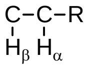
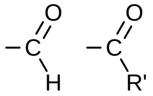
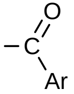
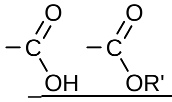
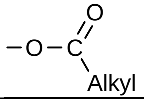
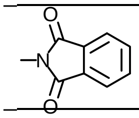
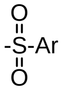
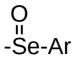
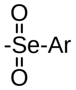
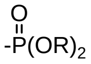
9.5 Curphy-Morrison Additivity Constants for Proton NMR

Substituent Effects on: 
$\underset{H_\beta}{C}-\underset{H_\alpha}{C}-R$

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

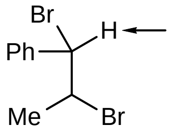
Substituent R		Alpha Shift	Beta Shift
Chlorine	-CH$_3$	2.30	0.60
	-CH$_2$-	2.30	0.55
	-CH-	2.55	0.15
Bromine	-CH$_3$	1.80	0.80
	-CH$_2$-	2.15	0.80
	-CH-	2.20	0.25
Iodine	-CH$_3$	1.30	1.10
	-CH$_2$-	1.95	0.60
	-CH-	2.70	0.35
Aryl	-CH$_3$	1.45	0.35
	-CH$_2$-	1.45	0.55
	-CH-	1.35	----
	-CH$_3$	1.25	0.25
	-CH$_2$-	1.10	0.30
	-CH-	0.95	----
	-CH$_3$	1.70(6)	0.28(4)
	-CH$_2$-	1.64(10)	0.50(3)
	-CH-	1.76(2)	0.76(1)
	-CH$_3$	1.20	0.25
	-CH$_2$-	1.00	0.30
	-CH-	0.95	----
−C≡N	-CH$_3$	1.10	0.45
	-CH$_2$-	1.10	0.40
	-CH-	0.95	----
-C=C-	-CH$_3$	0.90	0.05
	-CH$_2$-	0.75	0.10
	-CH-	0.65	----
−C≡C−	-CH$_3$	0.90	0.15
	-CH$_2$-	0.80	0.05
	-CH-	0.35	----
-OH	-CH$_3$	2.45	0.40
	-CH$_2$-	2.30	0.20
	-CH-	2.10	----
-O-Alkyl	-CH$_3$	2.45	0.30
	-CH$_2$-	2.30	0.15
	-CH-	2.10	----
-O-Aryl	-CH$_3$	2.95	0.40
	-CH$_2$-	2.65(11)	0.45
	-CH-	3.06(2)	----
	-CH$_3$	2.90	0.40
	-CH$_2$-	2.95	0.45
	-CH-	3.45	----
-O-SO$_2$Ar	-CH$_3$	2.84	0.39(1)
	-CH$_2$-	2.66(6)	0.28(5)
	-CH-	3.16(3)	0.32(2)
-O-SO$_2$Me	-CH$_3$	3.01(1)	0.47(2)
	-CH$_2$-	2.90(5)	0.43(2)
	-CH-	2.64(1)	0.61(1)

Substituent R		Alpha Shift	Beta Shift
-N(H)Alkyl -N(Alkyl)$_2$	-CH$_3$	1.25	0.20
	-CH$_2$-	1.40	0.15
	-CH-	1.35	----
-N(H)Aryl -N(Alkyl)(Aryl)	-CH$_3$	2.08(8)	0.28(10)
	-CH$_2$-	2.03(12)	0.34(2)
	-CH-	2.33(2)	?
$-\overset{+}{N}Me_3$	-CH$_3$	2.30(1)	?
	-CH$_2$-	2.06(4)	?
	-CH-	?	?
	-CH$_3$	2.14(1)	0.30(1)
	-CH$_2$-	2.25(10)	0.51(2)
	-CH-	?	?
-NO$_2$	-CH$_3$	3.50	0.65
	-CH$_2$-	3.15	0.85
	-CH-	3.05	----
-N$_3$	-CH$_3$	2.08(1)	0.45(1)
	-CH$_2$-	1.45(3)	-0.46(1)
	-CH-	1.46(2)	-0.22(1)
-SH -S-Alkyl	-CH$_3$	1.20	0.40
	-CH$_2$-	1.30	0.30
	-CH-	1.30	----
-S-Ar	-CH$_3$	1.47(2)	0.35(2)
	-CH$_2$-	1.45(8)	0.31(2)
	-CH-	1.60(4)	0.01(4)
 $-\overset{O}{\overset{\|}{S}}-Ar$	-CH$_3$	1.73(1)	0.23(2)
	-CH$_2$-	1.54(1)	0.63(1)
	-CH-	1.47(2)	?
 $-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-Ar$	-CH$_3$	2.13(1)	0.37(4)
	-CH$_2$-	1.75(9)	0.50(2)
	-CH-	1.53(3)	?
-Se-Ar	-CH$_3$	1.55(1)	0.45(8)
	-CH$_2$-	1.55(2)	0.36(5)
	-CH-	1.62(9)	0.32(2)
 $-\overset{O}{\overset{\|}{Se}}-Ar$	CH$_3$	1.72(1)	?
	-CH$_2$-	1.48(2)	?
	-CH-	?	?
 $-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{Se}}}}-Ar$	-CH$_3$	2.10(1)	?
	-CH$_2$-	?	?
	-CH-	?	?
-Te-Ph	-CH$_3$	1.20(1)	?
	-CH$_2$-	1.40(1)	?
	-CH-	?	?
 $-\overset{O}{\overset{\|}{P}}(OR)_2$	-CH$_3$	0.58(1)	0.22(3)
	-CH$_2$-	0.59(7)	0.34(3)
	-CH-	0.44(4)	?
-SiMe$_3$	-CH$_3$	-0.90(1)	0.06(2)
	-CH$_2$-	-0.39(2)	?
	-CH-	-0.83(8)	?
-SnMe$_3$	-CH$_3$	-0.81	?
	-CH$_2$-	?	?
	-CH-	?	?

From: P. L. Fuchs and C. A. Bunnell, "Carbon-13 NMR Based Spectral Problems," John Wiley, New York, 1979. Data with numbers in parentheses were added by HJR with limited number of examples (number is sample size)

Using the Curphy-Morrison Parameters

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.

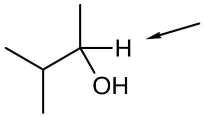


Calculate δ

1.55 (Base shift: tertiary CH)
0.95 (α-Ph for CH)
2.20 (α-Br for CH)
0.25 (β-Br for CH)

4.95 (δ Calculated)
5.00 (δ Observed)

Δδ 0.05



Calculate δ

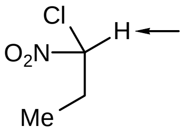
1.55 (Base shift: tertiary CH)
2.10 (α-OH for CH)

3.65 (δ Calculated)
3.54 (δ Observed)

Δδ 0.11

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.

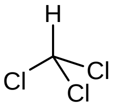


Calculate δ

1.55 (Base shift: tertiary CH)
2.55 (α-Cl for CH)
3.05 (α-NO_2 for CH)

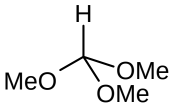
7.15 (δ Calculated)
5.80 (δ Observed)

Δδ 1.35



Obs: δ 7.26, Calc: 9.2

Δδ 1.94



Obs: δ 4.97, Calc: 8.9

Δδ 3.93

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.