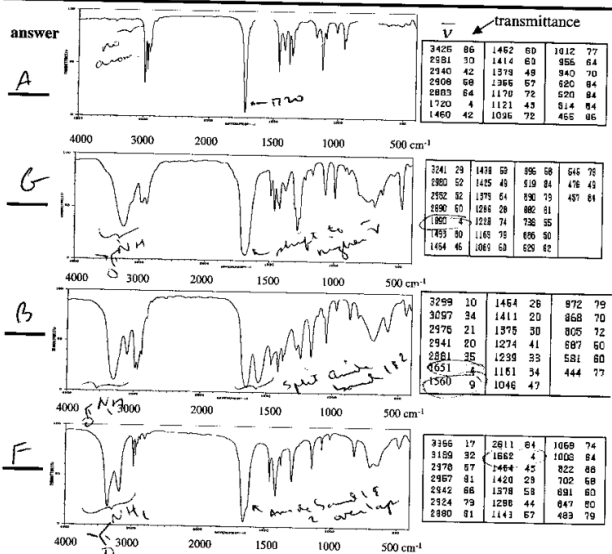
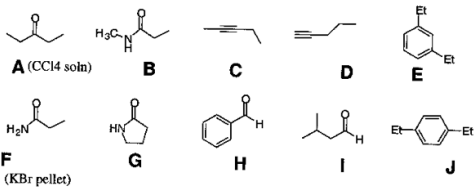
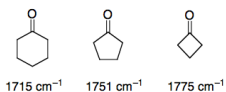


Cyclic Ketones

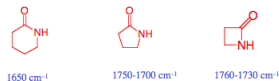
The bond angle influences the absorption frequency of the C=O



In strained rings, interaction with the adjacent C-C bonds increases the frequency of C=O stretching



Lactams

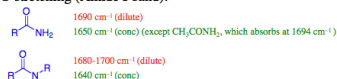


Secondary lactams do not have an NH bending band (Amide band II) near 1550 cm⁻¹. This is a characteristic of s-trans lactams.

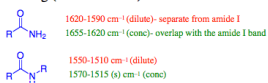
NH stretching:



C=O stretching (Amide I band):



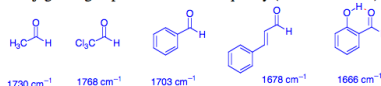
NH Bending (Amide II band):



Aldehydes

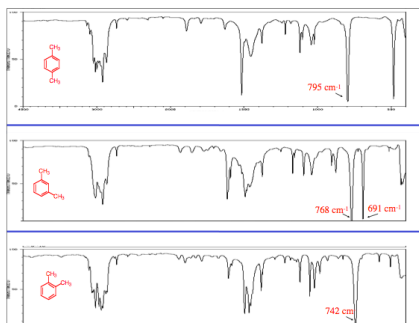
C=O stretch

- Aliphatic aldehydes: C=O stretch at 1740-1720 cm⁻¹
- Electron withdrawing groups shift to higher frequency
- Conjugative groups shift to lower frequency (1710-1685 cm⁻¹)



C-H stretch

2830-2695 cm⁻¹. Often, two bands are observed (the other is a result of an overtone of the C-H bend of the aldehyde)



Alkynes

- C≡C stretch: weak absorption at 2260-2100 cm⁻¹

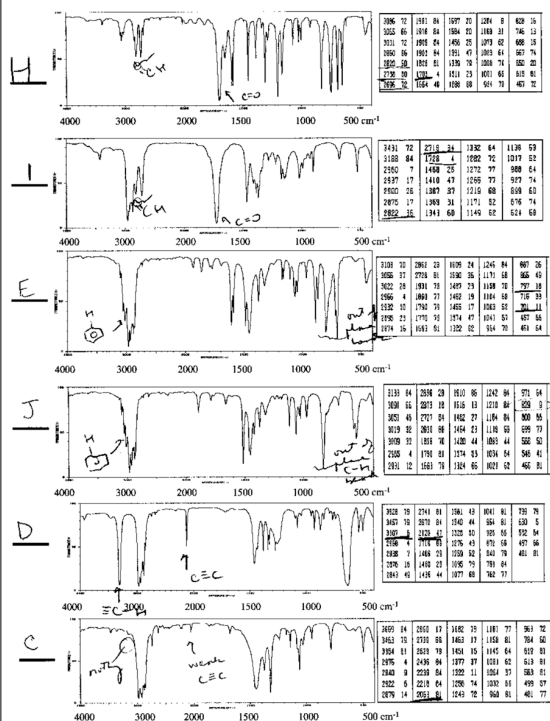
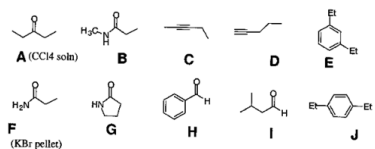
- not observed for symmetrical alkynes (v. weak for 'pseudo' symmetric alkynes)
- terminal alkynes (R-C≡C-H) absorptions are stronger than internal (R-C≡C-R) absorptions

C≡C-H stretch:

- 3333-3267 cm⁻¹
- strong, narrow (as compared to OH or NH)

C≡C-H bend:

- 700-610 cm⁻¹: broad, strong absorption
- 1400-1220 cm⁻¹: overtone of above



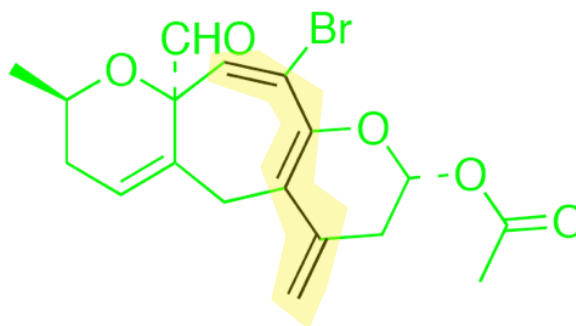
A.

TABLE 7.5

Rules of Diene Absorption ^a	
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+ 30
Alkyl substituent or ring residue	+ 5
Exocyclic double bond	+ 5
Polar groupings: OAc	
OAlk	+ 6
SAlk	+ 30
Cl, Br	+ 5
N(Alk) ₂	+ 60
Solvent correction ^b	+ 0
$\lambda_{\text{calc}} = \text{Total}$	

^aSee L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15-24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

^bSolvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.



use Table 7.5

Base (homoannular)	253
C=C (1 X 30)	+30
OR (1 x 6)	+6
Alkyl (3 X 5)	+15
Hal (1 x 5)	+5
Exocyclic	+5
$\lambda_{\text{max}}(\text{calc}) =$	314

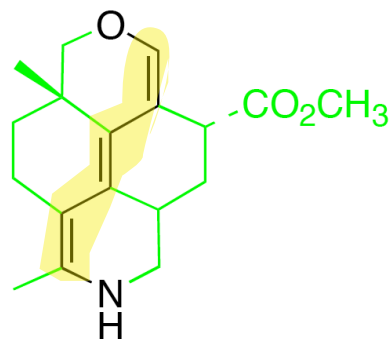
B.

TABLE 7.5

Rules of Diene Absorption ^a	
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+ 30
Alkyl substituent or ring residue	+ 5
Exocyclic double bond	+ 5
Polar groupings: OAc	
OAlk	+ 6
SAlk	+ 30
Cl, Br	+ 5
N(Alk) ₂	+ 60
Solvent correction ^b	+ 0
$\lambda_{\text{calc}} = \text{Total}$	

^aSee L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15-24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

^bSolvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.



Use Table 7.5

Base (hetero)	214
DBE	30
OR	6
Alkyl (5)	25
Exo (4)	20
NR ₂	60
$\lambda_{\text{max}}(\text{calc}) =$	355

TABLE 7.5

Rules of Diene Absorption	
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+ 30
Alkyl substituent or ring residue	+ 5
Exocyclic double bond	+ 5
Polar groupings: OAc	+ 0
OAlk	+ 6
SAlk	+ 30
Cl, Br	+ 5
N(Alk) ₂	+ 60
Solvent correction ^b	+ 0
$\lambda_{\text{calc}} = \text{Total}$	

^aSee L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15-24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

^bSolvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.

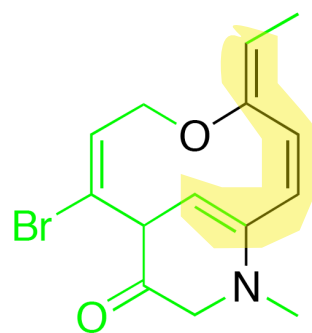


Table 7.5

Base (hetero)	253
C=C	30
Alkyl (2)	10
OR	6
NR ₂	60
Exo's	5
<hr/>	
λ_{max} (calc) =	364

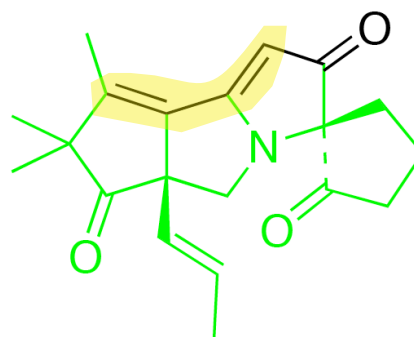
TABLE 7.12

Rules of Enone and Dienone Absorption (α, β -Unsaturated Carbonyl Compounds)	
β α β -C=C-C=O Enone	δ γ β α δ -C=C-C=C-C=O Dienone
Base values (nm)	
Acyclic α, β -unsaturated ketones	215
Six-membered cyclic α, β -unsaturated ketones	215
Five-membered cyclic α, β -unsaturated ketones	202
α, β -Unsaturated aldehydes	210
α, β -Unsaturated carboxylic acids and esters	195
Increments for	
Double bond extending conjugation	+ 30
Alkyl group, ring residue	+ 10
α	+ 10
β	+ 12
γ and higher	+ 18
Polar groupings: —OH	+ 35
α	+ 30
β	+ 30
δ	+ 50
—OAc α, β, δ	+ 6
—OMe α	+ 35
β	+ 30
γ	+ 17
δ	+ 31
—SAlk β	+ 85
—Cl α	+ 15
β	+ 12
—Br α	+ 25
β	+ 30
—NR ₂ β	+ 95
Exocyclic double bond	+ 5
Homodiene component ^a	+ 39
Solvent correction (see table below)	Variable
$\lambda_{\text{calc}} = \text{Total}^b$	

^aTwo conjugated double bonds, both in the same ring.

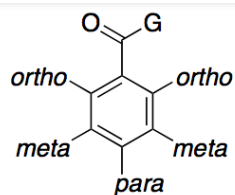
^bThe calculated values usually fall within ± 3 nm of the observed values. The molar absorptivities of *cisoid* enones are usually less than 10,000, whereas the molar absorptivities of *transoid* enones are greater than 10,000.

C



Use table 7.12

Base	202
C=C	30
β -NR ₂	95
Exo (2)	10
γ/δ alkyls (3x18)	54
<hr/>	
λ_{max} (calc) =	391



ArCOR/ArCHO/ArCO ₂ H/ArCO ₂ R	$\lambda_{\text{max}}^{\text{EtOH}}$ (nm)
Parent chromophore: Ar = C ₆ H ₅	
G = Alkyl or ring residue, (e.g., ArCOR)	246
G = H, (ArCHO)	250
G = OH, OAlk, (ArCO ₂ H and ArCO ₂ R)	230
Increment for each substituent on Ar:	
—Alkyl or ring residue	o-, m- +3 p- +10
—OH, —OCH ₃ , —OAlk	o-, m- +7 p- +25
—O ⁻ (oxyanion)	o- +11 m- +20 p- +78 ^b
—Cl	o-, m- +0 p- +10
—Br	o-, m- +2 p- +15
—NH ₂	o-, m- +13 p- +58
—NHCOCH ₃	o-, m- +20 p- +45
—NHCH ₃	p- +73
—N(CH ₃) ₂	o-, m- +20 p- +85

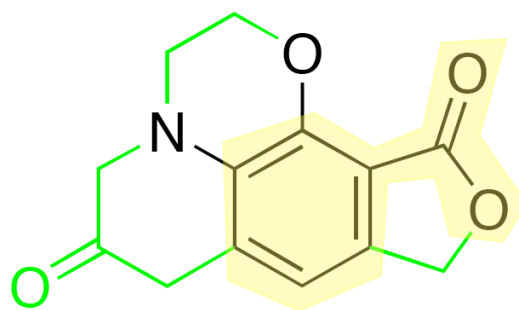
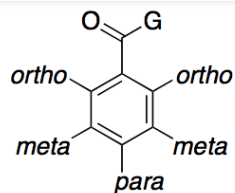
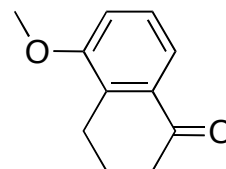


Table 7.21

Base (ArCO ₂ R)	230
<i>o</i> -OR	7
<i>o</i> -alk	3
<i>m</i> -NR ₂	20
<i>p</i> -Alkyl	10
<i>m</i> -alkyl	
λ_{max} (calc) =	270

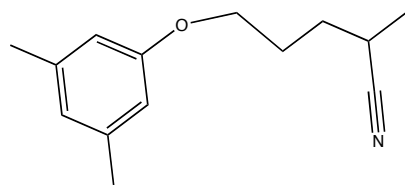


ArCOR/ArCHO/ArCO ₂ H/ArCO ₂ R	$\lambda_{\text{max}}^{\text{EtOH}}$ (nm)
Parent chromophore: Ar = C ₆ H ₅	
G = Alkyl or ring residue, (e.g., ArCOR)	246
G = H, (ArCHO)	250
G = OH, OAlk, (ArCO ₂ H and ArCO ₂ R)	230
Increment for each substituent on Ar:	
—Alkyl or ring residue	o-, m- +3 p- +10
—OH, —OCH ₃ , —OAlk	o-, m- +7 p- +25
—O ⁻ (oxyanion)	o- +11 m- +20 p- +78 ^b
—Cl	o-, m- +0 p- +10
—Br	o-, m- +2 p- +15
—NH ₂	o-, m- +13 p- +58
—NHCOCH ₃	o-, m- +20 p- +45
—NHCH ₃	p- +73
—N(CH ₃) ₂	o-, m- +20 p- +85

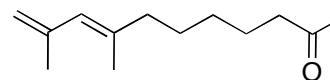


base	246
ortho alkyl: +3	
meta-OR (alkyl): +7	
<hr/>	
=	256 nm

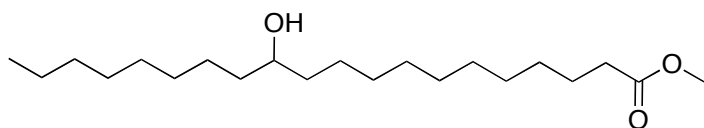
2. The key to solving this structure is first identifying the symmetric trisubstituted benzene ring from the C13 and the H1-NMR. The nitrile is more subtle, but (with the hint) and the IR it becomes clear that the Nitrogen and the remaining two IHD's are a nitrile.



3. UV indicates a conjugated double bond. IR confirms that the ketone is not conjugated. The substitution pattern of the diene is implied by the coupling constants.



4. The key is to identify the long chain ethyl ester (it is clearly ethyl by H-NMR and MS). The position of the alcohol is indicated by the alpha cleavage products in the MS: 243 and 143.



5. This cyclic ketone must be seven-membered or greater based on the IR absorbance at 1705. H-NMR shows that there are only three alpha protons (2.26-2.20 m, 3H) indicating that the substitution must be alpha to the carbonyl. The MS fragmentation for the McLafferty product (111) indicates loss of the isopentyl side-chain making it a seven membered-ring not larger.

