dd, J=7.95, 1.6 Hz), 9.77 (1H, s).

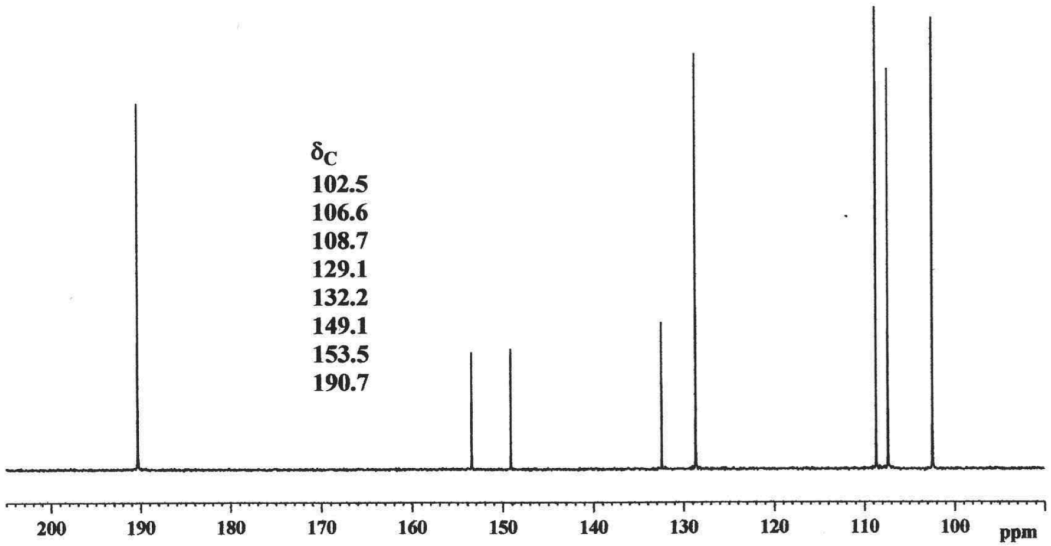


^{1}H NMR spectrum: (5 peaks, so 5 proton environments)

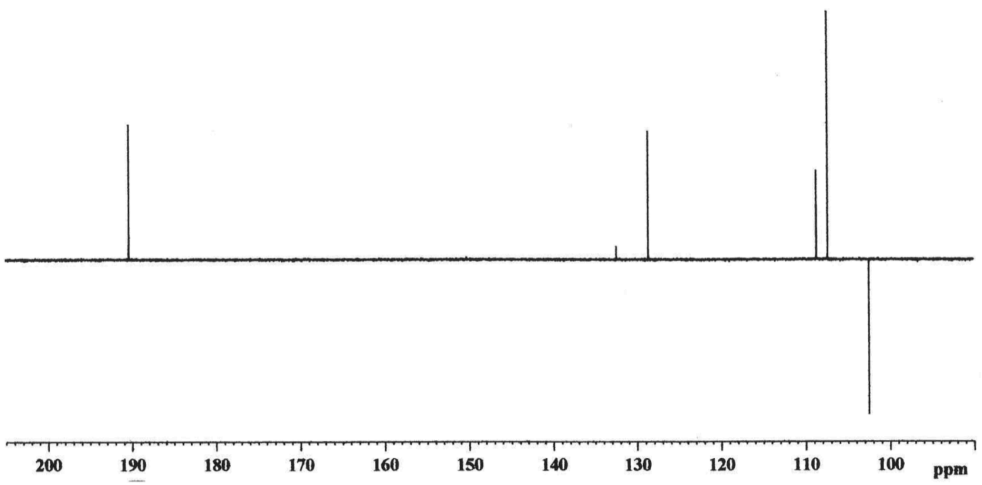
H_a	6.04	2H	s	
H_b	6.89	1H	d	J = 7.95 Hz
H_c	7.28	1H	d	J = 1.6 Hz
H_d	7.37	1H	dd	J = 7.95, 1.6 Hz
H_e	9.77	1H	s	

Solving Structures

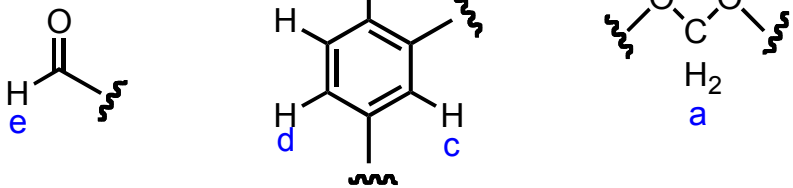
^{13}C NMR spectrum (125 MHz, proton decoupled):



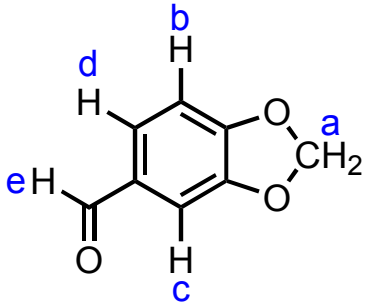
^{13}C DEPT spectrum (125 MHz, proton decoupled):

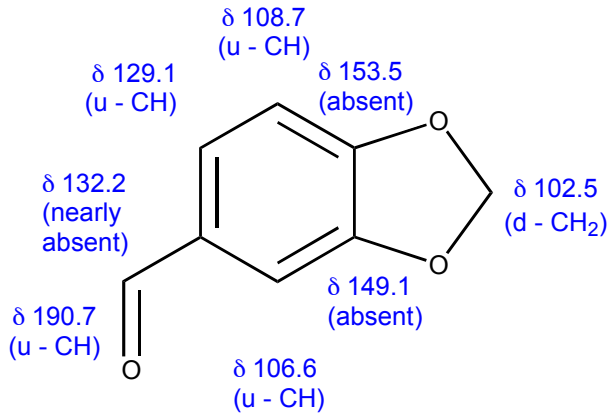


Structural fragments:



Structure of Y



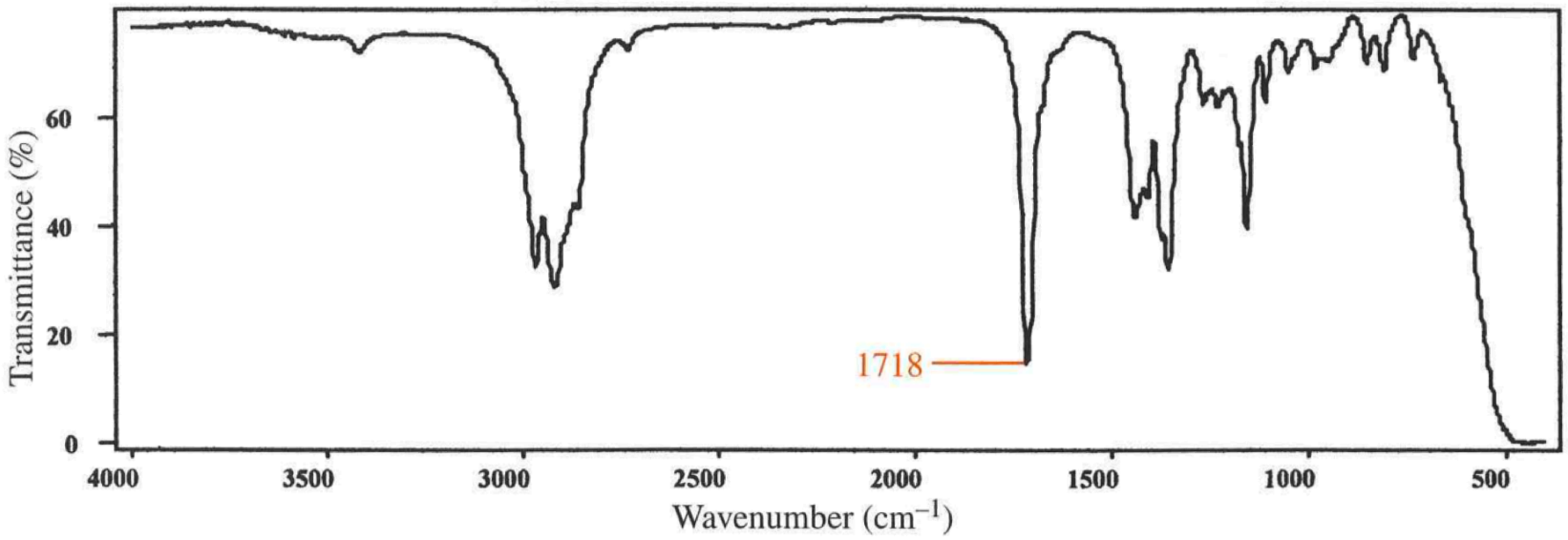


Solving Structures

Worked Problem: Determine the structure of **Z**, $C_8H_{14}O$ given the following spectroscopic data:

DBEs:
(8x2 + 2) -14 / 2 = 2

IR spectrum:

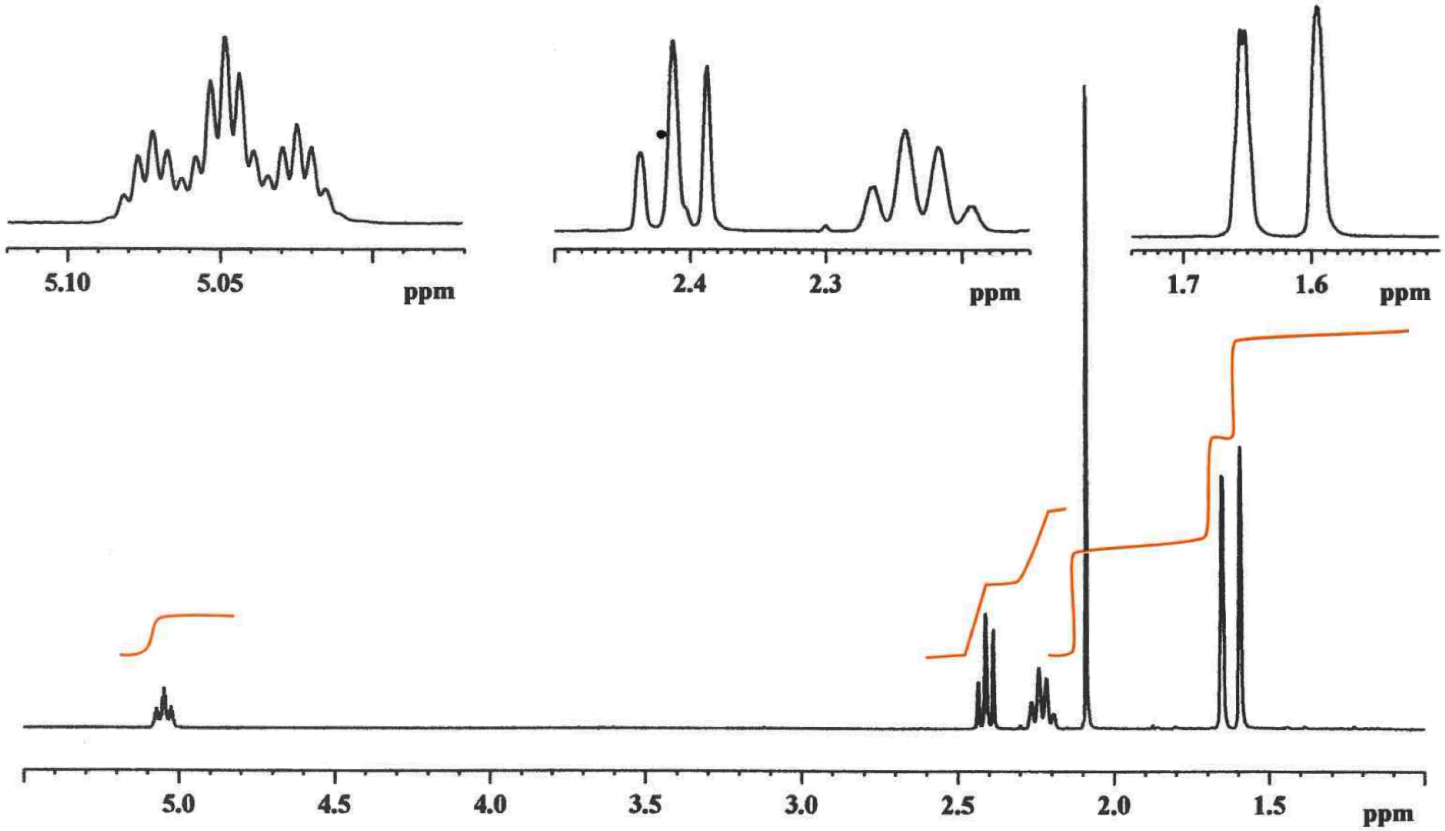


Diagnostic absorptions:

1718 (s) : ketone

Solving Structures

^{1}H NMR spectrum (300 MHz): δ 1.59 (3H, d, J=1.4 Hz) 1.67 (3H, d, J=1.4 Hz), 2.09 (3H, s), 2.24 (2H, q, J=7.2 Hz), 2.41 (2H, t, J=7.2 Hz), 5.05 (1H 3 x 7 lines, J=7.2, 1.4Hz)

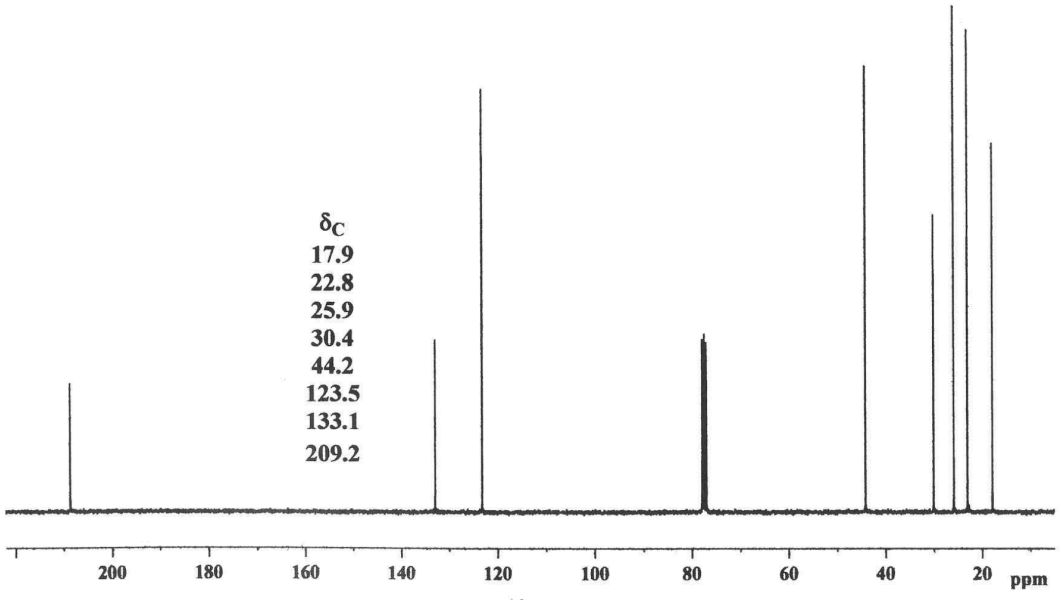


^{1}H NMR spectrum: (6 peaks, so 6 proton environments)

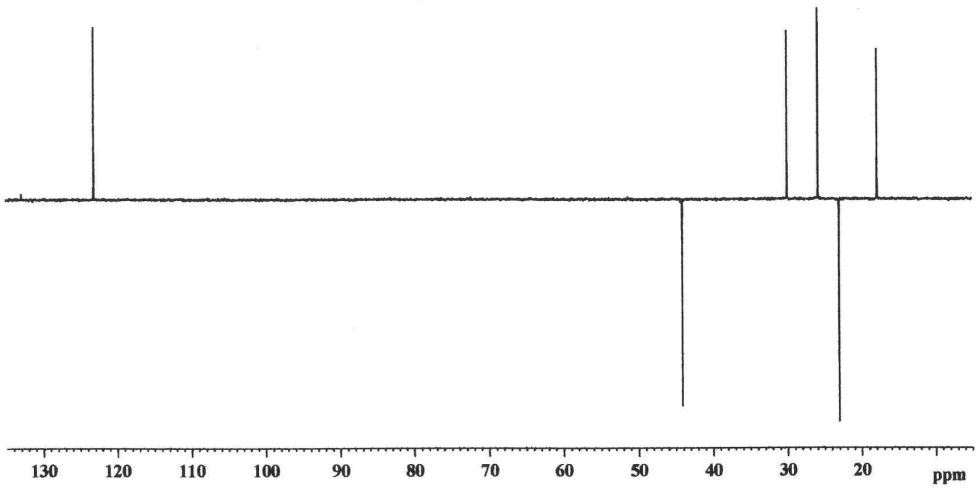
H_a	1.59	3H	d	J = 1.4 Hz
H_b	1.67	3H	d	J = 1.4 Hz
H_c	2.09	3H	s	
H_d	2.24	2H	q	J = 7.2 Hz
H_e	2.41	2H	t	J = 7.2 Hz
H_f	5.05	1H	3x7 lines	J = 7.2, 1.4 Hz

Solving Structures

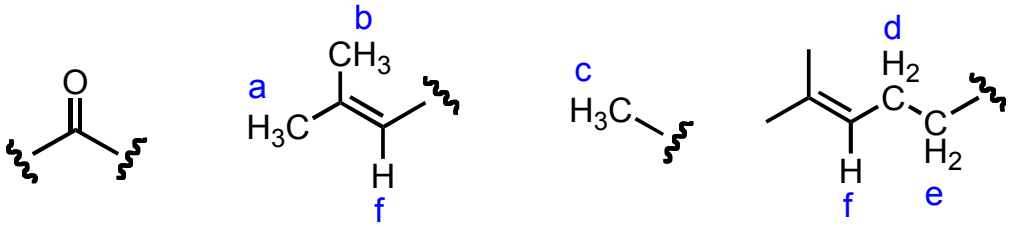
^{13}C NMR spectrum (75 MHz, proton decoupled):



^{13}C DEPT spectrum (125 MHz, proton decoupled):



Structural fragments:



Structure of Z