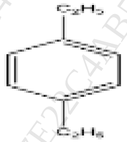
Duration: 3 hours **Marks: 75**

I. Do as directed 20M

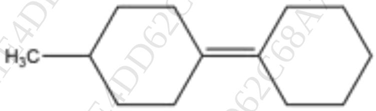
1. Name the fragmentation pathway for cyclic dienes that involves rearrangement
2. Draw structure of the ion responsible for the base peak of 1-propanamine at m/z=30 in the mass spectrum
3. Predict the number of signals in the ^{13}C NMR of-



4. Give an example of a molecule containing D_2O exchangeable proton/s
5. Calculate index of hydrogen deficiency for C_8H_7BrO
6. Predict the number of signals in ^1H NMR of isopropyl alcohol
7. Will the tropylium ion peak (m/z=91) be formed in the mass spectrum of toluene?
8. Explain why the M and M+2 peaks are equally intense in methyl bromide?
9. Give one application of GC AAS spectroscopy
10. Give any 2 points of difference between cation exchange and anion exchange chromatography
11. Which is the preferred method of ionization in LC-MS?
12. Enlist interfaces used in LC-MS
13. Give any 2 applications of ion-pair chromatography
14. How many peaks due to spin-spin coupling are expected for the signals of each of the protons a, b, c, d-

   $$\overset{a}{CH_3}\overset{b}{CH_2}O\overset{c}{CH_2}\overset{d}{CHCl_2}$$

15. Write any two differentiating points between 1D and 2D NMR spectroscopy
16. What is antistokes scattering with respect to Raman spectra?
17. Classify thermogravimetric methods of analysis
18. Enlist types of ELISA
19. What increment will you add to the parent value for the exocyclic double bond marked in the structure?



20. Predict the IR value of C≡C stretch in 1-butyne

II. **Long answer questions- (Answer <u>any two</u>)** **20M**

1.a. A compound with molecular weight 114 has the following spectral characteristics: **6M**

UV: λ_{max} -260 ϵ -19

IR – 1710, 1360 cm^{-1}

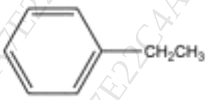
^1H NMR – δ 2.15 (s, 42sq), 2.74(s, 29sq)

Deduce structure and predict its ^{13}C NMR.

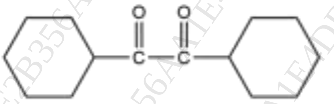
1.b. How will you distinguish between the following compounds using spectral techniques? **4M**

(i)

&



(ii)



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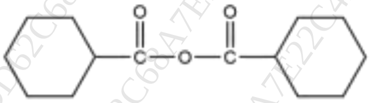


2.a. Elucidate the structure of compound with molecular formula $C_{10}H_{11}O_2Cl$ and the following spectral details – **6M**

IR - 1745, 1600, 1580cm^{-1}

^1H NMR – δ 2.00(s, 3H), 2.8(t,2H, J=6Hz), 4.1(t, 2H, J=6Hz), 7.1(d, 2H, J=8Hz), 7.3(2H, d, J=8Hz).

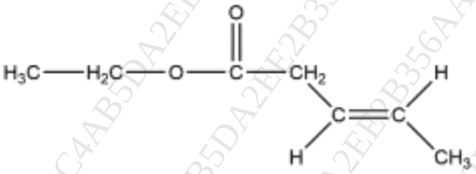
Deduce the structure and justify your answer.

2.b. A compound containing C, H and O shows presence of exchangeable proton in proton NMR spectroscopy and has the following mass spectrum- **4M**

m/e= 27, 31,41,43,56(base peak) and 74 (molecular ion).

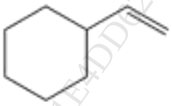
Give a reasonable structure for the molecule and depict how the molecular ion, base peak and peak of m/z-31 is formed

3. a. Predict the ^{13}C NMR and Mass spectra of- **6M**



3. b. Explain how you will distinguish between- **4M**

i.



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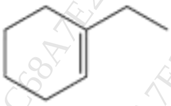
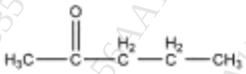
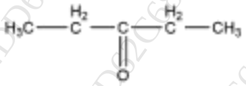


by Mass spectroscopy

ii.



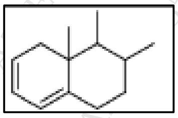
&

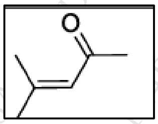


by IR spectroscopy

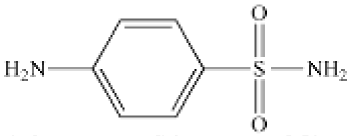
III. **Short answer questions- (Answer <u>any seven</u>)** **35M**

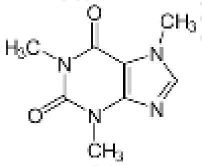
1. Predict the λ_{max} in the UV spectra of both the structures given below-





2. What is the difference berween 1D and 2 D NMR. Explain the term HETCOR
3. Predict IR values for major functional groups in the following structures





4. Explain the importance of GC-MS in brief and describe one interface
5. Explain the terms in brief- a) Base peak (b) % relative abundance
6. Elaborate on RIA technique
7. Explain the principle for flash chromatography. Give any one pharmaceutical application
8. Write principle and instrumentation for DSC
9. Explain ion exchange chromatography in brief

SPECTRAL CORRELATION TABLES

Chemical Shifts for Methylene Groups Attached to Two Functional Groups ($Y-CH_2-Z$)

GROUP	$-CH_3$	$-C=C$	$-C\equiv C$	$-Ph$	$-CF_2$	$-CF_3$	$-Cl$	$-Br$	$-I$	$-OH$	$-OR$	$-OPh$	$-OC(=O)R$	$-C(=O)R$	$-C(=O)Ph$	$-C(=O)OR$	$-C(=O)NR_2$	$-C\equiv N$	$-NR_2$	$-NHC(=O)R$	$-N_3$	$-SR$
$-CH_3$	1.17	1.90 2.02	2.14	2.55	1.91	1.84	3.37 3.23	3.43 3.03	3.20 2.52	3.70 3.26	3.40 3.06	3.93	4.25 3.83	2.47 2.40	2.54	2.25 2.25	2.25 2.29	[illegible] 2.40	2.63 2.27	2.97	2.67	2.63 2.34
$-C=C$		2.60 2.87	3.39 2.99	3.30 3.40	2.76	2.63	4.08	3.93 3.88	3.87 3.37	4.13	3.93 3.91	4.78	4.48	3.28	3.03	3.60 3.10	3.16	3.15 3.25	3.30 3.12	3.82	3.42	3.02 3.19
$-C\equiv C$			3.11	3.52	2.88	2.81	4.09 4.20	3.90 4.00	3.49	4.28	4.03	4.90	4.71 4.80	3.37	3.51	3.22	3.26	3.37	3.50 3.44	3.97	3.67	3.31
$-Ph$				3.87 3.93	3.29	3.50 3.32	4.50 4.61	4.33 4.41	3.90	4.58	4.70 4.44	4.91 5.31	5.08 5.21	3.35 3.78	3.92	3.40 3.63	3.66	3.65 3.78	3.48 3.65	4.34	4.04	3.42 3.72
$-CF_2$					2.63	2.58	3.97	3.76	3.26	4.01 4.01	3.80	4.47	4.57	3.12	3.28	2.99	3.03	3.42	3.01	3.71	3.41	3.08
$-CF_3$						2.51	3.90	3.70	3.36 3.19	3.93	4.73	4.80	4.34	3.07	3.11	2.97	2.96	3.07	2.94	3.64	3.34	3.01
$-Cl$							4.99 5.29	3.16 5.09	4.99 4.58	5.32	5.40 5.12	5.99	5.89	4.46	4.60	4.05 4.31	4.17 4.33	4.07 4.46	[illegible] 4.57	5.13	4.73	4.40
$-Br$								4.94 4.89	4.38	5.12	4.92	6.36 5.79	5.69	4.26	4.40 3.40	3.70 4.11	3.93 4.15	4.26	4.13	4.83	4.53	4.20
$-I$									3.90 3.87	4.61	4.41	5.16	5.06	3.75	3.89	3.60	3.65 3.64	3.65 3.75	3.62	4.32	4.02	3.69
$-OH$										4.55 4.35	[illegible]	[illegible]	3.92	4.48	4.43	4.34	4.38	4.49	4.35	5.04	4.78	[illegible]
$-OR$											[illegible] 4.95	[illegible]	5.72	4.29	4.43	4.13 4.22	4.18	4.30 4.27	4.15	4.94	4.64	4.33
$-OPh$												6.64	6.59	5.16	5.30	5.09	4.45 4.05	5.16	5.03	5.26	5.56	5.10
$-OC(=O)R$													6.46	4.42 5.10	5.20	4.91	4.95	5.10	4.92	5.63	5.37	5.00
$-C(=O)R$														3.60 3.63	3.77	3.37 3.48	3.52	3.63	3.50	4.10 4.20	3.90	3.57
$-C(=O)Ph$															3.91	3.62	3.66	3.77	3.64	4.34	4.02	3.71
$-C(=O)OR$																3.35 3.33	3.37	3.48	3.27 3.35	4.05	3.75	3.42
$-C(=O)NR_2$																	3.30 3.41	3.53	3.39	4.09	3.79	3.46
$-C\equiv N$																		3.53	3.50	4.20	3.90	3.57
$-NR_2$																			3.10 3.27	4.07	3.77	3.44
$-NHC(=O)R$																				4.75	4.45	4.14
$-N_3$																					4.15	3.84
$-SR$																						3.51

TURN OVER

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

Group		Range μ	Intensity	Range cm^{-1}
A. Hydrocarbon chromophore				
1. C—H STRETCHING				
a. Alkane		3.38–3.51	(m–s)	2962–2853
b. Alkene, monosubstituted (vinyl)		3.29–3.32	(m)	3040–3010
	and	3.23–3.25	(m)	3095–3075
Alkene, disubstituted, cis		3.29–3.32	(m)	3040–3010
Alkene, disubstituted, trans		3.29–3.32	(m)	3040–3010
Alkene, disubstituted, gem		3.23–3.25	(m)	3095–3075
Alkene, trisubstituted		3.29–3.32	(m)	3040–3010
c. Alkyne		~3.03	(s)	~3300
d. Aromatic		~3.30	(v)	~~~3030~~ 2900 3050
2. C—H BENDING				
a. Alkane, C—H		~7.46	(w)	~1340
Alkane, —CH₂—		6.74–6.92	(m)	1485–1445
Alkane, —CH₃		6.80–7.00	(m)	1470–1430
	and	7.25–7.30	(s)	1380–1370
Alkane, gem-dimethyl		7.22–7.25	(s)	1385–1380
	and	7.30–7.33	(s)	1370–1365
Alkane, tert-butyl		7.17–7.22	(m)	1395–1385
	and	~7.33	(s)	~1365
b. Alkene, monosubstituted (vinyl)		10.05–10.15	(s)	995–985
		10.93–11.05	(s)	915–905
	and	7.04–7.09	(s)	1420–1410
Alkene, disubstituted, cis		~14.5	(s)	~690
Alkene, disubstituted, trans		10.31–10.42	(s)	970–960
	and	7.64–7.72	(m)	1310–1295
Alkene, disubstituted, gem		11.17–11.30	(s)	895–885
	and	7.04–7.09	(s)	1420–1410
Alkene, trisubstituted		11.90–12.66	(s)	840–790
c. Alkyne		~15.9	(s)	~630
d. Aromatic, substitution type:‡				
five adjacent hydrogen atoms		~13.3	(v, s)	~750
	and	~14.3	(v, s)	~700
four adjacent hydrogen atoms		~13.3	(v, s)	~750
three adjacent hydrogen atoms		~12.8	(v, m)	~780
two adjacent hydrogen atoms		~12.0	(v, m)	~830
one hydrogen atom		~11.3	(v, w)	~880
3. C=C MULTIPLE BOND STRETCHING				
a. Alkene, nonconjugated		5.95–6.17	(v)	1680–1620
Alkene, monosubstituted (vinyl)		~6.08	(m)	~1645
Alkene, disubstituted, cis		~6.03	(m)	~1658
Alkene, disubstituted, trans		~5.97	(m)	~1675

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

‡ Substituted benzenes also show weak bands in the region 5.0–6.0 μ (2000–1670 cm^{-1}) which are characteristic of the substitution type. See Fig. 3-30.

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

Group		Range μ	Intensity	Range cm^{-1}
Alkene, disubstituted, gem		~6.05	(m)	~1653
Alkene, trisubstituted		~5.99	(m)	~1669
Alkene, tetrasubstituted		~5.99	(w)	~1669
Diene		~6.06	(w)	~1650
	and	~6.25	(w)	~1600
b. Alkyne, monosubstituted		4.67–4.76	(m)	2140–2100
Alkyne, disubstituted		4.42–4.57	(v, w)	2260–2190
c. Allene		~5.1	(m)	~1960
	and	~9.4	(m)	~1060
d. Aromatic		~6.25	(v)	~1600
		~6.33	(v)	~1580
		~6.67	(m)	~1500
	and	~6.90	(m)	~1450
B. Carbonyl chromophore				
1. KETONE STRETCHING VIBRATIONS				
a. Saturated, acyclic		5.80–5.87	(s)	1725–1705
b. Saturated, cyclic				
6-membered ring (and higher)		5.80–5.87	(s)	1725–1705
5-membered ring		5.71–5.75	(s)	1750–1740
4-membered ring		~~~5.63~~	(s)	~1775
c. α,β-Unsaturated, acyclic		5.94–6.01	(s)	1685–1665
d. α,β-Unsaturated, cyclic				
6-membered ring (and higher)		5.94–6.01	(s)	1685–1665
5-membered ring		5.80–5.85	(s)	1725–1708
e. α,β,α′,β′-Unsaturated, acyclic		5.99–6.01	(s)	1670–1663
f. Aryl		5.88–5.95	(s)	1700–1680
g. Diaryl		5.99–6.02	(s)	1670–1660
h. α-Diketones		~~5.78–5.85~~	(s)	1730–1710
i. β-Diketones (enolic)		6.10–6.50	(s)	1640–1540
j. 1,4-Quinones		5.92–6.02	(s)	1690–1660
k. Ketenes		~4.65	(s)	~2150
2. ALDEHYDES				
a. Carbonyl stretching vibrations				
Saturated, aliphatic		5.75–5.81	(s)	1740–1720
α,β-Unsaturated, aliphatic		5.87–5.95	(s)	1705–1680
α,β,γ,δ-Unsaturated, aliphatic		5.95–6.02	(s)	1680–1660
Aryl		5.83–5.90	(s)	1715–1695
b. C—H Stretching vibrations, two bands		3.45–3.55	(w)	2900–2820
	and	3.60–3.70	(w)	2775–2700
3. ESTER STRETCHING VIBRATIONS				
a. Saturated, acyclic		5.71–5.76	(s)	1750–1735
b. Saturated, cyclic				
δ-Lactones (and larger rings)		5.71–5.76	(s)	1750–1735
γ-Lactones		5.62–5.68	(s)	1780–1760
β-Lactones		~5.50	(s)	~1820

Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

TURN OVER

[CH]ARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

Group	Range μ	Intensity	Range cm⁻¹
c. Unsaturated:			
vinyl ester type	5.56–5.65	(s)	1800–1770
α,β-unsaturated and aryl	5.78–5.82	(s)	1730–1717
α,β-unsaturated δ-lactone	5.78–5.82	(s)	1730–1717
α,β-unsaturated γ-lactone	5.68–5.75	(s)	1760–1740
β,γ-unsaturated γ-lactone	~5.56	(s)	~1800
d. α-Ketoesters	5.70–5.75	(s)	1755–1740
e. β-Ketoesters (enolic)	~6.06	(s)	~1650
f. Carbonates	5.62–5.75	(s)	1780–1740
4. CARBOXYLIC ACIDS			
a. Carbonyl stretching vibrations:			
saturated aliphatic	5.80–5.88	(s)	1725–1700
α,β-unsaturated aliphatic	5.83–5.92	(s)	1715–1690
aryl	5.88–5.95	(s)	1700–1680
b. Hydroxyl stretching (bonded), several bands	3.70–4.00	(w)	2700–2500
c. Carboxylate anion stretching	6.21–6.45	(s)	1610–1550
	and 7.15–7.69	(s)	1400–1300
5. ANHYDRIDE STRETCHING VIBRATIONS			
a. Saturated, acyclic	5.41–5.56	(s)	1850–1800
	and 5.59–5.75	(s)	1790–1740
b. α,β-Unsaturated and aryl, acyclic	5.47–5.62	(s)	1830–1780
	and 5.65–5.81	(s)	1770–1720
c. Saturated, 5-membered ring	5.35–5.49	(s)	1870–1820
	and 5.56–5.71	(s)	1800–1750
d. α,β-Unsaturated, 5-membered ring	5.41–5.56	(s)	1850–1800
	and 5.47–5.62	(s)	1830–1780
6. ACYL HALIDE STRETCHING VIBRATIONS			
a. Acyl fluorides	~5.41	(s)	~1850
b. Acyl chlorides	~5.57	(s)	~1795
c. Acyl bromides	~5.53	(s)	~1810
d. α,β-Unsaturated and aryl	5.61–5.72	(s)	1780–1750
	and 5.72–5.82	(m)	1750–1720
e. COF₂	5.19	(s)	1928
f. COCl₂	5.47	(s)	~1828
g. COBr₂	5.47	(s)	1828
7. AMIDES			
a. Carbonyl stretching vibrations			
Primary, solid and concentrated solution	~6.06	(s)	~1650
Primary, dilute solution	~5.92	(s)	~1690
Secondary, solid and concentrated solution	5.95–6.14	(s)	1680–1630
Secondary, dilute solution	5.88–5.99	(s)	1700–1670
Tertiary, solid and all solutions	5.99–6.14	(s)	1670–1630
Cyclic, δ-lactams, dilute solution	~5.95	(s)	~1680
Cyclic, γ-lactams, dilute solution	~5.88	(s)	~1700

TURN OVER

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

Group	Range μ	Intensity	Range cm⁻¹
Cyclic, γ-lactams, fused to another ring, dilute solution	5.71–5.88	(s)	1750–1700
Cyclic, β-lactams, dilute solution	5.68–5.78	(s)	1760–1730
Cyclic, β-lactams, fused to another ring, dilute solution	5.62–5.65	(s)	1780–1770
Ureas, acyclic	~6.02	(s)	~1660
Ureas, cyclic, 6-membered ring	~6.10	(s)	~1640
Ureas, cyclic, 5-membered ring	~5.81	(s)	~1720
Urethanes	5.75–5.92	(s)	1740–1690
Imides, acyclic	~5.85	(s)	~1710
	and ~5.88	(s)	~1700
Imides, cyclic, 6-membered ring	~5.85	(s)	~1710
	and ~5.88	(s)	~1700
Imides, cyclic, α,β-unsaturated, 6-membered ring	~5.78	(s)	~1730
	and ~5.99	(s)	~1670
Imides, cyclic, 5-membered ring	~5.65	(s)	~1770
	and ~5.88	(s)	~1700
Imides, cyclic, α,β-unsaturated, 5-membered ring	~5.59	(s)	~1790
	and ~5.85	(s)	~1710
b. N—H Stretching vibrations			
Primary, free; two bands	~2.86	(m)	~3500
	and ~2.94	(m)	~3400
Primary, bonded; two bands	~2.99	(m)	~3350
	and ~3.15	(m)	~3180
Secondary, free; one band	~2.92	(m)	~3430
Secondary, bonded; one band	3.0–3.2	(m)	3320–3140
c. N—H Bending vibrations			
Primary amides, dilute solution	6.17–6.29	(s)	1620–1590
Secondary amides, dilute solution	6.45–6.62	(s)	1550–1510
C. Miscellaneous chromophoric groups			
1. ALCOHOLS AND PHENOLS			
a. O—H Stretching vibrations			
Free O—H	2.74–2.79	(v, sh)	3650–3590
Intermolecularly hydrogen bonded (change on dilution)			
single bridge compounds	2.82–2.90	(v, sh)	3550–3450
polymeric association	2.94–3.13	(s, b)	3400–3200
Intramolecularly hydrogen bonded (no change on dilution)			
single bridge compounds	2.80–2.90	(v, sh)	3570–3450
chelate compounds	3.1–4.0	(w, b)	3200–2500

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately

ARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

5

Group		Range, μ	Intensity	Range, cm^{-1}
b. O—H Bending and C—O stretching vibrations				
Primary alcohols		~9.5	(s)	~1050
	and	7.4–7.9	(s)	1350–1260
Secondary alcohols		~9.1	(s)	~1100
	and	7.4–7.9	(s)	1350–1260
Tertiary alcohols		~8.7	(s)	~1150
	and	7.1–7.6	(s)	1410–1310
Phenols		~8.3	(s)	~1200
	and	7.1–7.6	(s)	1410–1310
2. AMINES				
a. N—H Stretching vibrations				
Primary, free; two bands		~2.86	(m)	~3500
	and	~2.94	(m)	~3400
Secondary, free; one band		2.86–3.02	(m)	3500–3310
Imines (=N—H); one band		2.94–3.03	(m)	3400–3300
Amine salts		3.2–3.3	(m)	3130–3030
b. N—H Bending vibrations				
Primary		6.06–6.29	(s-m)	1650–1590
Secondary		6.06–6.45	(w)	1650–1550
Amine salts		6.25–6.35	(s)	1600–1575
	and	~6.67	(s)	~1500
c. C—N Vibrations				
Aromatic, primary		7.46–8.00	(s)	1340–1250
Aromatic, secondary		7.41–7.81	(s)	1350–1280
Aromatic, tertiary		7.36–7.64	(s)	1360–1310
Aliphatic		8.2–9.8	(w)	1220–1020
	and	~7.1	(w)	~1410
3. UNSATURATED NITROGEN COMPOUNDS				
a. C≡N Stretching vibrations				
Alkyl nitriles		4.42–4.46	(m)	2260–2240
α,β-Unsaturated alkyl nitriles		4.47–4.51	(m)	2235–2215
Aryl nitriles		4.46–4.50	(m)	2240–2220
Isocyanates		4.40–4.46	(m)	2275–2240
Isocyanides		4.50–4.83	(m)	2220–2070
b. C=N— Stretching vibrations (imines, oximes)				
Alkyl compounds		5.92–6.10	(v)	1690–1640
α,β-Unsaturated compounds		6.02–6.14	(v)	1660–1630
c. —N=N— Stretching vibrations, azo compounds		6.14–6.35	(v)	1630–1575
d. —N=C=N— Stretching vibrations, diimides		4.64–4.70	(s)	2155–2130
e. —N₃ Stretching vibrations, azides		4.63–4.72	(s)	2160–2120
	and	7.46–8.48	(w)	1340–1180

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

6

Group		Range, μ	Intensity	Range, cm^{-1}
f. C—NO₂, Nitro compounds:				
aromatic		6.37–6.67	(s)	1570–1500
	and	7.30–7.70	(s)	1370–1300
aliphatic		6.37–6.45	(s)	1570–1550
	and	7.25–7.30	(s)	1380–1370
g. O—NO₂, Nitrates		6.06–6.25	(s)	1650–1600
	and	7.70–8.00	(s)	1300–1250
h. C—NO, Nitroso compounds		6.25–6.67	(s)	1600–1500
i. O—NO, Nitrites		5.95–6.06	(s)	1680–1650
	and	6.15–6.21	(s)	1625–1610
4. HALOGEN COMPOUNDS, C—X STRETCHING VIBRATIONS				
a. C—F		7.1–10.0	(s)	1400–1000
b. C—Cl		12.5–16.5	(s)	800–600
c. C—Br		16.6–20.0	(s)	600–500
d. C—I		~20	(s)	~500
5. SULFUR COMPOUNDS				
a. S—H Stretching vibrations		3.85–3.92	(w)	2600–2550
b. C=S Stretching vibrations		8.33–9.52	(s)	1200–1050
c. S=O Stretching vibrations:				
sulfoxides		9.35–9.71	(s)	1070–1030
sulfones		8.62–8.77	(s)	1160–1140
	and	7.41–7.69	(s)	1350–1300
sulfites		8.13–8.70	(s)	1230–1150
	and	7.00–7.41	(s)	1430–1350
sulfonyl chlorides		8.44–8.59	(s)	1185–1165
	and	7.30–7.46	(s)	1370–1340
sulfonamides		8.48–8.77	(s)	1180–1140
	and	7.41–7.69	(s)	1350–1300
sulfonic acids		8.27–8.70	(s)	1210–1150
		9.43–9.71	(s)	1060–1030
	and	~15.4	(s)	~650

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† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp.
~ = approximately

TURN OVER

Proton Chemical Shifts (Values are given on the officially approved δ scale; τ = 10.00 − δ.)

Substituent Group	Methyl Protons	Methylene Protons	Methine Proton
HC—C—CH$_3$	0.95	1.20	1.55
HC—C—NR$_2$	1.05	1.45	1.70
HC—C—C=C	1.00	1.35	1.70
HC—C—C=O	1.05	1.55	1.95
HC—C—NRAr	1.10	1.50	1.80
HC—C—NH(C=O)R	1.10	1.50	1.90
HC—C—(C=O)NR$_2$	1.10	1.50	1.80
HC—C—(C=O)Ar	1.15	1.55	1.90
HC—C—(C=O)OR	1.15	1.70	1.90
HC—C—Ar	1.15	1.55	1.80
HC—C—OH (and OR)	1.20	1.50	1.75
HC—C—C≡CR	1.20	1.50	1.80
HC—C—C≡N	1.25	1.65	2.00
HC—C—SR	1.25	1.60	1.90
HC—C—OAr	1.30	1.55	2.00
HC—C—O(C=O)R	1.30	1.60	1.80
HC—C—SH	1.30	1.60	1.65
HC—C—(S=O)R and —SO$_2$R	1.35	1.70	
HC—C—NR$_3^+$	1.40	1.75	2.05
HC—C—O(C=O)CF$_3$	1.40	1.65	
HC—C—Cl	1.55	1.80	1.95
HC—C—O(C=O)Ar	1.65	1.75	1.85
HC—C—Br	1.80	1.85	1.90
HC—CH$_3$	0.90	1.30	1.50
HC—C=C	1.60	2.05	
HC—C≡C	1.70	2.20	2.80
HC—(C=O)OR (and NR$_2$)	2.00	2.25	2.50
HC—SR	2.05	2.55	3.00
HC—O—O	2.10	2.30	2.55
HC—(C=O)R	2.10	2.35	2.65
HC—C≡N	2.15	2.45	2.90
HC—CHO	2.20	2.40	
HC—Ar (and NR$_2$)	2.25	2.45	2.85
HC—SSR	2.35	2.70	
HC—(C=O)Ar	2.40	2.70	3.40
HC—SAr	2.40		
HC—NRAr	2.60	3.10	3.60
HC—SO$_2$R and —(SO)R	2.60	3.05	
HC—Br	2.70	3.40	4.10
HC—NR$_3^+$	2.95	3.10	3.60
HC—NH(C=O)R	2.95	3.35	3.85
HC—Cl	3.05	3.45	4.05
HC—OH and —OR	3.20	3.40	3.60
HC—NH$_2$	3.50	3.75	4.05
HC—O(C=O)R	3.65	4.10	4.95
HC—OAr	3.80	4.00	4.60
HC—O(C=O)Ar	3.80	4.20	5.05

TURN OVER

Substituent Group	Methyl Protons	Methylene Protons	Methine Proton
HC—F	4.25	4.50	4.80
HC—NO$_2$	4.30	4.35	4.60
Cyclopropane		0.20	0.40
Cyclobutane		2.45	
Cyclopentane		1.65	
Cyclohexane		1.50	1.80
Cycloheptane		1.25	

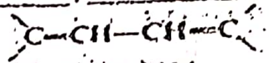
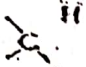
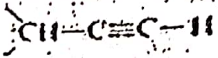
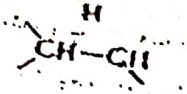
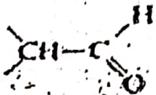
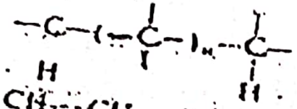
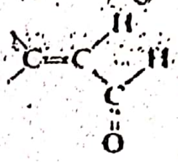
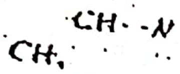
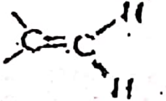
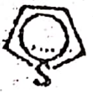
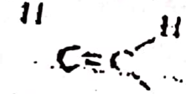
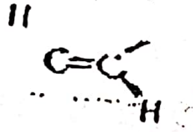
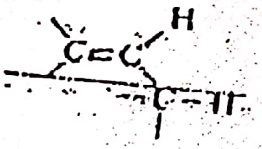
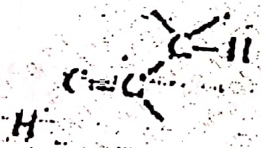
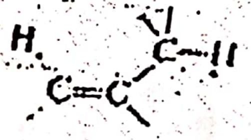
Substituent Group	Proton Shift	Substituent Group	Proton Shift
HC≡CH	2.35	HO—C=O	10–12
HC≡CAr	2.90	HO—SO$_2$	11–12
HC≡C—C=C	2.75	HO—Ar	4.5–6.5
HAr	7.20	HO—R	0.5–4.5
HCO—O	8.1	HS—Ar	2.8–3.6
HCO—R	9.4–10.0	HS—R	1–2
HCO—Ar	9.7–10.5	HN—Ar	3–6
HO—N=C(oxime)	9–12	HN—R	0.5–5

^{13}C Chemical Shifts (Values given on the δ scale, relative to TMS.)

Substituent Group	Primary Carbon	Secondary Carbon	Tertiary Carbon	Quaternary Carbon
Alkenes				
C—C≡	−20 to 30	25 to 45	30 to 60	35 to 70
C—O	40 to 60	40 to 70	60 to 75	70 to 85
C—N	20 to 45	40 to 60	50 to 70	65 to 75
C—S	10 to 30	25 to 45	40 to 55	55 to 70
C—Halide	−37 to 35 (I) (Cl)	−10 to 45 (I) (Cl)	30 to 65 (I) (Cl)	35 to 75 (I) (Cl)

Alkynes	70 to 100	Isocyanides	130 to 150
Alkenes	110 to 150	Carbonates	150 to 160
Aromatics	110 to 135	Oximes	155 to 165
C-substituted	125 to 145	Ureas	150 to 170
Heteroaromatics	115 to 140	Thioureas	165 to 185
C-α	135 to 155	Esters, Anhydrides	150 to 175
Cyanates	105 to 120	Amides	160 to 180
Isocyanates	115 to 135	Acids, Acyl chlorides	160 to 185
Thiocyanates	110 to 120	Aldehydes	175 to 205
Isothiocyanates	120 to 140	Ketones	175 to 225
Cyanides	110 to 130		

SPIN-SPIN COUPLING CONSTANTS

Type	J, cps	Type	J, cps
H_2	280		9–13
CH_4	12.4	H—C≡C—H	9.1
	12–15		2–3
	2–9		1–3
	~0		6–8
CH_3—CH_2—X	6.5–7.5		o- 6–9 m- 1–3 p- 0–1
	5.5–7.0		αβ 1.6–2.0 αβ' 0.6–1.0 αα' 1.3–1.8 ββ' 3.2–3.8
	a,a 5–10 a,e 2–4 e,e 2–4		αβ 2.0–2.6 αβ' 1.5–2.2 αα' 1.8–2.3 ββ' 2.8–4.0
	0.5–3		αβ 4.6–5.8 αβ' 1.0–1.8 αα' 2.1–3.3 ββ' 3.0–4.2
	7–12		αβ 4.9–5.7 αγ 1.6–2.6 αβ' 0.7–1.1 αα' 0.2–0.5 βγ 7.2–8.5 ββ' 1.4–1.9
	13–18		
	4–10		
	allyl 0.5–2.5		
	~0		

TURN OVER

Conjugated dienes & Trienes, Solvent: Ethanol

Parent value for Butadiene system or acyclic conjugated diene	217 nm
Acyclic triene	245 nm
Homoannular conjugated diene	253 nm
Hetroannular conjugated diene	215 nm
Increment for each substituents	
Alkyl substituents or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Auxochrome	
-OR	+6 nm
-SR	+30 nm
-Cl, -Br	+5 nm
NR_2	+60 nm
$-OCOCH_3$	0

Woodward Fieser rules for αβ-unsaturated carbonyl compounds:-

a) Parent values	
αβ-unsaturated acyclic or six membered ketone	215 nm
αβ-unsaturated five membered ring ketone	202 nm
αβ-unsaturated aldehyde	207 nm
b) Increments	
i) Each alkyl substituents or ring residue	
At α position	10 nm
At β position	12 nm
At gamma and higher position	18 nm
ii) Each exocyclic double bond	5 nm
iii) Double bond extending conjugation	30 nm
iv) Homoannular conjugated diene	39 nm

Auxochromes	Positions		
	α	β	gamma
-OH	35	30	50
-OR	35	30	17
-SR	-	85	-
$-OCOCH_3$	6	6	6
-Cl	15	12	-
-Br	25	30	-
$-NR_2$	-	95	-