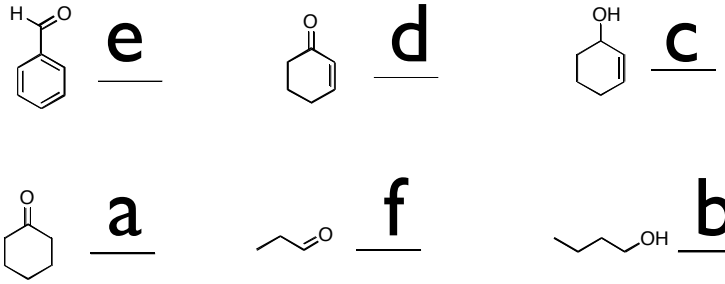
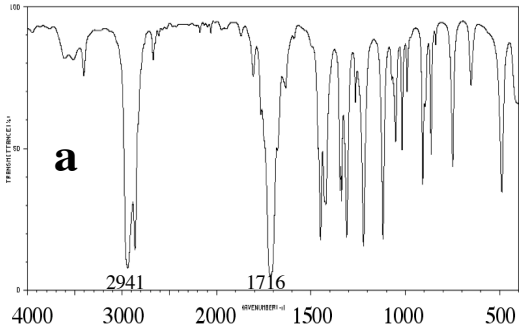
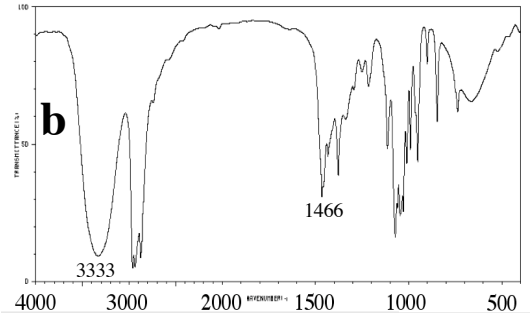
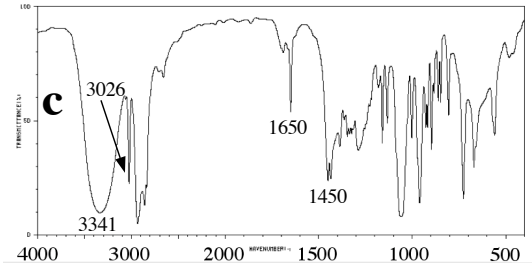
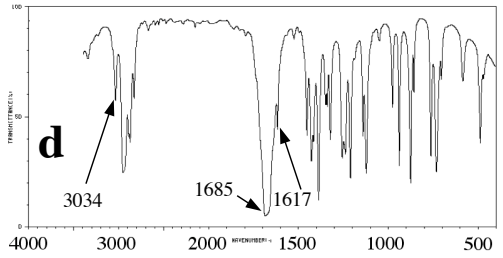
1. Match the following to their IR spectra (30 points)

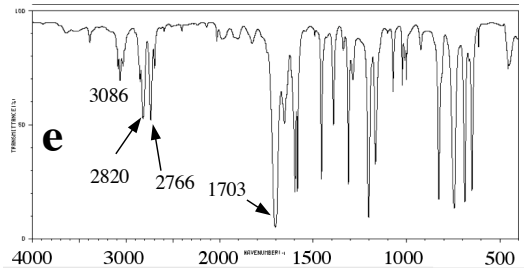


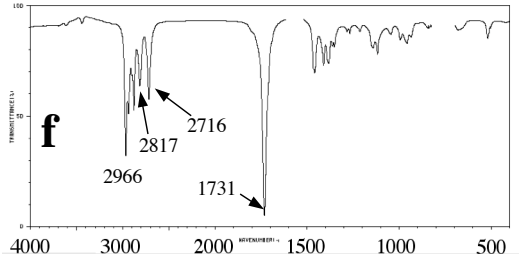












Look for absorption bands in decreasing order of importance:

1.the C-H absorption(s) between 3100 and 2850 cm-1. An absorption above 3000 cm-1 indicates C=C, either alkene or aromatic. Confirm the aromatic ring by finding peaks at 1600 and 1500 cm-1 and C-H out-of-plane bending to give substitution patterns below 900 cm-1. Confirm alkenes with an absorption generally at 1640-1680 cm-1. C-H absorption between 3000 and 2850 cm-1 is due to aliphatic hydrogens.

2. the carbonyl (C=O) absorption between 1690-1760cm-1; this strong band indicates either an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide. The an aldehyde may be confirmed with C-H absorption from 2840 to 2720 cm-1.

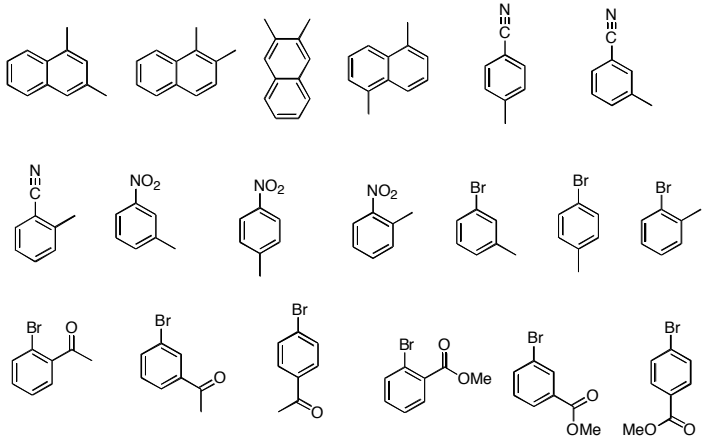
3.the O-H or N-H absorption between 3200 and 3600 cm-1. This indicates either an alcohol, N-H containing amine or amide, or carboxylic acid. For -NH2 a doublet will be observed.

4. the C-O absorption between 1080 and 1300 cm-1. These peaks are normally rounded like the O-H and N-H peak in 3. and are prominent. Carboxylic acids, esters, ethers, alcohols and anhydrides all containing this peak.

5. the CC and CN triple bond absorptions at 2100-2260 cm-1 are small but exposed.

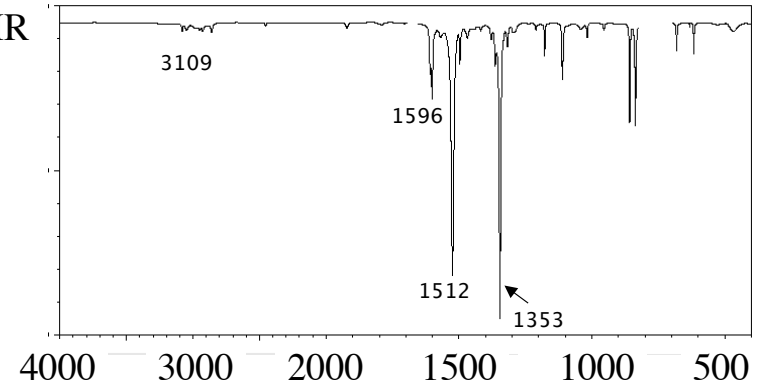
7. structure of aromatic compounds may also be confirmed from the pattern of the weak overtone and combination tone bands found from 2000 to 1600 cm-1.

1. Circle the structure of the product that corresponds to the 1H NMR and IR data below. Circle only one structure



^{1}H NMR 8.07 ppm (d, J=7.9 Hz, 2H)
7.32 ppm (d, J=7.9 Hz, 2H)
2.35 ppm (s, 3H)

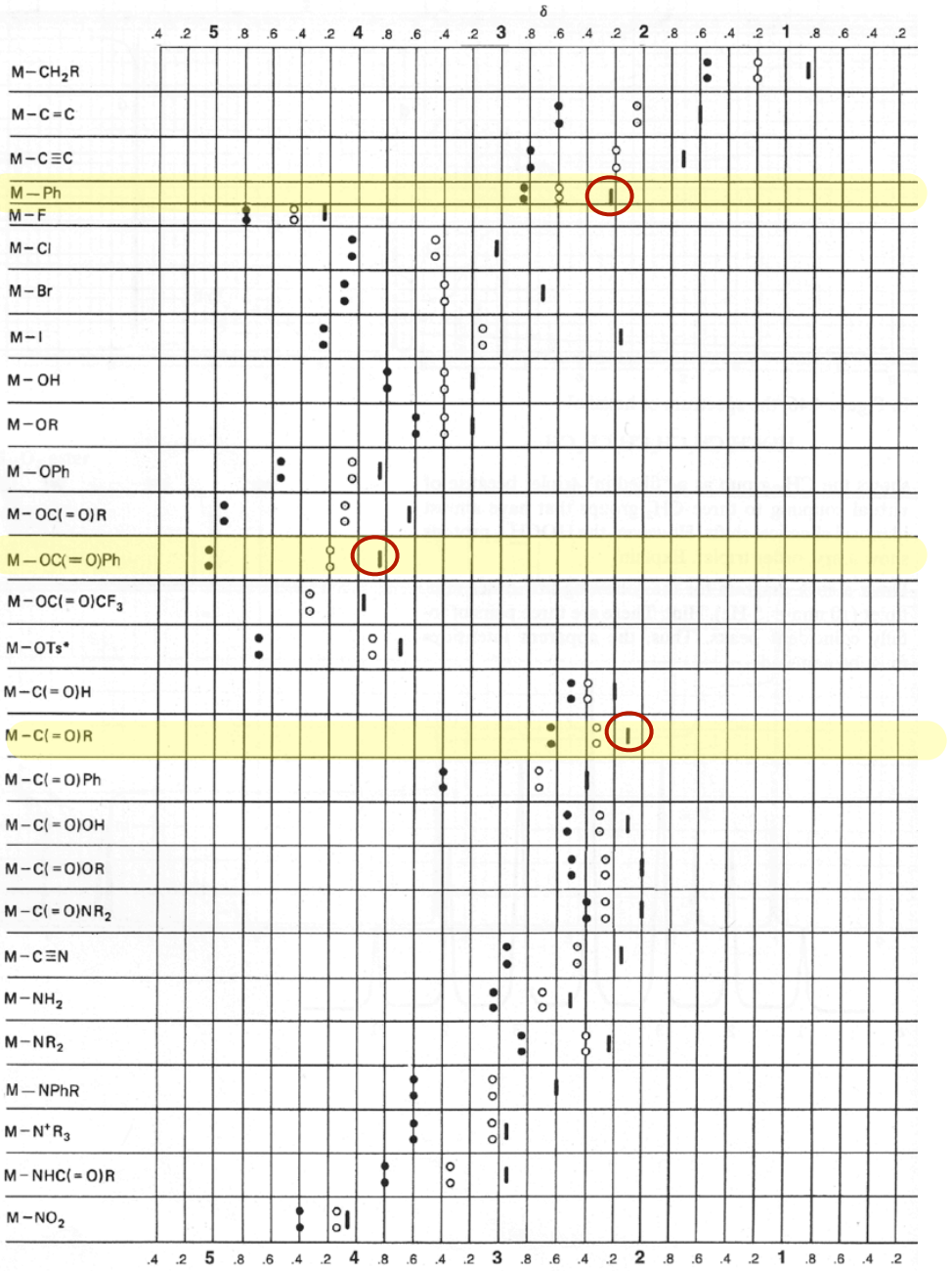
IR



- para substituted
- 2.35 ppm: Methyl ketone or Me-aromatic

Appendix A **CHART A.1 Chemical Shifts of Protons on a Carbon Atom Adjacent (α Position) to a Functional Group in Aliphatic Compounds (M—Y)**

▮ M = methyl
▮ M = methylene
▮ M = methine



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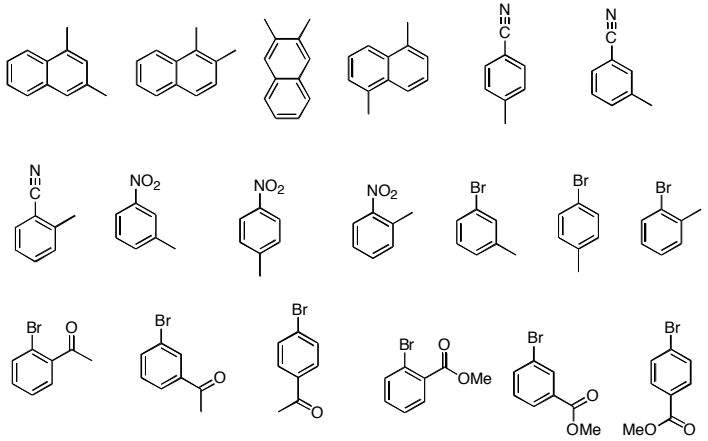

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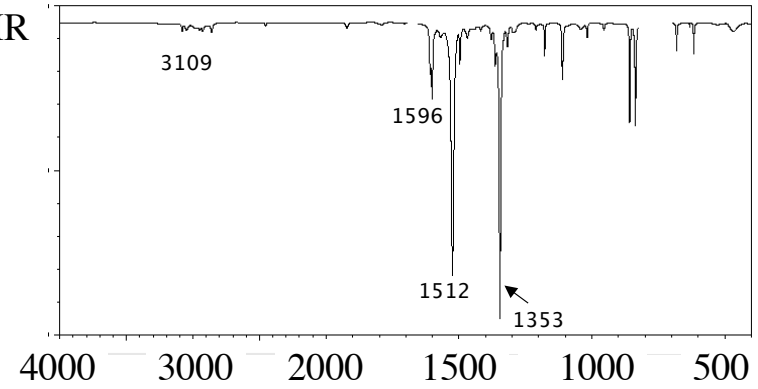

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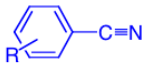
- IR: nitroarene, not a ketone

Nitriles

alkyl—C≡N 2260-2240 cm^{-1}

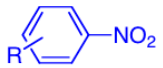


2240-2222 cm^{-1}

Nitro compounds

- 2 bands from the asymmetrical and symmetrical stretching of the N–O bond

alkylNO$_2$ 1550 cm^{-1} and 1372 cm^{-1}



1550-1500 cm^{-1} and 1360-1290 cm^{-1}

Ketones

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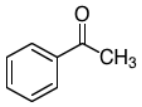
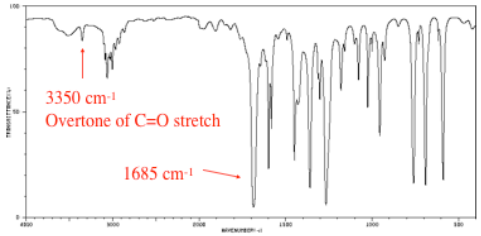


1685 cm^{-1}



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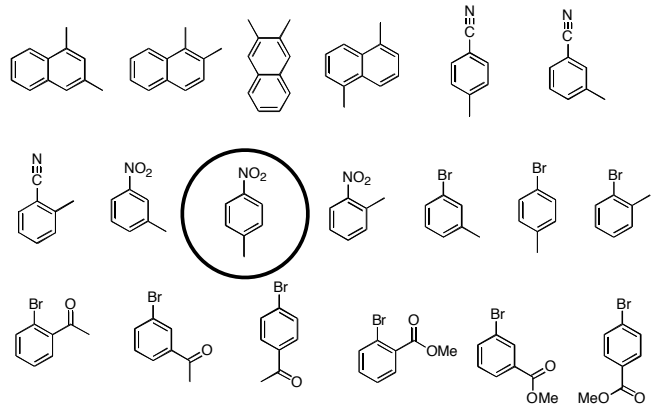

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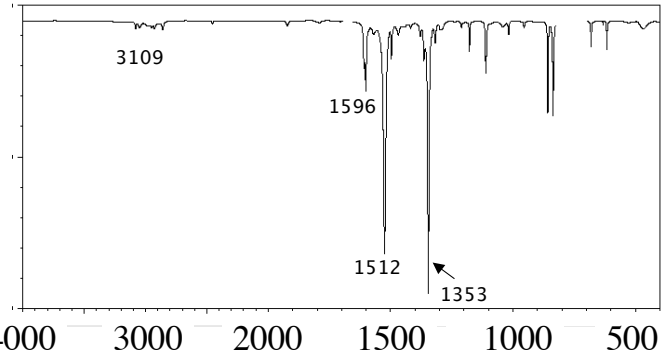

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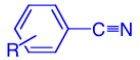

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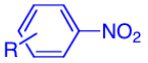

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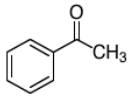

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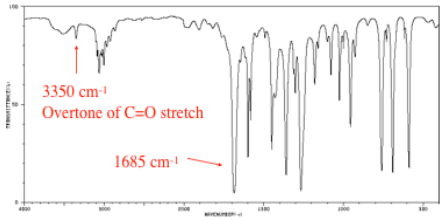

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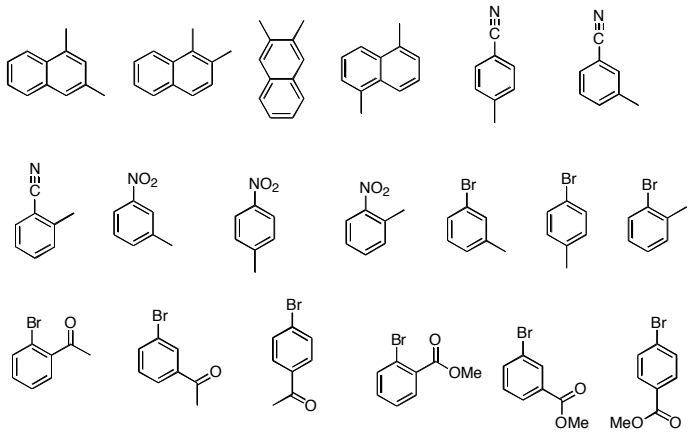

^{1}H NMR

7.22 ppm (d, J=7.9 Hz, 2H)
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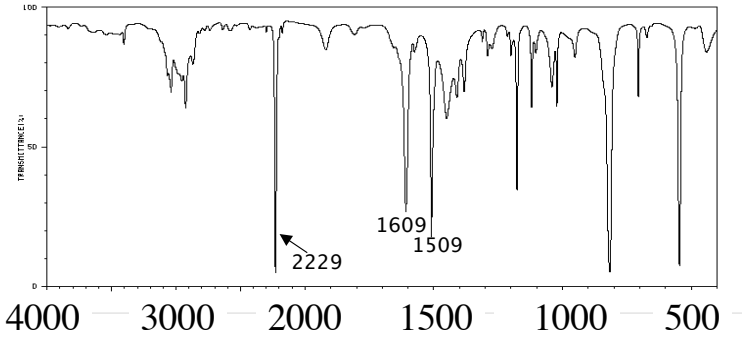

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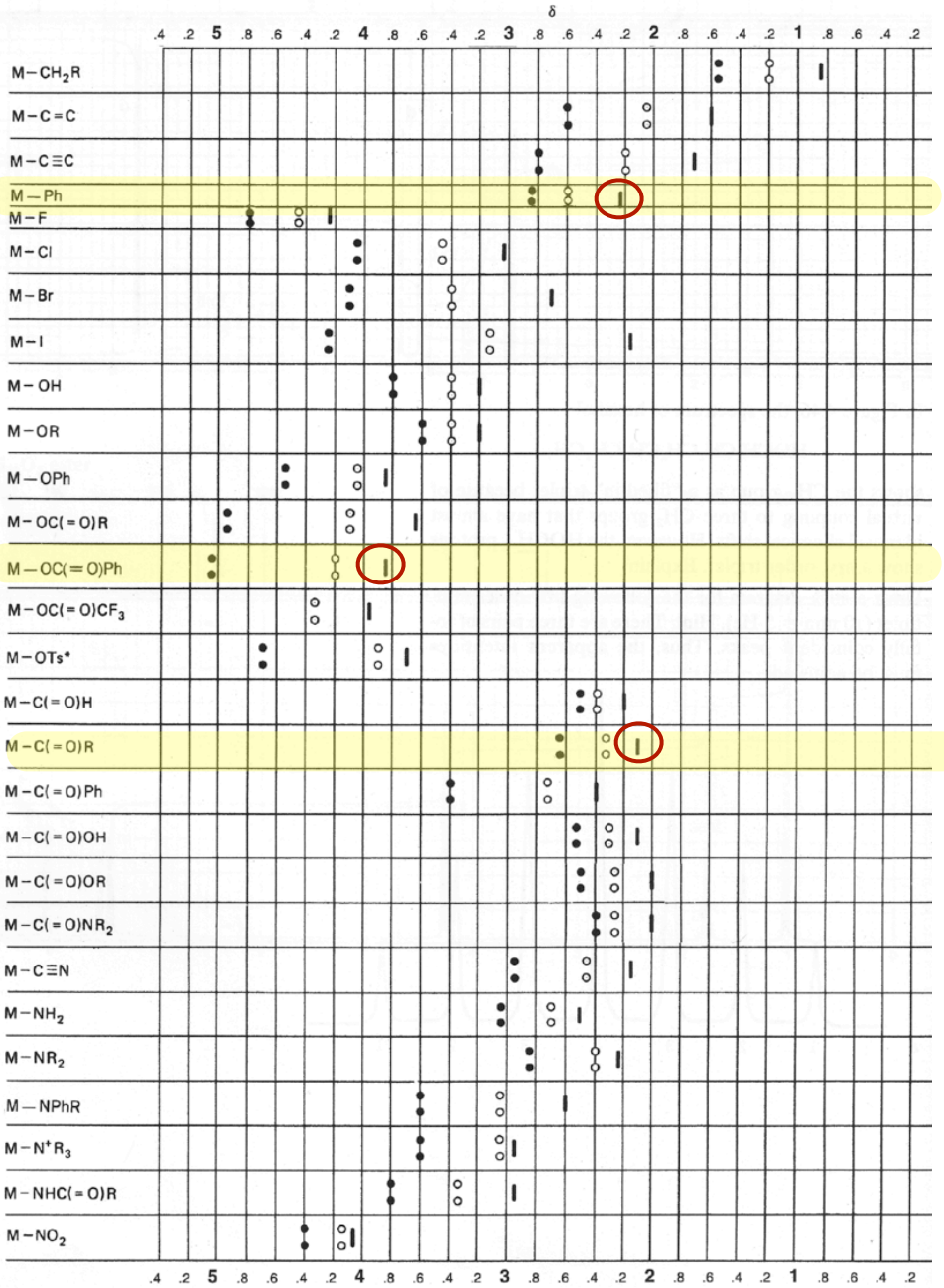

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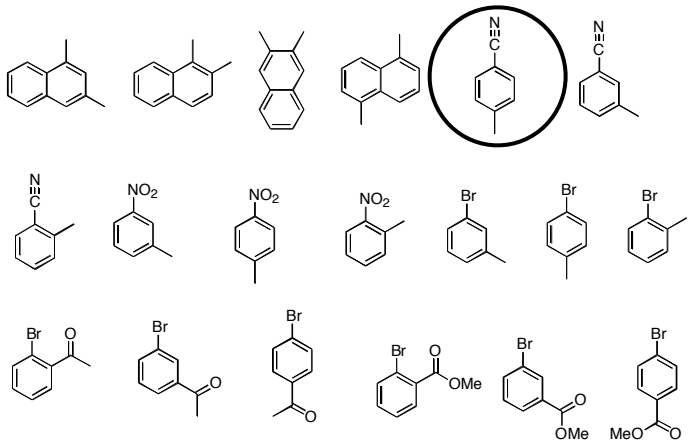

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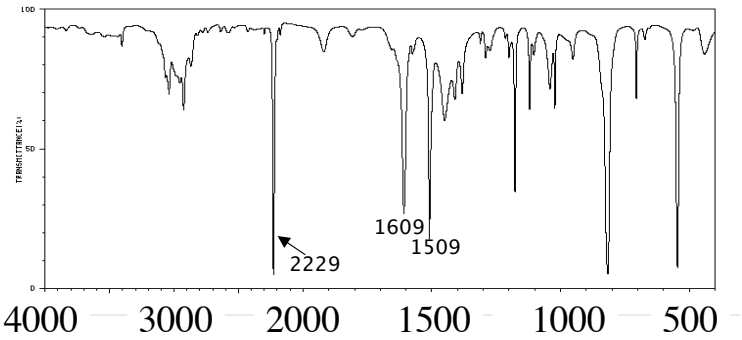

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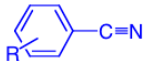

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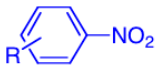

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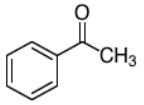

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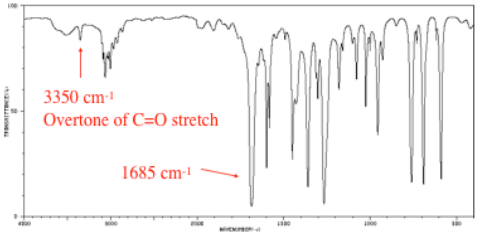

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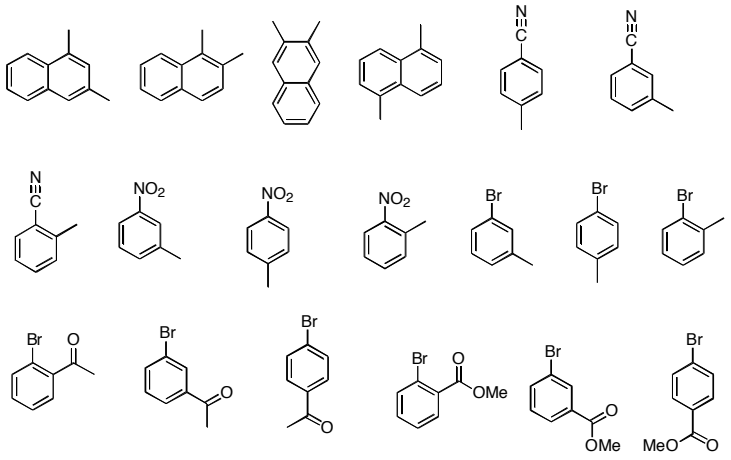

^{1}H NMR

8.17 ppm (t, J=2.1 Hz, 1H)
7.96 (dt, J=8.0, 2.1 Hz, 1H)
7.67 (dt, J=7.7,2.1 Hz, 1H)
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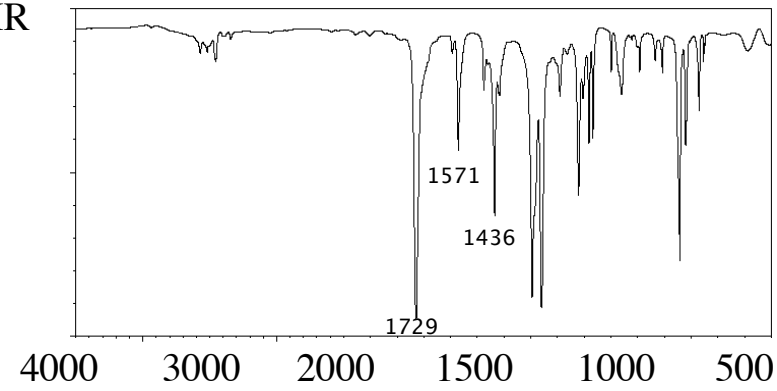
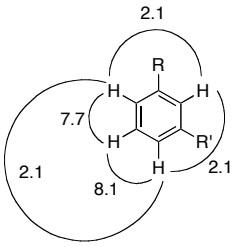
3.91 ppm (s, 3H)

IR



- meta substituted
- 3.91 ppm: Methyl ester



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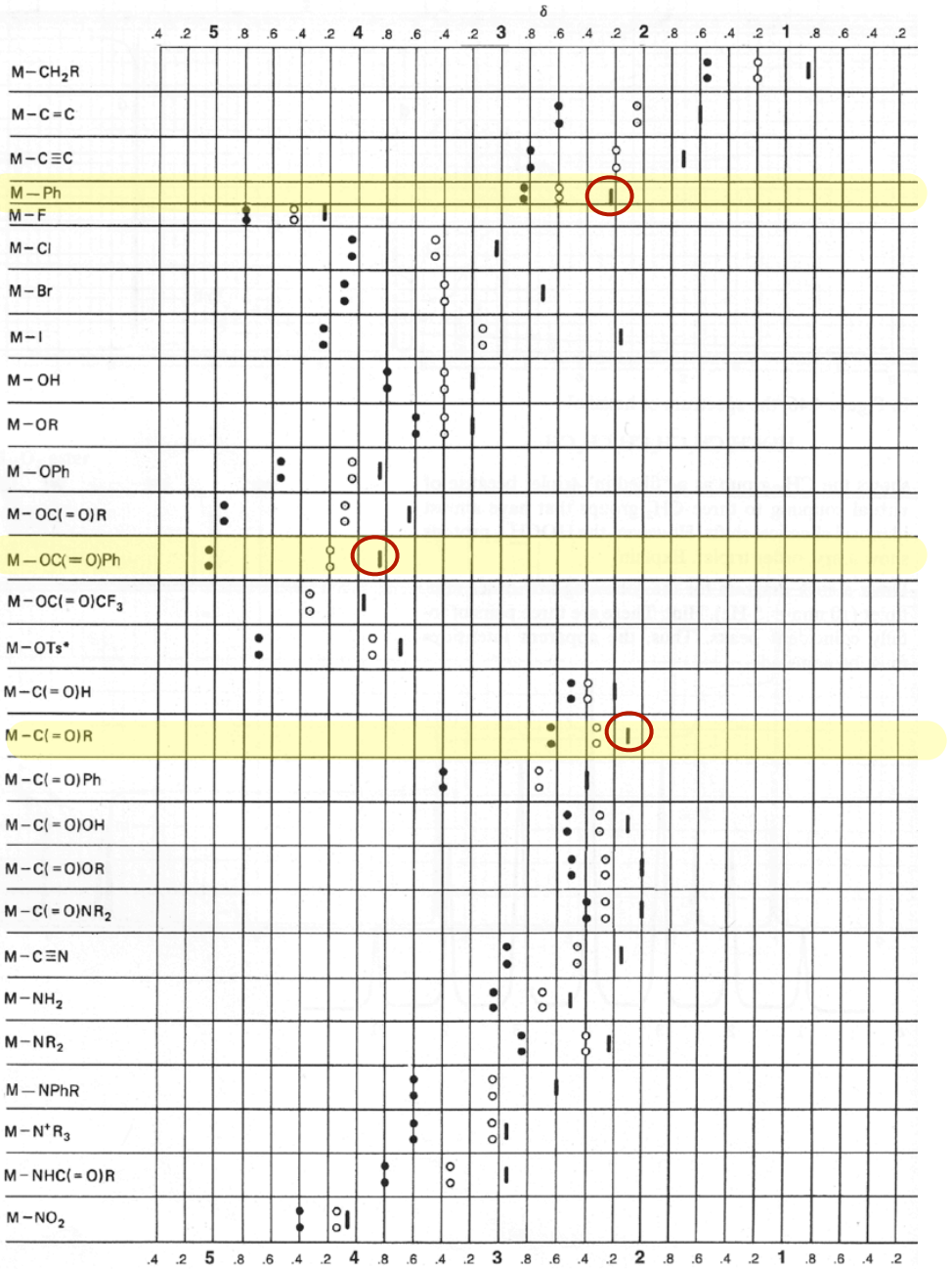

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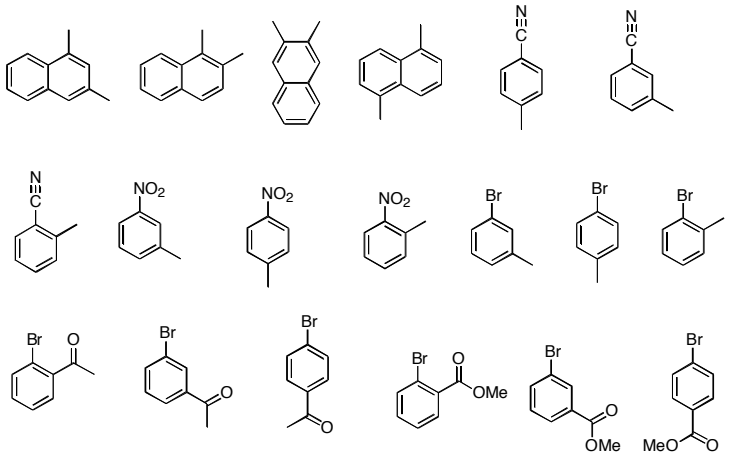

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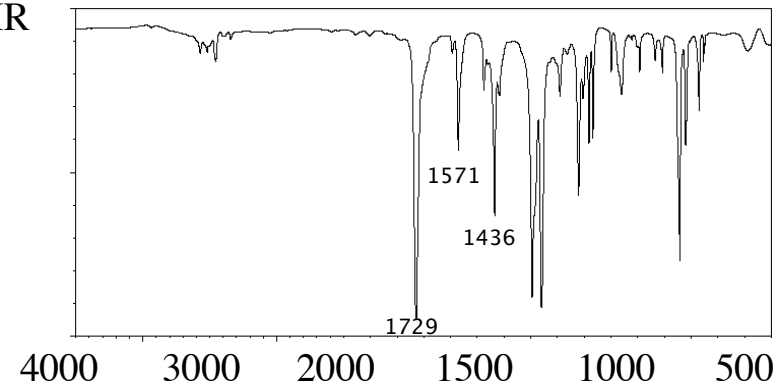

- meta substituted
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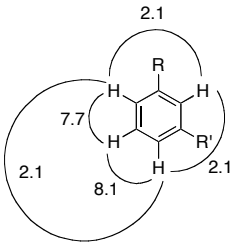


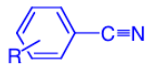
IR: arylester, 1729

no nitro, CN, ketone
from H NMR, we know there is not aryl-Me

Nitriles

alkyl—C≡N

2260-2240 cm^{-1}



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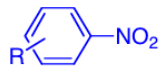

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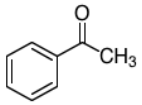
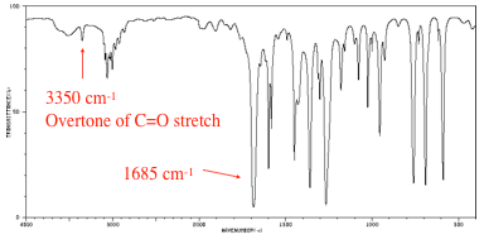


1685 cm^{-1}



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C=O stretch

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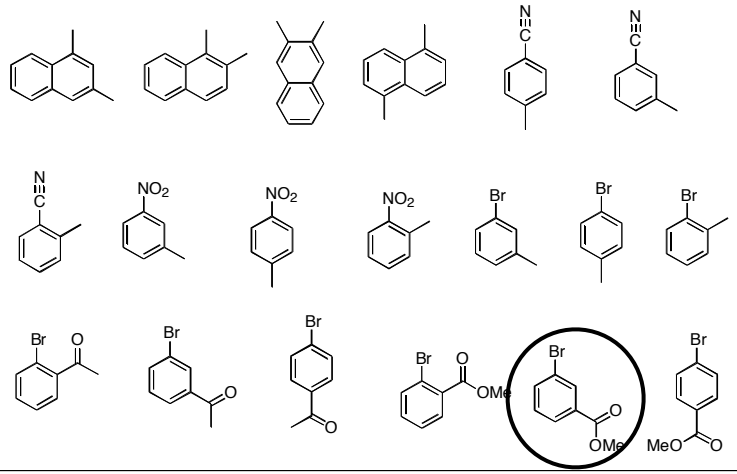
- formates, α,β-unsaturated, and benzoate esters: 1730-1715 cm^{-1}
- phenyl or vinyl esters: 1770-1780 cm^{-1}

C–O stretches (strong absorptions; asymmetrical coupled vibrations)

- saturated aliphatic esters (except acetates): C–O: 1210–1163 cm^{-1}
- acetates: 1240 cm^{-1}
- α,β-unsaturated esters: 1300–1160 cm^{-1}
- benzoate esters: 1310–1250 cm^{-1}

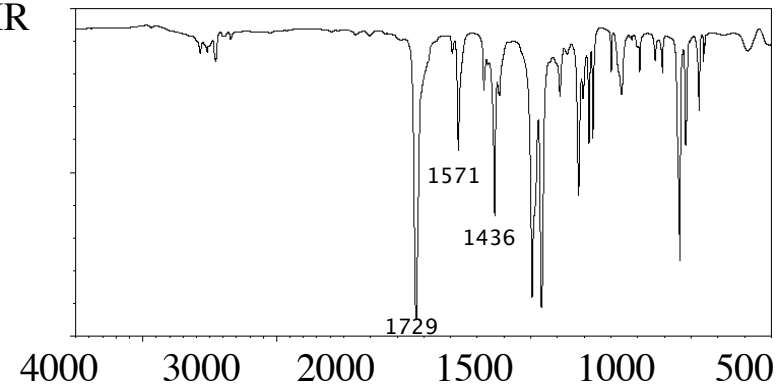
3. Circle the structure of the product that corresponds to the 1H NMR and IR data below. Circle only one structure



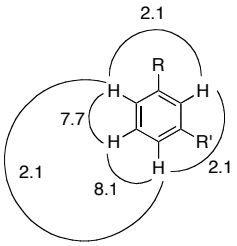
^{1}H NMR

8.17 ppm (t, J=2.1 Hz, 1H)
7.96 (dt, J=8.0, 2.1 Hz, 1H)
7.67 (dt, J=7.7,2.1 Hz, 1H)
7.31 (dd, J=8.0, 7.7 Hz, 1H)
3.91 ppm (s, 3H)

IR



- meta substituted
- 3.91 ppm: Methyl ester



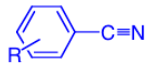
IR: arylester, 1729

no nitro, CN, ketone
from H NMR, we know there is not aryl-Me

Nitriles

alkyl—C≡N

2260-2240 cm^{-1}



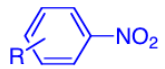
2240-2222 cm^{-1}

Nitro compounds

- 2 bands from the asymmetrical and symmetrical stretching of the N=O bond

alkylNO$_2$

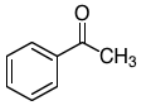
1550 cm^{-1} and 1372 cm^{-1}



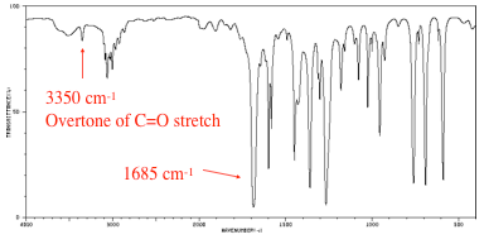
1550-1500 cm^{-1} and 1360-1290 cm^{-1}

Ketones

- conjugation: shifts position to lower frequency
  alkene or phenyl group causes absorption in the 1685-1666 cm^{-1} region. For α,β-unsaturated carbonyls, 2 absorptions may be observed



1685 cm^{-1}



Esters

C=O stretch

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- formates, α,β-unsaturated, and benzoate esters: 1730-1715 cm^{-1}
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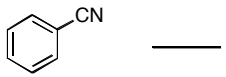
C–O stretches (strong absorptions; asymmetrical coupled vibrations)

- saturated aliphatic esters (except acetates): C–O: 1210–1163 cm^{-1}
- acetates: 1240 cm^{-1}
- α,β-unsaturated esters: 1300–1160 cm^{-1}
- benzoate esters: 1310–1250 cm^{-1}

(24 points) (not all compounds have a match)

1. Match the following to their IR spectra



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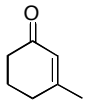
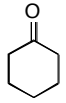


a

b

c

d



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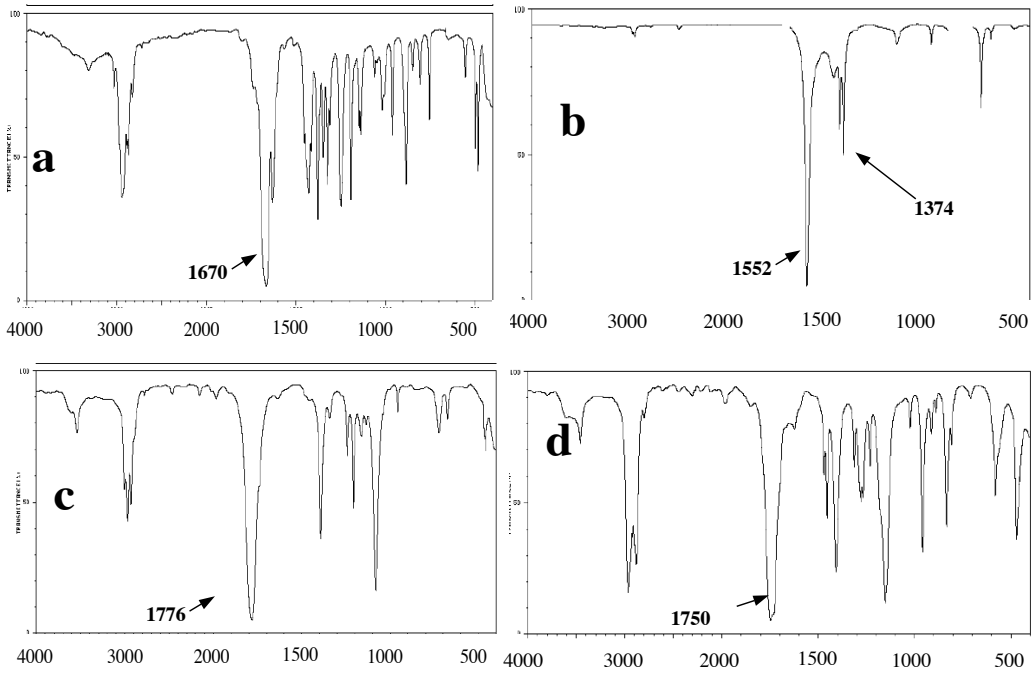
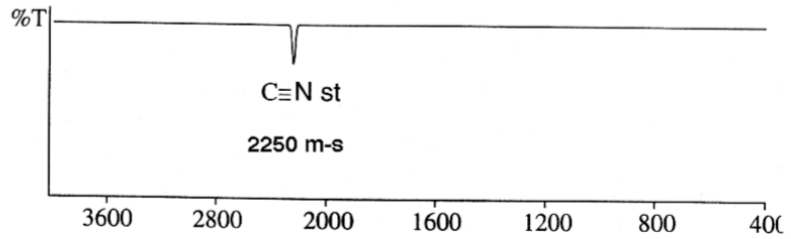
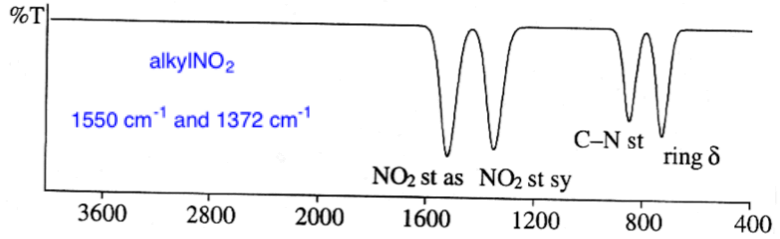


Nitriles

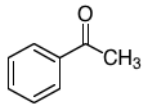


Nitro Compounds

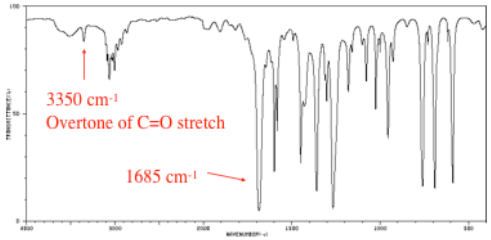


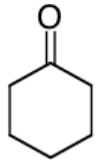
Ketones

- conjugation: shifts position to lower frequency
  alkene or phenyl group causes absorption in the 1685-1666 cm^{-1} region. For α,β-unsaturated carbonyls, 2 absorptions may be observed

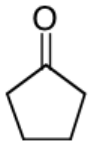


1685 cm^{-1}

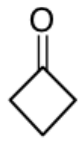




1715 cm^{-1}

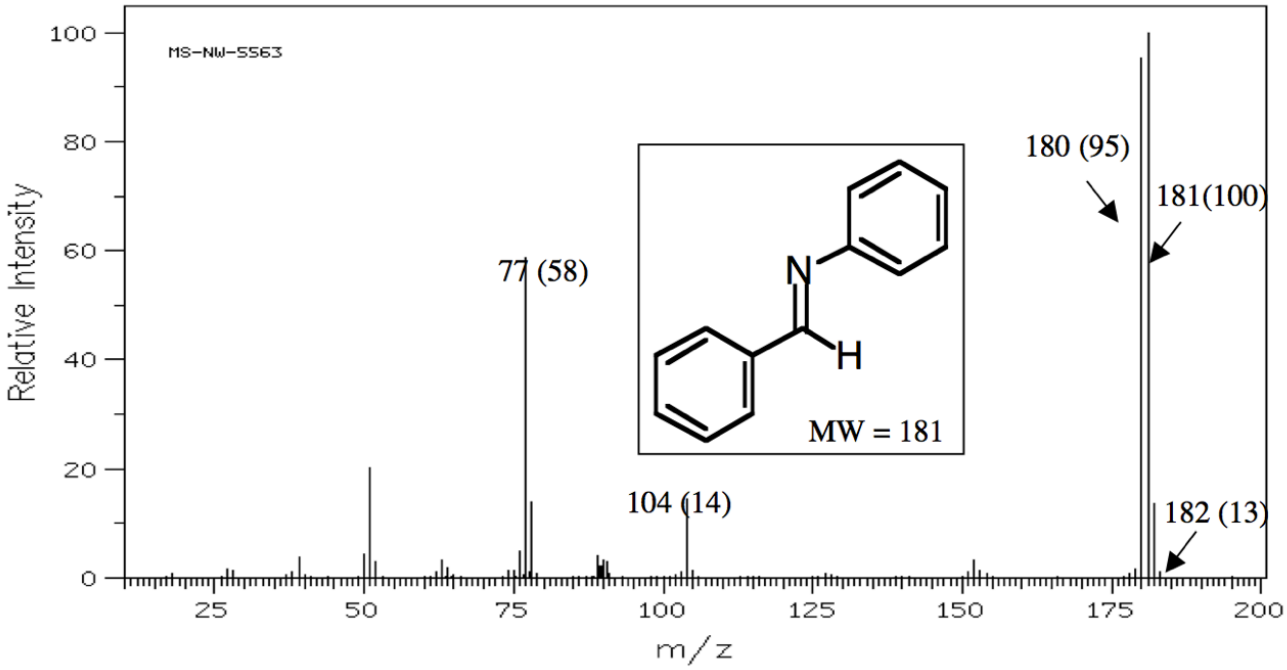


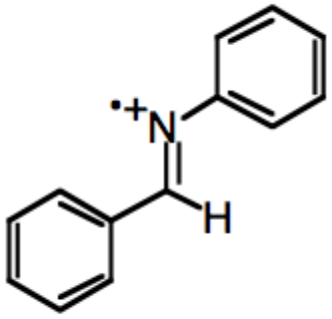
1751 cm^{-1}



1775 cm^{-1}

3. Explain how the labeled fragments are formed. Relative intensities are given in parentheses. (20 points





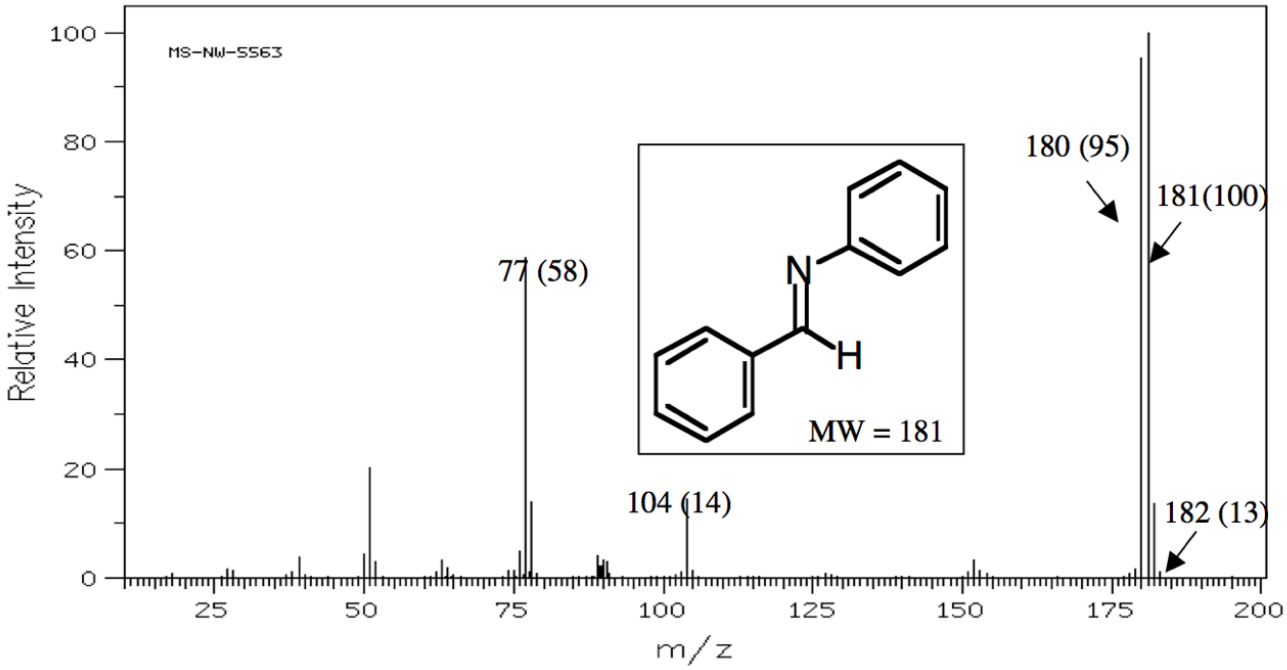
m/z 181 (parent)

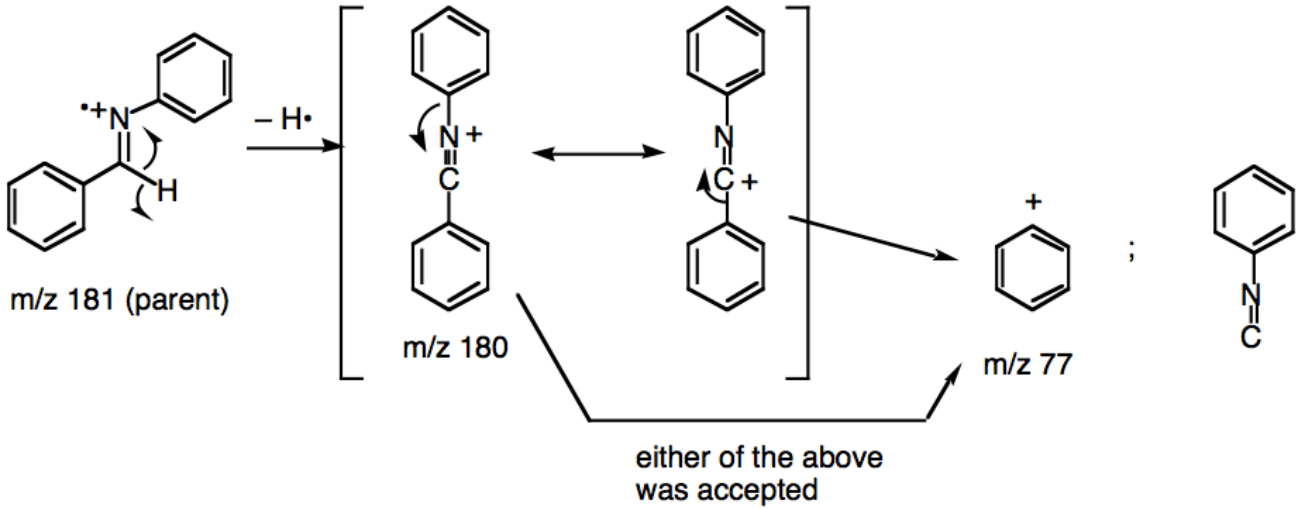
$(C^{12})_{12}(C^{13})_1H_{11}N$

m/z 182

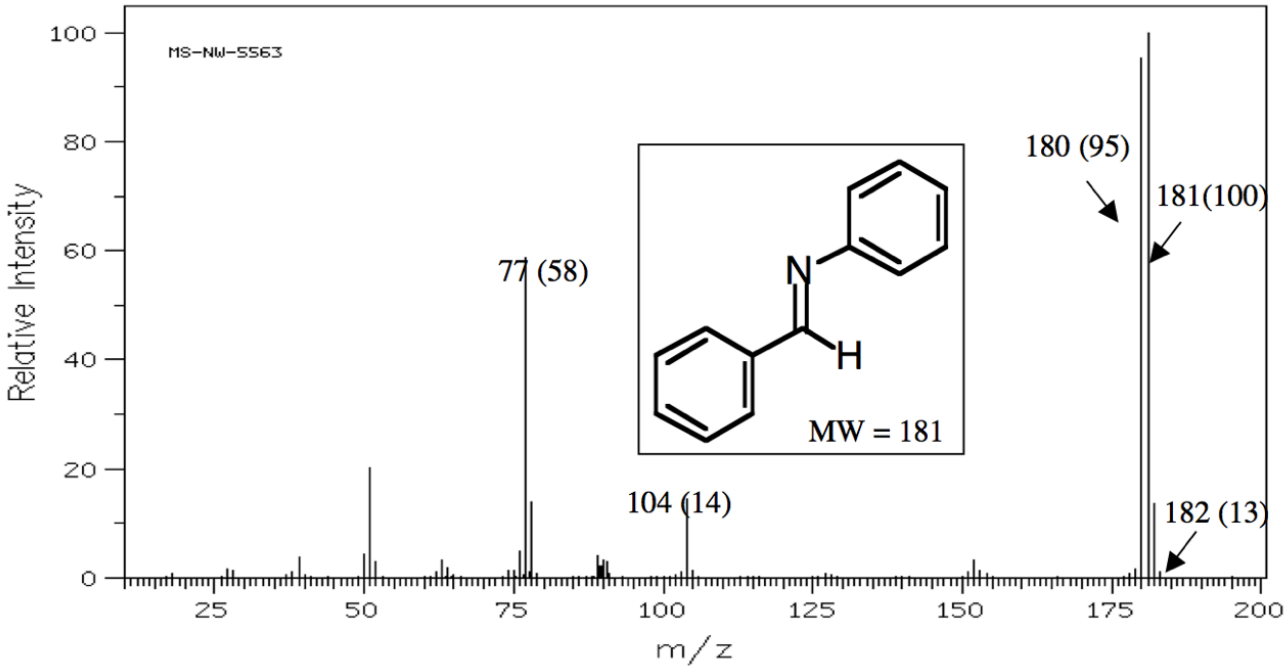
ratio of the parent peak to this peak is 100:13, because there are 13 carbons in the molecule, and the natural abundance of C^{13} is ca. 1%.

3. Explain how the labeled fragments are formed. Relative intensities are given in parentheses. (20 points

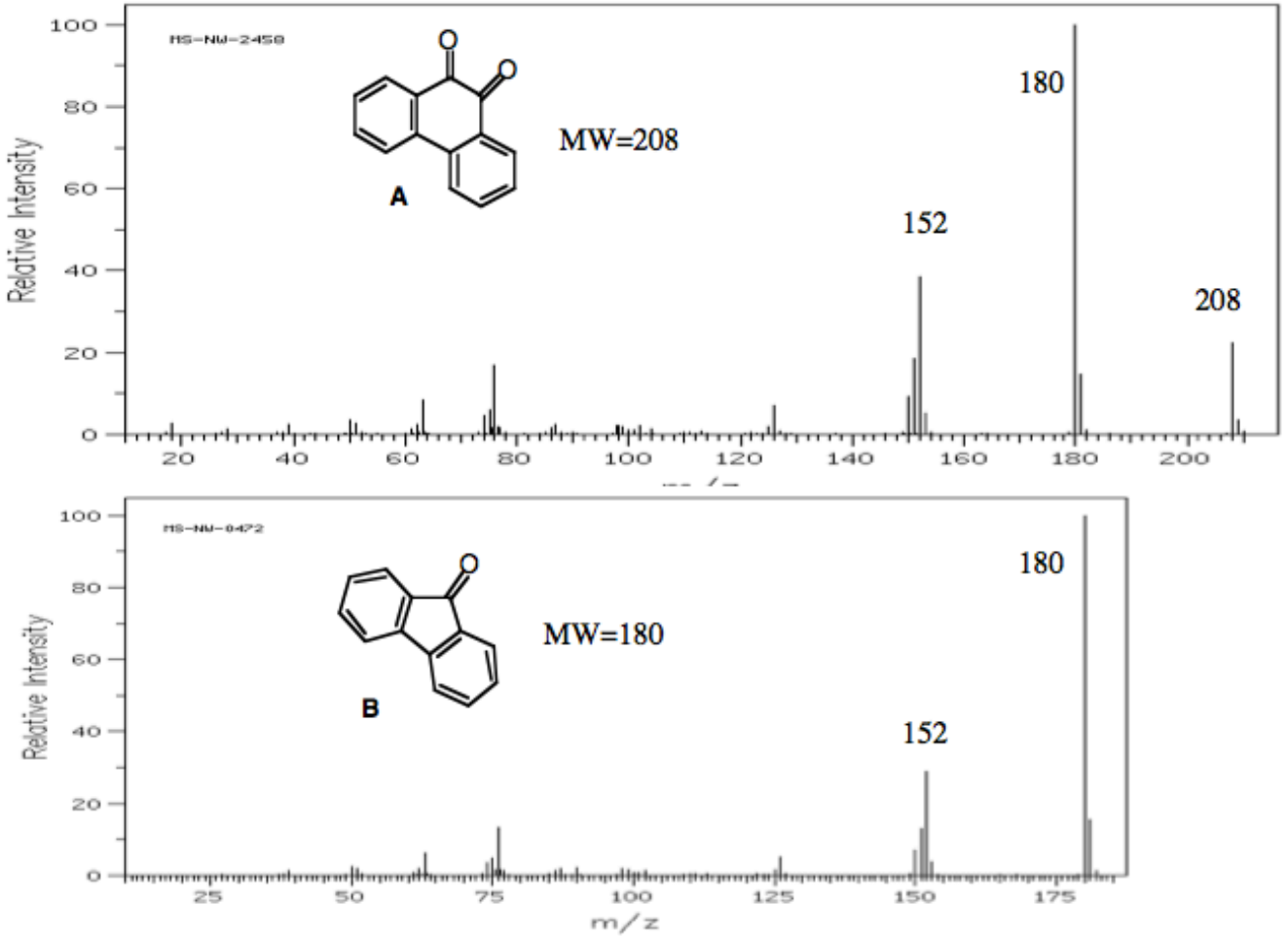


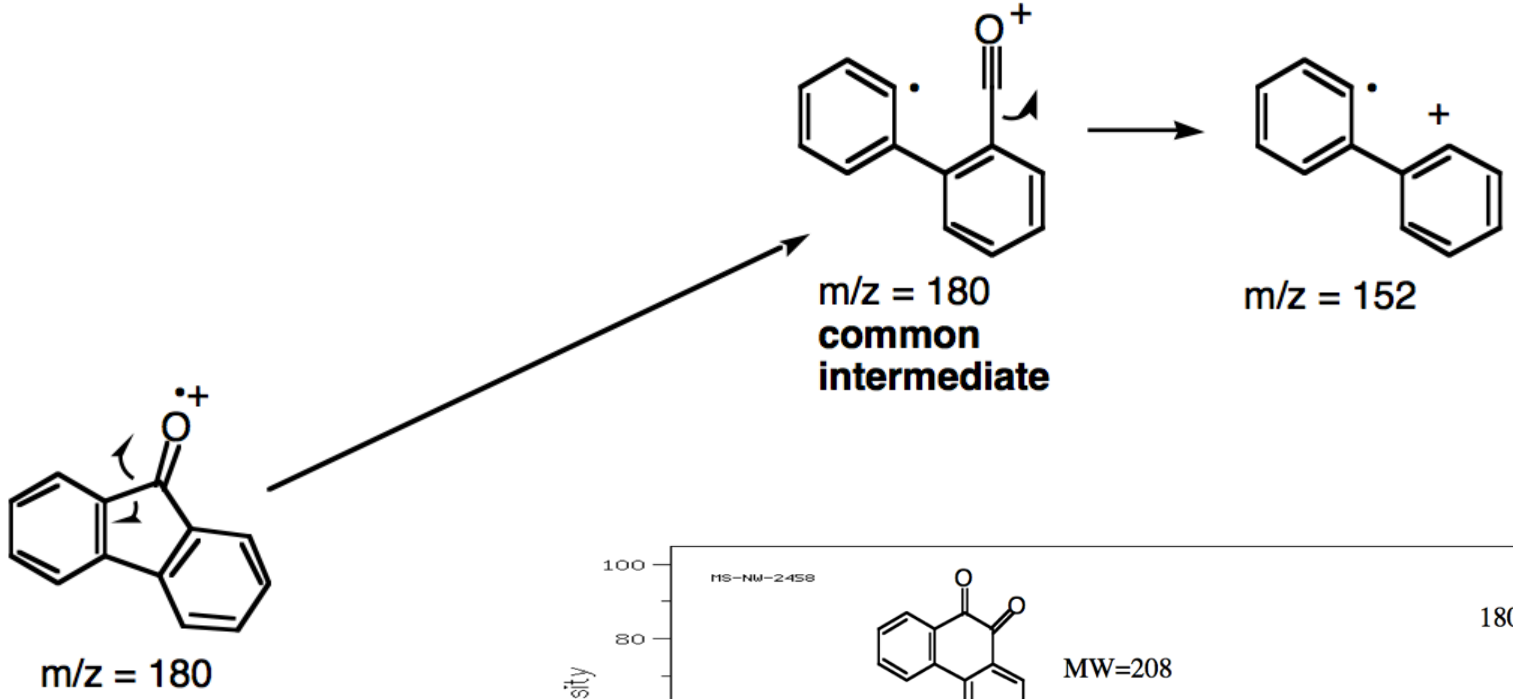


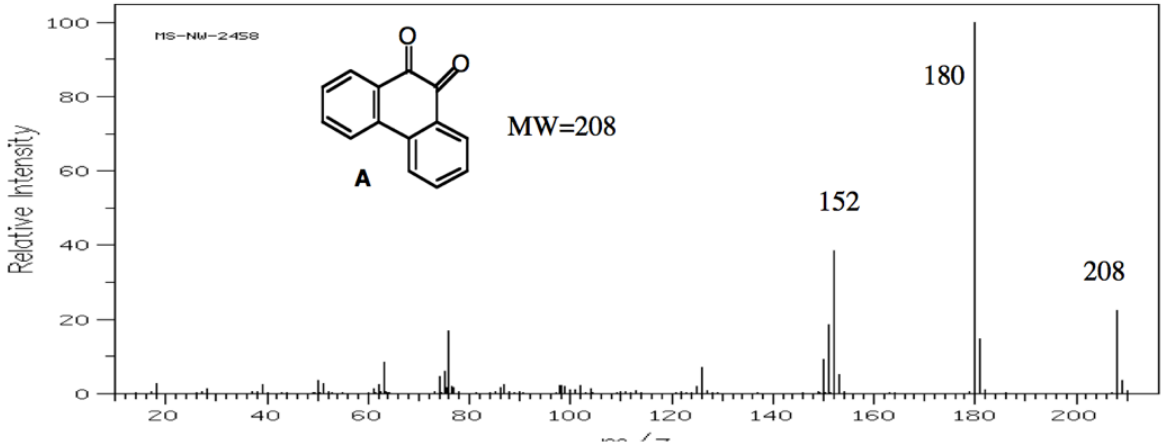
3. Explain how the labeled fragments are formed. Relative intensities are given in parentheses. (20 points

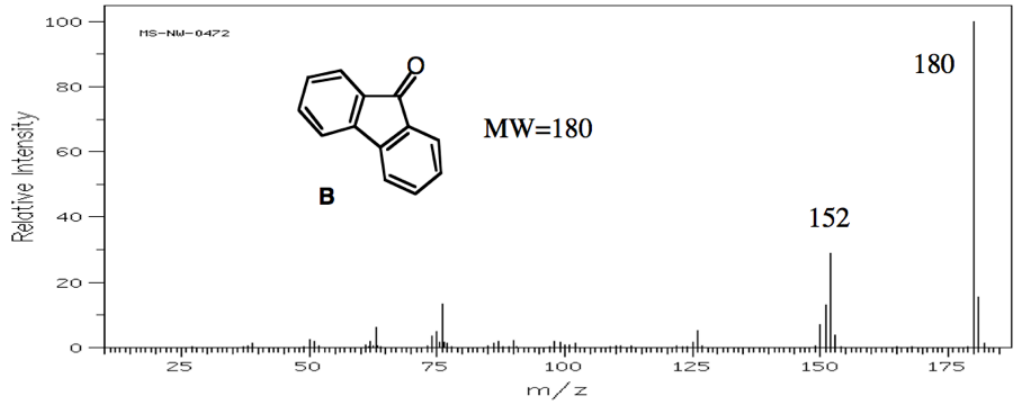


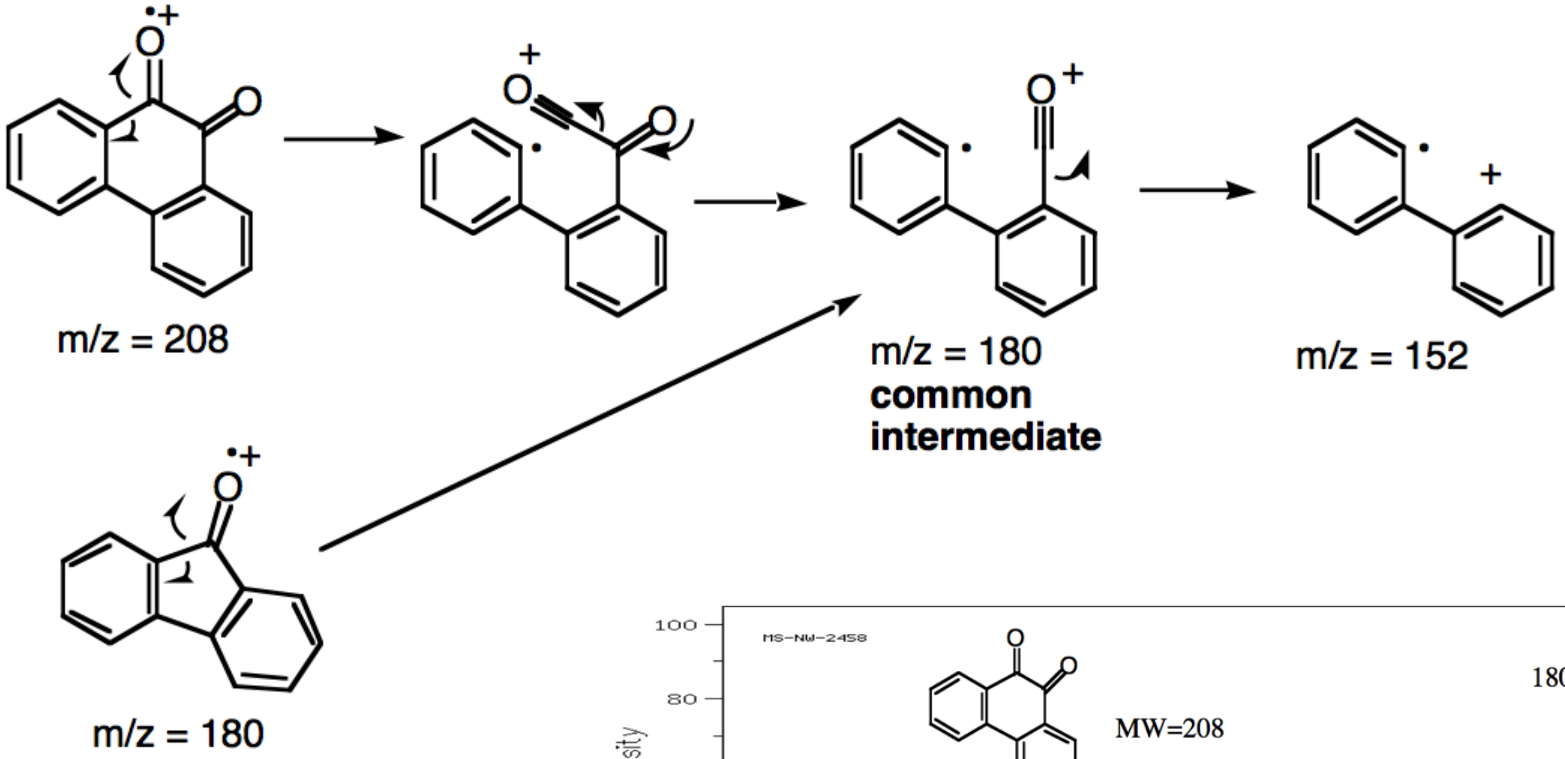
4. The mass spectra of compounds **A** and **B** are nearly identical, except for the additional peak at 208 in the spectrum of **A**. Explain why, and in doing so assign the labeled peaks in the mass spectrum. (20 points)

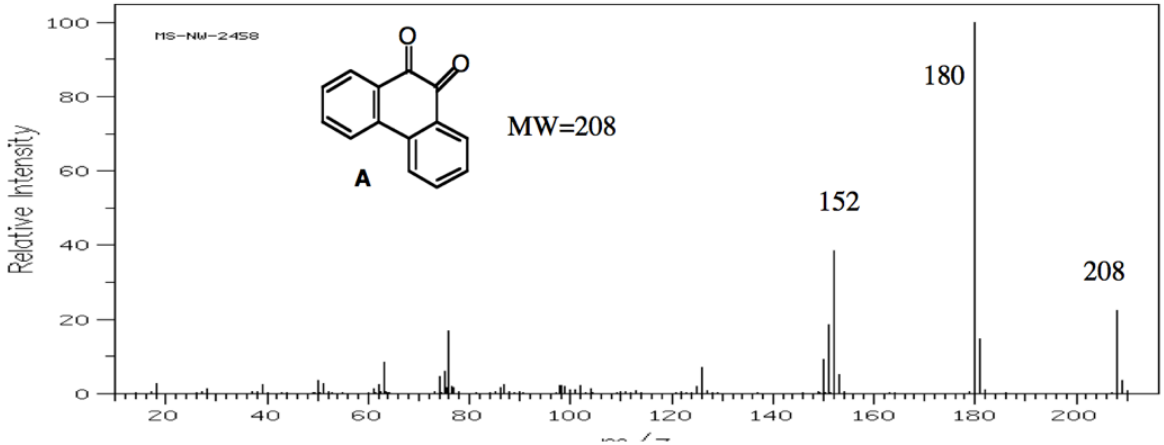


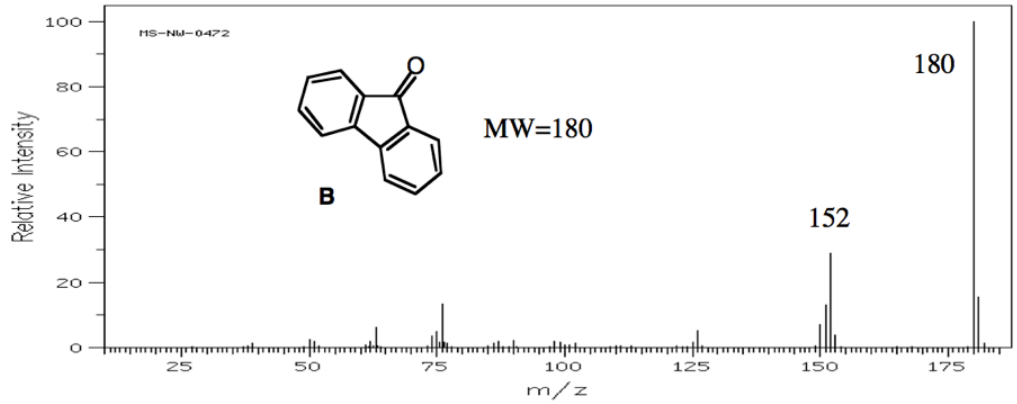

m/z = 180
m/z = 180
common
intermediate
m/z = 152


MS-NW-2458
A
MW=208
180
152
208
Relative Intensity
m/z

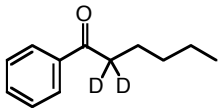
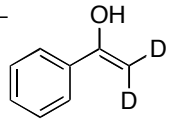
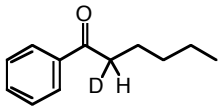
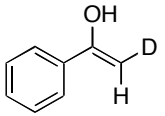
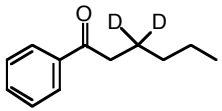
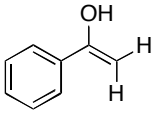
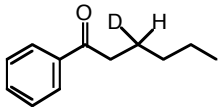
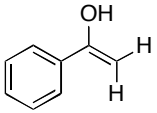
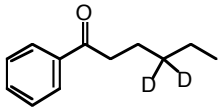
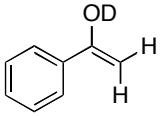
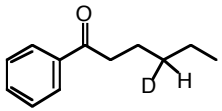
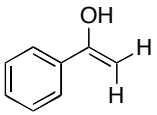
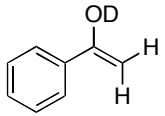
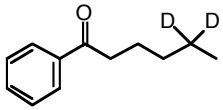
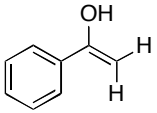
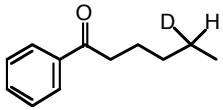
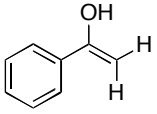

MS-NW-0472
B
MW=180
180
152
Relative Intensity
m/z


m/z = 208
m/z = 180
common
intermediate
m/z = 152
m/z = 180

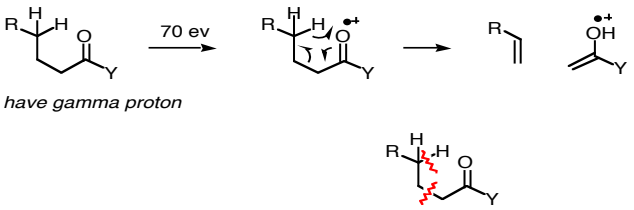

MS-NW-2458
A
MW=208
180
152
208
Relative Intensity
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200


MS-NW-0472
B
MW=180
180
152
Relative Intensity
100
80
60
40
20
0
25
50
75
100
125
150
175
m/z

5. McLafferty rearrangements of the molecules depicted below will give rise to fragments that can be detected by mass spectrometry. Circle the fragments that are observed. You may need to circle more than one answer for each! (24 points)

	120	121	**122**	
	120	**121**	122	
	**120**	121	122	
	**120**	121	122	
	120	**121**	122	
	**120**	**121**	122	 
	**120**	121	122	
	**120**	121	122	

The McLafferty Rearrangment:



must have gamma proton

1. Match the following to their IR spectra (24 points) (not all compounds have a match)