

Chemistry 333

Final Examination

May 22, 2000

Professor Charonnat

Name: _____

Be certain that your examination contains thirteen (13) pages including this cover page.

Put your name on each page of this examination booklet.

By putting your name on this examination booklet, you agree to abide by California State University, Northridge policies of academic honesty and integrity.

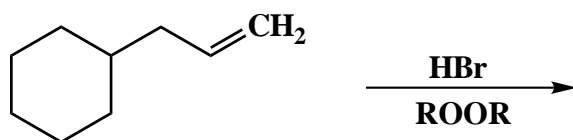
Molecular models are allowed for this examination. Calculators are unnecessary and are not allowed.

Name: _____

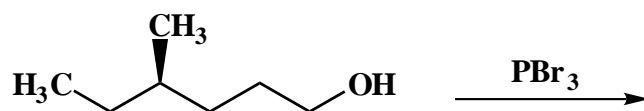
1. (50 points)

For each of the following ten (10) questions, draw the expected major organic product. If relevant, clearly specify the relative and/or absolute stereochemistry of the product.

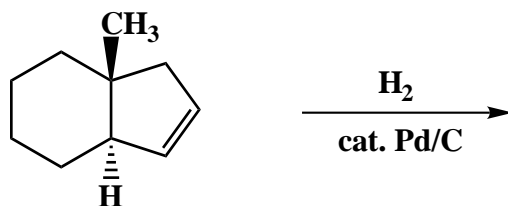
A.



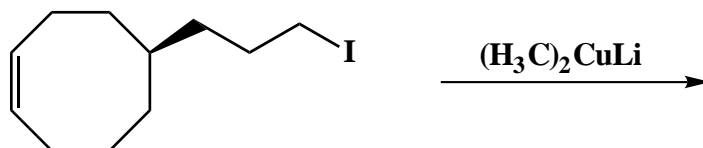
B.



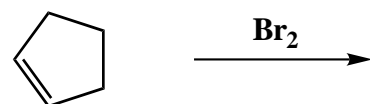
C.



D.



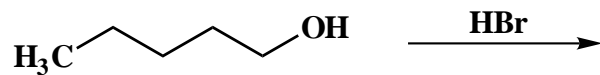
E.



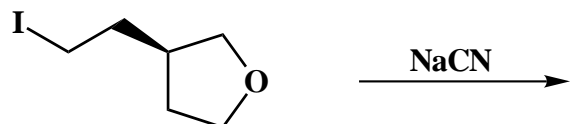
Name: _____

1. (continued)

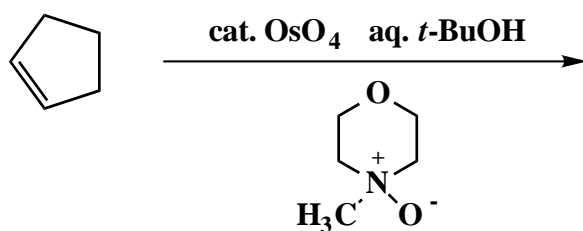
F.



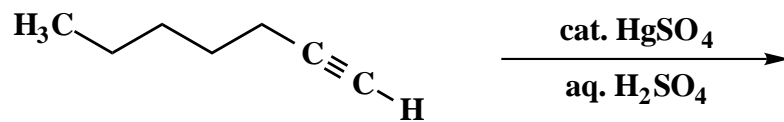
G.



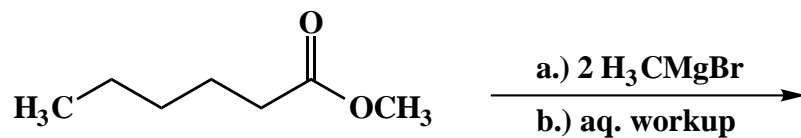
H.



I.



J.

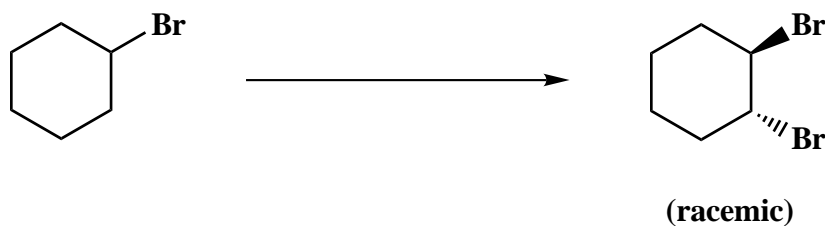


Name: _____

2. (25 points)

For each of the following five (5) questions, draw the specific reagent(s) necessary to effect the transformation shown. If more than one reaction is involved in an answer, be certain to distinguish the individual steps clearly.

A.



B.



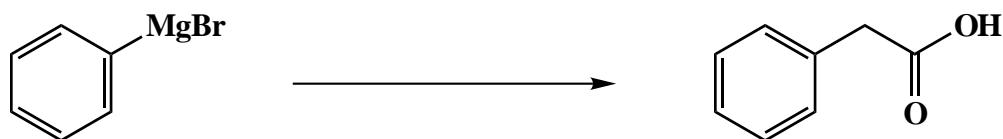
C.



D.



E.



Name: _____

3. (25 points)

For each of the following five (5) questions, circle the number that corresponds to the correct answer.

A. It is possible to determine the molecular formula of a compound with

1. ^1H NMR spectroscopy
2. low-resolution mass spectrometry
3. high-resolution mass spectrometry

B. A C–D bond has

1. a lower vibrational frequency compared to the corresponding C–H bond
2. an equal vibrational frequency compared to the corresponding C–H bond
3. a higher vibrational frequency compared to the corresponding C–H bond

C. The $\text{C}\equiv\text{C}$ stretching vibration of 2-butyne has

1. a strong infrared absorption
2. a moderate infrared absorption
3. an extremely weak or unobservable infrared absorption

D. The ^{13}C isotope has

1. one possible spin state
2. two possible spin states
3. three possible spin states

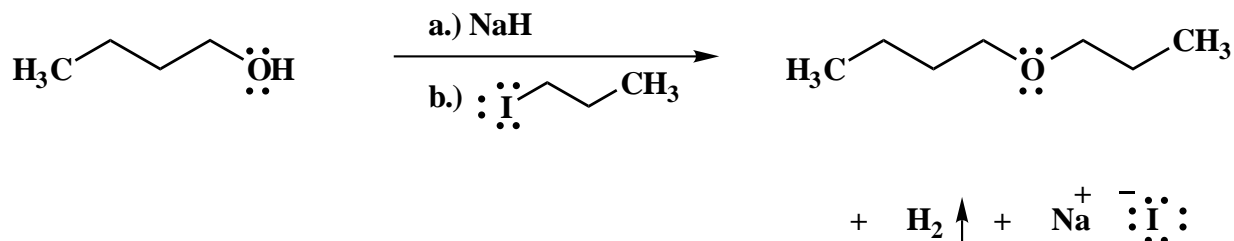
E. If the external magnetic field is increased, the NMR chemical shift (in ppm) of a specific proton will

1. decrease
2. remain constant
3. increase

Name: _____

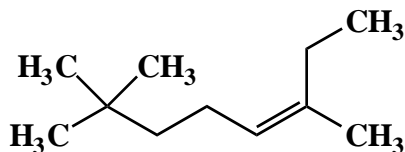
4. (10 points)

Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show all intermediates, unshared electrons, formal charges and countercharges. Specify reversibility or irreversibility for each primary mechanistic step.



5. (10 points)

Use IUPAC nomenclature to write the systematic name of the following alkene.

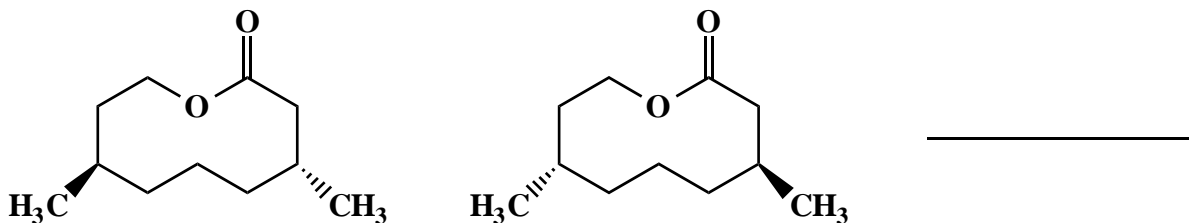


Name: _____

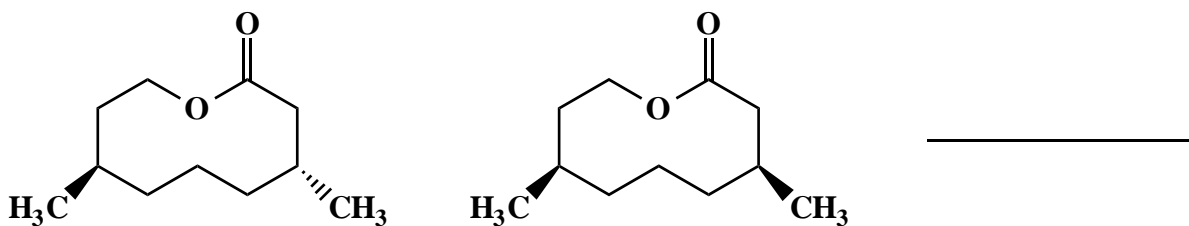
6. (10 points)

State the relationship between each of the following two (2) pairs of structures (identical, enantiomers, diastereomers, structural isomers, different compounds that are not isomeric).

A.



B



7. (20 points)

Answer the following two (2) questions precisely, succinctly and with correct grammar.

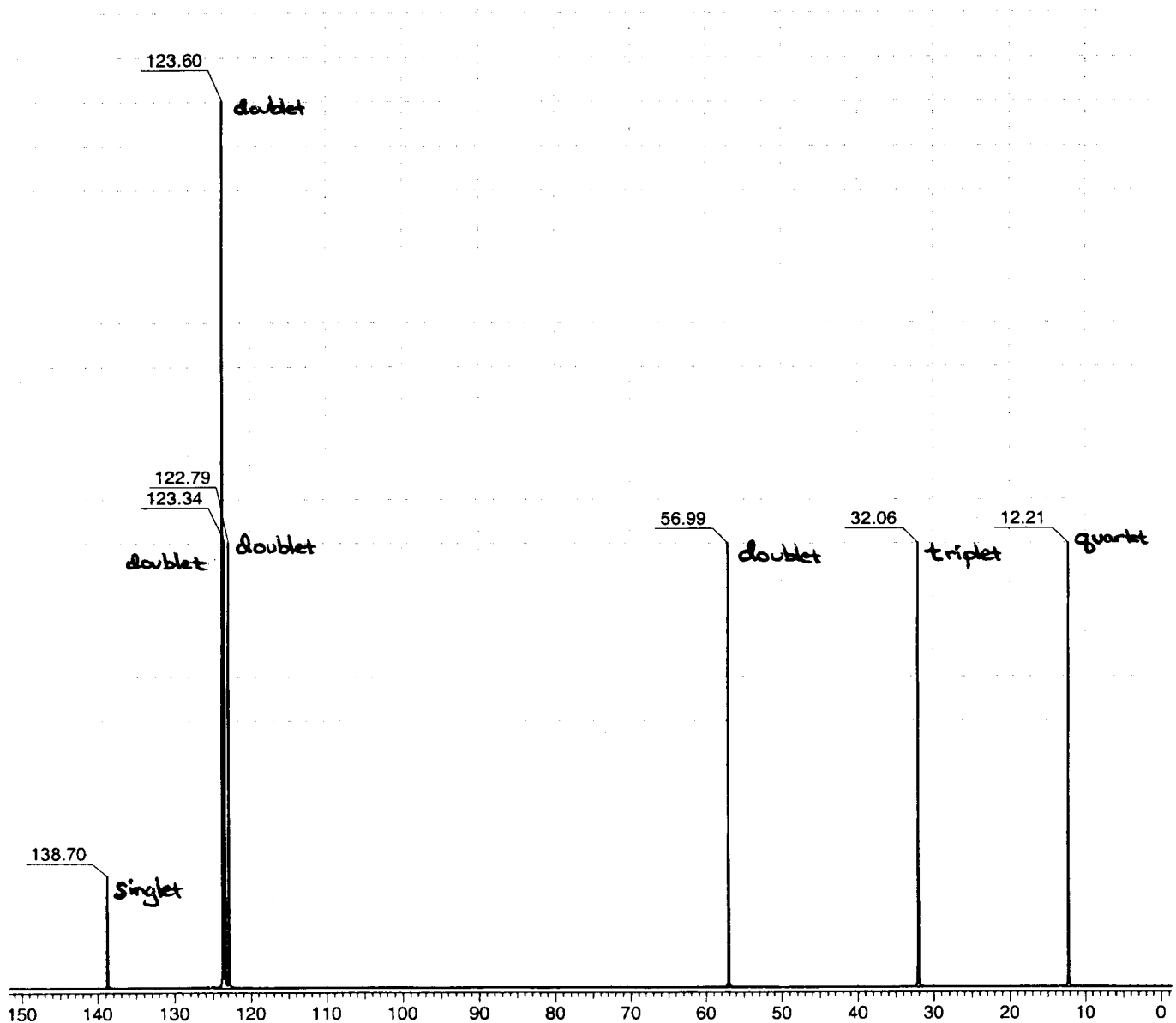
A. The mass spectrum of racemic 1-hepten-3-ol [$\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CHOHCH}=\text{CH}_2$] shows an apparent molecular ion at $m/z = 96$. Is this signal the molecular ion? If not, explain where the molecular ion should appear, and why it is not visible.

B. What is meant by the term, "fingerprint region"? How can it be used? What limitations exist, in this context?

Name: _____

8. (25 points)

The broadband proton-decoupled ^{13}C NMR spectrum of compound A ($\text{C}_9\text{H}_{11}\text{Br}$) is shown below. The multiplicities stated are those of the corresponding off-resonance proton-decoupled ^{13}C spectrum. Clearly assign all the resonances and draw the structure of compound A. (A ^{13}C NMR correlation table is included on page 12.)



Name: _____

8. (continued)

^{13}C NMR assignments:

chemical shift (ppm)

assignment

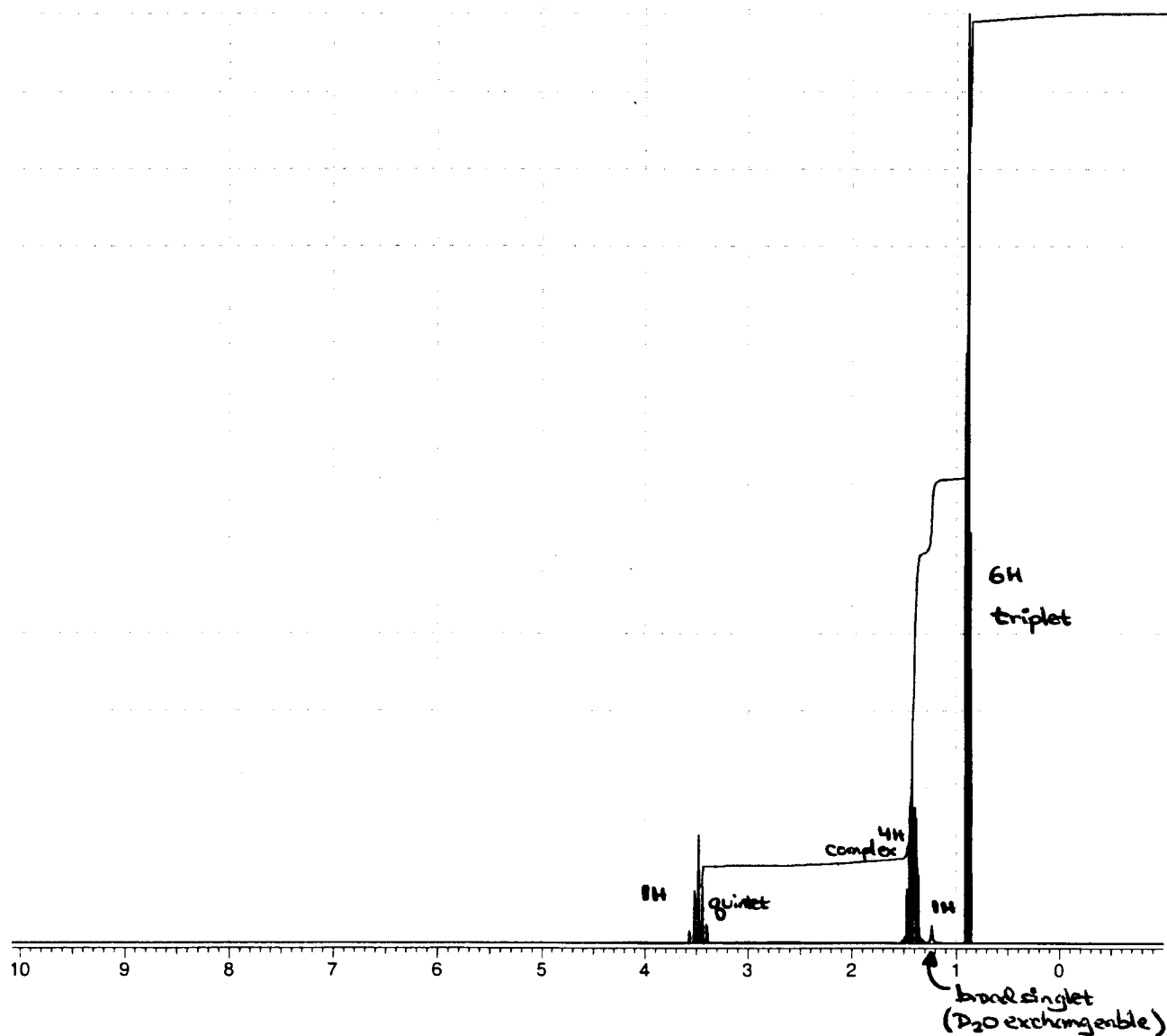
explanation of multiplicity

structure of compound A:

Name: _____

9. (25 points)

The ^1H NMR spectrum of compound B ($\text{C}_5\text{H}_{12}\text{O}$) is shown below. Clearly assign all the resonances and draw the structure of compound B. (A ^1H NMR correlation table is included on page 13.)



Name: _____

9. (continued)

¹H NMR assignments:

chemical shift (ppm)

assignment

explanation of multiplicity

structure of compound B:

Congratulations!

1	/50
2	/25
3	/25
4	/10
5	/10
6	/10
7	/20
8	/25
9	/25
<hr/> Total:	<hr/> /200

SELECTED ^{13}C NMR CORRELATIONS

structural type	chemical shift range (ppm)
cyclopropyl	- 10 - 10
$-\text{CH}_3$ (saturated)	10 - 30
$\begin{array}{c} \\ -\text{CH}_2 \\ \end{array}$ (saturated)	10 - 55
$\begin{array}{c} \\ -\text{CH} \\ \end{array}$ (saturated)	25 - 55
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$ (saturated)	30 - 55
$\begin{array}{c} \\ -\text{C}-\text{I} \\ \end{array}$	- 10 - 45
$\begin{array}{c} \\ -\text{C}-\text{Br} \\ \end{array}$	25 - 65
$\begin{array}{c} \\ -\text{C}-\text{Cl} \\ \end{array}$	35 - 80
$\begin{array}{c} \text{O} \\ // \\ \diagup \text{C} \diagdown \end{array}$	20 - 50
$-\text{C}-\text{N}'$	30 - 70
$\begin{array}{c} \\ -\text{C}-\text{O}- \\ \end{array}$	40 - 80
$-\text{C}\equiv\text{C}-$	65 - 85
$\begin{array}{c} \diagdown \text{C} \diagup \\ // \\ \diagup \text{C} \diagdown \end{array}$	100 - 150
$-\text{C}\equiv\text{N}$	110 - 125
ArH	110 - 160
$\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \text{OH} \end{array}$ $\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \text{X} \end{array}$	155 - 185
$\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \text{H} \end{array}$ $\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \diagdown \end{array}$	190 - 210

SELECTED ¹H NMR CORRELATIONS

structural type	chemical shift range (ppm)
cyclopropyl	0.0 - 0.9
RNH ₂ R ₂ NH	0.5 - 5.0 ^a
-CH ₃ (saturated)	0.7 - 1.3
$\text{H}_3\text{C}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{X}$ (X = halogen, O, N, carbonyl)	0.9 - 1.2
$-\overset{\text{I}}{\text{C}}\text{H}_2$ (saturated)	1.2 - 1.3
$-\overset{\text{I}}{\text{C}}\text{H}$ (saturated)	1.4 - 1.6
$\text{H}_3\text{C}-\overset{\text{I}}{\text{C}}-\text{X}$ (X = halogen, O, N, carbonyl)	1.0 - 2.0
ROH	1.0 - 5.0 ^a
$\text{H}_3\text{C}-\text{C}=\text{C}$	1.6 - 1.9
$\text{H}_3\text{C}-\text{C}\equiv\text{C}-$	1.8 - 2.2
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}$	1.9 - 2.6
H ₃ C-Ar	2.1 - 2.6
$\text{H}_3\text{C}-\text{N}$	2.1 - 3.0
-C≡C-H (nonconjugated)	2.0 - 2.6
-C≡C-H (conjugated)	2.8 - 3.1
H ₃ C-X (X = halogen, O)	2.6 - 4.4
Ar-NH ₂ Ar ₂ NH	3.0 - 5.0 ^a
H ₃ C-O-	3.3 - 4.2
ArOH	4.0 - 10.0 ^a
$\text{H}_2\text{C}=\overset{\text{I}}{\text{C}}$ (nonconjugated)	4.6 - 5.0
$\overset{\text{H}}{\text{C}}=\overset{\text{I}}{\text{C}}$ (nonconjugated)	5.1 - 5.9
$\text{H}_2\text{C}=\overset{\text{I}}{\text{C}}$ (conjugated)	5.3 - 6.3
$\overset{\text{H}}{\text{C}}=\overset{\text{I}}{\text{C}}$ (conjugated)	5.3 - 7.7
ArH	6.0 - 9.5
$\overset{\text{O}}{\parallel}{\text{R}}-\overset{\text{O}}{\parallel}{\text{C}}\text{H}$ $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}\text{H}$	9.5 - 10.5
$\overset{\text{O}}{\parallel}{\text{R}}-\overset{\text{O}}{\parallel}{\text{C}}\text{OH}$ $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}\text{OH}$	9.7 - 13.2