Estimating Chemical Shifts for ^{1}H NMR

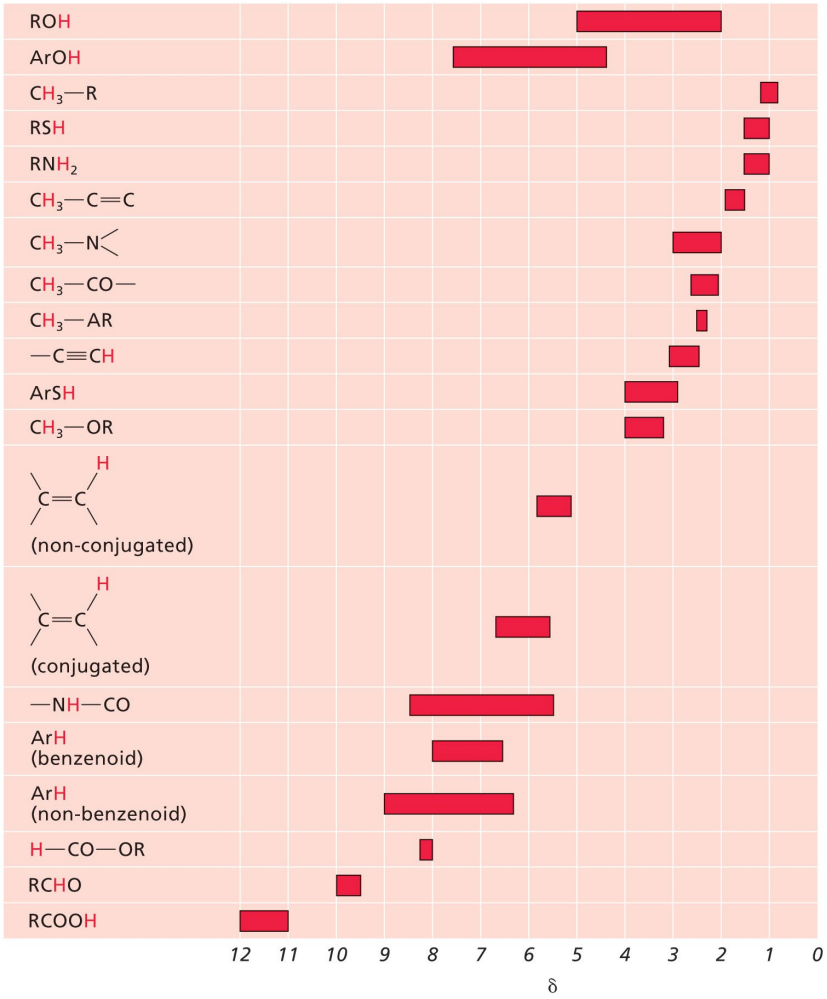


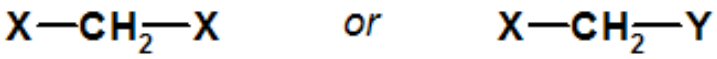
Table 13.1 Approximate chemical shift ranges for protons bonded to aliphatic carbon atoms.

Methyl protons	δ	*Methylene protons*	δ	*Methine protons*	δ
CH_3–C	0.9	–CH_2–C	1.3	–CH–C	1.5
CH_3–C–C=C	1.1	–CH_2–C–C=C	1.7	–CH–C–C=C	1.9
CH_3–C–O	1.4	–CH_2–C–O	1.9	–CH–C–O	2.0
CH_3–C=C	1.6	–CH_2–C=C	2.3	–CH–C=C	2.2
CH_3–Ar	2.3	–CH_2–Ar	2.7	–CH–Ar	3.0
CH_3–CO–R	2.2	–CH_2–CO–R	2.4	–CH–CO–R	2.7
CH_3–CO–Ar	2.6	–CH_2–CO–Ar	2.9	–CH–CO–Ar	3.5
CH_3–CO–O–R	2.0	–CH_2–CO–O–R	2.2	–CH–CO–O–R	2.5
CH_3–CO–O–Ar	2.4	–CH_2–CO–O–Ar	2.7	–CH–CO–O–Ar	2.9
CH_3–O–R	3.3	–CH_2–O–R	3.4	–CH–O–R	3.7
CH_3–O–H	3.5	–CH_2–O–H	3.6	–CH–O–H	3.9
CH_3–OAr	3.8	–CH_2–OAr	4.3	–CH–OAr	4.5
CH_3–O–CO–R	3.7	–CH_2–O–CO–R	4.1	–CH–O–CO–R	4.8
CH_3–N	2.3	–CH_2–N	2.5	–CH–N	2.8
CH_3–NO_2	4.0	–CH_2–NO_2	4.4	–CH–NO_2	4.7
CH_3–C–NO_2	1.6	–CH_2–C–NO_2	2.2	–CH–C–NO_2	2.6
CH_3–C=C–CO	2.0	–CH_2–C=C–CO	2.1	–CH–C=C–CO	2.4
CH_3–C–Cl	1.4	–CH_2–C–Cl	1.8	–CH–C–Cl	2.0
CH_3–C–Br	1.8	–CH_2–C–Br	1.8	–CH–C–Br	1.9
CH_3–Cl	3.0	–CH_2–Cl	3.4	–CH–Cl	4.0
CH_3–Br	2.7	–CH_2–Br	3.3	–CH–Br	3.9

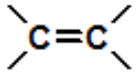
Data and Tables (with minor adaptations) from:

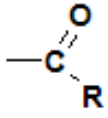
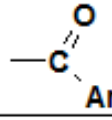
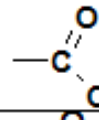
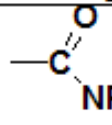
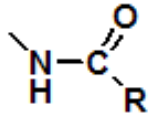
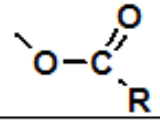
1. Sorrel "Organic Chemistry 2nd Edition (2006)
2. Pavia, Lampman and Kriz "Introduction to Spectroscopy" 2nd Edition (1996)

Calculating Chemical Shifts for Methylene (CH_2) Groups



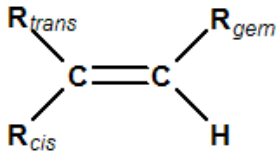
$$\delta_H = \left(0.23 + \sum \text{constants}\right) ppm$$

Substituent	Constant
-R (alkyl)	0.47
	1.32
-C≡C-	1.44
-Ar	1.85
-F	4.00
-Cl	2.53
-Br	2.33
-I	1.82
-C≡N	1.70
$-NO_2$	3.80
$-NR_2$	1.57
-OH	2.56
-OR	2.36
-OAr	3.23
-SR	1.64

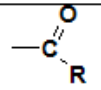
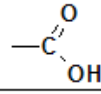
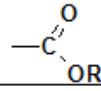
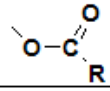
Substituent	Constant
	1.70
	1.84
	1.55
	1.59
	2.27
	3.13

Data and Tables (with minor adaptations) from:
1. Sorrel "Organic Chemistry 2nd Edition (2006)
2. Pavia, Lampman and Kriz "Introduction to Spectroscopy" 2nd Edition (1996)

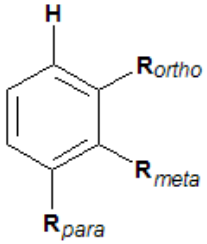
Calculating Chemical Shifts for Alkenes



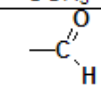
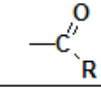
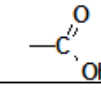
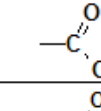
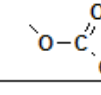
$$\delta_H = \left(5.25 + Z_{gem} + Z_{cis} + Z_{trans}\right) ppm$$

Substituent	Z_{gem}	Z_{cis}	Z_{trans}
-R (alkyl)	0.44	-0.26	-0.29
$-CH_2-OR$	0.67	-0.02	-0.07
-Ar	1.35	0.37	-0.10
-Cl	1.00	0.19	0.03
-Br	1.04	0.40	0.55
-C≡N	0.23	0.78	0.58
$-NO_2$	1.87	1.30	0.62
$-NR_2$	0.69	-1.19	-1.31
-OR	1.18	-1.06	-1.28
	1.10	1.13	0.81
	1.00	1.35	0.74
	0.84	1.15	0.56
	2.09	-0.40	-0.67

Calculating Chemical Shifts for Benzenes



$$\delta_H = \left(7.27 + \sum Z\right) ppm$$

Substituent	Z_{ortho}	Z_{meta}	Z_{para}
-H	0	0	0
-R (alkyl)	-0.14	-0.06	-0.17
$-CH_2-OH$	-0.07	-0.07	-0.07
-Cl	0.03	-0.02	-0.09
-Br	0.18	-0.08	-0.04
-C≡N	0.36	0.18	0.28
$-NO_2$	0.95	0.26	0.38
$-NH_2$	-0.75	-0.25	-0.65
-OH	-0.56	-0.12	-0.45
$-OCH_3$	-0.48	-0.09	-0.44
	0.56	0.22	0.29
	0.62	0.14	0.21
	0.85	0.18	0.27
	0.71	0.10	0.21
	-0.25	0.03	-0.13

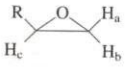
Data and Tables (with minor adaptations) from:

1. Sorrel "Organic Chemistry 2nd Edition (2006)
2. Pavia, Lampman and Kriz "Introduction to Spectroscopy" 2nd Edition (1996)

Estimating Coupling Constants for ^{1}H NMR

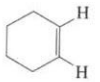
TYPICAL PROTON COUPLING CONSTANTS

Alkanes and Substituted Alkanes

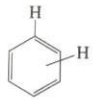
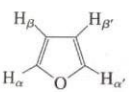
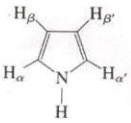
Type		Typical Value (Hz)	Range (Hz)	
	^2J geminal	12	12–15	(for a 109° H—C—H angle)
	^3J vicinal	7	6–8	(depends on HCCH dihedral angle)
	^3J a,a	10	8–14	in conformationally rigid systems
	^3J a,e	5	0–7	(in systems undergoing inversion,
	^3J e,e	3	0–5	all $J \approx 7$–8 Hz)
	^3J *cis* (H_bH_c)	9	6–12	
	^3J *trans* (H_aH_c)	6	4–8	
	^2J *gem* (H_aH_b)	6	3–9	
	^3J *cis* (H_bH_c)	4	2–5	
	^3J *trans* (H_aH_c)	2.5	1–3	
	^2J *gem* (H_aH_b)	6	4–6	
	^4J	0	0–7	(*W*-configuration obligatory—strained systems have the larger values)

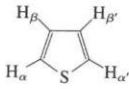
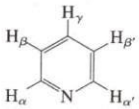
Alkenes and Cycloalkenes (^2J and ^3J)

Type		Typical Value (Hz)	Range (Hz)
	^2J *gem*	<1	0–5
	^3J *cis*	10	6–15
	^3J *trans*	16	11–18
	^3J	5	4–10
	^3J	10	9–13

Type		Typical Value (Hz)	Range (Hz)
	^3J	2	0–2
	^3J	4	2–4
	^3J	6	5–7
	^3J	10	8–11

Aromatics and Heterocycles

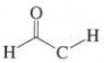
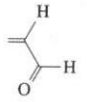
Type		Typical Value (Hz)	Range (Hz)
	^3J *ortho*	8	6–10
	^4J *meta*	3	1–4
	^5J *para*	<1	0–2
	^3J $\alpha\beta$		1.6–2.0
	^4J $\alpha\beta'$		0.3–0.8
	^4J $\alpha\alpha'$		1.3–1.8
	^3J $\beta\beta'$		3.2–3.8
	^3J $\alpha\beta$		2.0–2.6
	^4J $\alpha\beta'$		1.0–1.5
	^4J $\alpha\alpha'$		1.8–2.3
	^3J $\beta\beta'$		2.8–4.0

Type		Range (Hz)
	^3J $\alpha\beta$	4.6–5.8
	^4J $\alpha\beta'$	1.0–1.5
	^4J $\alpha\alpha'$	2.1–3.3
	^3J $\beta\beta'$	3.0–4.2
	^3J $\alpha\beta$	4.9–5.7
	^4J $\alpha\gamma$	1.6–2.0
	^5J $\alpha\beta'$	0.7–1.1
	^4J $\alpha\alpha'$	0.2–0.5
	^3J $\beta\gamma$	7.2–8.5
	^4J $\beta\beta'$	1.4–1.9

Alcohols

Type		Typical Value (Hz)	Range (Hz)
	^3J	5	4–10
(no exchange occurring)			

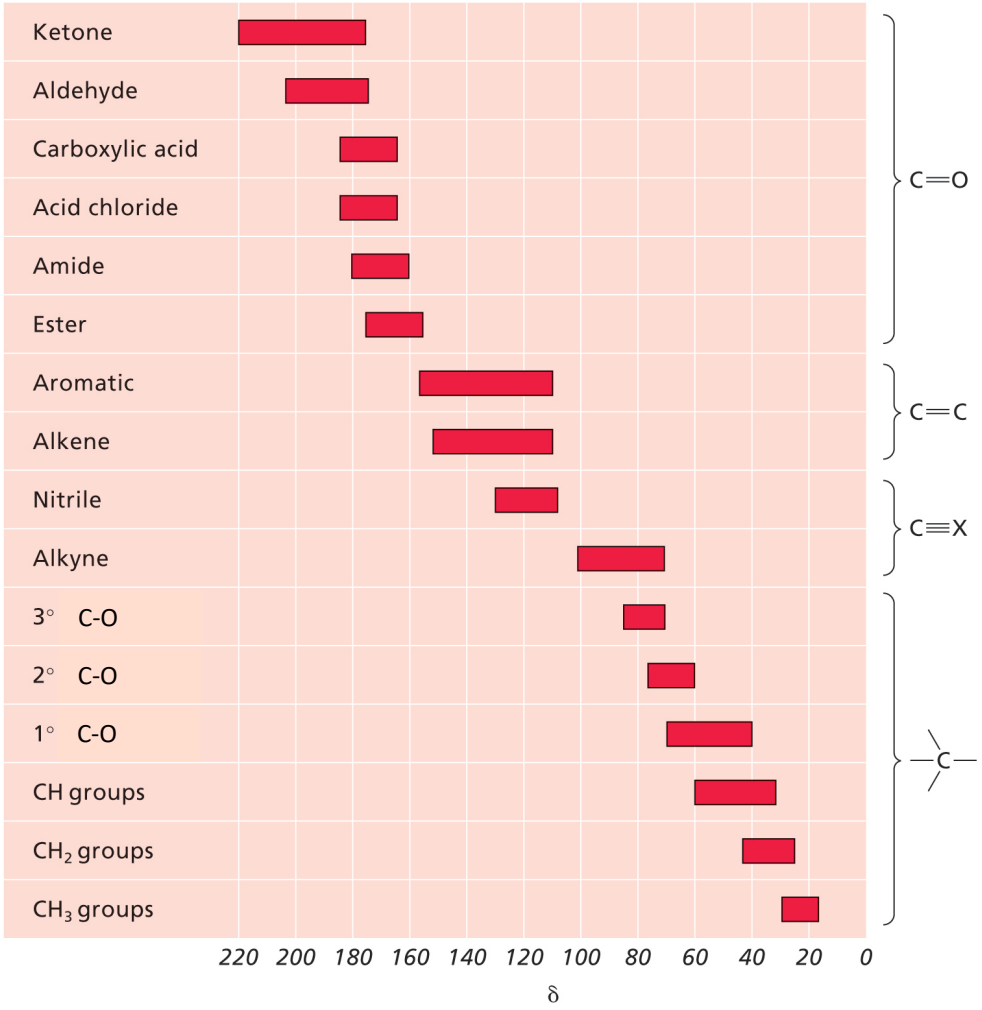
Aldehydes

Type		Typical Value (Hz)	Range (Hz)
	^3J	2	1–3
	^3J	6	5–8

^{4}J for terminal alkynes (H-C≡C-C-H) typically 2 Hz (range 2-3 Hz)
^{5}J for other alkynes (H-C-C≡C-C-H) typically 2 Hz (range 2-3 Hz)

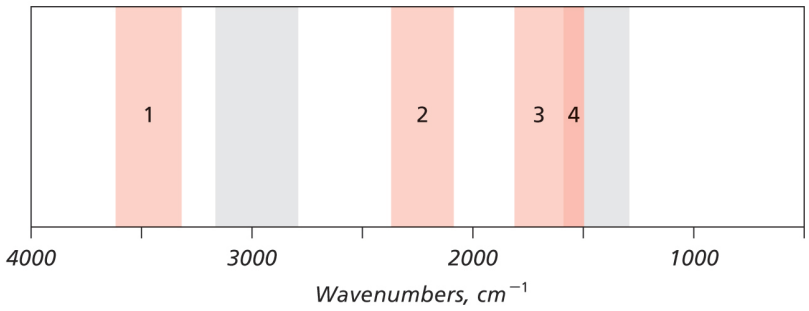
2. Pavia, Lampman and Kriz "Introduction to Spectroscopy" 2nd Edition (1996)

^{13}C NMR

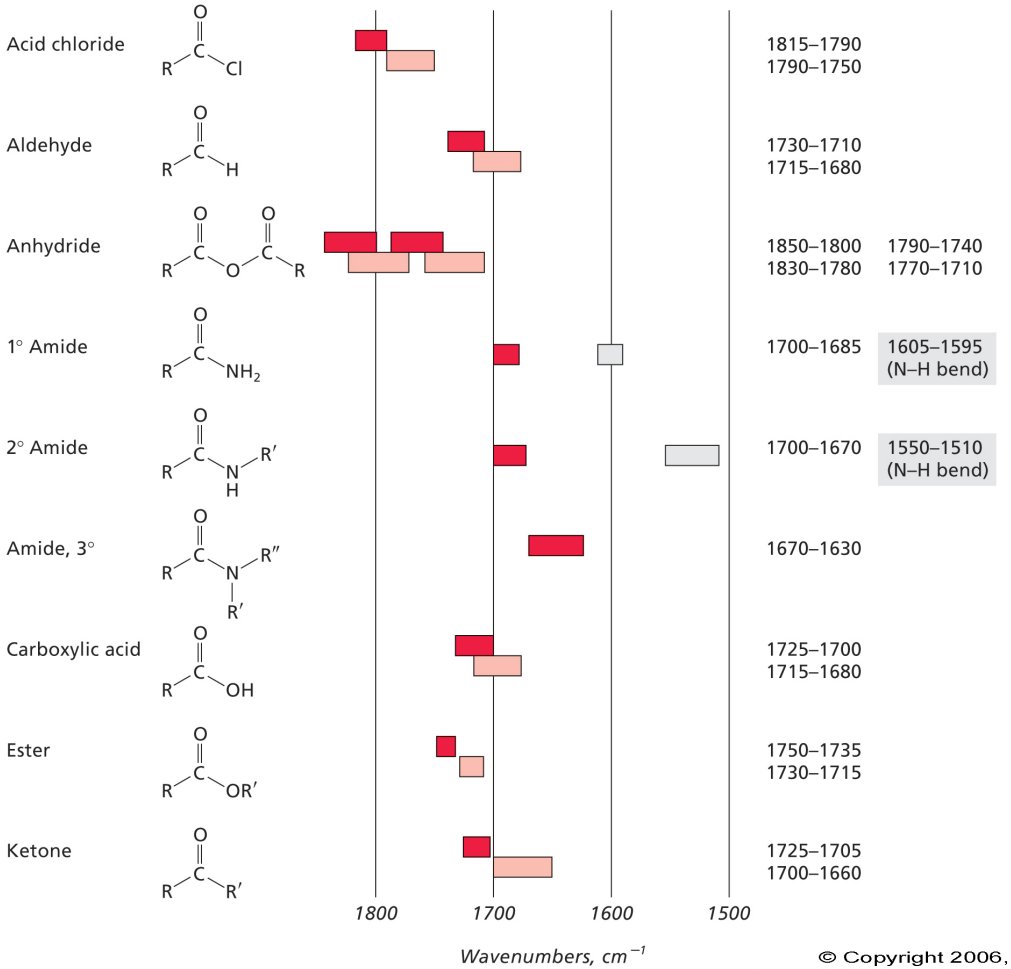


2. Pavia, Lampman and Kriz "Introduction to Spectroscopy" 2nd Edition (1996)

IR



Region	Frequency range, (cm^{-1})	Bond types	Functional groups
1	3500 – 3200	O—H	Alcohol, phenol
		N—H	Amine, amide
2	2300 – 2100	C≡C	Alkyne
		C≡N	Nitrile
3	1800 – 1650	C=O	Aldehyde
			Amide
			Anhydride (2 bands)
			Carboxylic acid
			Acid chloride
			Ester
4	1650 – 1500	C=C	Alkene
		C=C	Arene
		C=N	Imine
		N=O	Nitro compound



Data and Tables (with minor adaptations) from:

1. Sorrel "Organic Chemistry 2nd Edition (2006)
2. Pavia, Lampman and Kriz "Introduction to Spectroscopy" 2nd Edition (1996)