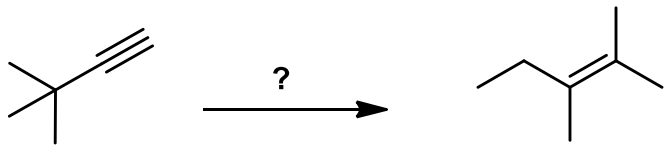
27.



A. i. H_2 / Lindlar's catalyst, ii. CH_3CO_3H, iii. CH_3MgBr, iv. H_3O^+

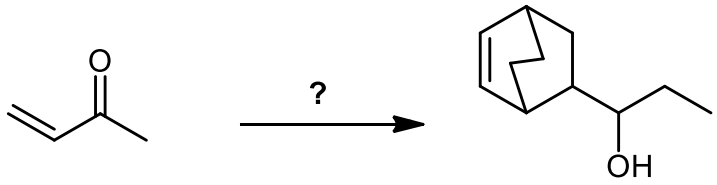
B. i. O_3, ii. H_2O, iii. CH_3CH_2MgBr, iv. H_3O^+

C. i. H_2 / Lindlar's cat. ii. BH_3, then aq. H_2O_2 / NaOH iii. PCC iv. MeMgBr then H^+ workup

D. i. $HgSO_4$, aq. H_2SO_4, ii. CH_3MgBr, iii. H_3O^+

E. i. BH_3, then aq. H_2O_2 / NaOH ii. $H_2C{=}P(Ph)_3$ iii. H^+, heat

28.



A. i. 1,3-cyclohexadiene, heat ii. MeMgBr iii. H_3O^+ iv. $LiAlH_4$ then H_2O

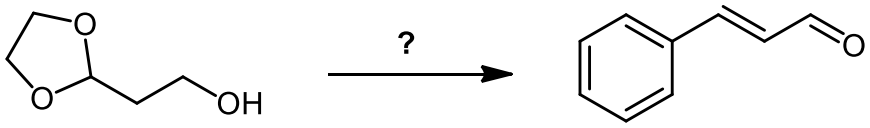
B. i. 1,3-cyclohexadiene, heat ii. $NaBH_4$, EtOH iii. PDC iv. MeMgBr v. H_3O^+

C. i. $NaBH_4$ ii. Na, CH_3I iii. 1,3-cyclohexadiene, heat

D. i. MeMgBr ii. H_3O^+ iii. cyclohexene, heat iv. PCC

E. i. LDA ii. Me-Br iii. 1,3-cyclohexadiene, heat iv. $NaBH_4$

29.



A. i. PCC ii. PhLi iii. H_3O^+, heat

B. i. aq. H_2SO_4 ii. PDC iii. PhMgBr iv. H_3O^+

C. i. $LiAlH_4$ ii. H_2O iii. Na, PhBr iv. H_3O^+

D. i. PhMgBr ii. H_3O^+ iii. PCC iv. $HgSO_4$, H_2SO_4, H_2O

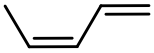
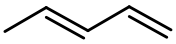
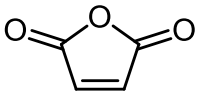
E. i. PDC ii. PhMgBr iii. H_3O^+ iv. $NaBH_4$

10% PART 5: EXPLANATION OF PHENOMENA

ANSWER ALL FIVE (5) OF THE QUESTIONS 30-34.

Choose the single explanation that best rationalises the phenomenon indicated.

30. The two pentadienes shown below are geometric (E/Z) isomers. One of them undergoes reaction with the anhydride shown significantly faster than the other. Which isomer is more reactive and why ?

X   **Y**  anhydride

A. **X** because it is the less stable isomer

B. **X** because steric effects destabilise its s-cis conformation

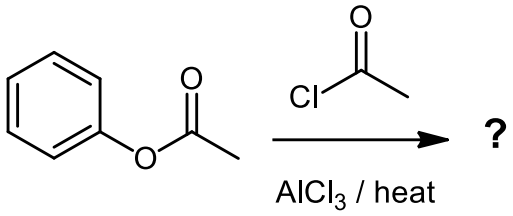
C. **X** because it has a more stable s-cis conformation

D. **Y** because it is the less stable isomer

E. **Y** because steric effects destabilise its s-cis conformation

AB. **Y** because it has a more stable s-cis conformation

31. When the aromatic ester is reacted as shown (right), which of the following best describes the major product and why it is formed ?



A. *para* because the ester group is electron donating directing *ortho/para*

B. *meta* because the ester group is electron donating directing *meta*

C. *para* because the ester group is electron withdrawing directing *ortho/para*

D. *meta* because the ester group is electron withdrawing directing *meta*

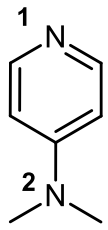
E. *meta* because the acyl group is electron withdrawing directing *meta*

AB. *no reaction* because the ester group is too deactivating for the Friedel-Crafts to work

32. What is the product of the reaction of butanoic acid with CH_3ONa / CH_3OH followed by work-up with aqueous acid ?

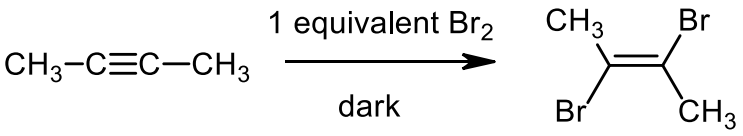
A. methyl butanoate because the carboxylic acid undergoes nucleophilic addition
B. methyl butanoate because the carboxylic acid undergoes nucleophilic acyl substitution
C. butyl methanoate because the carboxylic acid undergoes nucleophilic addition
D. butyl methanoate because the carboxylic acid undergoes nucleophilic acyl substitution
E. butanoic acid because the initial reaction forms a carboxylate that reprotonates
AB. pentan-2-one because the carboxylic acid undergoes nucleophilic acyl substitution

33. Dimethylaminopyridine has two basic nitrogen atoms labeled as **1** and **2** (shown below). Which N atom is more basic and why ?



A. N1 because the N1 lone pair is in an sp^2 hybrid orbital
B. N1 because the N1 lone pair is in a p orbital
C. N1 because its conjugate acid is resonance stabilised
D. N2 because the N2 lone pair is in an sp^3 hybrid orbital
E. N2 because its conjugate acid is resonance stabilised
AB. N2 because the N2 lone pair is in a p orbital

34. (E)-2,3-dibromobut-2-ene is the major product in the following reaction because:



A. *Trans* double bonds are generally more stable than *cis*
B. The stepwise reaction involves a vinyl cation
C. The stepwise reaction involves a cyclic bromonium ion
D. The stepwise reaction involves a vinyl radical
E. The two bromine atoms add in a concerted manner
AB. The reaction occurs in accord with Markovnikov's rule

10% PART 6: SYNTHESIS

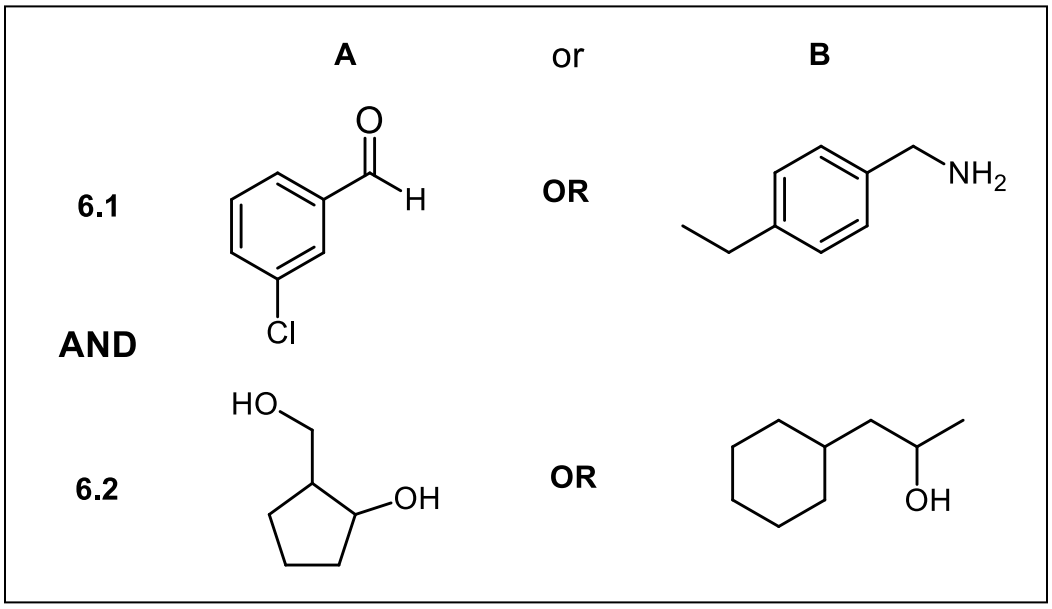
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED.

ANSWER TWO (2) QUESTIONS, ONE FROM EACH OF PART 6.1 AND PART 6.2

Design an efficient synthesis of TWO (2) of the following target molecules

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENT REQUIRED AND PRODUCT OF EACH STEP

DO NOT SHOW MECHANISMS (*i.e.* curly arrows are NOT required)



Permitted Materials and Reagents

NOTE: any materials that contribute carbon atoms to the target molecule must come from this allowed list:

- any organic compounds with no more than **FOUR** carbons
- benzene
- cyclohexene
- you can use any solvents or other reagents for the reactions provided that they do not contribute carbon atoms to the target.

10% PART 7: MECHANISM

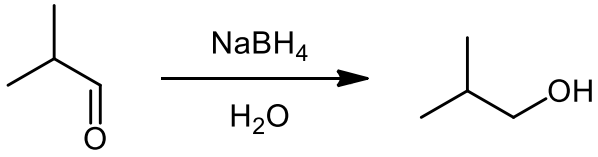
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED

ANSWER TWO (2) QUESTIONS, ONE FROM EACH OF PART 7.1 AND PART 7.2

Draw curly arrow mechanisms to explain the following reactions / observations. No other reagents are required.

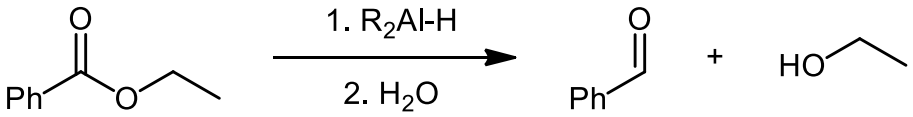
7.1. Draw the curly arrow mechanism for **one** of the following reactions:

A



OR

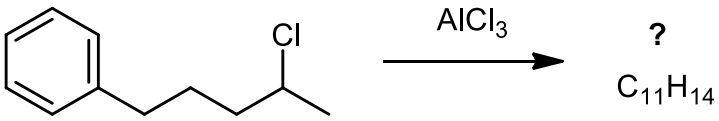
B



AND

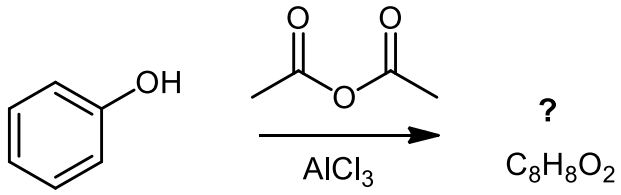
7.2. Predict the product and provide the curly arrow mechanism for **one** of the following reactions:

A



OR

B



13% PART 8: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE APPROPRIATE BOXES ON THE WRITTEN ANSWER SHEET PROVIDED

Use the information in the following paragraph to answer the questions below.

An unknown compound **A** was heated with **B** (C_4H_7OCl) and $AlCl_3$ to give compound **C** as the major product (IR : approx. 1685 cm^{-1}).

When **C** was then reacted with CH_3CO_3H, two isomeric products were isolated in about 2:1 ratio where **D** was the major isomer.

When **D** was subsequently reacted with $LiAlH_4$ / THF followed by an aqueous acid work up, extraction with Et_2O and then removal of the volatile components on a rotary evaporator, the major product obtained was **E** (mass spec : M+ = 122, 13C NMR / ppm = 6 peaks total with 4 peaks 140-125 range, and 65, 21. IR : broad 3370 cm^{-1}). When **E** was heated with acidic aq. $KMnO_4$ it gave **F** ($C_8H_6O_4$, H-NMR / ppm = 12.0 (1H broad singlet, D_2O exchangeable); 8.1 (2H singlet)) as the major product.

(**12**%) Identify the compounds **A** to **F** (drawn structures are sufficient).

(**1**%) Give the IUPAC name for **B**.

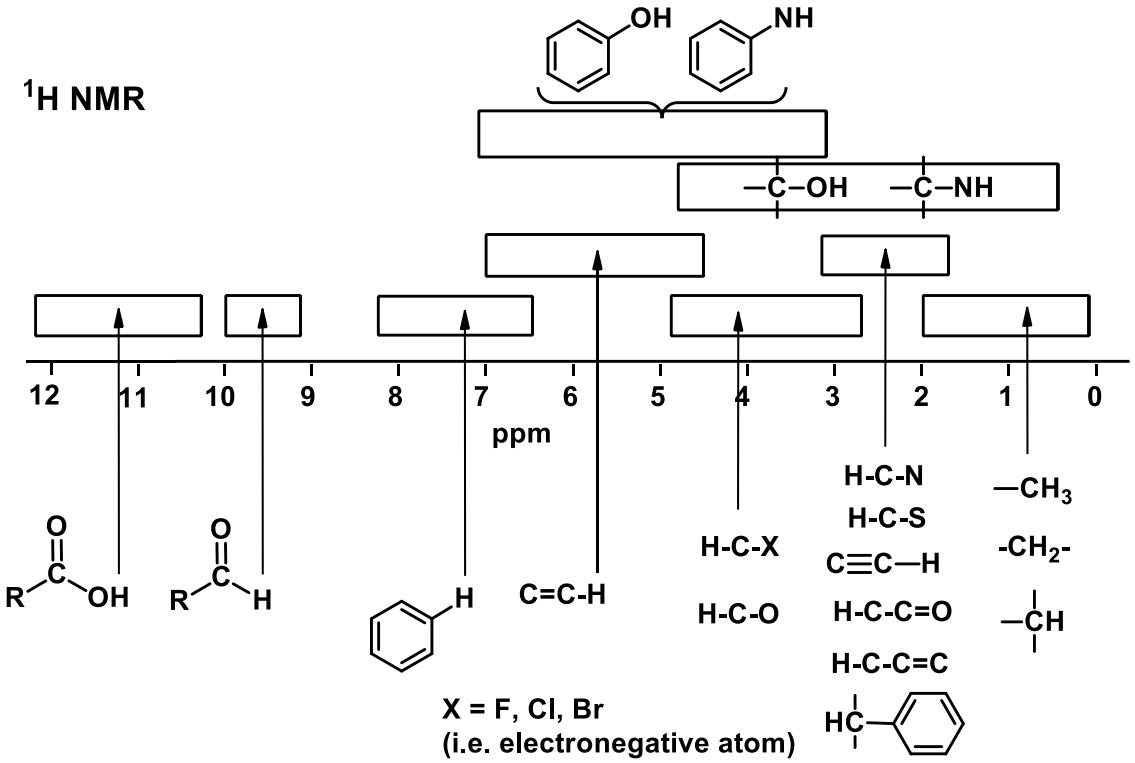
*****THE END*****

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

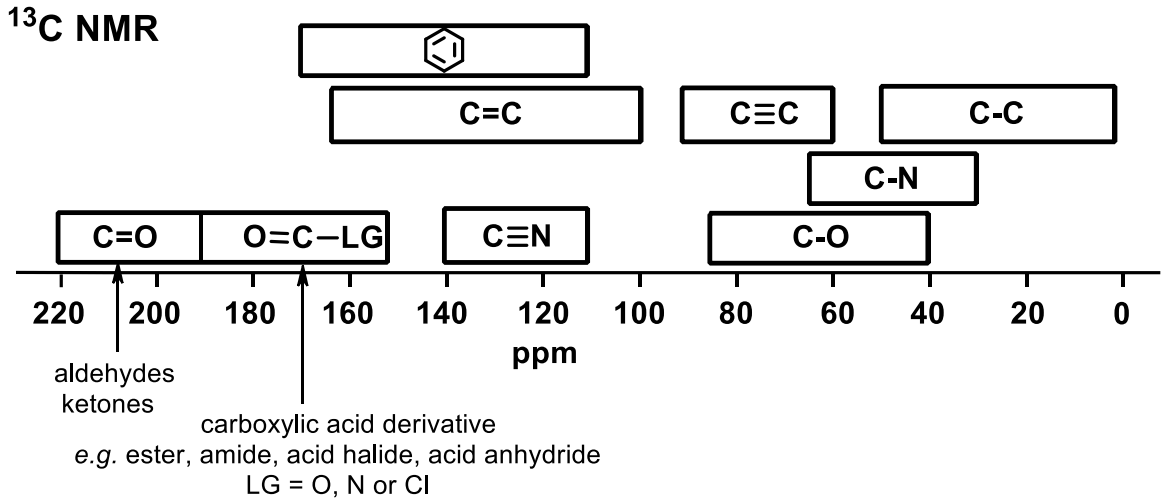
SPECTROSCOPIC TABLES



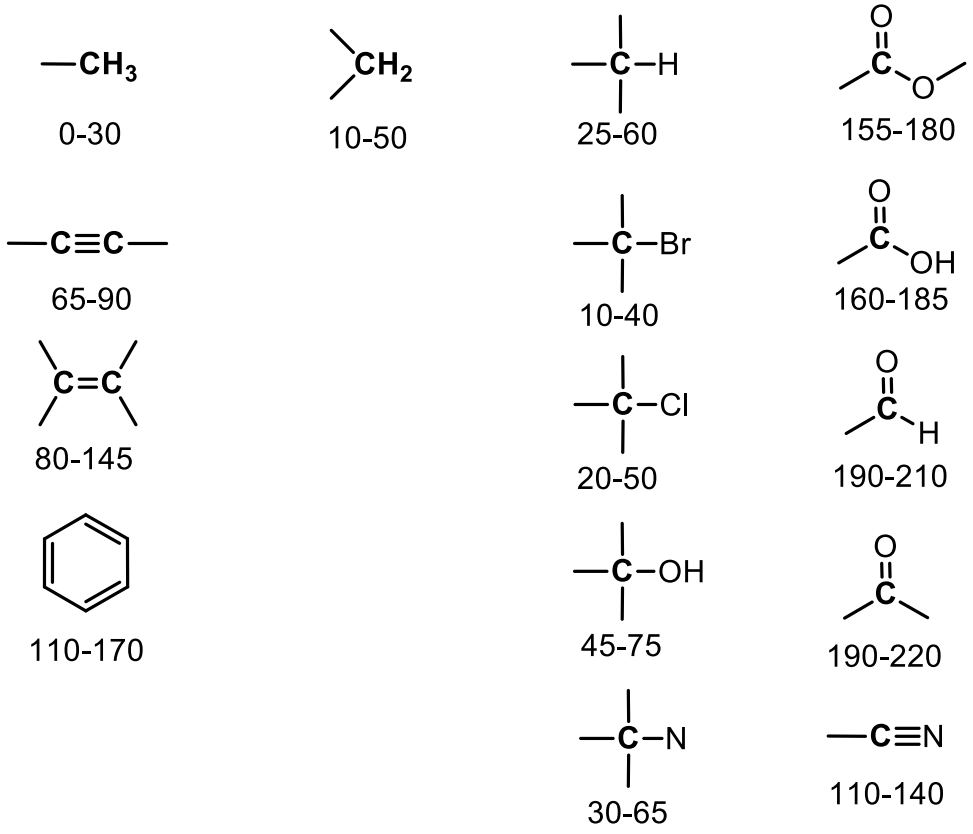
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

R = methyl	methylene	methyne
—CH_3	-CH_2-	—CH
0.9	1.4	1.5
1.6	2.3	2.6
2.1	2.4	2.5
2.2	2.5	2.9
2.3	2.7	3.0
2.7	3.3	4.1
3.1	3.4	4.1
3.3	3.4	3.7

other	
sp^3C-**OH**	1-5
sp^3C-**NH**	1-3
C≡CH	2.5
	4.5-6.5
	6.5-8
	9-10
	9-12



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	$-CH_3$	(bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids run as a nujol mull can be difficult to see as they may be very broad.

SCRAP PAPER

SCRAP PAPER

SCRAP PAPER