Answer Key Problem Set.

1a.

i. **Chemical shift** table shows that electron withdrawing influence of Bromine:
RCH2Br = 3.4 ppm
RCH2C-CH_xBr = 1.8 ppm
CH_3R = 0.9 ppm
ii. **Multiplicities** indicate that
A, having 2 neighboring protons should be a triplet. (N+1)
B, having 5 neighboring protons should be a sextet.
C, having 2 neighboring protons should be a triplet.

1b.

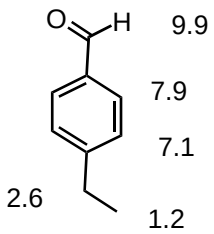
Chemical shifts from tables:
A, aproximately 47 (no exact example available)
B. Alkyne ; 70-90 ppm
C. Alkyne ; 70-90 ppm.
Multiplicities.
A, connected to 2 protons will be a triplet
B, connected to no protons will be a singlet
C, connected to one proton will be a doublet.

2a.

i. IHD = 0
ii. Only two resonances -> symmetry
iii. Resonance at 2.3 is septet that integrates to 1H; next to 6 neighboring protons (? 2 CH3's).
iv. Resonance at 1.7 is a doublet; next to one neightboring proton (methine) .
Propose: $CH_3CHBrCH_3$
v. Confirm chemical shifts: from tables 12.12 and hand out
R_2CHBr = 4.4 ppm
CH_3-C-Br = 1.7 ppm

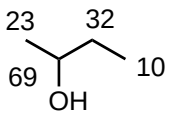
2b.

i. IHD = 5
ii. resonance at 9.9 indicates aldehyde.
iii. 2 aliphatic H's split into quartet = CH2-(CH3)
iv. 3 aliphatic H's split into quartet CH3-(CH2)
v. resonance above 7ppm (in the absence of other e-withdrawing groups) suggests aromatic ring; must be aromatic ring because only 4 HD's left (-1 for aldehyde) and 6 carbons remaining. Since there are not resonances consistent with the presence of an alkyne, the remaining 4 HD's must be 3 double bonds and a ring.
vi. The aromatic group is 1,4 substituted based on A,B quartet.
Vii: confirm chemical shifts from table:



3a.

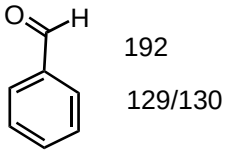
i. IHD = 0
ii. No symmetry
iii. Only one C next to O and total hydrogens attached to C's = 9 (of 10 total)
iv. Doublet at 69ppm corresponds to methine (not methylene or methyl) attached to OH.
iv. Quartet at 23 unique to methyl beta to alcohol.
v. Triplet at 33 consistent with metylene beta to OH.
Propose: 2-butanol
Confirm shifts from table.



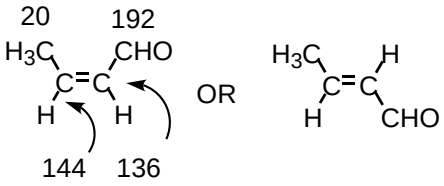
3b.

i. IHD = 5

ii. Symmetry (5peaks –7 C's)
iii. Shift at 193; C=O –doublet indicates aldehyde not ketone.
iv. Only sp^2 C's remaining, (No triplet bonds) must have 3 alkene's and a ring with only 6 carbons -> aromatic.
v. Monosubstituted aromatic.
Confirm shifts from tables:

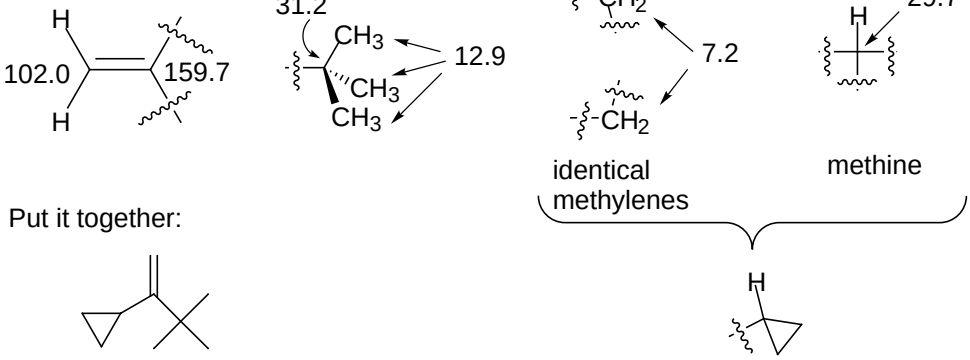


3d.
i. IHD =2
ii. No symmetry
iii. resonances at 193 = C=O; doublet indicates aldehyde.
iv. shifts at 154 or 135 = sp^2 C's; doublets either:
v. quartet at 18.2 methyl
Assemble:
confirm shifts from tables.



4.
IHD =2
Unsaturated groups:

Fragments:

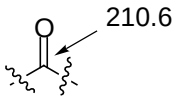


5.

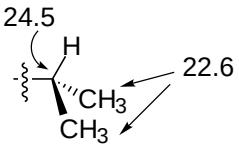
IHD =1

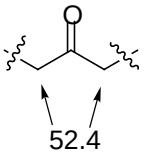
protons on carbon atoms= 18

Unsaturated groups:



Fragments:

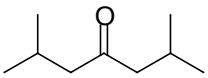




2 identical isopropyl groups

2 identical methylene groups next to the ketone

Put it together:

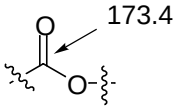


6.

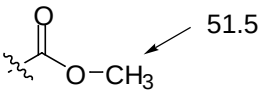
IHD =1

protons on carbon atoms= 11 (all of them)

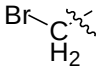
Unsaturated groups:



Fragments:

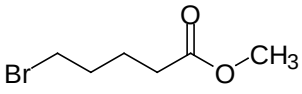


methyl ester

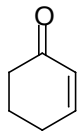


Bromo-methylene end group
Because all remaining peaks are triplets,
and because there are no remaining units
of unsaturation

Put it together:



7.



8.