^{13}C-NMR Spectroscopy

The number of signals in a ^{13}C-NMR spectrum tells you how many different kinds of Carbons a compound has. The principles behind ^{1}H-NMR and ^{13}C-NMR spectroscopy are essentially the same. There are, however, some differences that make ^{13}C-NMR easier to interpret. For example, ^{1}H is the most abundant isotope of hydrogen, but ^{13}C is only a minor isotope of carbon, representing about 1.1% of all carbon atoms found in nature. As a result, only one in every hundred carbon atoms will resonate, which demands the use of a sensitive receiver coil for ^{13}C NMR spectroscopy.

^{13}C-NMR requires Fourier transform techniques because the signals obtained from a single scan are too weak to be distinguished from background electronic noise. However, FT- ^{13}C-NMR scans can be repeated rapidly, so a large number of scans can be recorded and added.^{13}C- signals stand out when hundreds of scans are added.

Without Fourier transform, it could take days to record the number of scans required for a ^{13}C-NMR spectrum. The low abundance of ^{13}C means that the intensities of the signals in ^{13}C-NMR compared with those in ^{1}H- NMR are reduced by a factor of approximately 100. In addition, the gyromagnetic ratio (γ) of ^{13}C is about one-fourth that of ^{1}H. Therefore, the overall intensity of a ^{13}C signal is about 6400 times less than the intensity of an ^{1}H signal.

Overall sensitivity of ^{13}C compared to ^{1}H is 1/6000 approximately.

	^{13}C	^{1}H
Natural abundance	1.1%	99.98%
s.q.n (I)	1/2	1/2
precession frequency(ν_o)	25MHz	100MHz
magnetic moment	0.7	2.79
sensitivity	1.6%	100%
instrument(r.f.)	75MHz	300MHz

One advantage to ^{13}C-NMR spectroscopy is that the chemical shifts range over about 220 ppm, compared with about 12 ppm for ^{1}H-NMR . This means that signals are less likely to overlap.

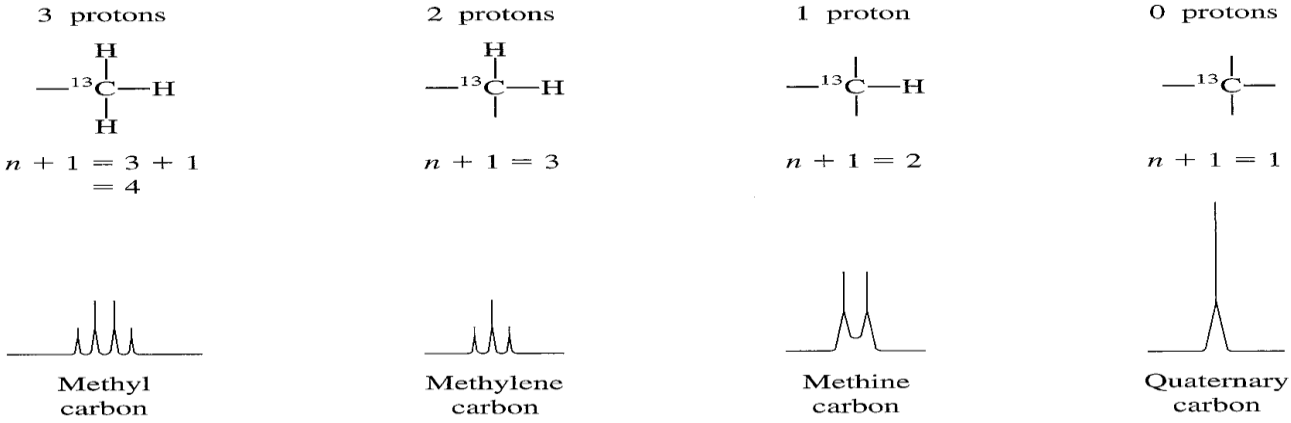
In ^{1}H NMR spectroscopy, we saw that each signal has three characteristics (chemical shift, integration, and multiplicity). In ^{13}C NMR spectroscopy, only the chemical shift is important. The integration and multiplicity of ^{13}C signals are not reported, which greatly simplifies the interpretation of ^{13}C NMR spectra. Integration values are not routinely calculated in ^{13}C NMR spectroscopy because the pulse technique employed by FT NMR spectrometers has the undesired effect of distorting the integration values, rendering

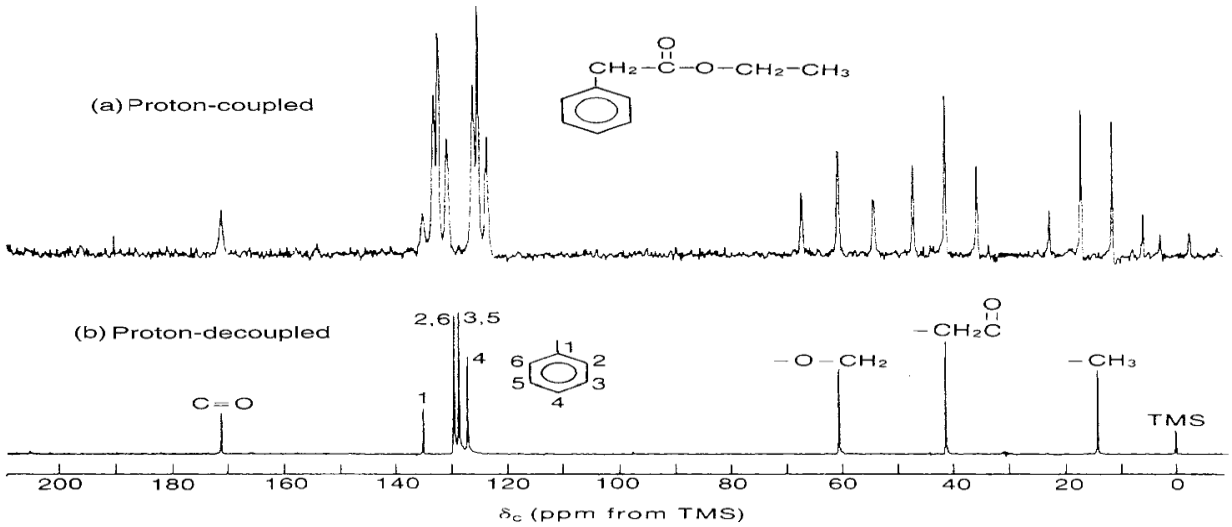
them useless in most cases. Multiplicity is also not a common characteristic of ^{13}C NMR spectra. Notice that all of the signals are recorded as singlets.

There are several good reasons for this:

First, no splitting is observed between neighboring carbon atoms because of the low abundance of ^{13}C. The likelihood of a compound having two neighboring ^{13}C atoms is quite small, so ^{13}C -^{13}C splitting is not observed. In contrast, ^{13}C -^{1}H splitting does occur, and it creates significant problems. The signal of each ^{13}C atom nucleus is split not only by the protons directly connected to it (separated by only one sigma bond) but also by the protons that are two or three sigma bonds removed. This leads to very complex splitting patterns, and signals overlap to produce an unreadable spectrum. To solve the problem, all ^{13}C -^{1}H splitting is suppressed with a technique called **broadband decoupling**, which uses two rf transmitters. The first transmitter provides brief pulses in the range of frequencies that cause ^{13}C nuclei to resonate, while the second transmitter continuously irradiates the sample with the range of frequencies that cause all ^{1}H nuclei to resonate. This second rf source effectively decouples the ^{1}H nuclei from the ^{13}C nuclei, causing all of the ^{13}C signals to collapse to singlets.

The advantage of broadband decoupling comes at the expense of useful information that would otherwise be obtained from spin-spin coupling. A technique called **off-resonance decoupling** allows us to retrieve some of this information. With this technique, only the one bond couplings are observed, so CH_3 groups appear as quartets(N+1), CH_2 groups appear as triplets, CH groups appear as doublets, and quaternary carbon atoms appear as singlets. Nonetheless, off-resonance decoupling is rarely used because it often produces overlapping peaks that are difficult to interpret.



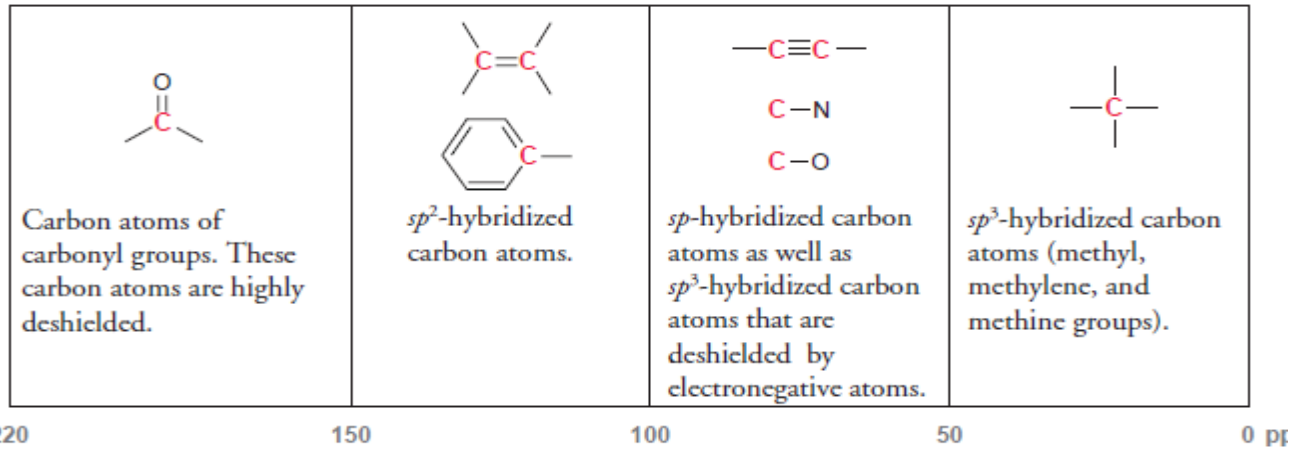


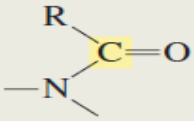
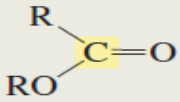
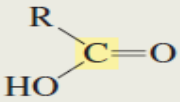
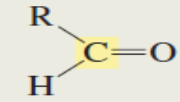
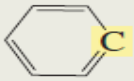
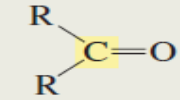
Chemical Shifts in ^{13}C NMR Spectroscopy

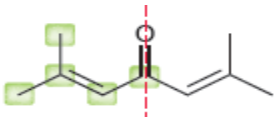
The range of rf frequencies in ^{13}C spectroscopy is different from that used in ^{1}H NMR spectroscopy, the position of each signal is defined relative to the frequency of absorption of a reference compound, TMS. With this definition, the chemical shift of each ^{13}C atom is constant, regardless of the operating frequency of the spectrometer. In ^{13}C NMR spectroscopy, chemical shift values typically range from 0 to 220 ppm.

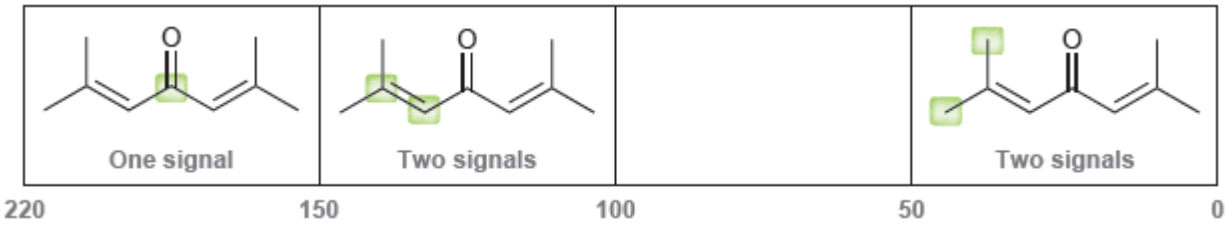
The number of signals in a ^{13}C NMR spectrum represents the number of carbon atoms in different electronic environments (not interchangeable by symmetry). Carbon atoms that are interchangeable by a symmetry operation (either rotation or reflection) will produce only one signal.

The ^{13}C-NMR chemical shifts of different kinds of carbons are shown below.



Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	C—I	0–40
R—CH_3	8–35	C—Br	25–65
R—CH_2—R	15–50	C—Cl C—N C—O	35–80 40–60 50–80
R—CH(R)—R	20–60		165–175
R—C(R)(R)—R	30–40		165–175
≡C	65–85		175–185
=C	100–150		190–200
	110–170		205–220

Q/ Consider the following compound. 



Electronegativity, hybridization, and anisotropy all affect ^{13}C chemical shifts in nearly the same fashion as they affect ^{1}H chemical shifts, however,^{13} C chemical shifts are about 20 times larger. Electronegativity produces the same deshielding effect in carbon NMR as in proton NMR—the electronegative element produces a large downfield shift. The shift is greater for a ^{13}C atom than for a proton since the electronegative atom is directly attached to the ^{13}C atom, and the effect occurs through only a single bond. In ^{1}H NMR, the effect of an electronegative element on chemical

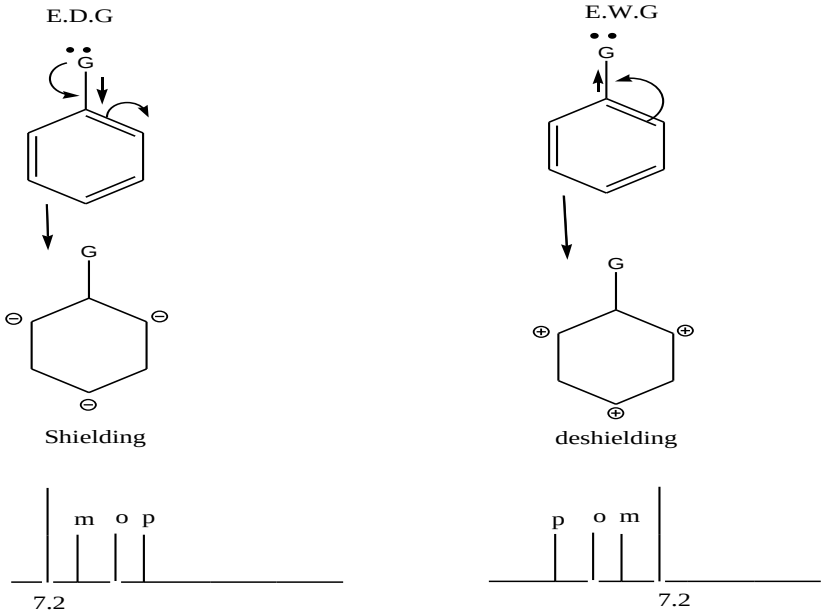
shift diminishes with distance, but it is always in the same direction (deshielding and downfield). In ^{13}C-NMR, an electronegative element also causes a downfield shift in the α and β carbons, but it usually leads to a small upfield shift for the γ carbon. This effect is clearly seen in the carbons of hexanol:

14.2 22.8 32.0 25.8 32.8 61.9 ppm
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-OH$
ω ε δ γ β α

Calculation of ^{13}C-NMR chemical shifts:

It is possible to predict the chemical shift of almost any ^{13}C-NMR atom from the Tables. Starting from a base value (128.5ppm) for the molecular skeleton and then adding increments that correct the value for each substituent.

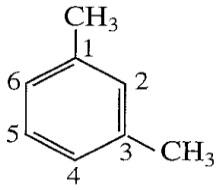
The largest chemical shifts are found for rings when E.W. groups such as NO_2 are attached to the ring. Conversely E.D. groups increase the shielding of these carbons causing them to move up field.



Consider *m*-xylene as an example. From the tables you will find that the base value for the carbons in benzene ring is 128.5ppm. These values are:

	ipso	*ortho*	*meta*	*para*
CH_3:	9.3	0.7	−0.1	−2.9 ppm

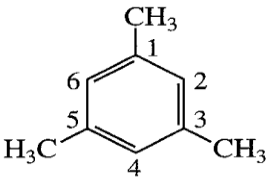
The ipso carbon is the one to which the substituent is directly attached. The calculations started with the base value and add these increments as follows:



C1 = base + *ipso* + *meta* = 128.5 + 9.3 + (−0.1) = 137.3 ppm
C2 = base + *ortho* + *ortho* = 128.5 + 0.7 + 0.7 = 129.9 ppm
C3 = C1
C4 = base + *ortho* + *para* = 128.5 + 0.7 + (−2.9) = 126.3 ppm
C5 = base + *meta* + *meta* = 128.5 + 2(−0.1) = 128.3 ppm
C6 = C4

The observed values for C1, C2, C4, and C5 of *m*-xylene are 137.6, 130.0, 126.2, and 128.2 ppm, respectively, and the calculated values agree well with those actually measured.

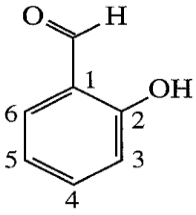
Example 1



Mesitylene

	Observed
C1,C3,C5 = 128.5 + 9.3 − 0.1 − 0.1 = 137.6 ppm	137.4 ppm
C2,C4,C6 = 128.5 + 0.7 + 0.7 − 2.9 = 127.0 ppm	127.1 ppm

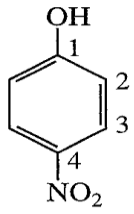
Example 2



Salicylaldehyde

	Observed
C1 = 128.5 + 8.2 − 12.7 = 124.0 ppm	121.0 ppm
C2 = 128.5 + 26.6 + 1.2 = 156.3 ppm	161.4 ppm
C3 = 128.5 − 12.7 + 0.6 = 116.4 ppm	117.4 ppm
C4 = 128.5 + 1.6 + 5.8 = 135.9 ppm	136.6 ppm
C5 = 128.5 − 7.3 + 0.6 = 121.8 ppm	119.6 ppm
C6 = 128.5 + 1.2 + 1.6 = 131.3 ppm	133.6 ppm

Example 3



4-Nitrophenol

	Observed
C1 = 128.5 + 26.6 + 6.0 = 161.1 ppm	161.5 ppm
C2 = 128.5 − 12.7 + 0.9 = 116.7 ppm	115.9 ppm
C3 = 128.5 + 1.6 − 5.3 = 124.8 ppm	126.4 ppm
C4 = 128.5 + 19.6 + 7.3 = 140.8 ppm	141.7 ppm

^{13}C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)[a]

Substituent Y	α (*ipso*)	o (*ortho*)	m (*meta*)	p (*para*)
$-CH_3$	9.3	0.7	−0.1	−2.9
$-CH_2CH_3$	15.6	−0.5	0	−2.6
$-CH(CH_2)_2$	20.1	−2.0	0	−2.5
$-C(CH_3)_3$	22.2	−3.4	−0.4	−3.1
$-CH=CH_2$	9.1	−2.4	0.2	−0.5
$-C\equiv CH$	−5.8	6.9	0.1	0.4
$-C_6H_5$	12.1	−1.8	−0.1	−1.6
−CHO	8.2	1.2	0.6	5.8
$-COCH_3$	7.8	−0.4	−0.4	2.8
$-COC_6H_5$	9.1	1.5	−0.2	3.8
−COOH	2.9	1.3	0.4	4.3
$-COOCH_3$	2.0	1.2	−0.1	4.8
−CN	−16.0	3.6	0.6	4.3
$-NH_2$	19.2	−12.4	1.3	−9.5
$-N(CH_3)_2$	22.4	−15.7	0.8	−11.8
$-NHCOCH_3$	11.1	−9.9	0.2	−5.6
$-NO_2$	19.6	−5.3	0.9	6.0
−OH	26.6	−12.7	1.6	−7.3
$-OCH_3$	31.4	−14.4	1.0	−7.7
$-OCOCH_3$	22.4	−7.1	−0.4	−3.2
−F	35.1	−14.3	0.9	−4.5
−Cl	6.4	0.2	1.0	−2.0
−Br	−5.4	3.4	2.2	−1.0
−I	−32.2	9.9	2.6	−7.3

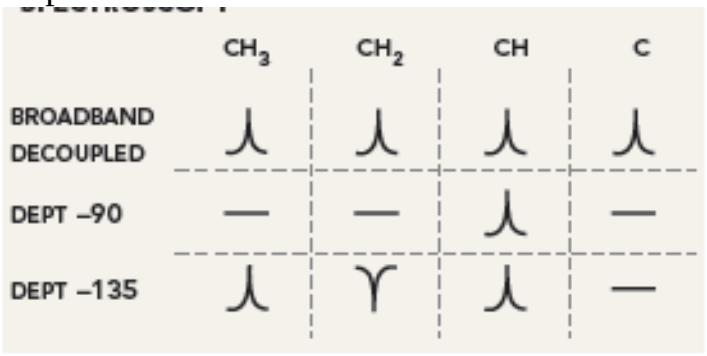
[a]*Add these increments to the base value for benzene-ring carbons (128.5 ppm).*

DEPT ^{13}C NMR Spectroscopy

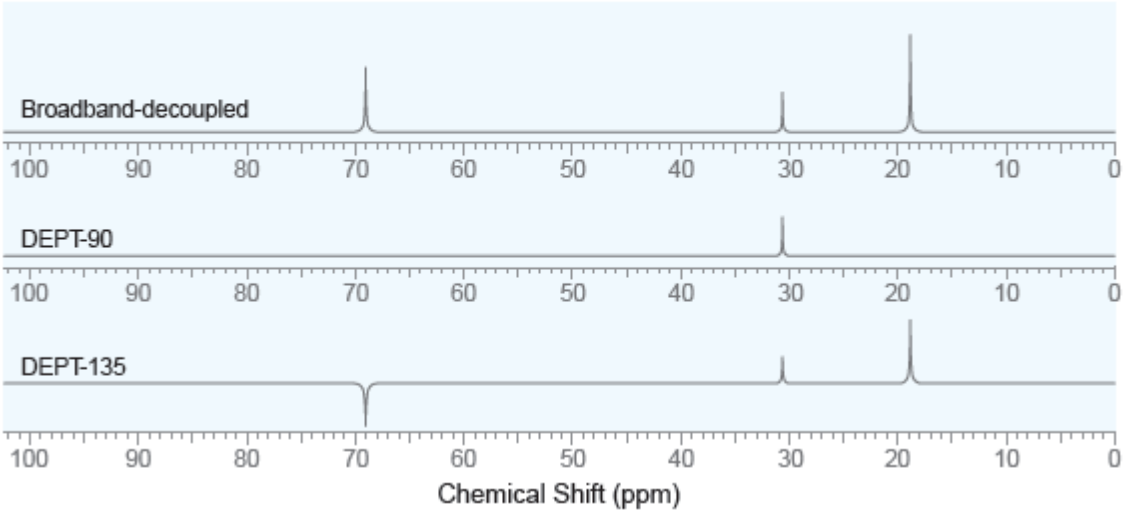
As mentioned before a broadband-decoupled ^{13}C spectrum does not provide information regarding the number of protons attached to each carbon atom in a compound. This information can be obtained through a variety of recently developed techniques, one of which is called distortionless enhancement by polarization transfer (DEPT). DEPT ^{13}C NMR spectroscopy utilizes two rf radiation emitters and relies on the fact that the intensity of each particular signal will respond to different pulse sequences in a predictable fashion, depending on the number of protons attached. This technique involves the acquisition of several spectra. First, a regular broadband-decoupled ^{13}C spectrum is acquired, indicating the chemical shifts associated with all carbon atoms in the compound. Then a special pulse sequence is utilized to produce a spectrum called a DEPT-45, in which only signals from protonated carbons appear, non-protonated carbon such as carbonyl is not seen. DEPT-90, in which only signals from CH groups appear. This spectrum does not show any signals resulting from CH_3 groups, CH_2 groups, or quaternary carbon atoms (C with no protons).

Then, a different pulse sequence is employed to generate a spectrum, called a DEPT-135,

in which CH_3 groups and CH groups appear as positive signals, CH_2 groups appear as negative signals (pointing down), and quaternary carbon atoms do not appear. By comparing all of the spectra, it is possible to identify each signal in the broadband decoupled spectrum as arising from either a CH_3 group, a CH_2 group, a CH group, or a quaternary carbon atom. This information is summarized in Table below. Notice that each type of group exhibits a different absorption pattern when all three spectra are compared. For example, only CH groups give positive signals in all three spectra, while CH_2 groups are the only groups that give negative signals in the DEPT-135 spectrum. This technique therefore produces a series of spectra that collectively contain all of the information in an off-resonance decoupled spectrum, but without the disadvantage of overlapping signals. The following example illustrates how DEPT spectra can be interpreted.



Determine the structure of an alcohol with molecular formula $C_4H_{10}O$ that exhibits the following ^{13}C NMR spectra.



The signal at approximately 69 ppm is a CH_2 group (signal is negative in the DEPT-135).

• The signal at approximately 30 ppm is a CH group (signal is positive in all spectra).

• The signal at approximately 19 ppm is a CH_3 group (signal is positive in the broadband-de coupled spectrum, absent in DEPT-90, and positive in DEPT-135).