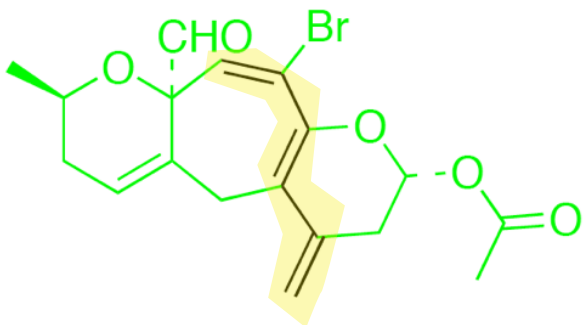
A.

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	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

[a]See 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.

[b]Solvents 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
λ_{max}(calc) =	314

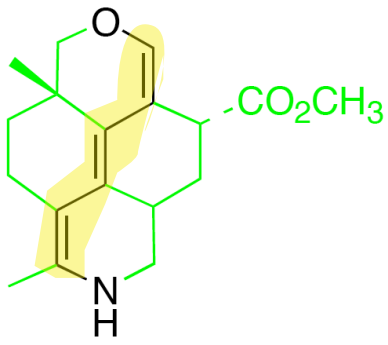
B.

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	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

[a]See 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.

[b]Solvents 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
λ_{max}(calc) =	355

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	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

[a]See 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.

[b]Solvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.

D

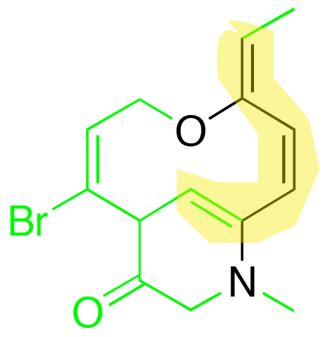
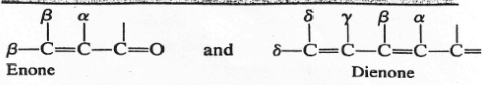


Table 7.5

Base (hetero)	253
C=C	30
Alkyl (2)	10
OR	6
NR_2	60
Exo's	5
λ_{max}(calc) =	364

TABLE 7.12

Rules of Enone and Dienone Absorption (α,β-Unsaturated Carbonyl Compounds)

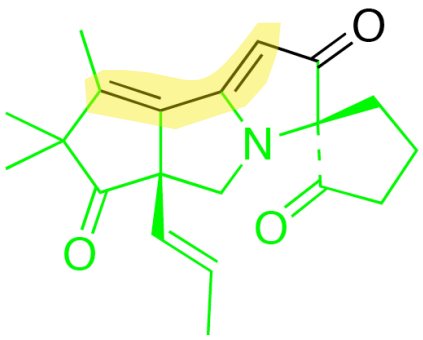


		(nm)
Base values		
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	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
λ_{calc} = Total[b]		

[a]Two conjugated double bonds, both in the same ring.

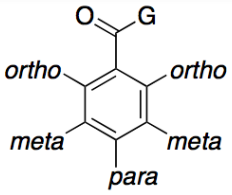
[b]The calculated values usually fall within ±3 nm of the observed values. The molar absorptivities of *cisoid* enones are usually less than 10,000, whereas the molar absorptivities of *transoid* enones are greater than 10,000.

C



Use table 7.12

Base	202
C=C	30
β-NR_2	95
Exo (2)	10
γ/δ alkyls (3x18)	54
λ_{max}(calc) =	391



ArCOR/ArCHO/$ArCO_2H$/$ArCO_2R$		λ_{max}^{EtOH} (nm)
Parent chromophore: Ar = C_6H_5		
G = Alkyl or ring residue, (e.g., ArCOR)		246
G = H, (ArCHO)		250
G = OH, OAlk, ($ArCO_2H$ and $ArCO_2R$)		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

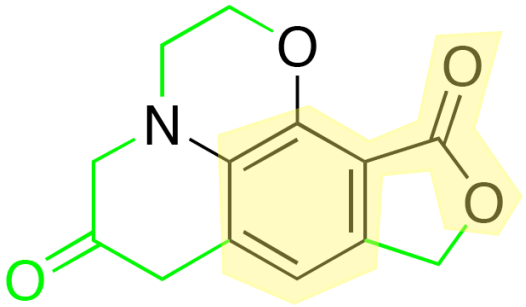
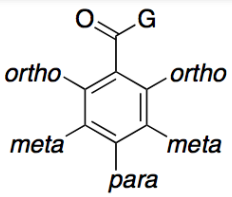
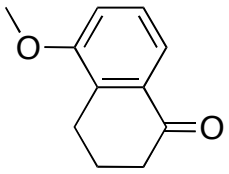


Table 7.21

Base (ArCO2R)	230
o-OR	7
o-alk	3
m-NR2	20
p-Alkyl	10
m-alkyl	
λ_{max}(calc) =	270



ArCOR/ArCHO/$ArCO_2H$/$ArCO_2R$		λ_{max}^{EtOH} (nm)
Parent chromophore: Ar = C_6H_5		
G = Alkyl or ring residue, (e.g., ArCOR)		246
G = H, (ArCHO)		250
G = OH, OAlk, ($ArCO_2H$ and $ArCO_2R$)		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

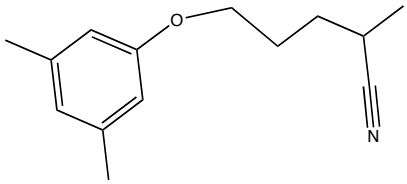
ortho alkyl: +3

meta-OR (alkyl): +7

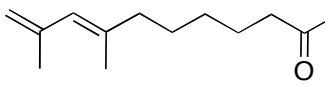
_____

= 256 nm

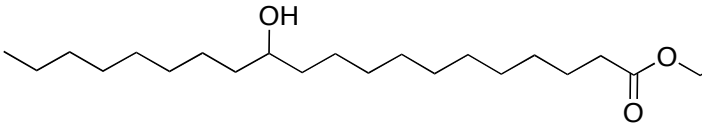
2. The key to solving this structure is first identifying the symmetric trisubstituted benzene ring from the C13 and the H1-NMR. The nitrile is more subtle, but (with the hint) and the IR it becomes clear that the Nitrogen and the remaining two IHD's are a nitrile.



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.