



(University of Choice)

**MASINDE MULIRO UNIVERSITY OF
SCIENCE AND TECHNOLOGY
(MMUST)**

MAIN CAMPUS

**UNIVERSITY EXAMINATIONS
2022/2023 ACADEMIC YEAR**

**FIRST YEAR SECOND SEMESTER EXAMINATIONS
MAIN EXAM**

**FOR THE DEGREE
OF
MASTERS OF SCIENCE (CHEMISTRY)**

COURSE CODE: SCH 830

COURSE TITLE: ADVANCED ORGANIC SPECTROSCOPY

DATE: 13/04/2023

TIME: 2.00-5.00 PM

INSTRUCTIONS TO CANDIDATES

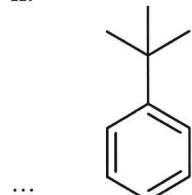
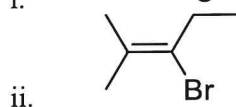
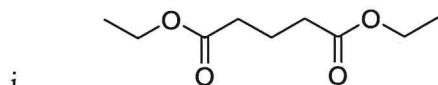
1. Answer all questions
2. Find IR chart and characteristic NMR chemical shifts tables attached to the question paper

TIME: 3 Hours

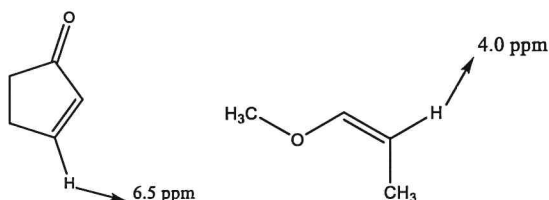
MMUST observes ZERO tolerance to examination cheating

QUESTION ONE (16 marks)

- a) For each of the compounds below, identify and label the chemically distinct hydrogen atoms. 6 marks

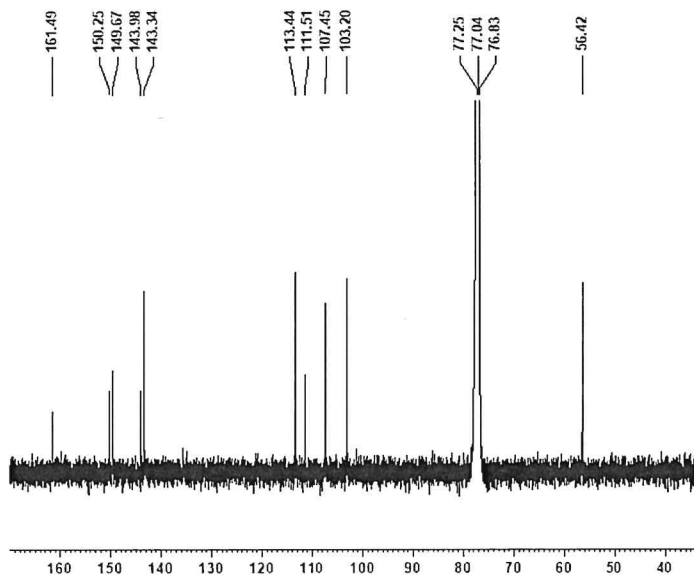


- b) Determine the splitting pattern for all the protons in the compound a(i) above. 2 marks
 c) The vinyl proton chemical shift in the two compounds shown below is substantially different. Explain 3 marks

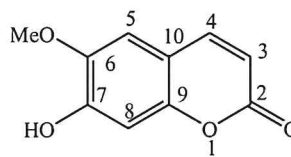


- d) Study the C-NMR spectrum of Scopoletin, whose structure is drawn alongside it

RMK49A (600) in CDCl3



¹³C-NMR spectrum of Scopoletin

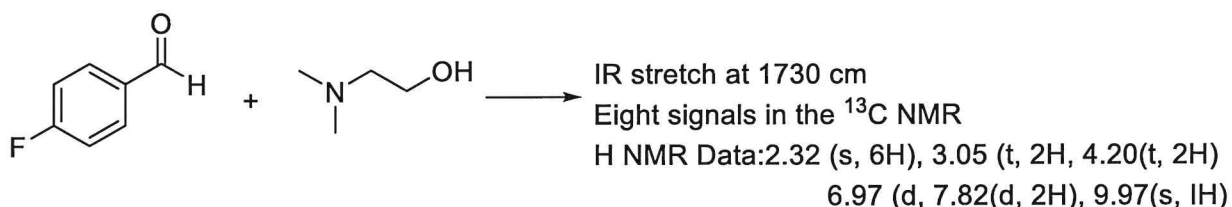


Scopoletin

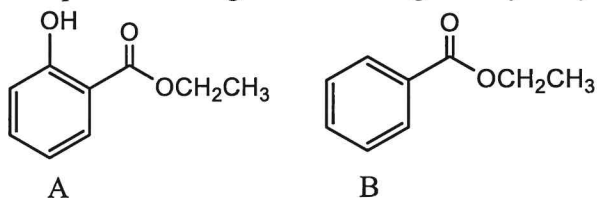
- i. Assign all the signals to the carbon atoms in the structure 5 marks

QUESTION TWO (15 marks)

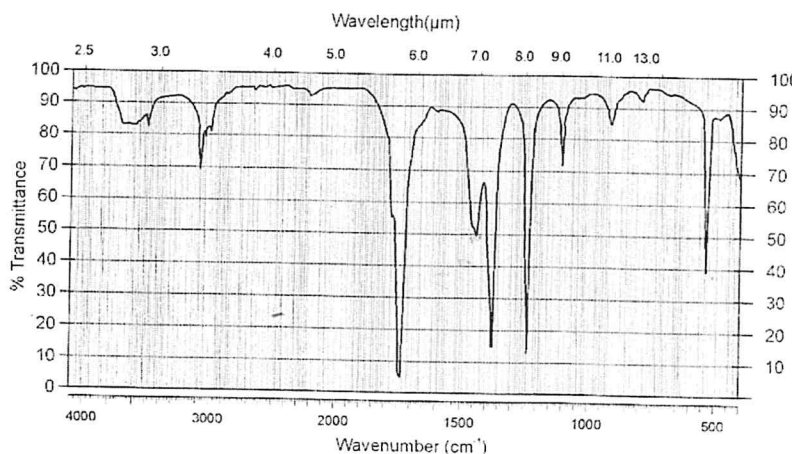
- a) The reaction below was carried out in the laboratory to yield a compound whose spectral information is as indicated.



- i. What interpretation would you give the IR data? 1 mark
 ii. Determine the types of protons represented by the ^1H NMR data obtained 5 marks
 iii. Draw the structure of the product obtained from the reaction 1 mark
 b) Describe two techniques of preparing a solid sample for IR analysis 2 marks
 c) Compound A was generated through the hydroxylation of compound B in the lab.



- i. How would you confirm the success of the reaction using the IR absorption frequencies of the carbonyl functional groups of both compounds? 2 marks
 ii. State any other evidence for the conversion, which would be obtained from the IR data 1 mark
 d) A compound with molecular formula $\text{C}_3\text{H}_6\text{O}$ shows the following IR spectrum.



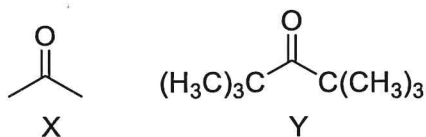
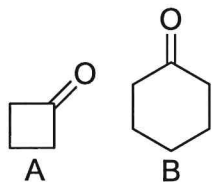
- i. What functional groups can be obtained from the above spectrum? 2 marks

ii. Suggest the molecular formula of the compound

1 mark

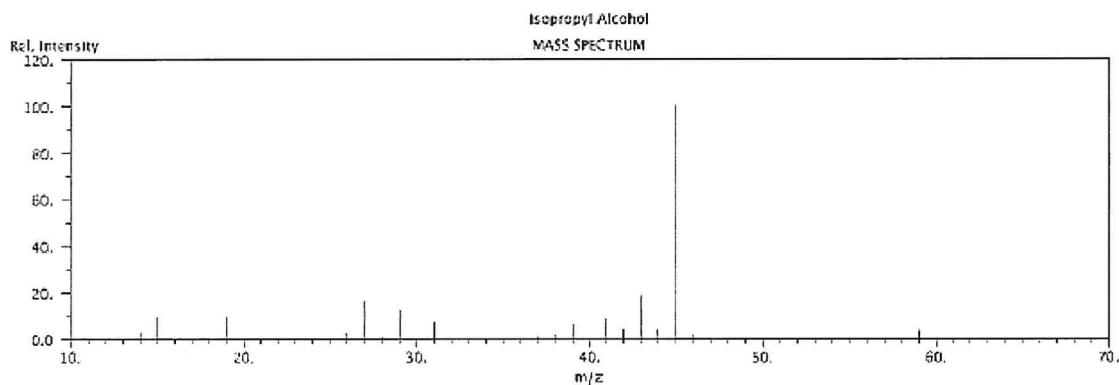
QUESTION THREE (14 marks)

a) Between the following pair of compounds, choose the one with a higher λ_{max} for the $n \rightarrow \pi^*$ transition. Explain your answer 3 marks



b) Describe the instrumentation of a single-crystal X-ray diffractometer 7 marks

c) The EI-MS for 2-propanol is given below. Using chemical formulae explain the origin of peaks at m/z 45 and m/z 43. 4 marks

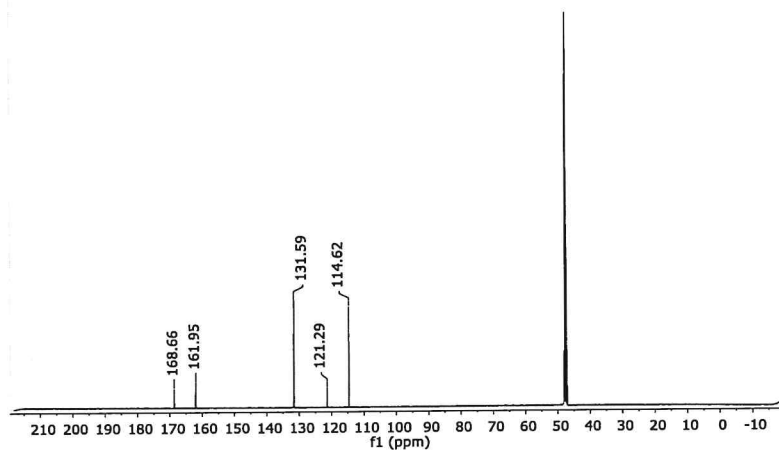


QUESTION FOUR (15 marks)

a) Carefully study the spectra of an unknown organic compound X and then answer the questions that follow.

i. What information can you gather from the ^{13}C NMR spectrum below? 2 marks

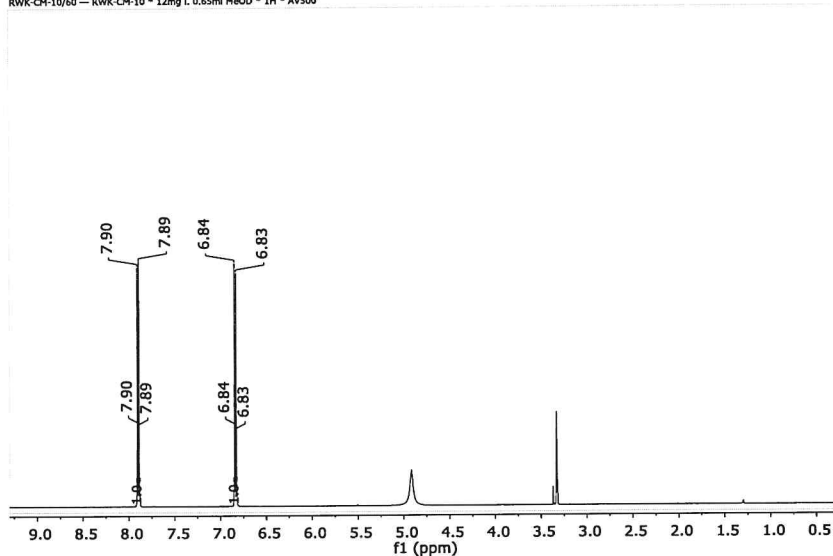
RWK-CH-10/64 — RWK-CH-10 * 12mg l. 0.65ml MeOD * 13C * AV500



^{13}C NMR spectrum of unknown organic compound X

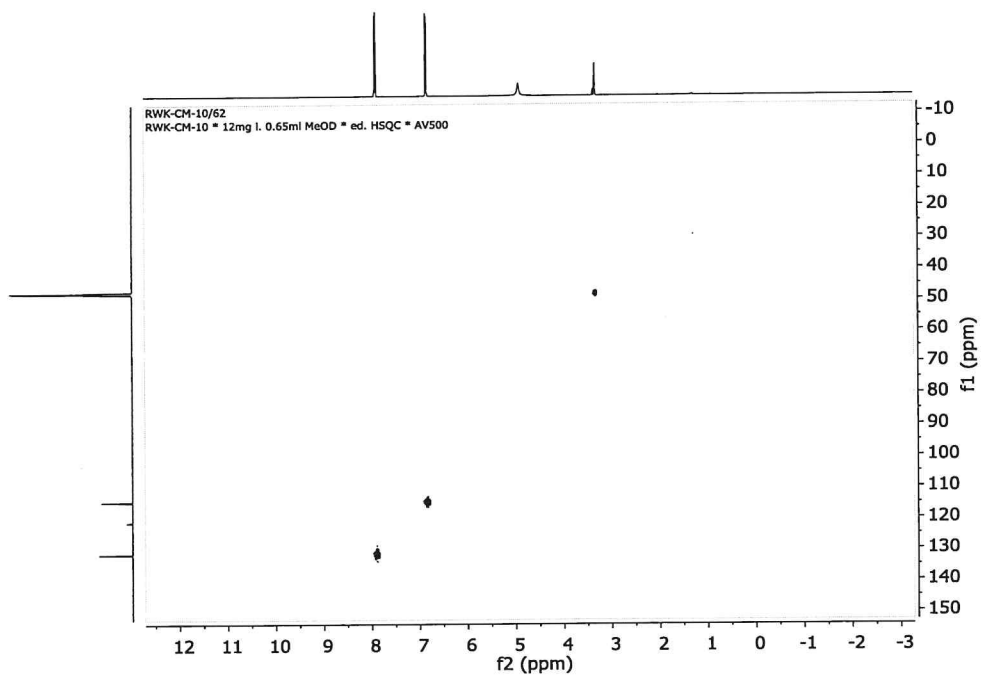
- ii. Considering the chemical shift and the splitting patterns in ^1H -NMR spectrum below establish the types of protons present in the compound 2 marks

RWK-CH-10/60 — RWK-CH-10 * 12mg l. 0.65ml MeOD * 1H * AV500



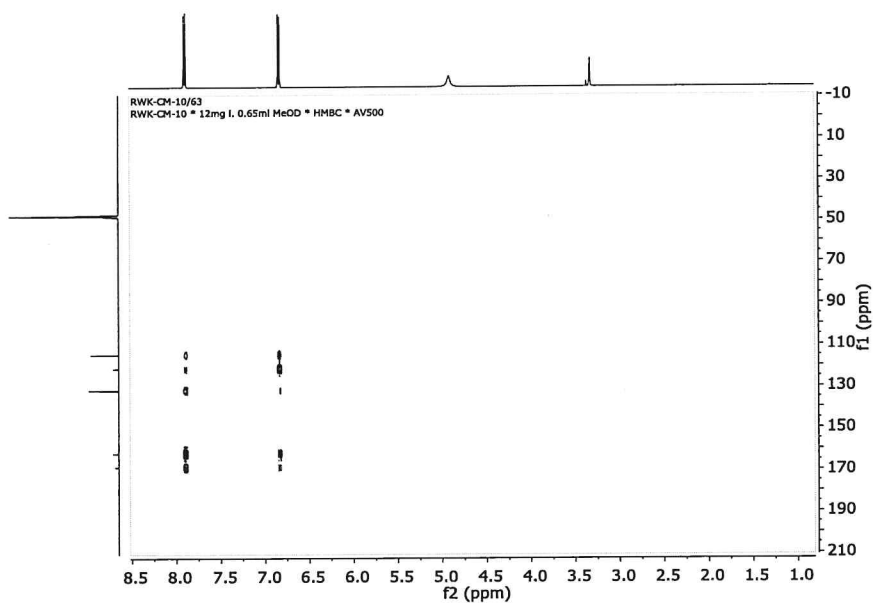
^1H NMR spectrum of unknown organic compound X

- iii. Determine the coupling constants of the peaks observed in the ^1H -NMR spectrum. Explain your answer 2 marks
- iv. Using the HSQC spectrum below, establish the attachment of the protons to their respective carbon atoms in the structure 2 marks



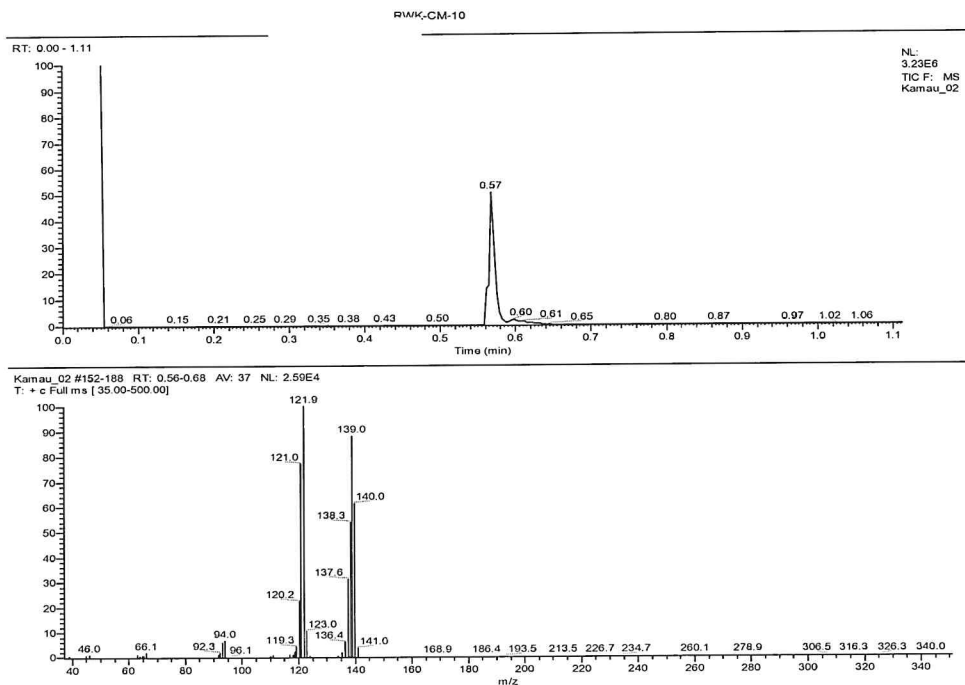
HSQC spectrum of unknown organic compound X

- v. Give all the HMBC correlations for the protons resonating at δ_H 7.90 ppm obtained from the spectrum below 3 marks



HMBC spectrum of unknown organic compound X

- vi. Using the pieces of information gathered in question (i-v) above, propose the structure of the compound 1 mark
- vii. Confirm the structure proposed in (vi) above by identifying its molecular ion peak from the mass spectrum below 1 mark



Mass spectrum of unknown organic compound X

- viii. Explain the origin of the remaining peaks in the mass spectrum of compound X 2 marks

Table of Characteristic IR Absorptions

<i>frequency, cm⁻¹</i>	<i>bond</i>	<i>functional group</i>
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β-unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β-unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in-ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in-ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH ₂ X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Characteristic ^{13}C -NMR Chemical Shifts

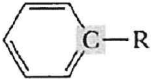
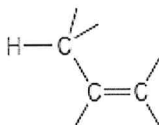
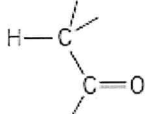
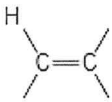
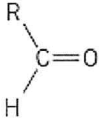
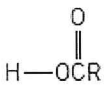
Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
$\text{R}\underline{\text{C}}\text{H}_3$	0–40		110–160
$\text{R}\underline{\text{C}}\text{H}_2\text{R}$	15–55	$\text{R}\overset{\text{O}}{\parallel}\text{C}\text{OR}$	160–180
$\text{R}_2\underline{\text{C}}\text{H}$	20–60	$\text{R}\overset{\text{O}}{\parallel}\text{C}\text{NR}_2$	165–180
$\text{R}\underline{\text{C}}\text{H}_2\text{I}$	0–40	$\text{R}\overset{\text{O}}{\parallel}\text{C}\text{OH}$	175–185
$\text{R}\underline{\text{C}}\text{H}_2\text{Br}$	25–65	$\text{R}\overset{\text{O}}{\parallel}\text{C}\text{H}, \text{R}\overset{\text{O}}{\parallel}\text{C}\text{R}$	180–210
$\text{R}\underline{\text{C}}\text{H}_2\text{Cl}$	35–80		
$\text{R}_2\underline{\text{C}}\text{OH}$	40–80		
$\text{R}_2\underline{\text{C}}\text{OR}$	40–80		
$\text{R}\underline{\text{C}}\equiv\text{CR}$	65–85		
$\text{R}_2\underline{\text{C}}=\text{CR}_2$	100–150		

TABLE 13.1 Approximate Chemical Shifts of Representative Protons

Compound class or type of proton		Chemical shift (δ), ppm*
Protons bonded to carbon		
Alkane	$\text{RCH}_3, \text{R}_2\text{CH}_2, \text{R}_3\text{CH}$	0.9–1.8
Allylic		1.5–2.6
Terminal alkyne	$\text{H}-\text{C}\equiv\text{C}$	1.8–3.1
C—H adjacent to $\text{C}=\text{O}$		2.0–2.5
C—H adjacent to $\text{C}\equiv\text{N}$	$\text{H}-\text{C}-\text{C}\equiv\text{N}$	2.1–2.3
Benzylic	$\text{H}-\text{C}-\text{Ar}$	2.3–2.8
Amine	$\text{H}-\text{C}-\text{NR}_2$	2.2–2.9
Alkyl chloride	$\text{H}-\text{C}-\text{Cl}$	3.1–4.1
Alkyl bromide	$\text{H}-\text{C}-\text{Br}$	2.7–4.1
Alcohol or ether	$\text{H}-\text{C}-\text{O}$	3.3–3.7
Vinyllic		4.5–6.5
Aryl	$\text{H}-\text{Ar}$	6.5–8.5
Aldehyde		9–10
Protons bonded to nitrogen or oxygen		
Amine	$\text{H}-\text{NR}_2$	1–3 [†]
Alcohol	$\text{H}-\text{OR}$	0.5–5 [†]
Phenol	$\text{H}-\text{OAr}$	6–8 [†]
Carboxylic acid		10–13 [†]

*Approximate values relative to tetramethylsilane; other groups within the molecule can cause a proton signal to appear outside of the range cited.

[†]The chemical shifts of O—H and N—H protons are temperature- and concentration-dependent.