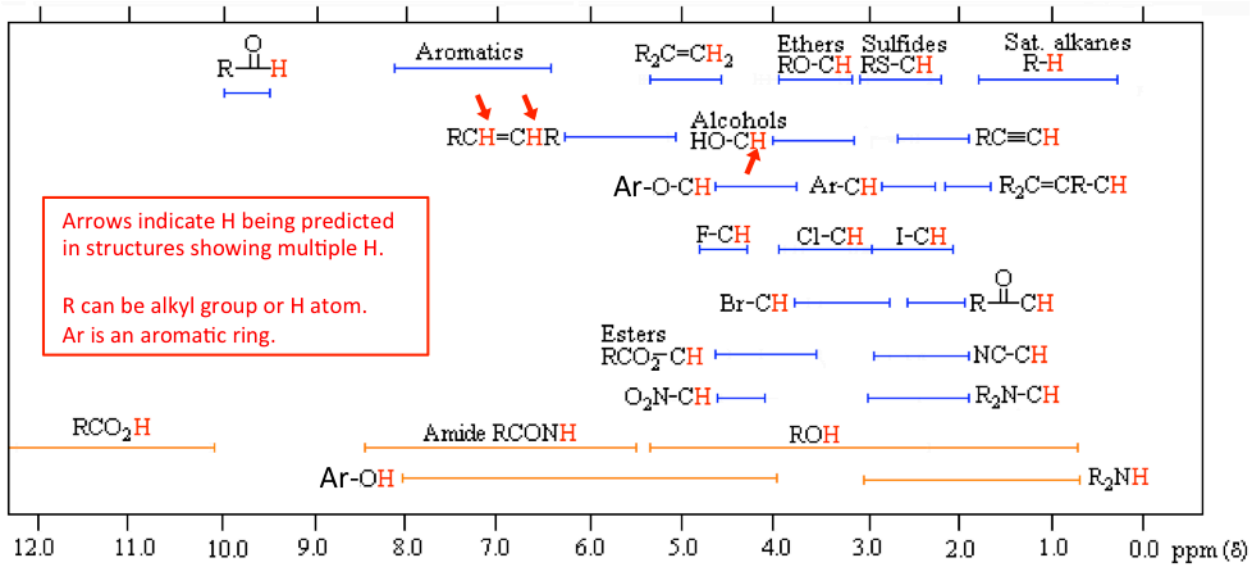
NMR Chemical Shift Prediction Tools for Chem 111 (keep this sheet!) (rev. 14 Nov, 2013)

^{1}H NMR chemical shift chart modified from Reusch *Virtual Organic Chemistry* (Nov. 2010)

(note: bottom two lines are for H attached to heteroatoms).



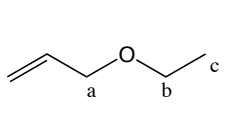
Predicting shifts for H on sp^3 carbons:

(Note: R can generally be any carbon or H atom, unless there is a separate listing for aromatic carbon (Ar) or for H)

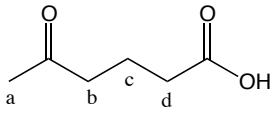
Prediction method for H on sp^3 C			Start with 0.9 ppm (CH_3),		
from Beauchamp & Marquez			1.2 ppm (CH_2), 1.5 ppm (CH)		
J. Chem. Educ. **1997,** *74*, 1483.			**alpha**	**beta**	**gamma**
atom	**–X group**	**shorthand**	**(HCX)**	**(HCCX)**	**(HCCCX)**
C(sp^2)	alkenyl	–CR=CR$_2$	0.8	0.2	0.1
C(sp^2)	amide	–C(O)NR$_2$	1.0	0.3	0.1
C(sp^2)	carboxylic acid	–C(O)OH	1.1	0.3	0.1
C(sp^2)	ester	–C(O)OR	1.1	0.3	0.1
C(sp^2)	aldehyde	–CHO	1.1	0.4	0.1
C(sp^2)	aliphatic ketone	–C(O)R	1.2	0.3	0.0
C(sp^2)	aryl	–Ar	1.4	0.4	0.1
C(sp^2)	aryl ketone	–C(O)Ar	1.7	0.3	0.1
C(sp^2)	acid chloride	–C(O)Cl	1.8	0.4	0.1
C(sp)	alkynyl	–C≡CR	0.9	0.3	0.1
C(sp)	nitrile	–C≡N	1.1	0.4	0.2
halide	iodo	–I	2.0	0.9	0.1
halide	bromo	–Br	2.1	0.7	0.2
halide	chloro	–Cl	2.2	0.5	0.2
halide	fluoro	–F	3.2	0.5	0.2
O	alkyl ether	–OR	2.1	0.3	0.1
O	alcohol	–OH	2.3	0.3	0.1
O	alkenyl ether	–OCR=CR$_2$	2.5	0.4	0.2
O	aryl sulfonate	–OS(O)$_2$Ar	2.8	0.4	0.0
O	aryl ether	–OAr	2.8	0.5	0.3
O	aliphatic ester	–OC(O)R	2.8	0.5	0.1
O	aryl ester	–OC(O)Ar	3.1	0.5	0.2
N	amine	–NH$_2$	1.5	0.2	0.1
N	amide	–NRC(O)R	2.1	0.3	0.1
N	nitro	–NO$_2$	3.2	0.8	0.1
S	thiol	–SH	1.3	0.4	0.1
S	thioether	–SR	1.3	0.4	0.1
S	sulfoxide	–S(O)R	1.6	0.5	0.3
S	sulfone	–S(O)$_2$R	1.8	0.5	0.3

Reference: A General Approach for Calculating Proton Chemical Shifts for Methyl, Methylene and Methine Protons ... by Beauchamp and Marquez, J. Chem. Educ., 1997, 74, 1483-85.

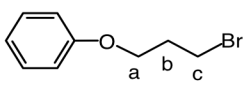
Examples. (First example corrected by RCS)



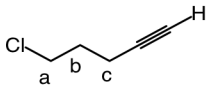
	a	b	c
start	1.2	1.2	0.9
–CR=CR$_2$	0.8	-	-
–OR	2.1	2.1	0.3
predicted	4.1	3.3	1.2
actual ∂ (ppm)	4.0	3.5	1.2



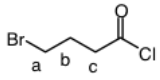
	a	b	c	d
start	0.9	1.2	1.2	1.2
–C(O)R	1.2	1.2	0.3	0.0
–C(O)OH	-	0.1	0.3	1.1
predicted	2.1	2.5	1.8	2.3
actual ∂ (ppm)	2.1	2.6	1.9	2.4



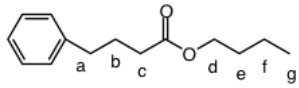
	a	b	c
Actual δ (ppm)	4.1	2.3	3.6
Calculated δ (ppm)	1.2	1.2	1.2
ArO–	2.8	0.5	0.3
Br–	0.2	0.7	2.1
Total	4.2	2.4	3.6



	a	b	c
	3.7	2.0	2.4
	1.2	1.2	1.2
Cl–	2.2	0.5	0.2
C≡C–	0.1	0.3	0.9
	3.5	2.0	2.3



	a	b	c
Actual δ (ppm)	3.4	2.2	3.1
Calculated δ (ppm)	1.2	1.2	1.2
Br–	2.1	0.7	0.2
ClOC–	0.1	0.4	1.8
Total	3.4	2.3	3.2



	a	b	c	d	e	f	g
	2.6	2.0	2.3	4.1	1.6	1.4	0.9
	1.2	1.2	1.2	1.2	1.2	1.2	0.9
Ar–	1.4	0.4	0.1	0.0	0.0	0.0	0.0
RO_2C–	0.1	0.3	1.1	0.0	0.0	0.0	0.0
RCO_2–	0.0	0.0	0.0	2.8	0.5	0.1	0.0
Total	2.7	1.9	2.4	4.0	1.7	1.3	0.9

Chemical shift predictions for hydrogens attached to sp² carbon atoms

(based on Silverstein, et al, *Spectrophotometric Identification of Organic Compounds,* 7th ed.).

Substituted Benzene (phenyl)

Start 7.27 ppm

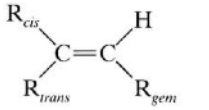
Add corrections for substituents as follows:

position:	ortho	meta	para
–R (alkyl)	-0.1	-0.1	-0.1
–CR*=CR*$_2$ (alkenyl)	0	0	0
–C≡CR* (alkynyl)	+0.2	0	0
–Phenyl	+0.2	0	-0.1
–F	-0.3	-0.2	0
–Cl	0	0	0
–Br	+0.3	0	0
–I	+0.5	-0.2	0
–OH	-0.5	-0.2	-0.35
–OR	-0.25	+0.1	-0.25
–OC(=O)R	-0.1	+0.2	0
–CHO	+0.7	+0.25	+0.4
–C(=O)R	+0.65	+0.3	+0.3
–C(=O)OH	+0.65	+0.1	+0.2
–C(=O)OR	+0.9	+0.2	+0.3
–C≡N	+0.3	+0.3	+0.3
–NH_2	-0.75	-0.1	-0.4
–NR_2	-0.55	-0.1	-0.55
–NR*C(O)R*	+0.35	+0.05	-0.1
–NO_2	+1.0	+0.3	+0.45
–SR	0	0	0

** - R* can either be alkyl or H*

Alkenes:

Start 5.25 ppm



$$\delta_H = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

TABLE D.1 Substituent Constants (*Z*) for Chemical Shifts of Substituted Ethylenes.

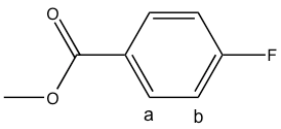
Substituent R	Z gem	Z cis	Z trans	Substituent R	Z gem	Z cis	Z trans
—H	0	0	0				
—Alkyl	0.44	−0.26	−0.29		1.03	0.97	1.21
—Alkyl-ring[a]	0.71	−0.33	−0.30				
—CH_2O, —CH_2I	0.67	−0.02	−0.07				
—CH_2S	0.53	−0.15	−0.15		1.37	0.93	0.35
—CH_2Cl, —CH_2Br	0.72	0.12	0.07				
—CH_2N	0.66	−0.05	−0.23		1.10	1.41	0.99
—C≡C	0.50	0.35	0.10				
—C≡N	0.23	0.78	0.58	—OR, R: aliph	1.18	−1.06	−1.28
—C=C	0.98	−0.04	−0.21	—OR, R: conj[b]	1.14	−0.65	−1.05
—C=C conj[b]	1.26	0.08	−0.01	—OCOR	2.09	−0.40	−0.67
—C=O	1.10	1.13	0.81	—Aromatic	1.35	0.37	−0.10
—C=O conj[b]	1.06	1.01	0.95	—Cl	1.00	0.19	0.03
—COOH	1.00	1.35	0.74	—Br	1.04	0.40	0.55
—COOH conj[b]	0.69	0.97	0.39	 R:aliph	0.69	−1.19	−1.31
—COOR	0.84	1.15	0.56	 R:conj[b]	2.30	−0.73	−0.81
—COOR conj[b]	0.68	1.02	0.33	—SR	1.00	−0.24	−0.04
				—SO_2	1.58	1.15	0.95

[a] Alkyl ring indicates that the double bond is part of the ring  .

[b] The *Z* factor for the conjugated substituent is used when either the substituent or the double bond is further conjugated with other groups.

Source: Pascual C., Meier, J., and Simon, W. (1966) *Helv. Chim. Acta,* **49,** 164.

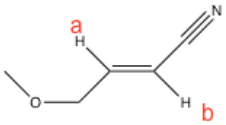
Example of chemical shift prediction for substituted benzene:



	a	b	-CH_3
start	7.27	7.27	0.9
-C(O)OR	+0.9 (o)	+0.2 (m)	3.1*
-F	-0.2 (m)	-0.3 (o)	
predicted	8.0	7.2	4.0
splitting	d	d	s
actual	8.05	7.10	3.90

* –OC(O)Ar, from table for H on sp^3 carbons

Example of chemical shift prediction for alkene:



	a	b
start	5.25	5.25
-CH_2O	+0.67 (gem)	-0.02 (cis)
-CN	+0.78(cis)	+0.23 (gem)
predicted	6.70	5.46
splitting	d of t	d

^{13}C NMR chemical shift chart, modified from Reusch *Virtual Organic Chemistry* (Nov. 2010)