

Chemistry 3371: Organic Chemistry

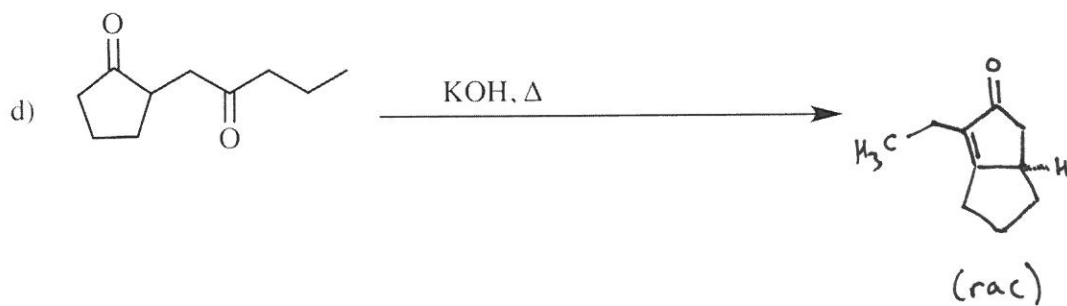
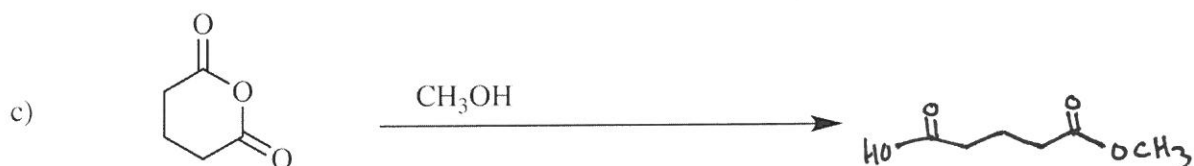
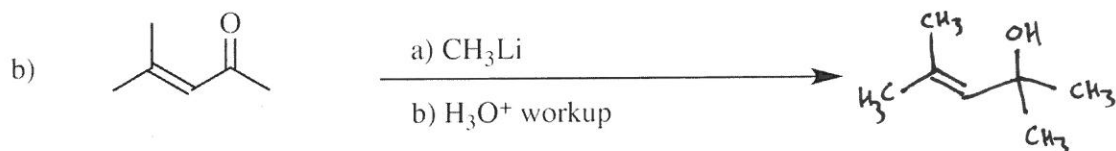
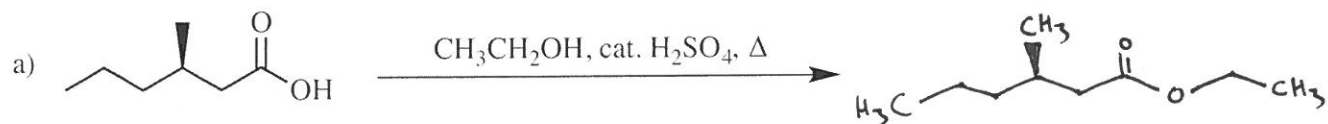
Instructor: Hubert Yin/TA: Adam Csakai

Tuesday: Apr. 12 @ 7:00 - 9:00 PM /3rd Exam

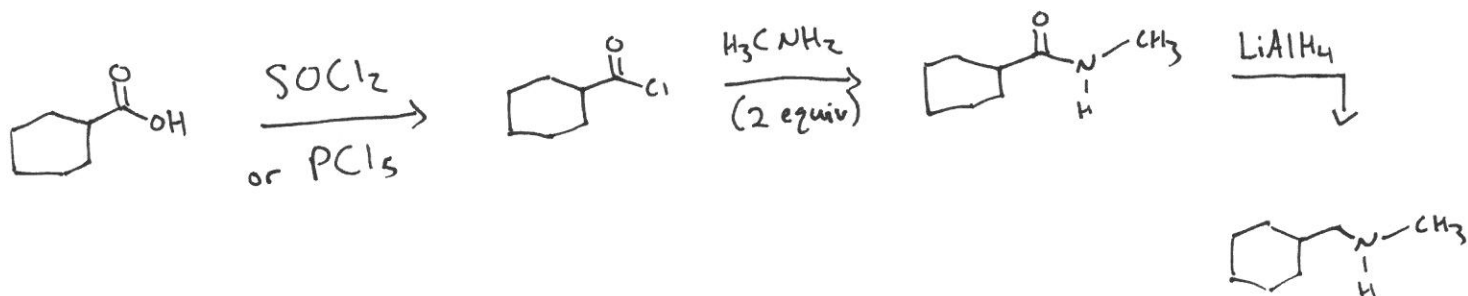
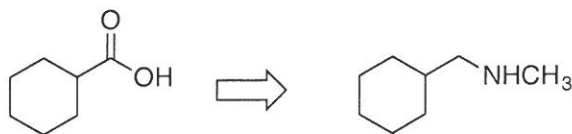
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Page	Possible Points	Score
1	<u>1</u>	<u> </u>
2	<u>12</u>	<u> </u>
3	<u>8</u>	<u> </u>
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5	<u>8</u>	<u> </u>
6	<u>15</u>	<u> </u>
7	<u>10</u>	<u> </u>
8	<u>8</u>	<u> </u>
9	<u>10</u>	<u> </u>
10	<u>10</u>	<u> </u>
11	<u>10</u>	<u> </u>
12	<u>Appendix: Periodic Table, common NMR, IR absorption</u>	
TOTAL	<u>100</u>	<u> </u>

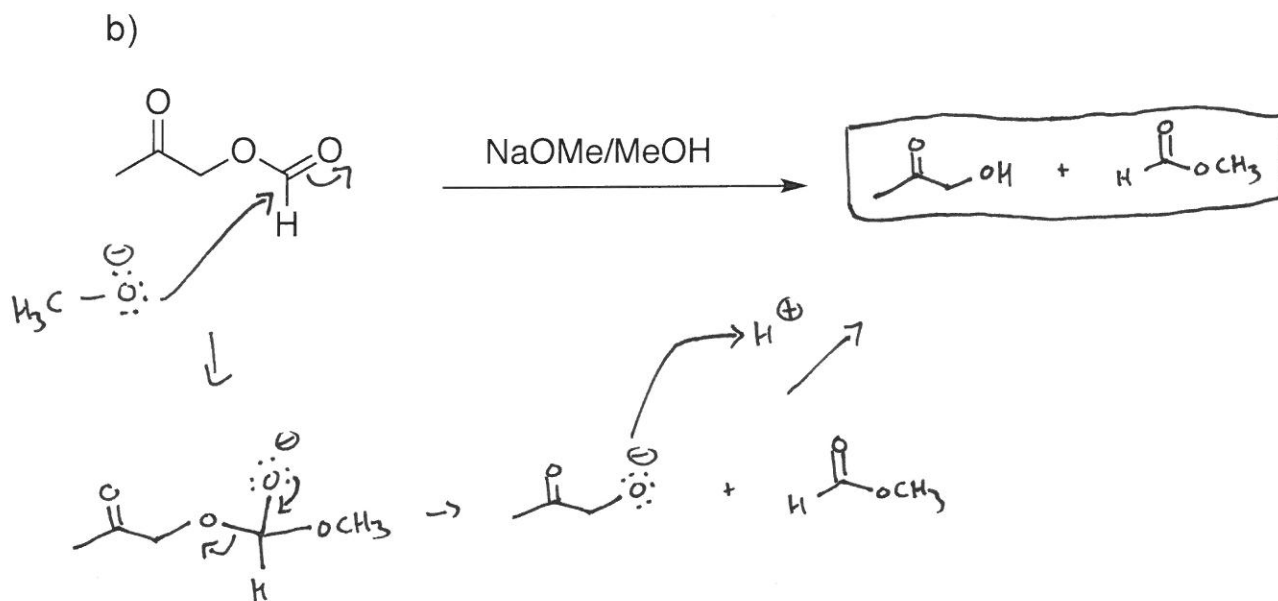
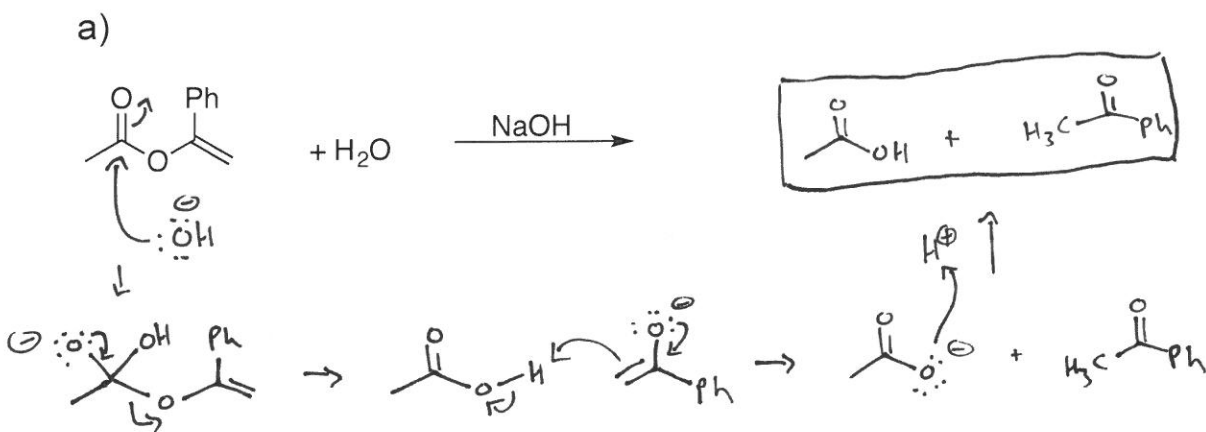
1. Give the **single major product** of each of the following reactions, carefully showing stereochemistry if appropriate. If a racemate is formed, show only one enantiomer, and label it "rac". Assume chiral starting materials are single pure enantiomers (3 pts each)



2. (8 pts) Outline a synthesis of (cyclohexylmethyl)methylamine from cyclohexanecarboxylic acid.

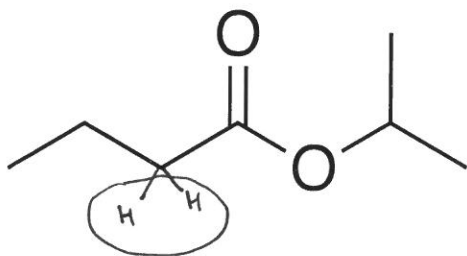


3. (8 pts) Complete the reactions by giving the principal organic products (assume an acidic workup). Provide curved arrows to indicate the electron flow.

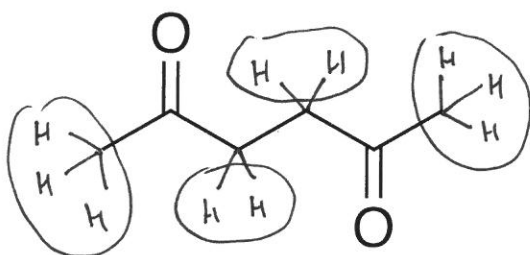


4. (8 pts) Draw and circle hydrogen atoms in each compound have a $pK_a \leq 25$

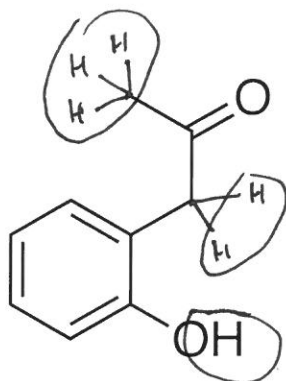
a)



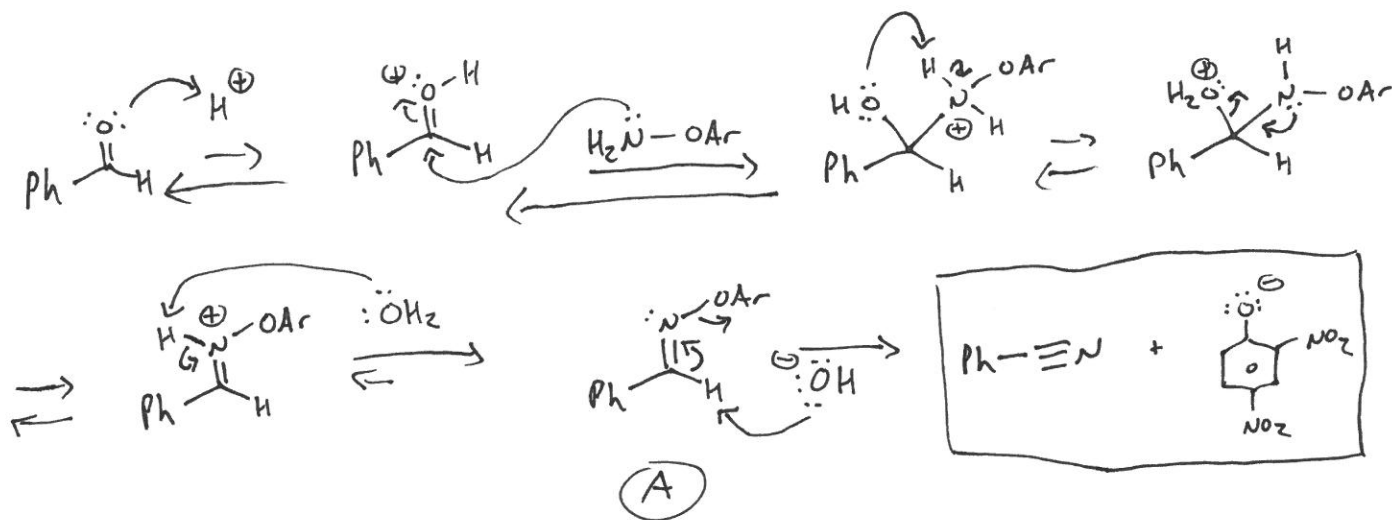
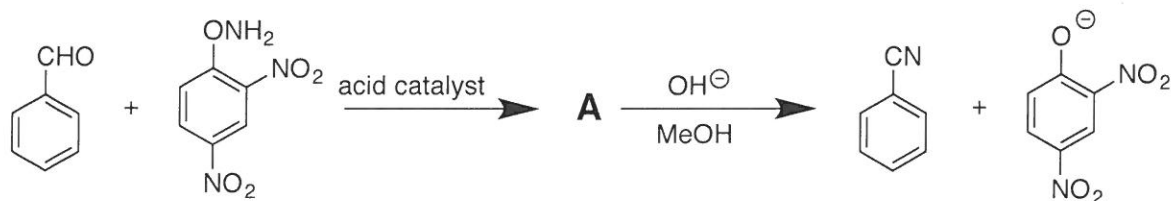
b)



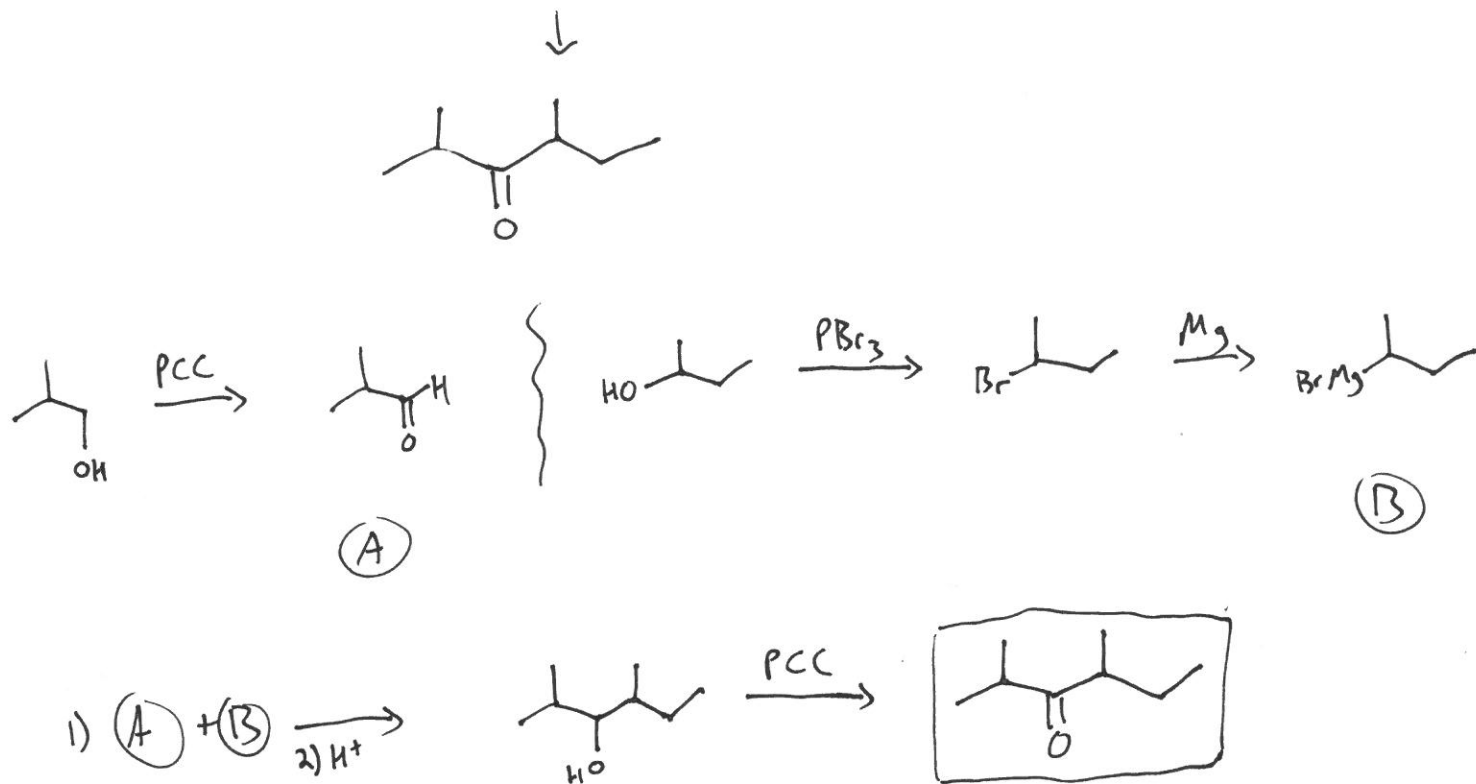
c)



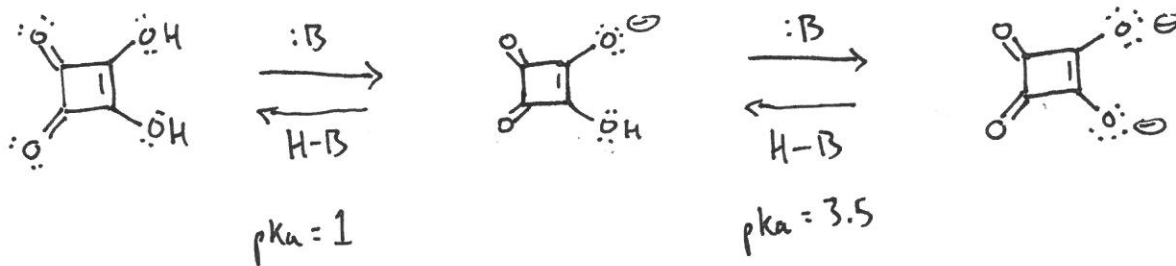
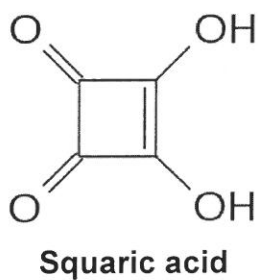
5. (15 pts) The sequence shown below illustrates a method for the preparation of nitriles from aldehydes. Identify compound A and give a curved-arrow mechanism for the conversion of A to the products.



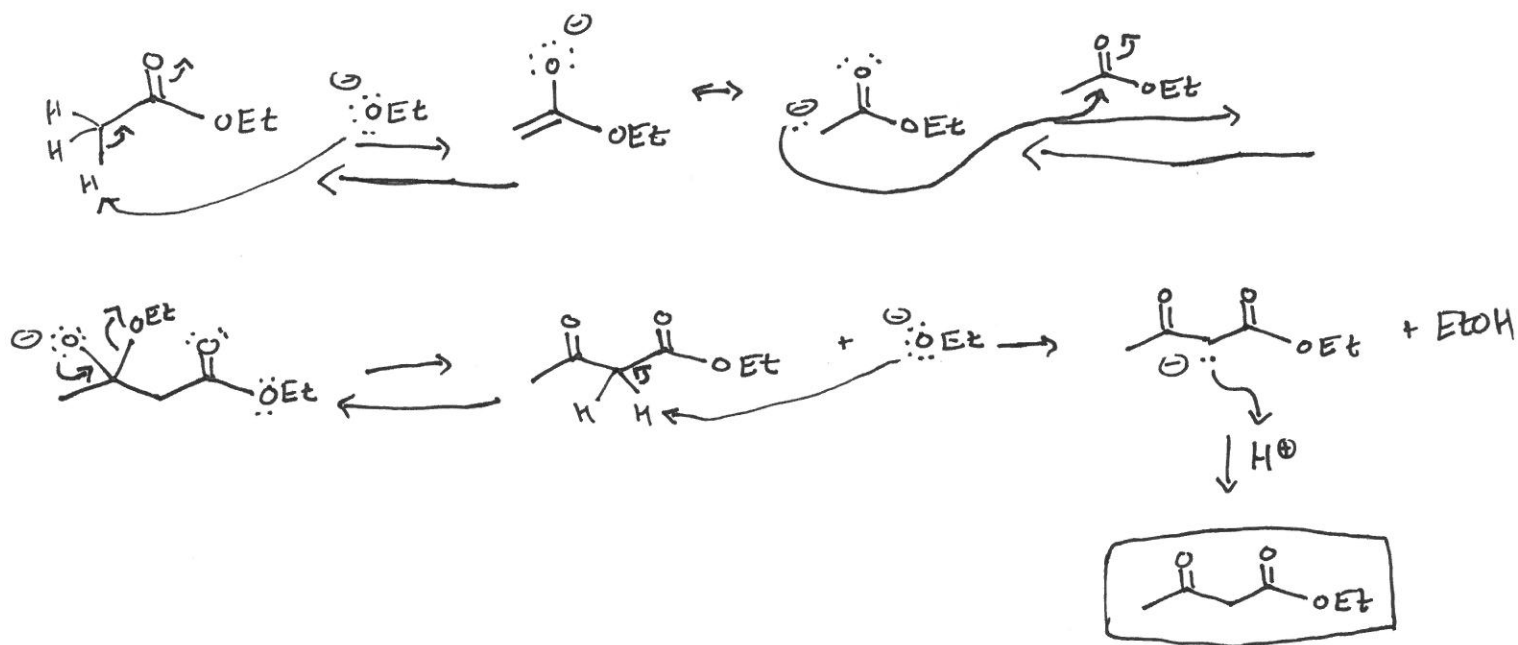
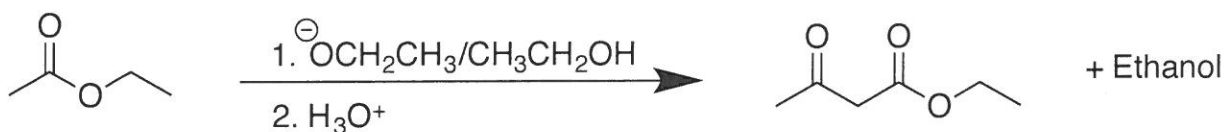
6. (10 pts) Synthesize 2,4-dimethylhexan-3-one from four carbon alcohols.



7. (8 pts) Squaric acid has pKa values of about 1 and 3.5. Draw the reactions corresponding to the two successive ionization of squaric acid and label each with the appropriate pKa value.

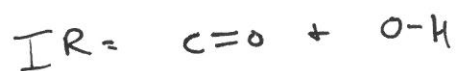


8. (10 pts) The Claisen condensation converts two molecules of an ester into a β -keto ester. The reaction starts with the ester in an alkoxide/alcohol solution and is worked up with acid to form the neutral β -keto ester product. Show the curved arrow mechanism for the Claisen condensation of ethyl ethanoate treated ethoxide ion. In each step, draw only the species that react in that step. If an enolate resonance form is possible, draw only the carbanionic form. Always omit ethanol byproducts.

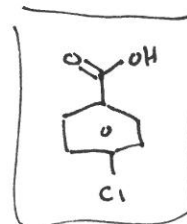


9. (10 pts) Give the structure of the compound $C_7H_5O_2Cl$ that has an IR absorption at 1685 cm^{-1} as well as a strong, broad O-H absorption, and the following proton NMR spectrum: $\delta = 7.56$ (2H, leaning d, $J = 10\text{ Hz}$); $\delta = 8.00$ (2H, leaning d, $J = 10\text{ Hz}$); $\delta = 8.27$ (1H, broad s, exchanges with D_2O).

$$\text{Deg. Unsat: } \frac{2(7)+2-(1)-(5)}{2} = 5$$



NMR = para subst. benzene
+ OH above aromatic
region (likely $\text{C}_6\text{H}_4\text{OH}$)



Appendix

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	seleonium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	niobium 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	* 57-70	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	* *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [265]	meitnerium 109 Mt [268]	unnilennium 110 Uun [271]	ununennium 111 Uuu [272]	unbinilium 112 Uub [273]	untrivalentium 114 Uuq [284]										

Group	Chemical shift, ppm
	0.7-1.5
	4.6-5.7
—O—H	varies with solvent and with acidity of O—H
$\text{—C}\equiv\text{C—H}$	1.7-2.5
	6.5-8.5

Group	Chemical shift, ppm
	9-11
	7.5-9.5
—C—NH—	0.5-1.5
	2.5-3.5

TABLE 12.1 Regions of the Infrared Spectrum

Wavenumber range, cm^{-1}	Type of absorptions	Name of region
3400-2800	O—H, N—H, C—H stretching	Functional group
2250-2100	$\text{C}\equiv\text{N}$, $\text{C}\equiv\text{C}$ stretching	
1850-1600	$\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}=\text{C}$ stretching	
1600-1000	C—C, C—O, C—N stretching; various bending absorptions	Fingerprint
1000-600	C—H bending	C—H bending