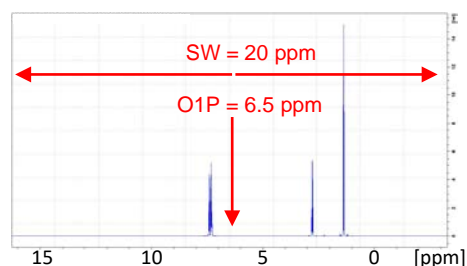
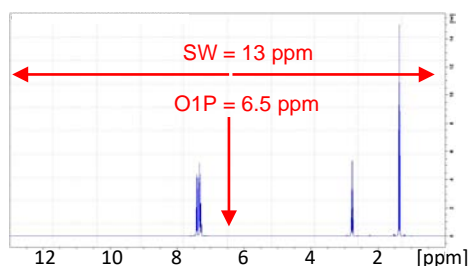


Setup ¹H 1d NMR experiment : (See as well manual experiment setup)

- Load your sample
- Command : **newnmr** (create a ¹H dataset)
- Command : **atma** (tuning) ; **rsh** (read standard shim file); **lock** (solvent); **topshim** (shim)
- Command : **zg** (start the experiment)

You can eventually change some parameters:

- **ns** : change number of scans.
Rem : The signal to noise (SNR) accumulate proportionally to the square root of the number of scans (ns)
Ex: if 16 scans are needed to have a SNR of 5, 64 scans will be needed to have a SNR of 10
→ Consider using cryoprobes if your SNR is still too small within a decent acquisition time
- **O1P** and **SW** : the centre and the width (in ppm) of the spectral window



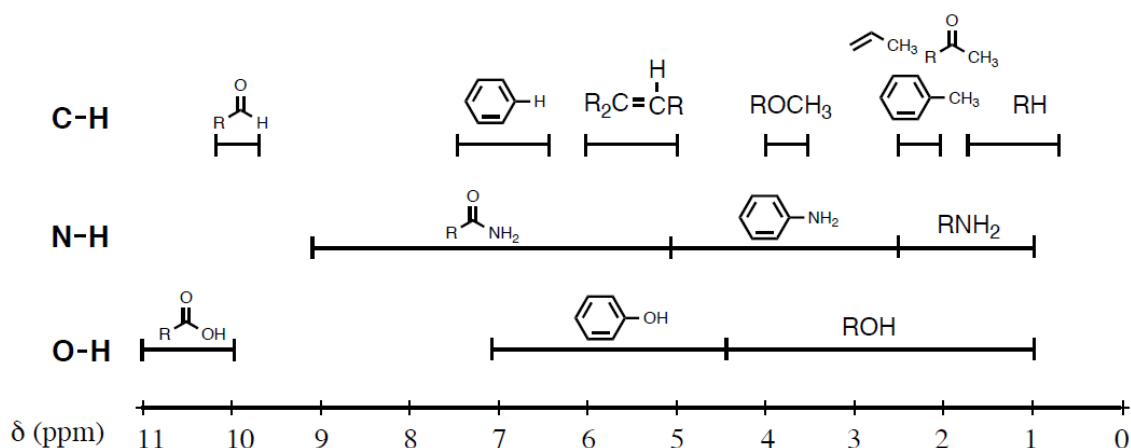
- **d1** : the relaxation time : to ensure the integral under the peak is quantitative
set d1 = 30 s or 5xT₁ (if you measured it)

¹H chemical shifts :

- See next table for general chemical shift
- See next tables for sp³, benzylic vinylic ¹H chemical shifts estimations (Curphy-Morrison constants)

¹H general chemical shifts table :

(source: Dr. Laurie S. Starkey California State Polytechnic University, Pomona)



Protons on Carbon

Type of C-H	δ (ppm)	Description of Proton
R-CH ₃	0.9	alkyl (methyl)
R-CH ₂ -R	1.3	alkyl (methylene)
R ₃ C-H	1.5-2	alkyl (methine)
	1.8	allylic (C is next to a pi bond)
	2-2.3	α to carbonyl (C is next to C=O)
Ar-CH ₃	2.3	benzylic (C is next to Ph)
RC \equiv C-H	2.5	alkynyl
R ₂ N-CH ₃	2-3	α to nitrogen (C is attached to N)
R-CH ₂ -X	2-4	α to halogen (C is attached to Cl, Br, I)
RO-CH ₃	3.8	α to oxygen (C is attached to O)
R-CH ₂ -F	4.5	α to fluorine (C is attached to F)
	5-5.3	vinylic (H is attached to alkene C)
Ar-H	7.3	aromatic (H is on phenyl ring)
	9.7	aldehyde (H is on C=O)

Note: aldehyde (-CHO) proton usually does not couple with neighboring H's so appears as a singlet

Protons on Oxygen/Nitrogen*

Type of H	δ (ppm)	Description
ROH	0.5-5	alcohol
ArOH	4-7	phenol
	10-13	carb. acid
RNH ₂	0.5-5	amine
ArNH ₂	3-5	aniline
	5-9	amide

*Protons on N or O typically have wide ranges of expected chemical shifts; the actual δ value depends on the solvent used, the concentration, temperature, etc. Because these protons are acidic and, therefore, *exchangeable*, they may be broad peaks and usually do not couple with neighboring protons (typically they are broad singlets). If a protic deuterated solvent is used (e.g., D₂O or CD₃OD), then the NH and OH protons will exchange with the deuterium and the peaks will shrink or disappear entirely, since D (²H) does not show up in the ¹H NMR spectrum.

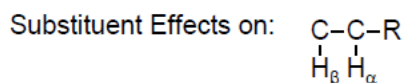
R = alkyl group
Ar = aromatic ring,
such as phenyl (Ph)

Estimating ¹H chemical shifts :

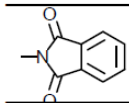
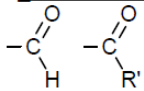

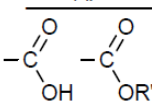

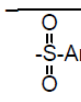
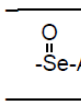
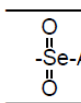
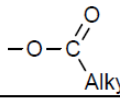
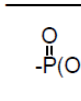
Curphy-Morrison Additivity Constants for Proton bonded to SP³ carbons

(source: Dr. Hans J. Reich. University of Wisconsin, Madison:

[Chem 605 - Structure Determination Using Spectroscopic Methods](#))



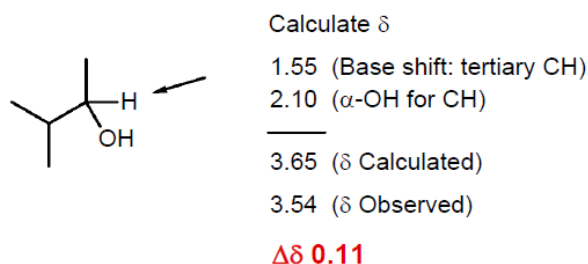
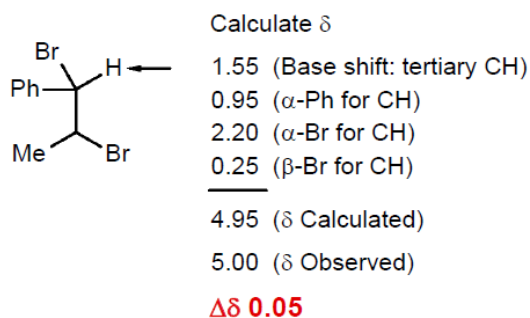
Standard Shift Positions:
Methyl 0.90 δ; Methylene 1.20 δ; Methine 1.55 δ

Substituent R		Alpha Shift	Beta Shift	Substituent R		Alpha Shift	Beta Shift
Chlorine	-CH ₃	2.30	0.60	-N(H)Alkyl	-CH ₃	1.25	0.20
	-CH ₂ -	2.30	0.55	-N(Alkyl) ₂	-CH ₂ -	1.40	0.15
	-CH-	2.55	0.15		-CH-	1.35	----
Bromine	-CH ₃	1.80	0.80	-N(H)Aryl	-CH ₃	2.08(8)	0.28(10)
	-CH ₂ -	2.15	0.80	-N(Alkyl)(Aryl)	-CH ₂ -	2.03(12)	0.34(2)
	-CH-	2.20	0.25		-CH-	2.33(2)	?
Iodine	-CH ₃	1.30	1.10	⁺ NMe ₃	-CH ₃	2.30(1)	?
	-CH ₂ -	1.95	0.60		-CH ₂ -	2.06(4)	?
	-CH-	2.70	0.35		-CH-	?	?
Aryl	-CH ₃	1.45	0.35		-CH ₃	2.14(1)	0.30(1)
	-CH ₂ -	1.45	0.55		-CH ₂ -	2.25(10)	0.51(2)
	-CH-	1.35	----		-CH-	?	?
	-CH ₃	1.25	0.25	-NO ₂	-CH ₃	3.50	0.65
	-CH ₂ -	1.10	0.30		-CH ₂ -	3.15	0.85
	-CH-	0.95	----		-CH-	3.05	----
	-CH ₃	1.70(6)	0.28(4)	-N ₃	-CH ₃	2.08(1)	0.45(1)
	-CH ₂ -	1.64(10)	0.50(3)		-CH ₂ -	1.45(3)	-0.46(1)
	-CH-	1.76(2)	0.76(1)		-CH-	1.46(2)	-0.22(1)
	-CH ₃	1.20	0.25	-SH	-CH ₃	1.20	0.40
	-CH ₂ -	1.00	0.30	-S-Alkyl	-CH ₂ -	1.30	0.30
	-CH-	0.95	----		-CH-	1.30	----
-C≡N	-CH ₃	1.10	0.45	-S-Ar	-CH ₃	1.47(2)	0.35(2)
	-CH ₂ -	1.10	0.40		-CH ₂ -	1.45(8)	0.31(2)
	-CH-	0.95	----		-CH-	1.60(4)	0.01(4)
-C=C-	-CH ₃	0.90	0.05		-CH ₃	1.73(1)	0.23(2)
	-CH ₂ -	0.75	0.10	-S-Ar	-CH ₂ -	1.54(1)	0.63(1)
	-CH-	0.65	----		-CH-	1.47(2)	?
-C≡C-	-CH ₃	0.90	0.15		-CH ₃	2.13(1)	0.37(4)
	-CH ₂ -	0.80	0.05	-S-Ar	-CH ₂ -	1.75(9)	0.50(2)
	-CH-	0.35	----		-CH-	1.53(3)	?
-OH	-CH ₃	2.45	0.40	-Se-Ar	-CH ₃	1.55(1)	0.45(8)
	-CH ₂ -	2.30	0.20		-CH ₂ -	1.55(2)	0.36(5)
	-CH-	2.10	----		-CH-	1.62(9)	0.32(2)
-O-Alkyl	-CH ₃	2.45	0.30		CH ₃	1.72(1)	?
	-CH ₂ -	2.30	0.15	-Se-Ar	-CH ₂ -	1.48(2)	?
	-CH-	2.10	----		-CH-	?	?
-O-Aryl	-CH ₃	2.95	0.40		-CH ₃	2.10(1)	?
	-CH ₂ -	2.65(11)	0.45	-Se-Ar	-CH ₂ -	?	?
	-CH-	3.06(2)	----		-CH-	?	?
	-CH ₃	2.90	0.40	-Te-Ph	-CH ₃	1.20(1)	?
	-CH ₂ -	2.95	0.45		-CH ₂ -	1.40(1)	?
	-CH-	3.45	----		-CH-	?	?
-O-SO ₂ Ar	-CH ₃	2.84	0.39(1)		-CH ₃	0.58(1)	0.22(3)
	-CH ₂ -	2.66(6)	0.28(5)	-P(OR) ₂	-CH ₂ -	0.59(7)	0.34(3)
	-CH-	3.16(3)	0.32(2)		-CH-	0.44(4)	?
-O-SO ₂ Me	-CH ₃	3.01(1)	0.47(2)	-SiMe ₃	-CH ₃	-0.90(1)	0.06(2)
	-CH ₂ -	2.90(5)	0.43(2)		-CH ₂ -	-0.39(2)	?
	-CH-	2.64(1)	0.61(1)		-CH-	-0.83(8)	?
				-SnMe ₃	-CH ₃	-0.81	?
					-CH ₂ -	?	?
					-CH-	?	?

Using the Curphy-Morrison Parameters

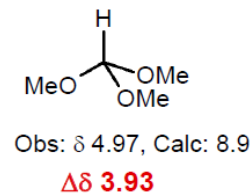
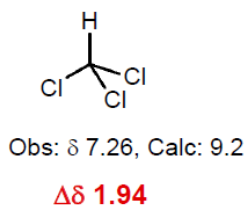
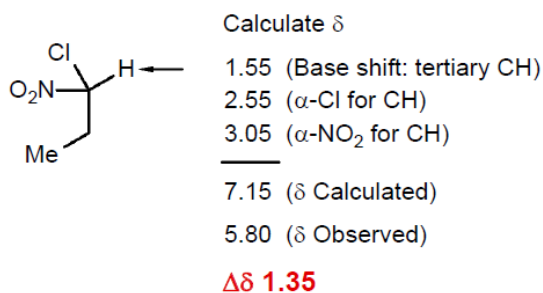
(source: Dr. Hans J. Reich, University of Wisconsin, Madison:
[Chem 605 - Structure Determination Using Spectroscopic Methods](#))

The Curphy-Morrison table is used to calculate the chemical shift of protons bonded to sp^3 carbons. Determine the type of proton to be calculated (CH_3 , CH_2 , or CH) and use the appropriate base shift. Then add corrections for all substituents at the α and β carbons: e.g. for a CH_2 group use δ 1.2 as base shift, and select parameters from the middle row (labelled CH_2) of all substituents at the α and β carbon of the molecule. The solvent should be innocuous (CCl_4 , $CDCl_3$, CD_2Cl_2 , acetone- d_6). In particular aromatic solvents (benzene- d_6 , pyridine- d_5) will give poorer results.



Alkyl substituents are already included in the base shift, so no additional corrections are applied for them

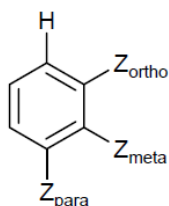
This method will usually give results within 0.5 ppm, except in situations where there are 2 or 3 strongly electronegative substituents (especially oxygen and nitrogen) on one carbon. Here the method overestimates the downfield shift.



This method will also give larger errors for cyclic compounds, as there are specific chemical shift effects associated with various ring systems that are not included in these parameters.

Curphy-Morrison Additivity Constants for Benzene Protons Chemical Shifts

(source: Dr. Hans J. Reich. University of Wisconsin, Madison:
[Chem 605 - Structure Determination Using Spectroscopic Methods](#))



$$\delta_{\text{Ar-H}} = 7.36 + Z_{\text{ortho}} + Z_{\text{meta}} + Z_{\text{para}}$$

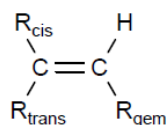
Zi for R (ppm)			
Substituent R	Zortho	Zmeta	Zpara
H	0.0	0.0	0.0
CH ₃ ^[a]	-0.18	-0.11	-0.21
C(CH ₃) ₃	0.02	-0.08	-0.21
CH ₂ Cl	0.02	-0.01	-0.04
CH ₂ OH	-0.07	-0.07	-0.07
CF ₃	0.32	0.14	0.20
CCl ₃	0.64	0.13	0.10
CH=CH ₂	0.04	-0.04	-0.12
CH=CHCOOH ^[a]	0.19	0.04	0.05
C C-H	0.15	-0.02	-0.01
C C-Ph ^[a]	0.17	-0.02	-0.03
Ph ^[a]	0.23	0.07	-0.02
COOH ^[a]	0.77	0.11	0.25
C(O)OCH ₃ ^[a]	0.68	0.08	0.19
C(O)OPh ^[a]	0.85	0.14	0.27
C(O)NH ₂ ^[a]	0.46	0.09	0.17
C(O)Cl ^[a]	0.76	0.16	0.33
C(O)CH ₃ ^[a]	0.60	0.10	0.20
C(O)C(CH ₃) ₃	0.44	0.05	0.05
C(O)H ^[a]	0.53	0.18	0.28
C(NPh)H	0.6	0.2	0.2
C(O)Ph ^[a]	0.45	0.12	0.23
C(O)C(O)Ph ^[a]	0.62	0.15	0.30
CN ^[a]	0.29	0.12	0.25
F	-0.29	-0.02	-0.23
Cl ^[a]	-0.02	-0.07	-0.13
Br ^[a]	0.13	-0.13	-0.08
I	0.39	-0.21	0.00
OH ^[a]	-0.53	-0.14	-0.43
OCH ₃ ^[a]	-0.45	-0.07	-0.41

Zi for R (ppm)			
Substituent R	Zortho	Zmet ^[a]	Zpara
OPh ^[a]	-0.36	-0.04	-0.28
O-C(O)CH ₃ ^[a]	-0.27	-0.02	-0.13
O-C(O)Ph ^[a]	-0.14	0.07	-0.09
O-SO ₂ Me	-0.05	0.07	-0.01
SH	-0.08	-0.16	-0.22
SMe	-0.08	-0.10	-0.24
SPh	0.06	-0.09	-0.15
SO ₂ Cl	0.76	0.35	0.45
NH ₂ ^[a]	-0.71	-0.22	-0.62
NMe ₂	-0.66	-0.18	-0.67
NEt ₂ ^[a]	-0.68	-0.15	-0.73
NMe ₃ +I-	0.69	0.36	0.31
NHC(O)CH ₃ ^[a]	0.14	-0.07	-0.27
NH-NH ₂	-0.60	-0.08	-0.55
N=N-Ph	0.67	0.20	0.20
N=O	0.58	0.31	0.37
NO ₂ ^[a]	0.87	0.20	0.35
P(O)(OMe) ₂	0.48	0.16	0.24
SiMe ₃	0.22	-0.02	-0.02
BPh ₃ ⁻	-0.16	-0.42	-0.56

^[a]Data in dilute CDCl₃ by Paul Schatz, University of Wisconsin, Madison. Original data from *J. Am. Chem. Soc.* **1956**, *78*, 3043 at 30 MHz with 50% solutions in cyclohexane.

Curphy-Morrison Additivity Constants for Vinylic Protons

(source: Dr. Hans J. Reich. University of Wisconsin, Madison:
[Chem 605 - Structure Determination Using Spectroscopic Methods](#))



$$\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

Zi for R (ppm)				Zi for R (ppm)			
Substituent R	Zgem	Zcis	Ztrans	Substituent R	Zgem	Zcis	Ztrans
H	0.0	0.0	0.0	F	1.54	-0.40	-1.02
Alkyl	0.45	-0.22	-0.28	Cl	1.08	0.18	0.13
Alkyl (cyclic)	0.69	-0.25	-0.28	Br	1.07	0.45	0.55
CH ₂ OH	0.64	-0.01	-0.02	I	1.14	0.81	0.88
CH ₂ SH	0.71	-0.13	-0.22	OR (R, aliphatic)	1.22	-1.07	-1.21
CH ₂ X (X = F, Cl, Br)	0.70	0.11	-0.04	OR (R, conjugated)	1.21	-0.60	-1.00
CH ₂ NR ₂	0.58	-0.10	-0.08	O-C(O)-R	2.11	-0.35	-0.64
CF ₃	0.66	0.61	0.32	O-P(O)(OEt) ₂	0.66	0.88	0.67
C=CR ₂ (isolated)	1.00	-0.09	-0.23	SR	1.11	-0.29	-0.13
C=CR ₂ (conjugated)	1.24	0.02	-0.05	S(O)R	1.27	0.67	0.41
C≡C-R	0.47	0.38	0.12	S(O) ₂ R	1.55	1.16	0.93
C≡N	0.27	0.75	0.55	S-C N	0.80	1.17	1.11
COOH (isolated)	0.97	1.41	0.71	SF ₅	1.68	0.61	0.49
COOH (conjugated)	0.80	0.98	0.32	SePh (5)	1.36	0.17	0.24
COOR (isolated)	0.80	1.18	0.55	Se(O)Ph (1)	1.86	0.97	0.63
COOR (conjugated)	0.78	1.01	0.46	Se(O ₂)Ph (1)	1.76	1.49	1.21
C(O)H	1.02	0.95	1.17	NR ₂ (R, aliphatic)	0.80	-1.26	-1.21
C(O)NR ₂	1.37	0.98	0.46	NR ₂ (R, conjugated)	1.17	-0.53	-0.99
C(O)Cl	1.11	1.46	1.01	N=N-Ph	2.39	1.11	0.67
C=O (isolated)	1.10	1.12	0.87	NO ₂	1.87	1.30	0.62
C=O (conjugated)	1.06	0.91	0.74	N-C(O)R	2.08	-0.57	-0.72
CH ₂ -C(O)R; CH ₂ -CN	0.69	-0.08	-0.06	N ₃	1.21	-0.35	-0.71 ^[2]
CH ₂ Ar	1.05	-0.29	-0.32	P(O)(OEt) ₂	0.66	0.88	0.67
Ar	1.38	0.36	-0.07	SiMe ₃ (1)	0.77	0.37	0.62
Ar (o-subst)	1.65	0.19	0.09	GeMe ₃ (1)	1.28	0.35	0.67

The increments 'R conjugated' are to be used instead of 'R isolated' when either the substituent or the double bond is conjugated with further substituents. The increment alkyl (cyclic) is to be used when both the substituent and the double bond form part of a ring. (Data for compounds containing 3- and 4-membered rings have not been considered.) Numbers in parentheses represent the number of examples used to calculate the parameters.

^[1] Pascual, C. *Helv. Chem. Acta* **1966**, 49, 164.

^[2] L'Abbe, G. *Chem. & Ind. (London)* **1971**, 278