CHEM 2430 – Organic Chemistry 1 for Majors – Fall 2019

Instructor: Paul Bracher

Quiz #4

Due: Monday, December 9th, 2019 by 1:10 p.m.

in class on Monday, at office hours on Sunday, or to the box outside Monsanto Hall 103

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

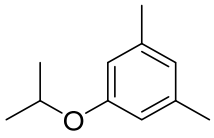
- Please write your answers on the official answer sheet. Nothing else will be graded.
- You may collaborate with others and use any resources you wish.
- All questions must be posed to the official class discussion forum so everyone has equal access to the answers.

Problem	Points Earned	Points Available
I		24
II		16
III		18
IV		18
V		24
TOTAL		100

Questions, Required Information, Supplementary Explanation, Grading Notes, Where You've Seen It

Problem I. Multiple Choice (24 points total). Correct answers score +3 points, intentionally blank answers score +1 point, and incorrect answers score 0 points. For each question, select the best and most complete answer of the choices given. Write your answer clearly in the spaces provided on the answer sheet.

(1) B How many signals (arising from sets of inequivalent carbon atoms) appear in the ^{13}C NMR spectrum of compound **A**?

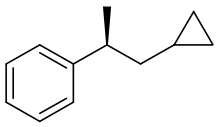


A

(A) 5 or fewer signals
(B) 6 or 7 signals
(C) 8 or 9 signals
(D) 10 or 11 signals

This compound will have 7 signals in its ^{13}C NMR spectrum.

(2) D How many signals (arising from sets of inequivalent hydrogens) appear in the ^{1}H NMR spectrum of compound **B**?



B

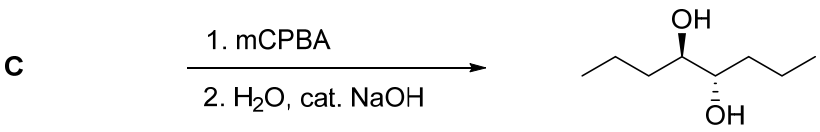
(A) eight or fewer signals
(B) nine signals
(C) ten signals
(D) eleven or more signals

Refer to the discussion in class. The *cis* pair and *trans* pair of protons on the ring would normally be enantiotopic, so in this case, they are diastereotopic because there is a stereocenter elsewhere. In practice, we would probably expect some of the 12 chemical shifts to be accidentally equivalent.

(3) C The EI-MS of a mystery compound has its largest peaks at m/z 59, 69, 41, and 87. What is the most likely identity of the compound?

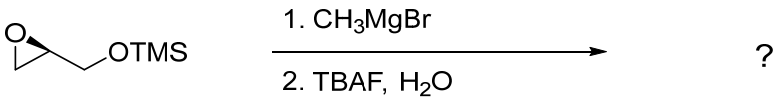
(A) 1-heptanol
(B) 2-heptanol
(C) 3-heptanol
(D) 4-heptanol

(4) B What is the identity of compound **C**?



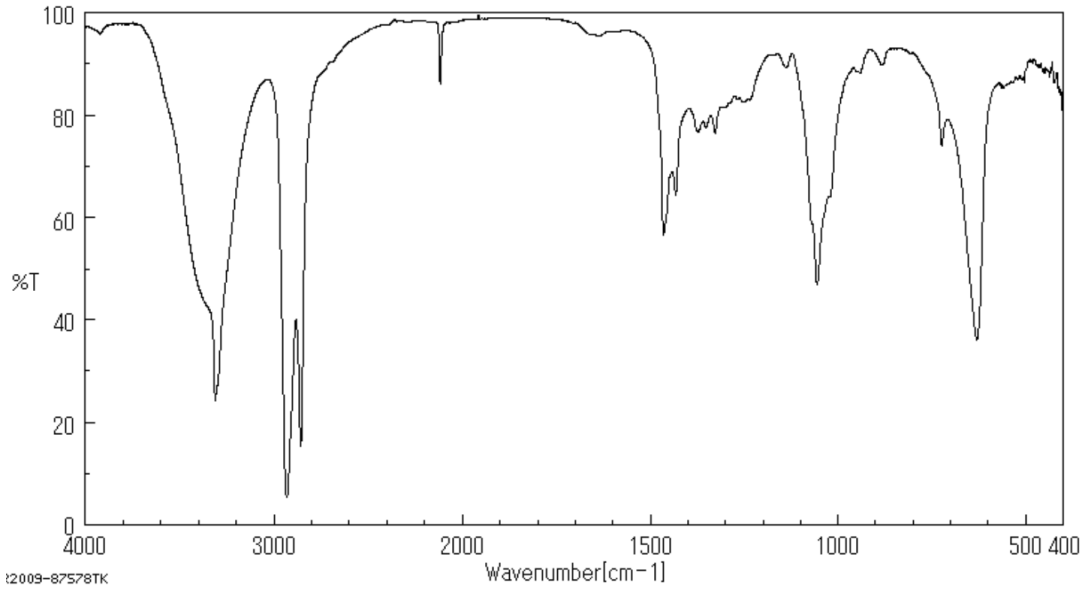
(A) 4-octyne
(B) (*E*)-4-octene
(C) (*Z*)-4-octene
(D) both (B) and (C) will give the indicated product

(5) C What is the major product of the following reaction?

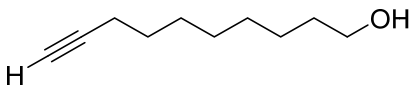


(A) (B) (C) (D)

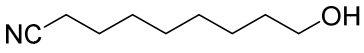
(6) A The IR spectrum below corresponds to which of the following compounds?



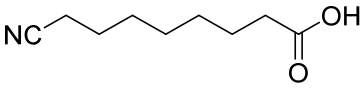
Source: Spectral Database for Organic Compounds, 9-decyn-1-ol, #52499
http://sdbs.db.aist.go.jp/



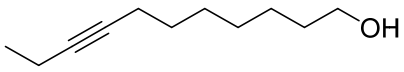
(A)



(B)

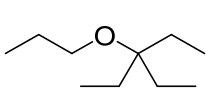


(C)

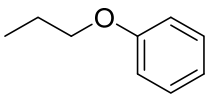


(D)

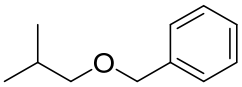
(7) B Which of the following ethers will not react with excess HI to form two alkyl and/or aryl iodides?



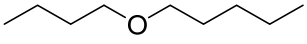
(A)



(B)

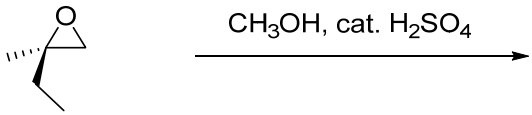


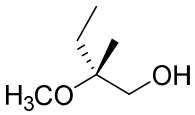
(C)



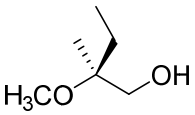
(D)

(8) B What is the major product of the following reaction?

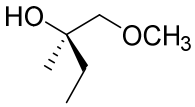




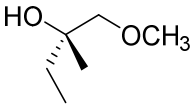
(A)



(B)

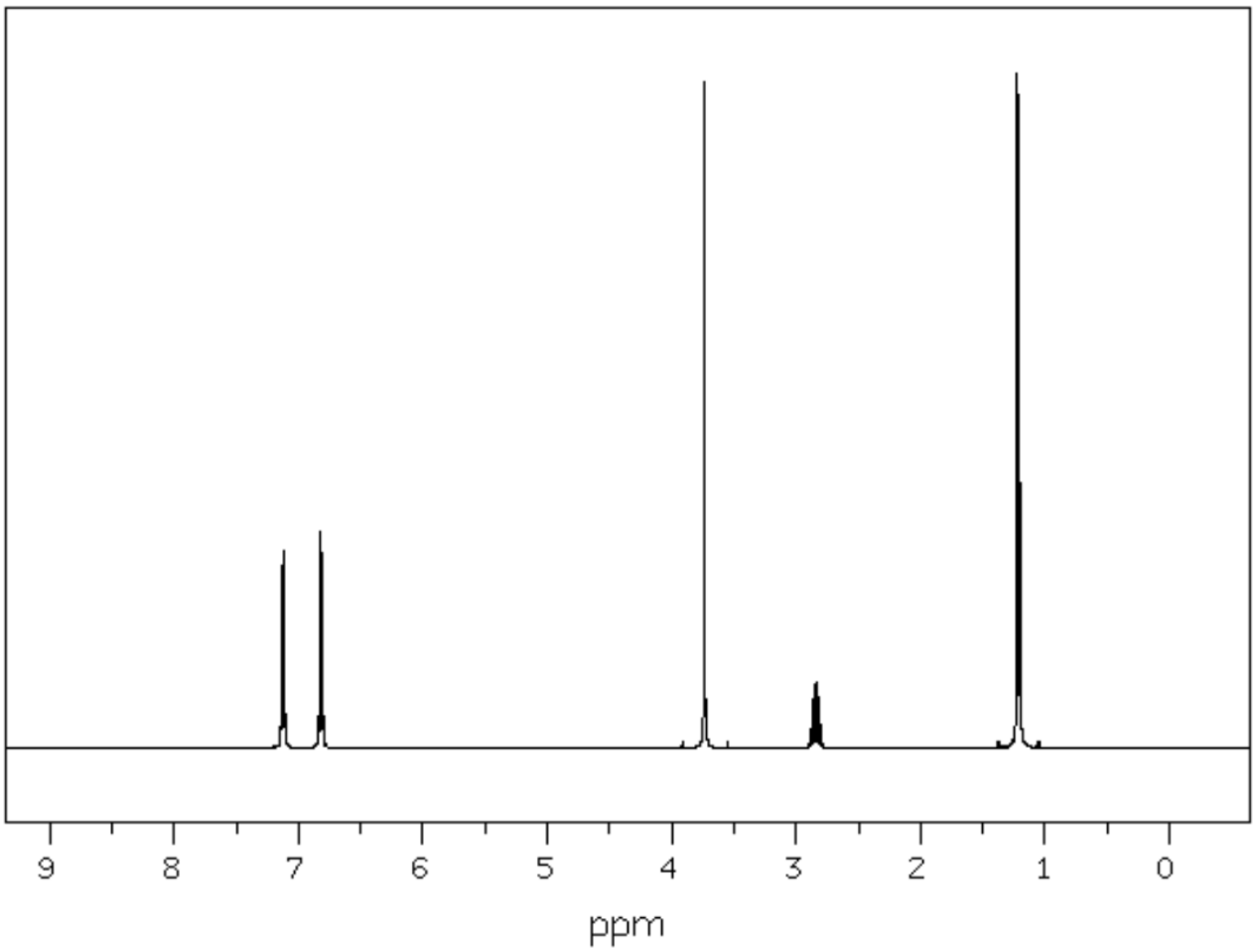


(C)



(D)

Problem II. Assignment of an NMR Spectrum (16 points). High-resolution mass spectral analysis of a pure sample of compound **AA** reveals it to have a molecular formula of $C_{10}H_{14}O$. The ^1H NMR spectrum of **AA** is:



Source: Spectral Database for Organic Compounds, *p*-isopropylanisole, #17111
http://sdbs.db.aist.go.jp/

Label	Chemical Shift (ppm)	Multiplicity	Integration
A	7.12	doublet	85
B	6.82	doublet	82
C	3.74	singlet	124
D	2.84	septet	42
E	1.21	doublet	249

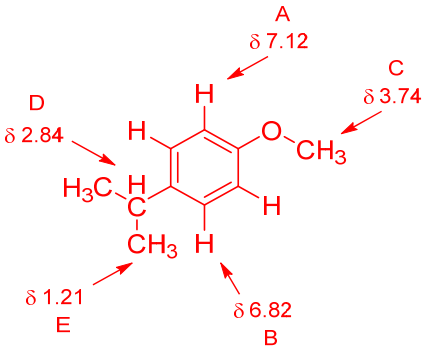
In the space provided on your official answer sheet:

(i) Draw a Lewis structure for compound **AA** consistent with the data provided above. (Molecular formula: $C_{10}H_{14}O$)

(ii) For each chemical shift, draw an arrow from that signal to a hydrogen that gives rise to it. (Or you can use letters/labels instead—essentially, make sure to assign the spectrum.)

AA

4-isopropylanisole



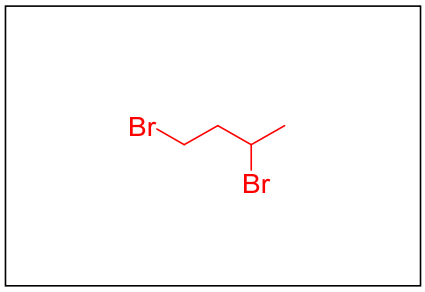
Ω (RAPB) = 4

Full credit if signals A & B are swapped in assignment.

Problem III. Structure Determination (18 points). Given the four spectra shown below for compound **BB**, provide its structure.

Grading and partial credit: Your structure will be scored +6 points if correct and zero points if incorrect. The remaining 12 points are based on three multiple choice questions about **BB** that can be answered independently without knowing the full structure of **BB**. These questions are scored +4 points for a correct answer and zero points for an incorrect answer or blank answer.

Compound **BB** (6 points)



1,3-dibromobutane
SDBS No. 4094

(1) A Which of the following elements is present in compound **BB**?

(A) bromine
(B) chlorine
(C) nitrogen
(D) none of the above elements is in compound **BB**

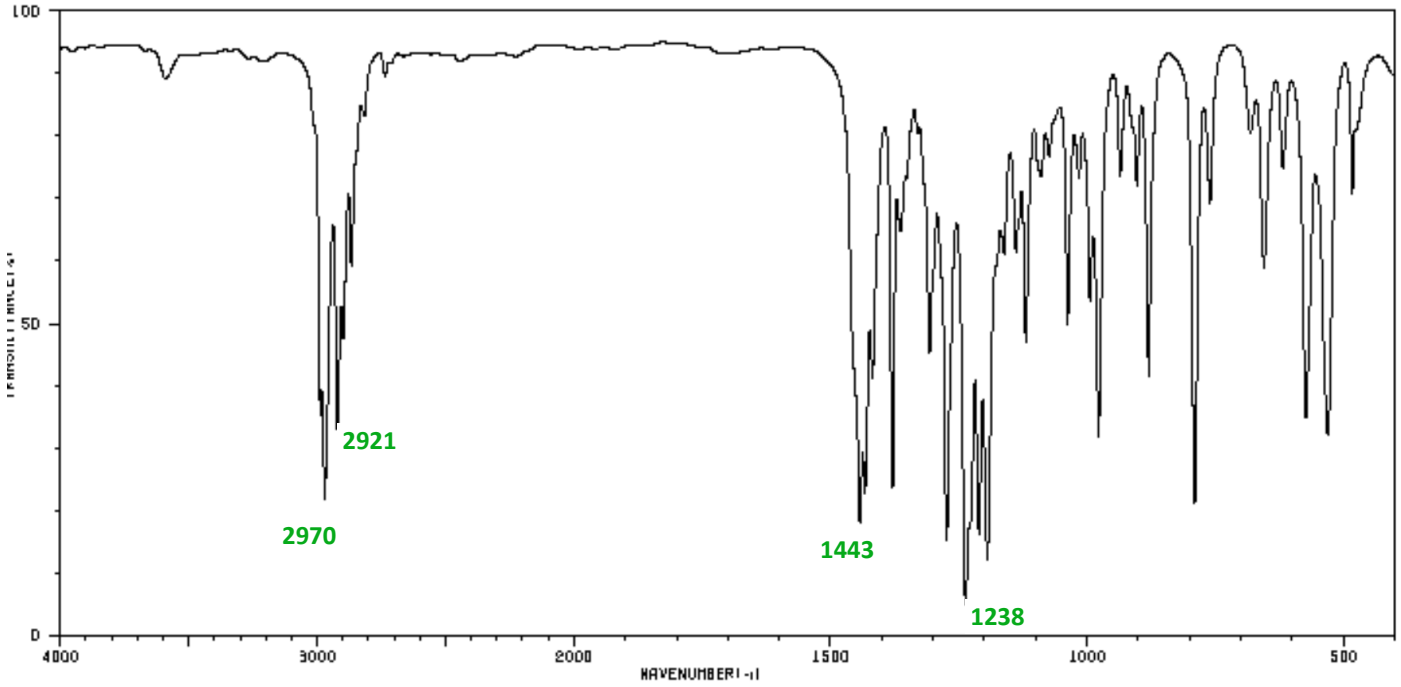
(2) D Which of the following functional groups is present in compound **BB**?

(A) alcohol
(B) ester
(C) nitrile
(D) none of the above functional groups is in compound **BB**

(3) C Which of the following is <u>not</u> present in compound **BB**?

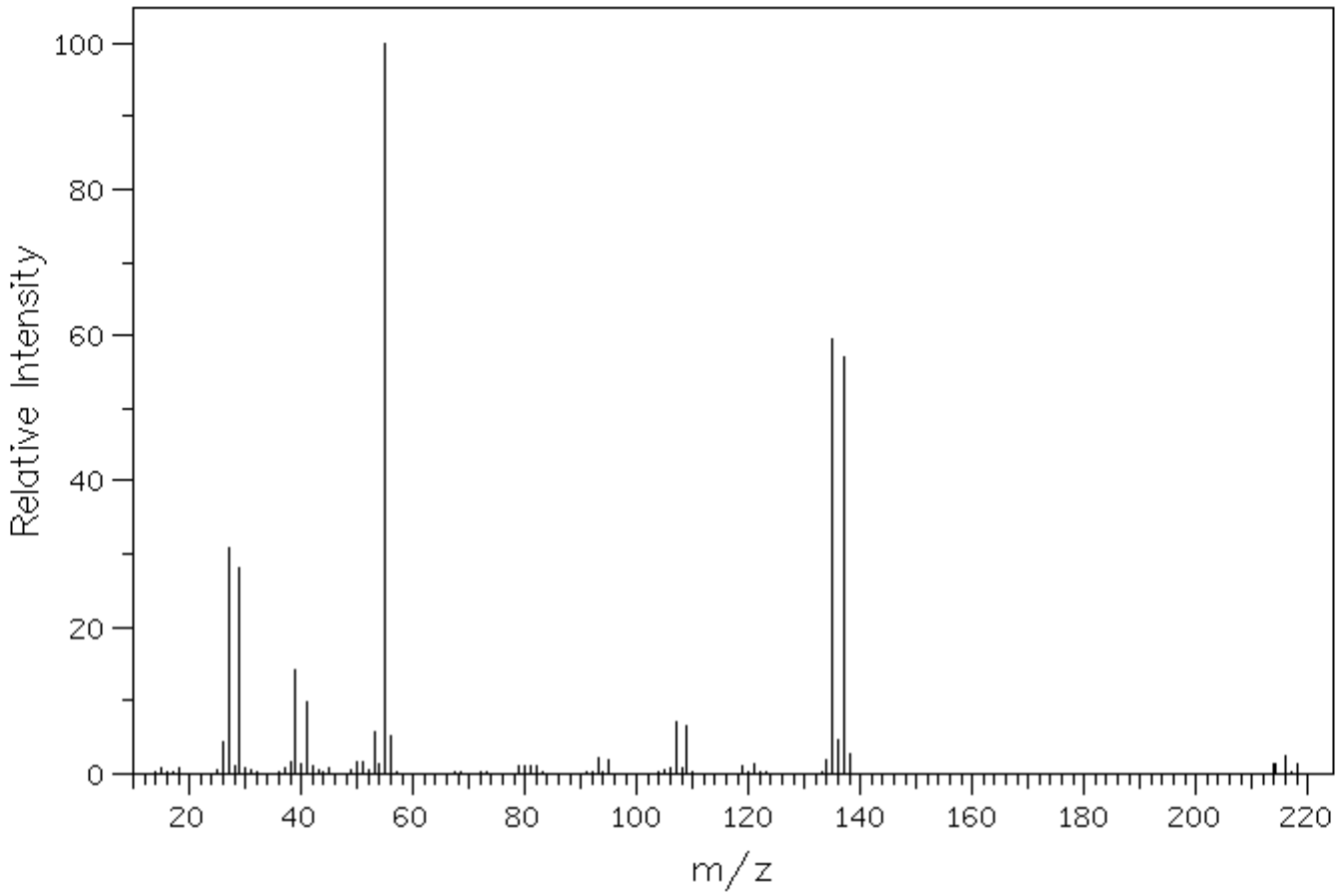
(A) a primary (1°) carbon atom
(B) a secondary (2°) carbon atom
(C) a tertiary (3°) carbon atom
(D) none of the above (i.e., the compound has all of the above)

IR Spectrum:



Source: Spectral Database for Organic Compounds, 1,3-dibromobutane, #4094
http://sdbs.db.aist.go.jp/

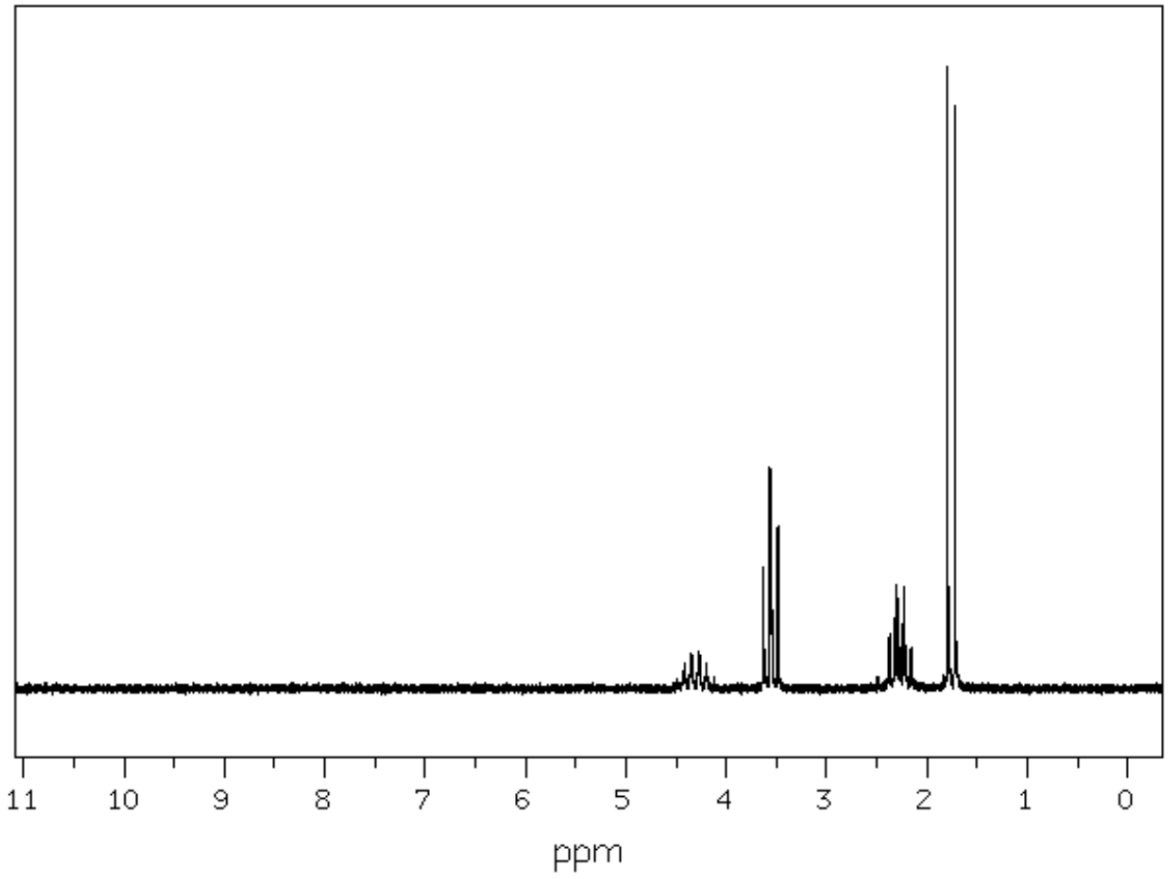
Mass Spectrum:



Source: Spectral Database for Organic Compounds, 1,3-dibromobutane, #4094
http://sdbs.db.aist.go.jp/

m/z	intensity
26.0	4.2
27.0	30.7
28.0	1.0
29.0	28.1
38.0	1.5
39.0	14.3
40.0	1.3
41.0	9.9
42.0	1.1
50.0	1.6
51.0	1.7
53.0	5.8
54.0	1.4
55.0	100.0
56.0	5.2
79.0	1.0
80.0	1.0
81.0	1.0
82.0	1.1
93.0	2.1
95.0	2.0
107.0	7.0
109.0	6.5
119.0	1.1
121.0	1.4
134.0	1.9
135.0	59.4
136.0	4.6
137.0	57.2
138.0	2.7
214.0	1.3
216.0	2.5
218.0	1.2

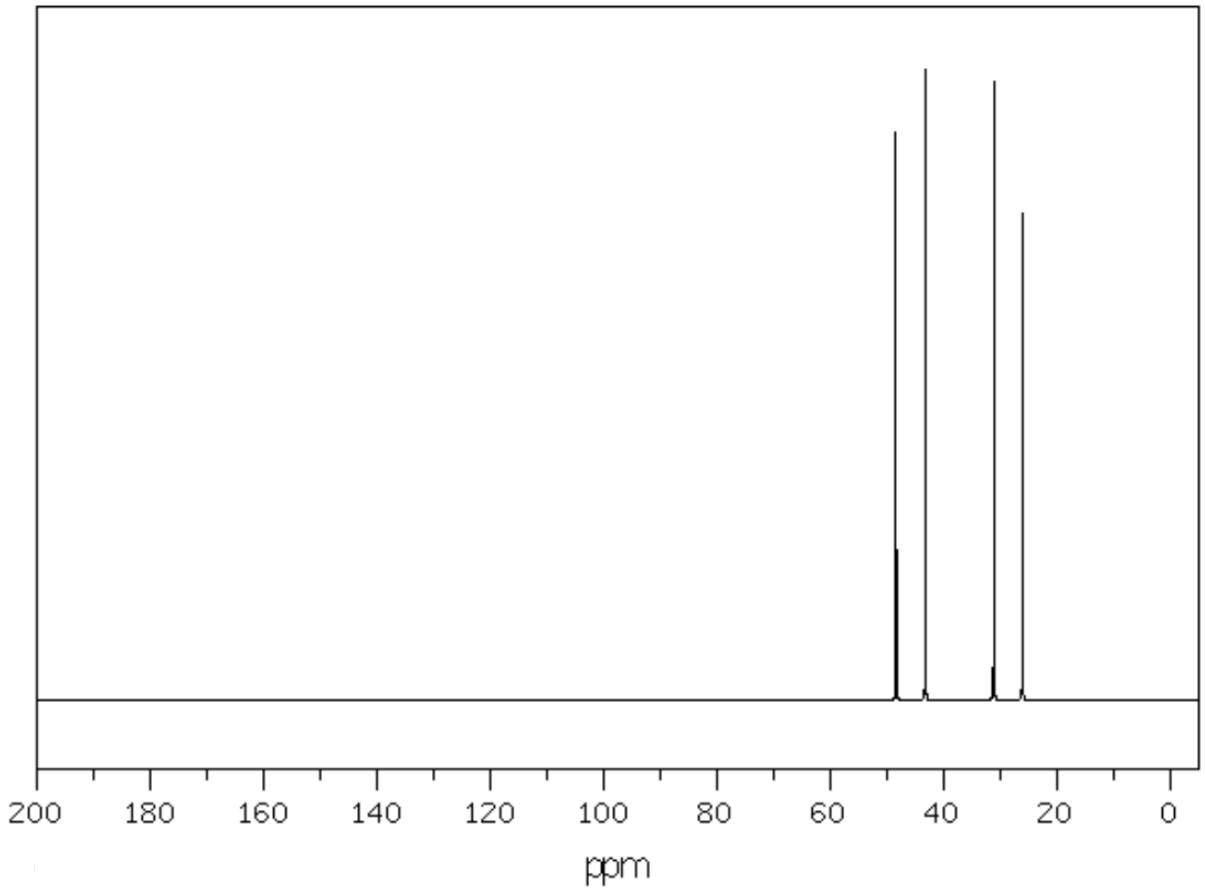
^{1}H NMR Spectrum:



Source: Spectral Database for Organic Compounds, 1,3-dibromobutane, #4094
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Multiplicity	Integration
4.31	apparent sextet	37
3.55	triplet	76
2.27	6 (dt)	75
1.76	doublet	118

^{13}C NMR Spectrum:

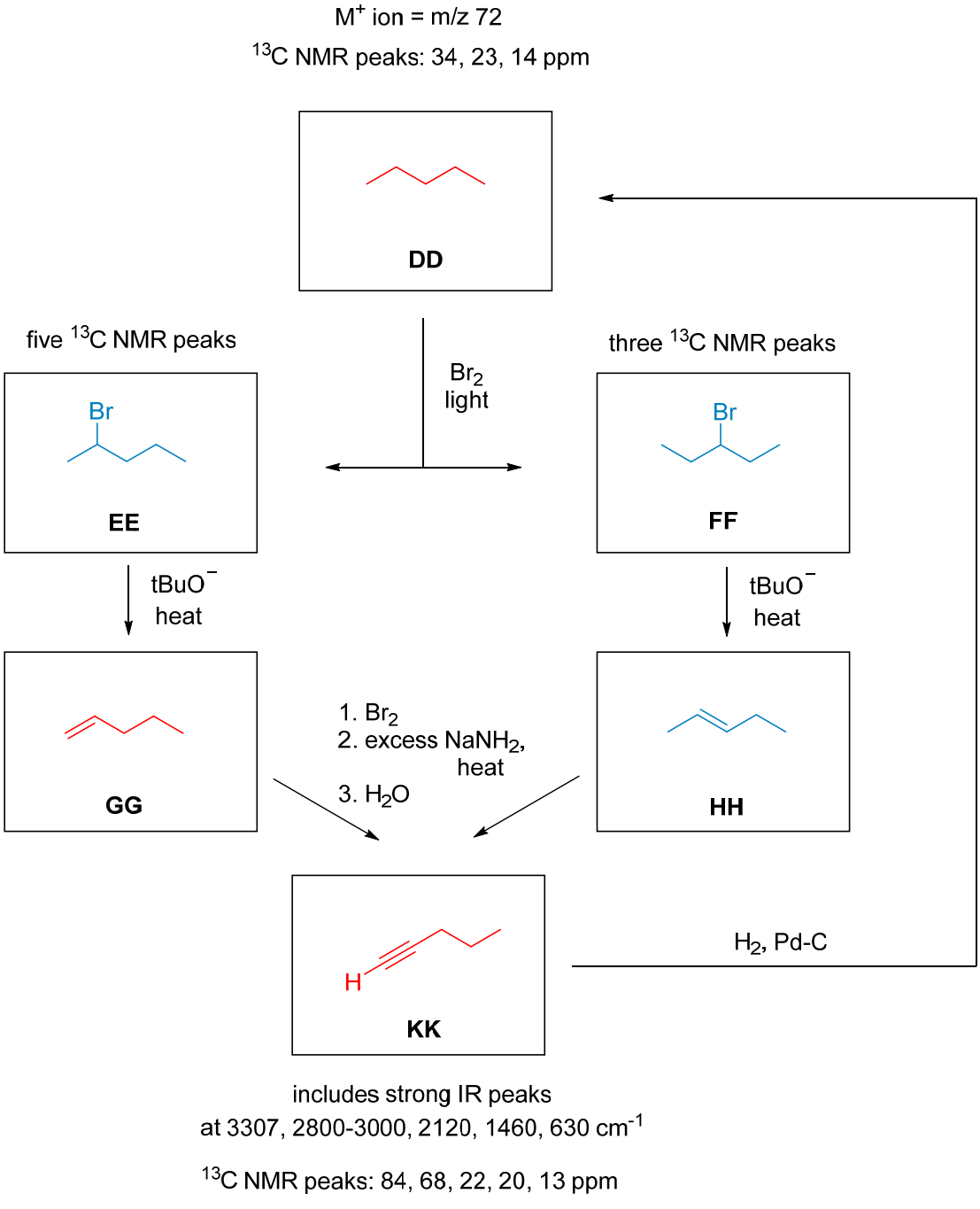


Source: Spectral Database for Organic Compounds, 1,3-dibromobutane, #4094
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Intensity
48.42	900
43.22	1000
31.13	980
26.08	771

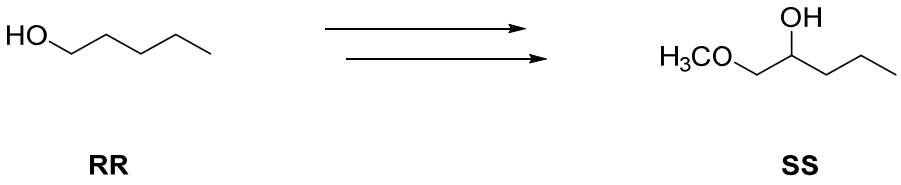
Problem IV. Reaction Roadmap (18 points). Unknown compound **DD**, with molecular ion of 72 a.m.u., has a ^{13}C NMR spectrum with three signals: 34, 23, ad 14 ppm. Compound **DD** undergoes radical bromination to form two major products: compounds **EE** and **FF**. Compound **EE** has five signals in its ^{13}C NMR spectrum, while **FF** has three signals. Compounds **EE** and **FF** react with potassium *tert*-butoxide and heat to form major products **GG** and **HH**, respectively. Both **GG** and **HH** react with bromine, followed by excess sodium amide and aqueous workup to form the same product, **KK**. Compound **KK** has a ^{13}C NMR spectrum with signals at 84, 68, 22, 20, and 13 ppm. Compound **KK** has strong IR absorptions at 3307, 2800–3000, 2120, 1460, and 630 cm^{-1} (among others).

On your answer sheet, provide structures for compounds **DD**, **GG**, and **KK**. Your proposals should be consistent with all of the data provided above.

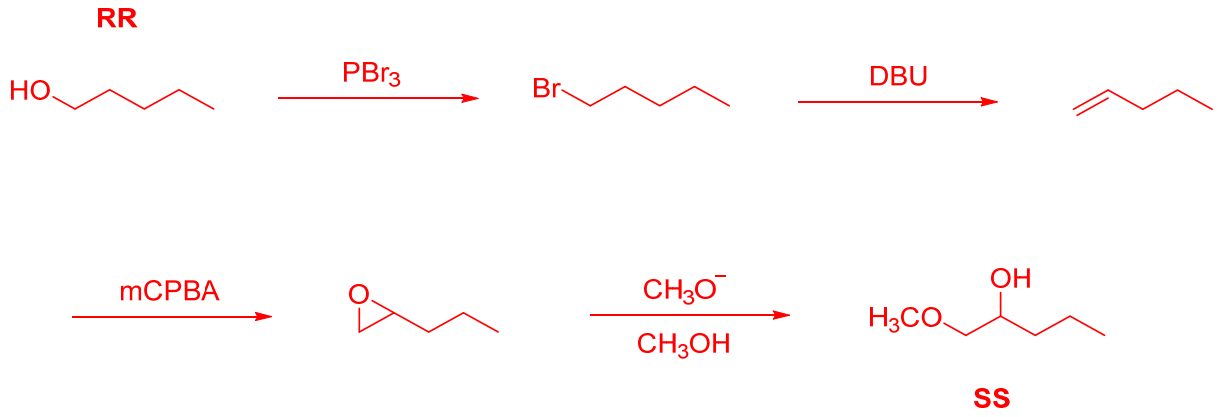


Problem V. Synthesis (24 points). These transformations will require multiple steps. Provide the reagents for each step and draw out your proposed synthetic intermediates. Please do not draw curved arrows; this problem is not asking for mechanisms. You do not need to provide solvents for the reactions.

(1) (12 points) Provide a synthetic route—i.e., a sequence of reactions—to produce compound **SS** from compound **RR** using any other starting materials and reagents you wish.



RR **SS**



Other options include generating pent-1-ene from pent-1-ol by $POCl_3$/pyridine (though it is questionable whether this reaction presented in textbooks actually works well). Using $SOCl_2$ or TsCl/py in place of PBr_3 to generate a good leaving group. (Treatment with H_2SO_4 will probably generate dipentyl ether rather than pent-1-ene. You can also use other non-nucleophilic, bulky bases rather than DBU.

(2) (12 points) Provide a synthetic route—i.e., a sequence of reactions—to produce compound **VV** using compound **TT** as the only source of carbon atoms in your target product. You may use any reagents you wish so long as they do not contribute carbon atoms to the product.